

# Crystal structures of diastereomeric styrene complexes of the chiral rhenium fragment $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^+$ : effect of ligating enantioface upon bonding and conformation

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## Abstract

The styrene complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H}_2\text{C}=\text{CHC}_6\text{H}_5)]^+\text{BF}_4^-$  (**1**) can exist as two configurational diastereomers, *RS,SR* and *RR,SS*, that differ in the C=C enantioface bound to rhenium. Crystal structures show that the eleven atom  $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})\text{-}(\text{P})(\text{C}:\text{C})$  units of each are virtually superimposable (*RS,SR*-**1**; triclinic,  $P\bar{1}$ ,  $a = 11.438(2)$  Å,  $b = 12.449(3)$  Å,  $c = 10.712(2)$  Å,  $\alpha = 99.86(1)^\circ$ ,  $\beta = 105.01(1)^\circ$ ,  $\gamma = 99.43(1)^\circ$ ,  $Z = 2$ ; *RR,SS*-**1**; monoclinic,  $P2_1/n$  (No. 14),  $a = 9.673(1)$  Å,  $b = 9.517(1)$  Å,  $c = 30.928(2)$  Å,  $\beta = 94.98(1)^\circ$ ,  $Z = 4$ ). Steric interactions between the styrene phenyl group and cyclopentadienyl ligand in the less stable diastereomer (*RR,SS*-**1**) are apparent. These and other structural features are analyzed in detail.

**Keywords:** Rhenium; Chiral recognition; Styrene complexes; Enantioface binding

## 1. Introduction

Adducts of alkenes and chiral metal fragments are key intermediates in numerous enantioselective syntheses [1]. In order to provide well-defined models for these transient species, we have conducted an extensive study of  $\pi$  complexes of alkenes [2,3] and aldehydes [4] with the chiral rhenium Lewis acid  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^+$  (**I**). This sixteen-valence-electron fragment is a strong  $\pi$  donor, with the d orbital HOMO shown in Scheme 1.

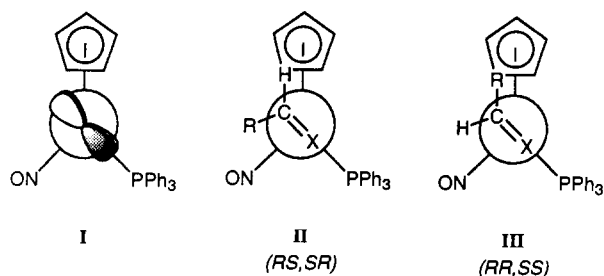
With adducts of **I** and monosubstituted alkenes or aldehydes, two configurational diastereomers are possible. These differ in the X = CHR enantioface bound to rhenium, as illustrated with the idealized structures **II** (*RS,SR*) and **III** (*RR,SS*) in Scheme 1 [5]. The Re–(X = CHR) conformations maximize overlap of the HOMO of **I** and the X = C  $\pi^*$  acceptor orbitals, while directing the larger = CHR terminus *anti* to the bulky  $\text{PPh}_3$  ligand. The *RR,SS* diastereomer **III**, in which the = CHR substituent is *syn* to the cyclopentadienyl ligand, is

always less stable than the *RS,SR* diastereomer **II**, in which the = CHR substituent is *syn* to the small nitrosyl ligand.

The *RS,SR/RR,SS* or **II/III** equilibrium ratios can be viewed as a measure of “chiral recognition”, and have been measured for a variety of monosubstituted alkene [2b,d,e] and aldehyde [4c,d] ligands. In particular, there is a fascinating electronic effect upon the *RS,SR/RR,SS* ratios with aromatic aldehydes that ultimately derives from variations in the rhenium–carbon bond lengths [4c,d]. However, the diastereomeric aldehyde complexes rapidly interconvert via  $\sigma$  complexes [4b], and in all cases examined to date crystallize in the more stable form **II** [4a,c,d]. Hence, structural characterization of the less stable *RR,SS* aldehyde complexes has not proved possible. However, diastereomeric monosubstituted alkene complexes interconvert only at 95–100 °C [2b,c], and in most cases are easily separated.

In order to interpret better the data with aromatic aldehyde complexes, we sought to determine the crystal structures of both diastereomeric adducts of **I** and an aryl-substituted alkene. Any unanticipated differences would potentially require revised chiral recognition models. In this paper, we report that the diastereomeric styrene complexes of **I**,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(\text{H}_2\text{C}$

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Scheme 1. d-orbital HOMO of the pyramidal rhenium fragment  $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)]^+$  (**I**), and idealized structures of diastereomeric monosubstituted alkene and aldehyde complexes (**II**, **III**;  $\text{X} = \text{CH}_2, \text{O}$ ).

$= \text{CHC}_6\text{H}_5]^+ \text{BF}_4^-$  (**1**) [2a], exhibit solid state structures that are close to those of **II** and **III**, and, excluding the  $\text{CC}_6\text{H}_5$  moiety, remarkable in their similarity.

## 2. Results

X-ray data were collected on the diastereomers (*RS,SR*)-**1** and (*RR,SS*)-**1** as outlined in Table 1. Refinement, described in the experimental section, gave the structures shown in Figs. 1 and 2. The three hydrogens bound to the ligated  $\text{C}\equiv\text{C}$  moieties were located. Atomic coordinates, and selected bond lengths, bond angles, and torsion angles, are summarized in Tables 2 and 3.

Fig. 1 shows that the more stable diastereomer (*RS,SR*)-**1** adopts a  $\text{Re}(\text{C}\equiv\text{C})$  conformation close to that of the idealized structure **II**. In **II**, the  $\text{Re}-\text{C}\equiv\text{C}$  plane defines angles of  $0^\circ$  and  $\pm 90^\circ$ , respectively, with the  $\text{Re}-\text{P}$  and  $\text{Re}-\text{N}$  bonds. In (*RS,SR*)-**1**, the corresponding angles are  $23.5^\circ$  and  $63.2^\circ$ . The angle of the  $\text{Re}-\text{C}\equiv\text{C}$  plane with that defined by the cyclopentadienyl centroid, rhenium, and  $\text{C}\equiv\text{C}$  centroid provides another

Table 1  
Summary of crystallographic data for styrene complexes (*RS,SR*)-**1** and (*RR,SS*)-**1**

	( <i>RS,SR</i> )- <b>1</b>	( <i>RR,SS</i> )- <b>1</b>
Molecular formula	$\text{C}_{31}\text{H}_{28}\text{BF}_4\text{NOPRe}$	$\text{C}_{31}\text{H}_{28}\text{BF}_4\text{NOPRe}$
Molecular weight	734.55	734.55
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
Cell dimensions (16°C)		
$a$ (Å)	11.438(2)	9.673(1)
$b$ (Å)	12.449(3)	9.517(1)
$c$ (Å)	10.712(2)	30.928(2)
$\alpha$ (deg)	99.86(1)	–
$\beta$ (deg)	105.01(1)	94.98(1)
$\gamma$ (deg)	99.43(1)	–
$V$ (Å <sup>3</sup> )	1416.25	2836.45
$Z$	2	4
$d$ calc $\text{g cm}^{-3}$	1.722 (16°C)	1.720 (16°C)
$d$ obs $\text{g cm}^{-3}$ ( $\text{CCl}_4/\text{CH}_2\text{I}_2$ )	1.715 (22°C)	1.718 (22°C)
Crystal dimensions (mm)	$0.30 \times 0.25 \times 0.21$	$0.30 \times 0.15 \times 0.12$
Diffractometer	Syntex $P\bar{1}$	Syntex $P\bar{1}$
Radiation ( $\lambda$ Å)	$\text{Cu K}\alpha$ (1.54184)	$\text{Cu K}\alpha$ (1.54184)
Data collection method	$\theta-2\theta$	$\theta-2\theta$
Scan speed $\text{deg min}^{-1}$	4.5	4.5
Reflections measured	3037	3323
Range/indices ( $h, k, l$ )	0 to 11, –12 to 12, –10 to 10	0 to 9, 0 to 9, –30 to 30
Scan range	$\text{K}\alpha 1 - 1.3$ to $\text{K}\alpha 2 + 1.3$	$\text{K}\alpha 1 - 1.3$ to $\text{K}\alpha 2 + 1.3$
$2\theta$ limit (deg)	3.00–98.00	2.00–98.00
No. of reflections between std	98	98
Total no. of unique data	2795	3040
No. of observed data, $I > 3\sigma(I)$	2733	2614
Abs. coefficient ( $\text{cm}^{-1}$ )	90.70	90.58
Min. transmission (%)	69.80	60.30
Max. transmission (%)	99.99	99.99
No. of variables	382	379
Goodness of fit	2.2498	1.7381
$R$ (averaging) ( $I_{\text{obs}}, F_{\text{obs}}$ )	0.0289, 0.0163	0.0302, 0.0169
$R = \sum   F_o  -  F_c   / \sum  F_o $	0.0345	0.0301
$R_w = \sum   F_o  -  F_c   w^{1/2} / \sum  F_o  w^{1/2}$	0.0397	0.0526
$\Delta/\sigma$ (max)	0.010	0.006
$\Delta/\rho$ (max) ( $\text{e}/\text{Å}^3$ )	0.927	0.528

measure of Re–C=C conformation. This value is 76.9° for (*RS,SR*)-**1**, as opposed to 45° for **II**.

As expected, the C=C substituents in (*RS,SR*)-**1** are significantly bent out of the  $\pi$  nodal plane of the free alkene. In order to quantify this feature, a plane was defined that contained the C=C carbons (C1, C2) but

was perpendicular to the Re–C=C plane. The angles of the C1–H1, C1–H2, C2–H3, and C2–C3 bonds [6] with this plane were 14°, 22°, 12°, and 15.4°, respectively. Also, the H1–C1–C2–C3 torsion angle was –145°. All of these values would be 0° in an idealized sp<sup>2</sup> hybridized alkene. In this context, the

Table 2

Atomic coordinates and equivalent isotropic thermal parameters of located atoms in (*RS,SR*)-**1** and (*RR,SS*)-**1**

	( <i>RS,SR</i> )- <b>1</b>				( <i>RR,SS</i> )- <b>1</b>			
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> ) <sup>a</sup>	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> ) <sup>a</sup>
Re	0.80760(3)	0.14215(3)	0.31946(3)	2.429(8)	0.21427(2)	0.11630(3)	0.33201(1)	2.641(8)
P	0.6919(2)	0.2870(2)	0.3106(2)	2.39(5)	0.1300(2)	0.0900(2)	0.40301(5)	2.59(3)
O	0.6992(6)	0.0586(6)	0.5169(6)	5.5(2)	0.1617(6)	0.4207(5)	0.3323(2)	5.5(1)
N	0.7409(6)	0.0944(6)	0.4351(7)	4.0(2)	0.1896(5)	0.2974(6)	0.3344(1)	3.4(1)
C1	0.6674(8)	0.0669(7)	0.1233(8)	3.4(2)	0.4200(7)	0.0886(8)	0.3713(2)	4.7(2)
C2	0.7111(7)	–0.0208(7)	0.1716(8)	3.4(2)	0.4476(7)	0.1522(6)	0.3318(2)	3.8(1)
C3	0.6434(8)	–0.1082(7)	0.2199(8)	3.2(2)	0.5255(6)	0.0853(7)	0.2982(2)	3.4(1)
C4	0.6969(9)	–0.1930(7)	0.261(1)	5.0(3)	0.5936(7)	–0.0402(8)	0.3050(2)	5.0(2)
C5	0.635(1)	–0.2722(8)	0.307(1)	6.0(3)	0.6666(8)	–0.0979(8)	0.2742(3)	6.9(2)
C6	0.5188(9)	–0.2702(9)	0.318(1)	5.6(3)	0.6768(8)	–0.037(1)	0.2368(3)	9.0(2)
C7	0.4623(8)	–0.1877(8)	0.279(1)	4.6(3)	0.6104(9)	0.088(1)	0.2287(3)	8.8(3)
C8	0.5252(8)	–0.1058(8)	0.2291(9)	4.1(2)	0.5367(8)	0.1504(8)	0.2591(2)	5.3(2)
C9	0.9712(8)	0.1307(8)	0.2331(9)	4.4(2)	0.2444(6)	–0.0640(8)	0.2842(2)	3.9(1)
C10	0.9636(8)	0.2397(8)	0.253(1)	5.2(3)	0.1468(8)	–0.1063(6)	0.3118(2)	3.7(2)
C11	0.9832(7)	0.2793(8)	0.3937(9)	3.9(2)	0.0313(6)	–0.0175(7)	0.3061(2)	4.2(2)
C12	1.0076(8)	0.1896(9)	0.453(1)	4.9(3)	0.0600(8)	0.0787(8)	0.2727(2)	5.1(2)
C13	0.9934(8)	0.0948(8)	0.352(1)	5.8(3)	0.1929(7)	0.0498(8)	0.2603(2)	4.4(2)
C14	0.7378(7)	0.3800(6)	0.2102(8)	2.6(2)	0.0899(6)	–0.0897(6)	0.4140(2)	3.0(1)
C15	0.7069(8)	0.3427(7)	0.0719(8)	3.5(2)	0.1930(6)	–0.1916(7)	0.4166(2)	3.8(1)
C16	0.7500(9)	0.4095(8)	–0.0026(8)	4.3(2)	0.1642(8)	–0.3336(7)	0.4207(2)	4.7(2)
C17	0.8232(9)	0.5143(8)	0.0556(8)	4.5(2)	0.030(1)	–0.3756(6)	0.4210(3)	5.7(2)
C18	0.8564(8)	0.5521(7)	0.1915(8)	3.6(2)	–0.0757(8)	–0.2798(8)	0.4189(3)	6.1(2)
C19	0.8123(7)	0.4861(7)	0.2676(8)	3.1(2)	–0.0476(8)	–0.1362(6)	0.4147(3)	4.5(2)
C20	0.7185(7)	0.3825(6)	0.4711(7)	2.5(2)	–0.0294(6)	0.1891(6)	0.4104(2)	2.6(1)
C21	0.8010(8)	0.3740(7)	0.5866(8)	3.3(2)	–0.1117(6)	0.2419(7)	0.3751(2)	4.0(1)
C22	0.8248(8)	0.4532(8)	0.7023(8)	3.7(2)	–0.2333(7)	0.3146(8)	0.3809(2)	4.8(2)
C23	0.7662(8)	0.5411(7)	0.7031(8)	3.8(2)	–0.2731(7)	0.3317(8)	0.4221(2)	4.6(2)
C24	0.6814(8)	0.5486(7)	0.5909(9)	3.7(2)	–0.1941(7)	0.2804(8)	0.4568(2)	5.0(2)
C25	0.6560(7)	0.4697(7)	0.4749(8)	3.0(2)	–0.0710(6)	0.2069(7)	0.4512(2)	3.9(1)
C26	0.5233(7)	0.2430(6)	0.2520(7)	2.7(2)	0.2417(6)	0.1539(6)	0.4494(2)	3.0(1)
C27	0.4501(7)	0.2752(7)	0.1458(8)	3.3(2)	0.2818(7)	0.0716(8)	0.4862(2)	4.4(2)
C28	0.3226(8)	0.2341(8)	0.1049(9)	4.1(2)	0.3633(9)	0.1290(7)	0.5200(2)	5.5(2)
C29	0.2683(8)	0.1623(8)	0.1664(1)	4.5(3)	0.4080(7)	0.2654(9)	0.5181(2)	5.7(2)
C30	0.3394(8)	0.1326(8)	0.2742(9)	4.7(2)	0.3702(9)	0.3483(8)	0.4823(3)	5.5(2)
C31	0.4659(7)	0.1713(7)	0.3160(9)	3.6(2)	0.2882(7)	0.2907(8)	0.4484(2)	4.8(2)
B	1.0553(9)	0.8215(7)	0.133(1)	6.5(3)	–0.5017(4)	0.6034(3)	0.3553(1)	2.23(7)
F1	1.1738(9)	0.853(1)	0.134(2)	10.5(5)	–0.6130(5)	0.6865(5)	0.3362(2)	7.7(1)
F2	0.9862(8)	0.7337(7)	0.0269(8)	8.3(3)	–0.5490(5)	0.5169(6)	0.3874(2)	9.4(1)
F3	1.032(1)	0.8218(9)	0.2537(8)	9.8(3)	–0.4824(9)	0.4996(9)	0.3238(2)	6.1(2)
F4	1.005(1)	0.906(1)	0.088(1)	8.3(4) <sup>b</sup>	–0.3761(9)	0.663(1)	0.3675(3)	7.2(2)
F1'	1.121(2)	0.769(2)	0.207(2)	6.8(5) <sup>b</sup>				
F2'	1.107(2)	0.913(1)	0.109(2)	7.9(4) <sup>b</sup>				
F3'	0.945(3)	0.856(2)	0.138(3)	6.1(7) <sup>b</sup>	–0.449(1)	0.714(1)	0.3813(4)	9.7(3) <sup>b</sup>
F4'	1.065(3)	0.722(2)	0.094(3)	6.3(7) <sup>b</sup>	–0.423(1)	0.576(1)	0.3297(4)	10.0(3) <sup>b</sup>
H1	0.688(7)	0.089(7)	0.063(8)	5.0 <sup>b</sup>	0.410(6)	–0.011(6)	0.372(2)	5.0 <sup>b</sup>
H2	0.580(7)	0.072(7)	0.109(8)	5.0 <sup>b</sup>	0.444(7)	0.123(5)	0.406(2)	5.0 <sup>b</sup>
H3	0.758(7)	–0.043(7)	0.139(8)	5.0 <sup>b</sup>	0.434(6)	0.252(6)	0.336(2)	5.0 <sup>b</sup>

<sup>a</sup> Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:  $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$ .

<sup>b</sup> These atoms were refined isotropically.

informative but derivationally more complex  $\alpha$ ,  $\beta$ , and  $\beta'$  angles utilized by Ibers were also calculated ( $56^\circ$ ,  $31^\circ$ ,  $25^\circ$ ) [7].

Fig. 2 shows that the less stable diastereomer (*RR,SS*)-**1** adopts a  $\text{Re}-(\text{C}=\text{C})$  conformation close to that of the idealized structure **III**. The  $\text{Re}-\text{C}=\text{C}$  plane gave angles of  $19.3^\circ$ ,  $68.4^\circ$ , and  $71.6^\circ$ , respectively, with the  $\text{Re}-\text{P}$  bond,  $\text{Re}-\text{N}$  bond, and the plane defined by the cyclopentadienyl centroid, rhenium, and  $\text{C}=\text{C}$  centroid. The alkene substituents in (*RR,SS*)-**1** were also bent out of the  $\pi$  nodal plane of the free alkene. A plane was again defined that contained C1 and C2 but was perpendicular to the  $\text{Re}-\text{C}=\text{C}$  plane. The angles of the C1–H1, C1–H2, C2–H3, and C2–C3 bonds [6] with this plane were  $6^\circ$ ,  $24^\circ$ ,  $5^\circ$ , and  $19.4^\circ$ , respectively. The Ibers  $\alpha$ ,  $\beta$ , and  $\beta'$  angles were  $45^\circ$ ,  $18^\circ$ , and  $18^\circ$ . The distance between the centroid of the styrene phenyl ring and the nearest cyclopentadienyl hydrogen (H9) was calculated to be 2.96 Å.

### 3. Discussion

To our knowledge, this study provides the first structural comparison of two diastereomeric alkene complexes that differ only in the  $\text{C}=\text{C}$  enantioface bound to a chiral metal fragment. A surprising degree of homology is evident in Figs. 1 and 2, and the metrical

parameters in Table 3. This is particularly striking on a stereoscopic viewing screen, where it is readily seen that the three atoms of the  $\text{Re}-\text{C}=\text{C}$  moiety, the seven atoms of the cyclopentadienyl and nitrosyl ligands, and the  $\text{PPh}_3$  ligand phosphorus are virtually superimposable. A two-dimensional perspective is given in Fig. 3. Since the  $\text{Re}-\text{P}$  conformations differ slightly, the remaining  $\text{PPh}_3$  ligand atoms do not superimpose. In order to quantify this feature,  $\text{N}-\text{Re}-\text{P}-\text{C}$  and  $\text{C1}-\text{Re}-\text{P}-\text{C}$  torsion angles are included in Table 3.

To a first approximation, the styrene ligand phenyl rings in (*RS,SR*)-**1** and (*RR,SS*)-**1** might be expected to occupy reciprocal positions with respect to the  $\text{Re}-\text{C}=\text{C}$  plane. However, as would be expected from steric interactions with the cyclopentadienyl ligand, the phenyl ring in the less stable diastereomer (*RR,SS*)-**1** is “bent back” slightly more from the perpendicular plane ( $19.4^\circ$  vs  $15.4^\circ$ ). Similarly, the  $\text{Re}-\text{CH}-\text{C}_6\text{H}_5$  ( $\text{Re}-\text{C2}-\text{C3}$ ) angle is greater in (*RR,SS*)-**1** than (*RS,SR*)-**1** ( $120.1(5)^\circ$  vs  $116.8(6)^\circ$ ). Although the standard deviations are too large for a rigorous conclusion, the  $\text{Re}-\text{CH}_2$  ( $\text{Re}-\text{C1}$ ) and  $\text{Re}-\text{CHC}_6\text{H}_5$  ( $\text{Re}-\text{C2}$ ) bonds in (*RR,SS*)-**1** ( $2.255(7)^\circ$ ,  $2.284(7)^\circ$ ) appear to be longer than in (*RS,SR*)-**1** ( $2.225(9)^\circ$ ,  $2.258(9)^\circ$ ). In each diastereomer, the  $\text{Re}-\text{CH}_2$  bond is shorter.

The (*RS,SR*)-**1**/*(RR,SS)*-**1** equilibrium ratio is 90:10 in chlorobenzene at  $100^\circ\text{C}$  [2b,c]. Interestingly, when (*RR,SS*)-**1** is viewed on a stereoscopic screen with the

Table 3  
Key bond lengths (Å), bond angles (deg) and torsion angles (deg) in styrene complexes (*RS,SR*)-**1** and (*RR,SS*)-**1**

	( <i>RS,SR</i> )- <b>1</b>	( <i>RR,SS</i> )- <b>1</b>		( <i>RS,SR</i> )- <b>1</b>	( <i>RR,SS</i> )- <b>1</b>
Re–P	2.406(2)	2.420(2)	Re–C13	2.25(1)	2.299(6)
Re–N	1.75(1)	1.742(7)	N–O	1.21(1)	1.205(8)
Re–C1	2.225(9)	2.255(7)	C1–C2	1.40(1)	1.41(1)
Re–C2	2.258(9)	2.284(7)	C2–C3	1.47(1)	1.48(1)
Re–C9	2.305(9)	2.301(7)	P–C14	1.814(8)	1.793(7)
Re–C10	2.325(9)	2.287(6)	P–C20	1.836(8)	1.838(6)
Re–C11	2.272(9)	2.269(6)	P–C26	1.822(9)	1.823(7)
Re–C12	2.280(9)	2.289(7)			
P–Re–N	90.9(2)	90.3(2)	C14–P–C20	102.9(4)	105.6(3)
P–Re–C1	81.7(3)	81.4(2)	C14–P–C26	107.3(4)	106.9(3)
P–Re–C2	114.8(2)	115.4(2)	C20–P–C26	102.4(4)	100.2(3)
N–Re–C1	105.1(4)	102.1(3)	Re–C1–C2	73.2(6)	73.0(4)
N–Re–C2	89.5(3)	89.5(3)	Re–C2–C1	70.6(5)	70.8(4)
C1–Re–C2	36.3(3)	36.2(3)	Re–C2–C3	116.8(6)	120.1(5)
Re–N–O	176.9(7)	172.8(5)	C1–C2–C3	127.4(9)	124.8(7)
Re–P–C14	111.3(3)	111.5(2)	C2–C3–C4	121.3(9)	122.3(7)
Re–P–C20	114.5(3)	114.3(2)	C2–C3–C8	120.7(9)	120.6(7)
Re–P–C26	117.1(3)	117.1(2)			
P–Re–C1–C2	–156.2(5)	–160.4(4)	H1–C1–C2–C3	–144.6(66)	–30.2(40)
N–Re–C1–C2	–67.5(6)	–72.0(4)	N–Re–P–C26	62.0(4)	–70.9(3)
P–Re–C2–C1	26.0(6)	21.5(4)	N–Re–P–C14	174.0(4)	165.5(3)
Re–C1–C2–C3	109.5(9)	–113.9(6)	N–Re–P–C20	57.8(4)	45.9(2)
C1–C2–C3–C4	178.9(9)	–8.4(9)	C1–Re–P–C20	162.9(4)	148.1(3)
C1–C2–C3–C8	–4.2(13)	–174.2(7)	C1–Re–P–C14	–80.9(4)	–92.3(3)
Re–C2–C3–C4	–97.1(9)	–95.0(7)	C1–Re–P–C26	43.0(4)	31.4(3)
Re–C2–C3–C8	81.0(9)	87.6(7)			

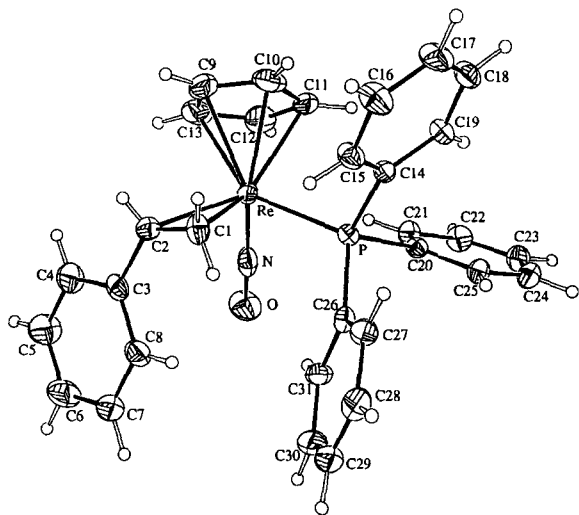


Fig. 1. Structure of the cation of styrene complex (*RS,SR*)-1: top, numbering diagram; bottom, Newman-type projection with  $\text{PPh}_3$  phenyl rings omitted.

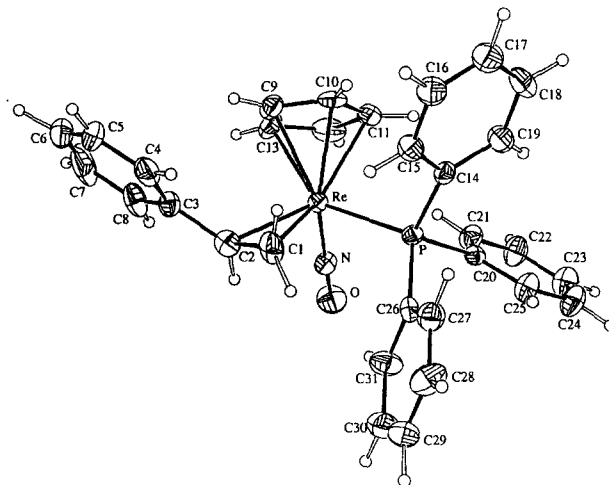


Fig. 2. Structure of the cation of styrene complex (*RR,SS*)-1: top, numbering diagram; bottom, Newman-type projection with  $\text{PPh}_3$  phenyl rings omitted.

atoms set at van der Waals radii, the spatial overlap of the styrene phenyl ring and cyclopentadienyl ligand is modest. Thus, the steric interactions that give rise to the approx.  $1.64 \text{ kcal mol}^{-1}$  stability difference are not visually conspicuous. There is also the possibility of slight attractive interactions between the cyclopentadienyl hydrogens and the styrene phenyl  $\pi$  cloud in (*RR,SS*)-1, as documented for a variety of  $\text{C-H} \cdots \pi(\text{arene})$  systems [8]. Regardless, severe steric repulsion would occur in the corresponding *pentamethylcyclopentadienyl* complexes. Indeed, the *RS,SR/RR,SS* equilibrium ratio in this series of compounds is much greater ( $> 99: < 1$ ) [3d].

The crystal structures of seven other alkene complexes of **I** have been reported [2a,b,d,e,3a,b]. The angles of the  $\text{Re}-\text{C}=\text{C}$  planes with the  $\text{Re}-\text{P}$  bonds range from  $8.8^\circ$  (cyclopentene) [3a] to  $22.6^\circ$  (*trans*-2-butene) [3b], with an average of  $16.7^\circ$ . Thus, the angle in (*RS,SR*)-1 ( $23.5^\circ$ ) constitutes the largest deviation

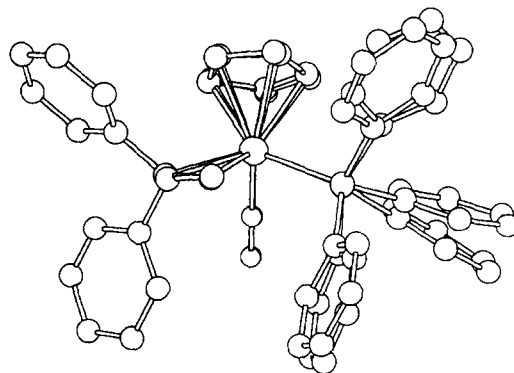
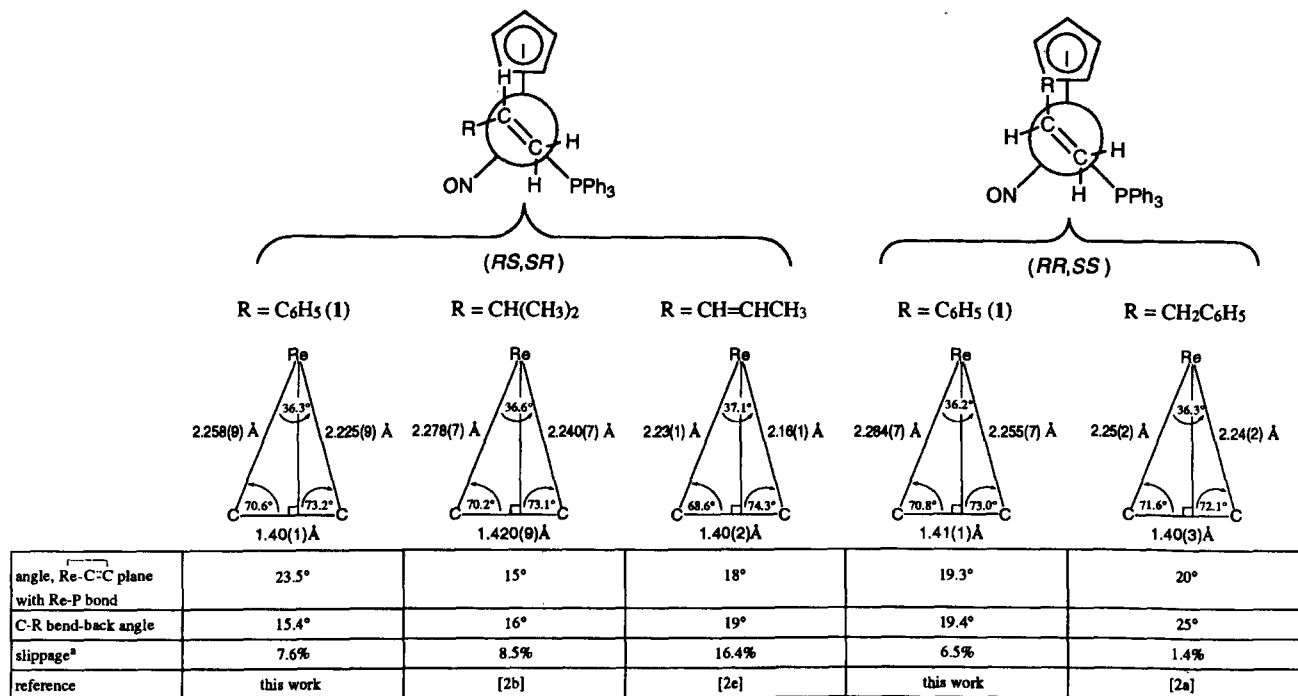


Fig. 3. Superposition of the cations of (*RS,SR*)-1 and (*RR,SS*)-1.



<sup>a</sup>See reference [4b].

Fig. 4. Views of the Re-C≡C planes of monosubstituted alkene complexes of I.

from those in the idealized structures **II** and **III** (0°) found to date. In all cases, the Re-(C≡C) conformation differs from those in **II** and **III** by a slight counterclockwise rotation. Three other monosubstituted alkene complexes have been structurally characterized [2a,b,e], and key data are summarized pictorially in Fig. 4. From this limited sampling, there are no trends or generalizations that we consider statistically significant at this time. Indeed, except for a short Re-CH<sub>2</sub> bond in the piperylene complex (2.16(1) Å) [2e], the data are remarkably uniform.

In summary, this study has filled an important gap of missing structural data involving  $\pi$  complexes of **I** with monosubstituted alkenes, and provided support for structures proposed for the *RR,SS* diastereomers of the corresponding  $\pi$  aldehyde complexes. All of the preceding will be integrated into a comprehensive review in the near future [9].

## 4. Experimental

### 4.1. Crystallography

Yellow prisms were grown by vapor diffusion of ether into CH<sub>3</sub>CN solutions of (*RS,SR*)-**1** and (*RR,SS*)-**1** [2a]. Data were collected as summarized in Table 1. Cell constants were obtained from 16 (30° < 2 $\theta$  < 45°) and 26 reflections (20° < 2 $\theta$  < 45°), respectively. Space

groups were obtained from systematic absences (none;  $h0l$   $h+l=2n+1$ ,  $0k0$   $k=2n+1$ ) and subsequent least-squares refinement. With (*RR,SS*)-**1**, standard reflections showed 8.6% decay during data collection. Lorentz, polarization, decay, and empirical absorption ( $\psi$  scans) corrections were applied. The structures were solved by standard heavy-atom techniques with the Molen/VAX package [10]. Non-hydrogen atoms were refined with anisotropic thermal parameters. The H<sub>2</sub>C = CH hydrogens were located. Other hydrogen atom positions were calculated and added to the structure factor calculations but were not refined. The BF<sub>4</sub><sup>-</sup> anions were disordered, and were refined isotropically with partial site occupancy. Scattering factors, and  $\Delta f'$  and  $\Delta f''$  values were taken from the literature [11].

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## Supplementary material available

Tables of anisotropic thermal parameters for (*RS,SR*)-**1** and (*RR,SS*)-**1** (two pages) and calculated and observed structure factors (20 pages).

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