33. Thermodynamic Enantioface-Binding Selectivities of Monosubstituted Alkenes to a Highly Discriminating Chiral Transition-Metal *Lewis* Acid; Equilibration of Diastereoisomeric (Cyclopentadienyl)(alkene)(nitrosyl)(triphenylphosphine)rhenium Complexes ($[Re(\eta^5\text{-}C_5H_5)(CH_2{=}CHR)(NO)(PPh_3)]^+BF_4^-$)

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Reactions of monosubstituted alkenes $RCH{=}CH_2$ and $[Re(\eta^5\text{-}C_5H_5)(CH_2Cl_2)(NO)(PPh_3)]^+BF_4^-$ give complexes ($[Re(\eta^5\text{-}C_5H_5)(CH_2{=}CHR)(NO)(PPh_3)]^+BF_4^-$ (**1a–g**) in 63–99% yields as mixtures of (*RS,SR*)- and (*RR,SS*)-diastereoisomers (**1a** (R = Me), 66:34; **1b** (R = Pr), 63:37; **1c** (R = $PhCH_2$), 70:30; **1d** (R = Ph), 75:25; **1e** (R = i-Pr), 64:36; **1f** (R = *t*-Bu), 84:16; **1g** (R = Me_3Si), 69:31; *Scheme 2*). These differ in the C=C enantioface bound to the chiral Re fragment. In most cases, the analogous reactions of $RCH{=}CH_2$ and $[Re(\eta^5\text{-}C_5H_5)(C_6H_5Cl)(NO)(PPh_3)]^+BF_4^+$ give comparable results. When **1a–e, g** are heated in PhCl at 95–100°, equilibration to 96:4, 97:3, 97:3, 90:10, > 99: < 1, and > 99: < 1 (*RS,SR*)/(*RR,SS*) mixtures occurs (79–99% recoveries; *Tables 1* and *2*). Thus, thermodynamic enantioface-binding selectivities are much higher than kinetic binding selectivities. This phenomenon is analyzed in detail. A crystal structure of (*RS,SR*)-**1e** (monoclinic, $P2_1/c$, $a = 10.256(1)$ Å, $b = 17.191(1)$ Å, $c = 16.191(1)$ Å, $\beta = 101.04(1)°$, $Z = 4$) shows that the Re–C(1)–C(2) plane (see *Fig. 2*) is nearly coincident with the Re–P bond (angle 15°), and that the i-Pr group is '*syn*' to the nitrosyl ligand.

The asymmetric hydrogenation of alkenes by chiral transition-metal catalysts has seen widespread use in organic synthesis over the last two decades [1]. Mechanisms of enantioselection have been studied in detail [2] and can depend upon either the alkene-binding event or subsequent H_2-addition and hydride-transfer steps. Many other metal-catalyzed asymmetric transformations of alkenes were subsequently developed (for asymmetric oligomerization and polymerization phenomena, see [3]; for asymmetric oxidations, see [4]). In most cases, similar considerations are relevant to product stereogenesis.

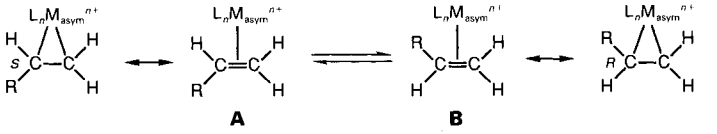
In general, two diastereoisomers are possible for most π complexes of substituted alkenes and chiral metal fragments[1]). These differ in the alkene enantioface bound to the metal, as illustrated for monosubstituted alkenes in **A** and **B** (*Scheme 1*). When viewed as metallacyclopropanes, **A** and **B** can be differentiated by conventional (*R*)/(*S*) descriptors for absolute configuration [6][2]). Although such configurational diastereoisomers were characterized for several classes of chiral alkene complexes [7–11][3]), relatively few studies

[1]) The C=C π faces must be enantiotopic (or equivalently, the alkene must be prochiral). Thus, symmetrical *cis* and geminally disubstituted alkenes can not give π diastereoisomers. If the alkene is itself chiral, additional diastereoisomers are possible. For further analyses, see [5].

[2]) We specify the configuration of the asymmetric C-atom *after* that of the asymmetric metal center.

[3]) For $[Mo(\eta^5\text{-}C_5H_5)(CH_2{=}CHR)(CO)(NO)]_2$, see [7]; for $[Ru(\eta^5\text{-}C_5H_5)(CH_2{=}CHR)(L)(L')]$, see [8]; for $[Fe(\eta^5\text{-}C_5H_5)(CH_2{=}CHR)(CO)(PPh_3)]^+X^-$, see [9]; for other cyclopentadienyl-containing complexes, see [10]; for lead ref. to chiral Pt^{II} complexes, see [11].

Scheme 1. *Configurational Diastereoisomerism in Alkene Complexes of Chiral Metal Fragments*



of binding selectivity are known, either in kinetic or thermodynamic contexts [2a] [8] [11]. Obviously, a rationally designed and efficient receptor for binding one alkene enantioface would be of considerable significance.

We previously reported the synthesis of several chiral (monosubstituted alkene)-rhenium complexes of the formula $[Re(\eta^5\text{–}C_5H_5)(CH_2{=}CHR)(NO)(PPh_3)]^+BF_4^-$ (**1**) [12] from the substitution-labile chlorohydrocarbon complexes $[Re(\eta^5\text{–}C_5H_5)(CH_2Cl_2)(NO)(PPh_3)]^+BF_4^-$ [13] (**2**) and $[Re(\eta^5\text{–}C_5H_5)(C_6H_5Cl)(NO)(PPh_3)]^+BF_4^-$ [14] (**3**; *Scheme 2*). The *Lewis*-acidic, pyramidal Re fragment $[Re(\eta^5\text{–}C_5H_5)(NO)(PPh_3)]^+$ (**I**) was well studied theoretically [15] and possesses the high-lying d orbital (= HOMO) shown in *Fig. 1*.

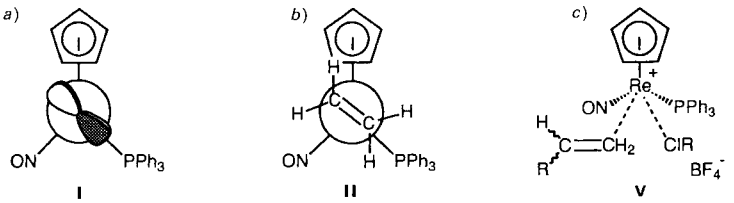


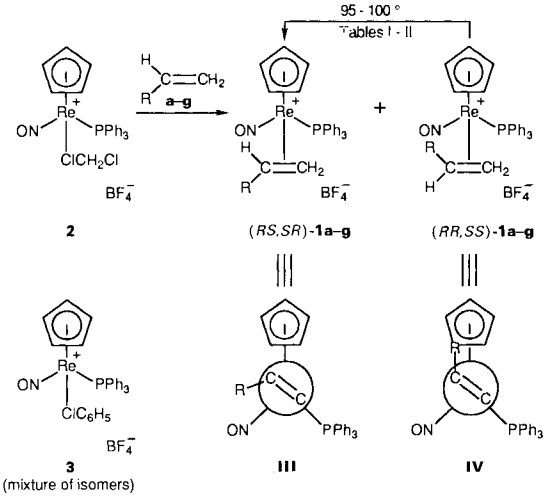
Fig. 1. a) *HOMO of the pyramidal 16-valence-electron Re fragment* $[Re(\eta^5\text{–}C_5H_5)(NO)(PPh_3)]^+$ (**I**), b) *idealized structure of ethylene complex* $[Re(\eta^5\text{–}C_5H_5)(CH_2{=}CH_2)(NO)(PPh_3)]^+$ (**II**), *and* c) *associative transition state*

Accordingly, alkene-ligand conformations of the type shown in the idealized structure **II** were found crystallographically and by ^{1}H-NMR NOE experiments in solution [12] [16]. In the cases examined to date, complexes **1** were obtained as *ca.* 2:1 mixtures of (*RS,SR*)/(*RR,SS*)-diastereoisomers **III** and **IV** [6][2]) (see **1a–d** in *Scheme 2*). In the major diastereoisomer, the alkene substituent is '*syn*' to the small nitrosyl ligand, whereas in the minor diastereoisomer, the substituent is '*syn*' to the medium-sized cyclopentadienyl ligand. Thus, steric factors rationalize the observed diastereoselectivity. However, we had anticipated that the Re fragment **I** would exhibit somewhat greater binding selectivity.

In this paper, we report that this expectation is in fact fully realized under appropriate thermodynamically controlled conditions. The data described herein provide, to our knowledge, the first detailed picture of thermodynamic alkene-enantioface-binding selectivities involving a highly discriminating receptor. A portion of this work was communicated [12a] and a companion mechanistic paper is in press [17].

Results. – 1. *Reactions of Dichloromethane Complex* **2** *and Alkenes: Kinetic Enantioface-Binding Selectivities.* As reported earlier, **2** was combined with propene (**a**) (9 atm), pent-1-ene (**b**), allylbenzene (**c**), and styrene (**d**) at −80°. Workup gave the corresponding alkene complexes $[Re(\eta^5\text{–}C_5H_5)(CH_2{=}CHR)(NO)(PPh_3)]^+BF_4^-$ (**1a**, R=Me; **1b**, R=Pr; **1c**, R=$PhCH_2$; **1d**, R=Ph) in 88–95% yields. The (*RS,SR*)/(*RR,SS*)-diastereoisomer ratios were determined by replicate integrations of cyclopentadienyl ^{1}H-NMR resonances

Scheme 2. *Synthesis of Monosubstituted Alkene Complexes* $[Re(\eta^5\text{–}C_5H_5)(CH_2{=}CHR)(NO)(PPh_3)]^+ BF_4^-$ (**1**)[a])



1 R	From **2**	
	Yield [%]	(*RS,SR*)/(*RR,SS*) Ratio[b])
a Me	95	66:34[c])
b Pr	94	63:37[c])
c $PhCH_2$	88	70:30[c])
d Ph	93	75:25[c])
e i-Pr	99[d])	64:36
f *t*-Bu	73[d])	84:16
g Me_3Si	63	69:31

1 R	From **3**	
	Yield [%]	(*RS,SR*)/(*RR,SS*) Ratio[b])
a Me	90	68:32
b Pr	95	67:33
c $PhCH_2$	90	67:33
d Ph	94	80:20
e i-Pr	99	62:38
f *t*-Bu	82	96:4[e])
g Me_3Si	92	69:31

[a]) Only one enantiomer of the racemic products is depicted.

[b]) Determined by integration of cyclopentadienyl ^{1}H-NMR resonances. Each integer of a diastereoisomer ratio is considered accurate to ±2, *i.e.*, 66:34 = (66 ± 2): (34 ± 2).

[c]) Similar diastereoisomer ratios are reported in [12]. The somewhat higher yields represent optimizations realized in replicate experiments.

[d]) These are yields of crude products; purification gave 59% (**1e**) and 67% (**1f**) yields of analytically pure material.

[e]) The product contained a trace impurity.

(see *Scheme 2*). Importantly, crude and purified reaction mixtures gave identical diastereoisomer ratios, within experimental error. Also, in the case of **1a**, the ratio was independent of propene pressure over the range of 1–9 atm.

Next, bulkier monosubstituted alkenes branched in the allylic positions were studied. The reaction of **2** and 3-methylbut-1-ene (**e**; 5 equiv.) was monitored by ^{31}P-NMR spectroscopy and was markedly slower than that of alkenes **a**–**d**. Some alkene complex $[Re(\eta^5\text{-}C_5H_5)\{CH_2{=}CH(i\text{-}Pr)\}(NO)(PPh_3)]^+BF_4^-$ (**1e**) slowly formed at −20°, but the reaction was complete only after warming to room temperature. Crude **1e** was isolated in 99% yield as a (64 ± 2):(36 ± 2) mixture of (*RS,SR*)/(*RR,SS*)-diastereoisomers. However, detectable quantities of the bridging chloride complex $[[Re(\eta^5\text{–}C_5H_5)(NO)(PPh_3)]_2(\mu\text{-}Cl)]^+BF_4^-$ (**4**), a decomposition product derived from **2**, were present [13]. Silica-gel chromatography gave analytically pure **1e** in 59% yield as a (67 ± 2):(33 ± 2) mixture of diastereoisomers[4]). Thus, the bulkier i-Pr substituent does not give higher kinetic enantioface-binding selectivities than primary alkyl substituents.

A similar reaction of **2** and 3,3-dimethylbut-1-ene (**f**; 5 equiv.) gave crude $[Re(\eta^5\text{–}C_5H_5)\{CH_2{=}CH(t\text{-}Bu)\}(NO)(PPh_3)]^+BF_4^-$ (**1f**) in 73% yield as a (84 ± 2):(16 ± 2) mixture of (*RS,SR*)/(*RR,SS*)-diastereoisomers. Recrystallization gave analytically pure

[4]) Some diastereoisomers of **1** fractionate on silica gel [12b]. Care was taken to avoid any separation in this purification.

1f (67%) as an identical mixture of diastereoisomers. The bridging chloride complex **4** was also isolated in 21% yield. Thus, the bulky *t*-Bu substituent gives a modestly higher kinetic enantioface-binding selectivity.

The analogous reaction of **2** and (trimethylsilyl)ethylene (**g**; 5 equiv.) yielded 63% of analytically pure $[Re(\eta^5\text{-}C_5H_5)(CH_2{=}CHSiMe_3)(NO)(PPh_3)]^+BF_4^-$ (**1g**) as a (69 ± 2):(31 ± 2) mixture of (*RS,SR*)/(*RR,SS*)-diastereoisomers. An identical ratio was present in the crude reaction mixture, and some bridging chloride complex **4** (33%) was also isolated. Thus, a trimethylsilyl substituent does not enhance the kinetic enantioface-binding selectivity.

2. *Reactions of Chlorobenzene Complex* **3** *and Alkenes: Kinetic Enantioface-Binding Selectivities.* The chlorobenzene complex **3** exists as a mixture of linkage and constitutional isomers [16]. However, it is stable with respect to the formation of the bridging chloride complex **4** and, thus, preparatively superior to **2** as a functional equivalent of the *Lewis* acid **I**. Hence, **3** and monosubstituted alkenes **a–g** (5 equiv.) were combined at −45°; workup gave the alkene complexes **1a–g** (*Scheme 2*). All complexes (except **1f**) were pure, and in several cases, their yields improved significantly in comparison with their formation from **2**. The enantioface-binding selectivity of 3,3-dimethylbut-1-ene was also appreciably higher than that obtained with **2**; this effect was reproducible. However, the remaining diastereoisomer ratios were similar.

3. *Thermodynamic Enantioface-Binding Selectivities.* We previously showed that the (*RS,SR*)/(*RR,SS*)-diastereoisomers of **1a–d** interconvert in chlorohydrocarbon solvents at 95–100° [12]. However, a number of precautions are necessary to obtain reliable equilibrium data. *E.g.*, many organometallic compounds undergo decomposition in this temperature region. Also, when equilibrations of (*RS,SR*)/(*RR,SS*)-**1** were attempted in nitrile solvents (PF_6^- salts) [18], some alkene-ligand displacement was observed. Thus, there is the possibility that the competing-decomposition or reaction of one diastereoisomer could lead to an erroneous equilibrium value. Hence, it is essential to verify good mass balance. Further, alkene complexes **1** become less soluble in less polar solvents, and the preferential precipitation of one diastereoisomer could also give misleading data.

Samples of **1a–e, g** were prepared as described above and dissolved in C_6D_5Cl (*ca.* 0.01M) in NMR tubes. Dilute solutions were required to maintain homogeneity, especially in the case of the sparingly soluble styrene complex **1d**[5]). The tubes were kept in a 100° bath, and periodically monitored by ^{1}H-NMR spectroscopy. Resonances of the (*RR,SS*)-diastereoisomers diminished, while those of the (*RS,SR*)-diastereoisomers intensified. Data are given as a function of time in *Table 1*. After equilibrium had been reached, the alkene complexes were recovered in > 99–84% yields. In view of the 3–4 mg scales involved, the error limits on these yields are considerable (±5%). Thus, no special significance should be attached to the runs with the lower recoveries. An analogous series of larger-scale, preparative reactions were conducted under homogeneous conditions (*Table 2*). In all cases, similar diastereoisomer ratios were obtained. Furthermore, mass recoveries were comparable and subject to much smaller error limits (±1%).

Since (trimethylsilyl)ethylene complex **1g** gave the lowest mass balances in *Tables 1* and *2*, a sample of the less stable diastereoisomer (*RR,SS*)-**1g** was isolated by column

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[5]) Alternatively, optically active alkene complexes are much more soluble. Analogous equilibrium data were obtained with (−)-(*SS*)-**1d** [17].

Table 1. *Equilibration of Diastereoisomeric Alkene Complexes* $[Re(\eta^5\text{-}C_5H_5)(CH_2{=}CHR)(NO)(PPh_3)]^+BF_4^-$ (**1**) *in* C_6D_5Cl *at 100°. (*RS,SR*)/(*RR,SS*) Ratios as a Function of Time*[a])

1	R	Time [h]						After isolation (yield [%][b]))
		0	6	12	24	48	72	
a	Me	67:33	91:9	96:4	96:4	95:5	–	96:4 (94)
b	Pr	50:50	86:14	94:6	97:3	97:3	–	97:3 (100)
c	$PhCH_2$	64:36	90:10	96:4	97:3	97:3	–	97:3 (89)
d	Ph	63:37	82:18	88:12	90:10	92:8[c])	90:10	90:10 (88)
e	i-Pr	73:27	> 99: < 1	> 99: < 1	–	–	–	> 99: < 1 (94)
g	Me_3Si	73:27	> 99: < 1	> 99: < 1	–	–	–	> 99: < 1 (84)

[a]) Determined by integration of cyclopentadienyl ^{1}H-NMR resonances. Each integer of a diastereoisomer ratio is considered accurate to ±2, *i.e.* 67:33 = (67 ± 2):(33 ± 2).

[b]) Weights ranged from 3.1 to 3.6 mg. Thus, error limits on the yields are ±5%.

[c]) The C_5H_5 and =C*H*R ^{1}H-NMR resonances of (*RS,SR*)-**1d** overlap in C_6D_5Cl. Thus, the (*RS,SR*)/(*RR,SS*)-**1d** ratios are subject to greater error. However, the ratio subsequent to isolation was measured in CD_2Cl_2 which removed the overlap.

Table 2. *Preparative-scale Equilibration of Diastereoisomeric Alkene Complexes* **1** *in PhCl at 100°*

1	R	Weight [mg]		Time [h]	Yield [%]	(*RS,SR*)/(*RR,SS*)	
		starting	isolated			starting	isolated
a	Me	64	60	36	94	66:34	96:4[a])
b	Pr	70	61	36	87	63:37	97:3[a])
c	$PhCH_2$	64	63	36	99	64:36	98:2[a])
d	Ph	49	44	48	90	65:35	89:11
e	i-Pr	176	175	24	99	67:33	> 99: < 1
g	Me_3Si	37	29	18	79	72:28	> 99: < 1

[a]) Similar preparative data were reported in [12].

chromatography [12b] and submitted to an analogous thermolysis in CD_2ClCD_2Cl (95°, 24 h); diastereoisomerically pure (*RS,SR*)-**1g** was isolated in > 99% yield. This unequivocally demonstrates that (*RR,SS*)-**1g** undergoes isomerization to (*RS,SR*)-**1g**. An identical experiment with styrene complex (*RR,SS*)-**1d** gave (*RS,SR*)/(*RR,SS*)-**1d** (89 ± 2):(11 ± 2) in > 99% yield.

Data for the 3,3-dimethylbut-1-ene complex **1f** are absent in *Tables 1* and *2*. In experiments with (*RS,SR*)/(*RR,SS*)-**1f** (84 ± 2):(16 ± 2), mass recoveries never exceeded the original amount of the more stable diastereoisomer. Furthermore, the rates of disappearance of (*RR,SS*)-**1f** were actually slower than those of (*RR,SS*)-**1e**, **g** (*Table 1*). By-products were also detected. One possibility is that the bulky *t*-Bu group induces a change of the Re–(C$\ddot{-}$C) conformation in **IV**, yielding a less reactive rotamer. Regardless, the (*RS,SR*)/(*RR,SS*) equilibrium ratio should be at least as great as those of **1e**, **g**.

Finally, we sought an expedient preparative route to samples enriched in the (*RS,SR*)-diastereoisomers. Thus, chlorobenzene complex **3** was treated with alkenes **a**–**g** at −45°, and the mixtures brought directly to 95–100°. After 24–48 h, workup gave alkene complexes **1a**–**g** in spectroscopically pure form as (96 ± 2):(4 ± 2) (95%), (97 ± 2):(3 ± 2) (87%), (97 ± 2):(3 ± 2) (96%), (91 ± 2):(9 ± 2) (83%), > 99: < 1 (96%), > 99: < 1 (96%), and > 99: < 1 (95%) mixtures of (*RS,SR*)/*RR,SS*)-diastereoisomers,

respectively. When the reaction mixture containing **1e** was kept for seven days at room temperature, single crystals of (*RS,SR*)-**1e** formed and were isolated in 55% yield.

4. *Spectroscopic and Structural Properties.* The new alkene complexes **1e–g** were characterized by IR and NMR (^{1}H, ^{13}C, ^{31}P) spectroscopy, as described in the *Exper. Part.* Properties generally paralleled those previously noted for **1a–d** [12b]. *E.g.*, the CH_2=CHR C-atoms, which are '*syn*' to the PPh_3 ligand, exhibited larger ^2J(C,P) values (4–6 Hz) than the CH_2=*C*HR C-atoms. However, some NMR chemical shift trends of the (*RS,SR*)- and (*RR,SS*)-diastereoisomers were reversed in **1f, g** (*e.g.*, the (*RR,SS*) CH_2=CHR and CH_2=CH*C* ^{13}C resonances, and *CHH'*=CHR ^{1}H resonances), possibly due to the bulk of the alkene substituents.

We sought to probe, whether the bulkier substituents might effect a significant deviation from the idealized structure **II** (*Fig. 1b*). Thus, X-ray data were collected for the 3-methylbut-1-ene complex (*RS,SR*)-**1e** (*Table 3*). Refinement (see *Exper. Part*) gave the structure shown in *Fig. 2*. All vinylic and allylic protons were located. Selected bond lengths, bond angles, and torsion angles are given in *Table 4*.

Table 3. *Crystallographic Data for the 3-Methylbut-1-ene Complex (*RS,SR*)-[Re(η^5–C_5H_5){CH_2=CH(*i*-Pr)}(NO)(PPh_3)]$^+BF_4^-$ ((*RS,SR*)-**1e**)*

Molecular formula	$C_{28}H_{30}BF_4NOPRe$	Scan speed [deg/min]	variable
Formula weight	700.54	Range/indices (h,k,l)	0 11, 0 20, −18 18
Crystal system	monoclinic	Scan range	0.8 + 0.14 tan θ
Space group	$P2_1/c$	No. of reflections between stds.	1 X-ray h
Cell dimensions: a [Å]	10.256(1)	Total unique data	5245
b [Å]	17.191(1)	Observed data, $I > 3\sigma(I)$	4761
c [Å]	16.191(1)	Abs. coeff. (μ) [cm^{-1}]	91.34
β [deg]	101.04(1)	Min. transmission [%]	54.41
V [Å^3]	2801.82	Max. transmission [%]	99.66
Z	4	No. of variables	343
d_{calc} [g/cm^3] (15°)	1.661	$R\,\Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0415
d_{obs}, g/cm^3 (22°)	1.653	$R_w[\Sigma\omega(\|F_o\| - \|F_c\|)^2/\Sigma\omega\|F_o\|^2]^{1/2}$	0.0494
Crystal dimensions [mm]	0.31 × 0.24 × 0.18	Goodness of fit	1.7629
Radiation [Å]	λ (CuKα) 1.54056	Δ/σ (max)	0.014
Data-collection method	θ–2θ	$\Delta\rho$ (max) [eÅ^{-3}]	1.082 (0.9 Å from Re)

Fig. 2b shows that (*RS,SR*)-**1e** adopts a Re–(C=C) conformation that is rotated slightly counter-clockwise from that of **II**. This feature can be quantified in several ways.

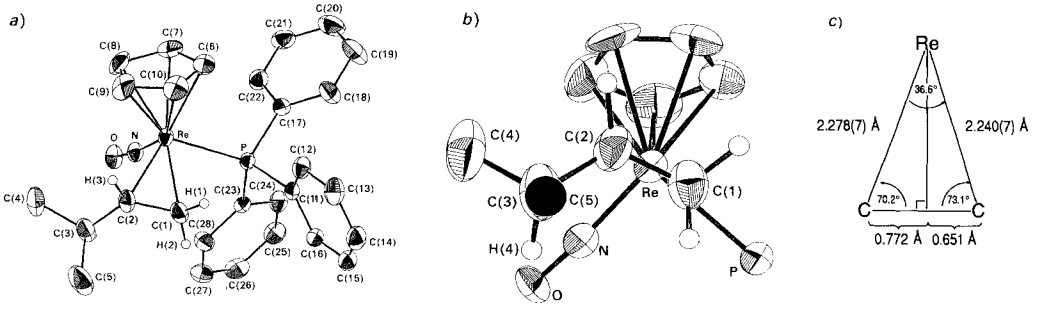


Fig. 2. *Structure of the cation of the 3-methylbut-1-ene complex (*RS,SR*)-[Re(η^5–C_5H_5){CH_2=CH(*i*-Pr)}(NO)(PPh_3)]$^+BF_4^-$ ((*RS,SR*)-**1e**).*
a) Numbering diagram; *b*) *Newman*-type projection; *c*) view of the Re–C(1)–C(2) plane.

Table 4. *Key Bond Lengths* [Å], *Bond Angles* [°], *and Torsion Angles* [°] *in (*RS,SR*)*-**1e**

Re–P	2.413(1)	Re–N	1.775(5)
Re–C(1)	2.240(7)	Re–C(2)	2.278(7)
Re–C(6)	2.335(7)	Re–C(7)	2.292(7)
Re–C(8)	2.294(7)	Re–C(9)	2.323(7)
Re–C(10)	2.336(7)	N–O	1.156(7)
P(1)–C(11)	1.817(6)	P–C(17)	1.819(6)
P(1)–C(23)	1.826(6)	C(1)–C(2)	1.420(9)
C(2)–C(3)	1.52(1)	C(3)–C(4)	1.52(1)
C(3)–C(5)	1.51(1)	C(6)–C(7)	1.43(1)
C(6)–C(10)	1.38(1)	C(7)–C(8)	1.44(1)
C(8)–C(9)	1.40(1)	C(9)–C(10)	1.42(1)
P–Re–N	90.2(2)	P–Re–C(1)	77.9(2)
P–Re–C(2)	113.1(2)	N–Re–C(1)	104.1(3)
N–Re–C(2)	93.9(2)	C(1)–Re–C(2)	36.6(2)
Re–P–C(11)	115.9(2)	Re–P–C(17)	112.0(2)
Re–P–C(23)	113.8(2)	Re–N–O	173.1(5)
Re–C(1)–C(2)	73.1(4)	Re–C(2)–C(1)	70.2(4)
Re–C(2)–C(3)	116.1(5)	C(1)–C(2)–C(3)	121.0(7)
C(2)–C(3)–C(4)	110.8(8)	C(2)–C(3)–C(5)	105.8(8)
C(4)–C(3)–C(5)	110.6(8)	C(7)–C(6)–C(10)	108.4(7)
C(6)–C(7)–C(8)	106.5(8)	C(7)–C(8)–C(9)	107.8(8)
C(8)–C(9)–C(10)	108.2(8)	C(6)–C(10)–C(9)	109.0(8)
Re–C(1)–C(2)–C(3)	109(1)	Re–C(1)–C(2)–H(3)	– 91(1)
H(1)–C(1)–C(2)–Re	98(1)	H(1)–C(1)–C(2)–C(3)	– 153(1)
H(1)–C(1)–C(2)–H(3)	6(1)	H(2)–C(1)–C(2)–Re	– 117(1)
H(2)–C(1)–C(2)–C(3)	– 7(1)	H(2)–C(1)–C(2)–H(3)	152(1)
Re–C(2)–C(3)–C(4)	– 81(1)	Re–C(2)–C(3)–C(5)	159(1)
Re–C(2)–C(3)–H(4)	35(1)	C(1)–C(2)–C(3)–C(4)	– 163(1)
C(1)–C(2)–C(3)–C(5)	77(1)	C(1)–C(2)–C(3)–H(4)	– 47(1)
H(3)–C(2)–C(3)–C(4)	36(1)	H(3)–C(2)–C(3)–C(5)	– 84(1)
H(3)–C(2)–C(3)–H(4)	152(1)	P–Re–C(1)–C(2)	– 164(1)
N–Re–C(1)–C(2)	– 77(1)		

E.g., the Re–C(1)–C(2) plane and Re–P and Re–N bonds define angles of 0 and 90°, respectively, in **II**. In (*RS,SR*)-**1e**, the corresponding angles are 15 and 71°. Alternatively, the angle of the Re–C(1)–C(2) plane with the plane defined by the cyclopentadienyl centroid, Re and C(1)–C(2) centroid is 45° in **II** and 66° in (*RS,SR*)-**1e**. These deviations move C(2) further away from and bring C(1) closer to the cyclopentadienyl ligand. Thus, distances between the olefinic atoms H(3) and H(1) and the cyclopentadienyl-ligand C-atoms were calculated to be H(3)–C(9) 2.51, H(3)–C(10) 2.93, H(1)–C(10) 3.12, and H(1)–C(9) 3.73 Å.

Fig. 2 further shows that the i-Pr group in (*RS,SR*)-**1e** adopts a conformation that directs the smallest allylic substituent (H-atom) towards the nitrosyl ligand, diminishing steric interactions. Also, the C=C substituents are bent out of the π nodal plane of the free alkene. This was measured by several methods. First, a plane was defined that contained C(1) and C(2) and was perpendicular to the Re–C(1)–C(2) plane. The angles of the C(2)–C(3), C(2)–H(3), C(1)–H(1), and C(1)–H(2) bonds with this plane were 16, 1, 7, and 24°, respectively. This plane also made a 23° angle with the H(2)–C(1)–C(2)–C(3) least-squares plane. All these angles would be 0° in an idealized sp^2-hybridized alkene.

Finally, the more informative but derivationally more complex α, β, and β' angles utilized by *Ibers* were also calculated (49, 57, and 73°) [19].

The C(1)–C(2) and Re–C bond lengths in (*RS,SR*)-**1e** (1.420(9), 2.240(7), and 2.278(7) Å) were similar to those found earlier in the crystal structure of allylbenzene complex (*RR,SS*)-**1c** (1.40(3), 2.24(2), 2.25(2) Å; PF_6^- salt) [12]. However, these constitute opposite diastereoisomers, with the latter directing an alkyl substituent towards the cyclopentadienyl ligand. Nonetheless, the Re–(C=C) conformation of (*RS,RS*)-**1c** shows a comparable counter-clockwise deviation from that of **II**, as judged by the angles of the Re–C(1)–C(2) plane with the Re–P and Re–N bonds (18 and 70°, resp.).

Discussion. 1. *Chiral Recognition in Alkene Complexes* **1**. In order to best interpret the modest kinetic enantioface-binding selectivities summarized in *Scheme 2*, mechanistic data are required. In work in progress, we have studied the kinetics of substitution of the CH_2Cl_2 ligand in **2** by tropone and several related reactions [20]. In all cases, data are best accommodated by *associative* mechanisms. In fact, experiments described elsewhere establish that the equilibration of (*RS,SR*)- and (*RR,SS*)-**1** occurs *without* alkene dissociation [17]. Thus, the free *Lewis* acid **I** does not appear to play a role in *Scheme 2*. Nonetheless, many properties of **I**, such as binding constants and frontier orbitals, remain applicable to and can be addressed by this chemistry.

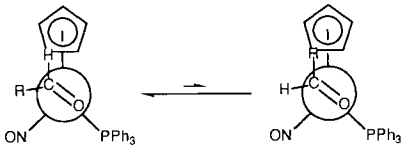
All substitution reactions of **2** and **3** studied to date occur with *retention* of configuration at the Re-atom [13] [14]. Thus, we suggest 'frontside' displacements of the coordinated chlorohydrocarbons as sketched in **V** (one of several possible transition states; see *Fig. 1*). It is further possible that the nitrosyl ligand might 'bend' or the cyclopentadienyl ligand 'slip' to a η^3-coordination mode [21] at some point on the reaction coordinate. The CH_2= terminus of simple monosubstituted alkenes is commonly more nucleophilic or prone to electrophilic attack. Thus, the =CHR terminus, which becomes an asymmetric center in **1**, will be remote from the existing asymmetric Re-center in the transition state. We propose that this accounts for the low degree of chiral recognition in the binding event.

We further propose that the much higher thermodynamic enantioface-binding selectivities (*Tables 1* and *2*) simply reflect the closer proximity of the asymmetric Re- and C-centers in the products **1**, and the relative sizes of the cyclopentadienyl and nitrosyl ligands as analyzed above. We consider the values in the last column in *Table 1* to best represent the true equilibrium constants. Several trends are evident in both the kinetic and thermodynamic data.

First, the highest kinetic enantioface-binding selectivities (*Scheme 2*) are found with the bulkiest and least reactive alkene 3,3-dimethylbut-1-ene (**f**). The larger (*RS,SR*)/(*RR,SS*)-**1f** ratio obtained from chlorobenzene complex **3** may indicate a departure from the substitution mechanism shown in **V**. NMR data suggest that with less reactive *Lewis* bases, **3** can undergo chlorobenzene-ligand oxidative addition prior to adduct formation [14]. The lower kinetic enantioface-binding selectivity of (trimethylsilyl)ethylene is likely due to the greater Si–C bond length (1.86 *vs. ca.* 1.54 Å for C–C bonds) [22]. Second, the highest thermodynamic enantioface-binding selectivities are found with aliphatic alkenes that are branched in the allylic position or with silicon analogs ($> 99 : < 1$). However, alkenes that are unbranched give only slightly lower selectivities ((96–97):(4–3)). Finally, the Ph substituent in styrene gives still lower selectivity ((90–89):(10–11)), and a rationale is suggested below.

2. *Chiral Recognition in Other π Adducts of* **I**. It is instructive to compare the preceding data (*Scheme 2* and *Tables 1* and *2*) with that obtained for the corresponding π aldehyde complexes $[Re(\eta^5\text{–}C_5H_5)(NO)(PPh_3)(\eta^2\text{–}RCH{=}O)]^+BF_4^-$ (**5**) [23]. Aldehydes and monosubstituted alkenes differ only at one π terminus (CH_2= *vs.* O=) and, thus, are approximately 'isosteric'. Accordingly, aldehyde complexes **5** adopt Re–(X$\ddot{}$–CHR) conformations analogous to those of **1** [23] [24], as shown in **VI** and **VII** (*Scheme 3*). In contrast to **III** and **IV**, these rapidly interconvert below room temperature and readily attain equilibrium. The isomerization mechanism involves intermediate σ complexes, a type of energy minimum not available to alkene complexes **1**. Some thermodynamic aldehyde enantioface-binding selectivities that were determined by low-temperature NMR are given in *Scheme 3*. Aliphatic aldehydes appear to exhibit somewhat higher binding selectivities towards **I** (> 99:1) than unbranched aliphatic alkenes. However, these equilibria are established at temperatures that differ by > 100°, and thus are not exactly comparable. In both series of compounds, a Ph substituent lowers selectivity. This may have two origins. First, by some steric criteria, a Ph group can be smaller than a Me group [25]. Second, a Ph group should allow greater positive-charge localization onto the X=C C-atom, resulting in 'slippage' [26] away from the Re-atom. The resulting increase in distance between the asymmetric Re- and C-centers would attenuate chiral recognition. This electronic effect is being systematically probed in aldehyde complexes **5** by X-ray crystallography [27].

Scheme 3. *Selected Aldehyde-Enantioface-Binding Selectivities in* $[Re(\eta^5\text{–}C_5H_5)(NO)(PPh_3)(\eta^2\text{–}RCH{=}O)]^+BF_4^-$ (**5**)



VI **VII**

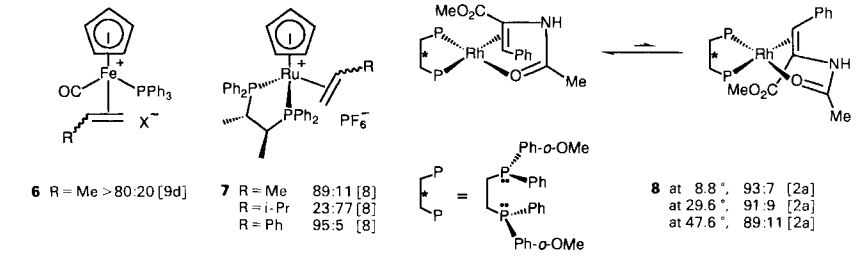
R of **5**	(*RS,SR*)/(*RR,SS*) Ratio (**VI**/**VII**) [23]
alkyl	> 99:1
4-CF_3–C_6H_4	88:12
Ph	86:14
4-Me–C_6H_4	82:18

In preliminary work, we analogously probed the kinetic and thermodynamic enantioface-binding selectivities of unsymmetrical geminally disubstituted alkenes, RR′C=CH_2 [28]. In all cases, kinetic and thermodynamic selectivities are lower. *E.g.*, reaction of **2** and 2-methylpent-1-ene gives a (50 ± 2):(50 ± 2) mixture of diastereoisomeric alkene complexes. Upon equilibration, a (68 ± 2):(32 ± 2) mixture is obtained. The dominant diastereoisomer has the smaller Me substituent '*syn*' to the cyclopentadienyl ligand and the larger Pr substituent '*syn*' to the NO ligand. Thus, the size difference between Me and H substituents is sufficient to provide good thermodynamic enantioface-binding selectivity (**1a**), but the size difference between Me and Et substituents is not.

A logical approach to enhanced thermodynamic binding selectivities would be to increase the bulk of the cyclopentadienyl ligand. This should further disfavor **IV** relative to **III** (see *Scheme 2*). Accordingly, pentamethylcyclopentadienyl analogs of **1** are currently under study. The related complex $[Re(\eta^5\text{–}C_5Me_5)(CH_2{=}CHMe)(CO)(PMe_3)]$ was prepared by *Zhuang* and *Sutton* and appears to be diastereoisomerically homogeneous [10c].

3. *Chiral Recognition in Other Alkene Complexes.* (Alkene)iron complexes of the formula $[Fe(\eta^5\text{–}C_5H_5)(CH_2{=}CHR)(CO)(PPh_3)]^+X^-$ (**6**; *Scheme 4*) can be viewed as isoelectronic and isosteric to **1** [9]. However, metal-ligand bonds are commonly 6–9% shorter in this series of compounds [12b]. Thus, thermodynamic alkene-enantioface-binding selectivities greater than those in *Tables 1* and *2* might be expected. Most syntheses appear to give mixtures of diastereoisomers [9a, c]. However, *Brookhart* finds that the less stable diastereoisomer of the propene complex $[Fe(\eta^5\text{–}C_5H_5)(CH_2{=}CHMe)(CO)(PPh_3)]^+TfO^-$ can be generated by rearrangement of the corresponding propylidene complex, and it equilibrates to a > 80:20 mixture of diastereoisomers between −40 and 0° [9d]. Thus, equilibrium is much more readily achieved than for Re complexes **1**.

Scheme 4. *Other Thermodynamic Binding Selectivities for Complexes of Chiral Metal Fragments and Alkenes*



6 R = Me >80:20 [9d]

7 R = Me 89:11 [8]
R = i-Pr 23:77 [8]
R = Ph 95:5 [8]

8 at 8.8 °, 93:7 [2a]
at 29.6 °, 91:9 [2a]
at 47.6 °, 89:11 [2a]

9 R = Me 56:44 [11a]
Et 45:55 [11a]
i-Pr 34:66 [11a]
Ph 75:25 [11a]

10 R = Me 51:49 [11b]
t-Bu 55:45 [11b]
Ph 65:35 [11b]
4-Cl–C_6H_4 59:41 [11b]
4-Me–C_6H_4 62:38 [11b]

Faller et al. reported that one diastereoisomer of the sterically similar neutral (propene)iron complex $[Fe(\eta^5\text{–}C_5H_5)(CH_2{=}CHMe)(CO)(SnR_3)]$ (R=Ph, Me) is thermally more stable than the other [10a]. Also, *Kegley et al.* recently found that acrylate esters and styrenes can bind to Mo fragments of the formulae $[Mo(\eta^5\text{–}C_5H_5)(CO)(PR_2CH_2CH_2PR_2)]^+$ with high thermodynamic selectivities [10d]. In some cases, high kinetic selectivities are also observed.

In other relevant work, *Consiglio* and coworkers prepared optically active (monosubstituted alkene)ruthenium complexes of the formulae $[Ru(\eta^5\text{–}C_5H_5)\{PPh_2CH(Me)CH(Me)PPh_2\}(CH_2{=}CHR)]^+PF_6^-$ (**7**; *Scheme 4*) [8]. In all cases, the diastereoisomers readily equilibrate at or below room temperature. Representative thermodynamic enantioface-binding selectivities are given in *Scheme 4*. Interestingly, propene exhibits an enantioface-binding preference *opposite* to that of 3-methylbut-1-ene (R=i-Pr). Also, styrene binds *more* selectively than propene. *Consiglio* and coworkers concluded, based upon these and other data, that binding selectivities in **7** do not depend solely upon steric factors. Crystallographic data that would enable diastereoisomer assignments are not yet available.

Halpern and *Landis* demonstrated very high enantioface-binding selectivities for adducts **8** of chiral Rh fragments and the chelating methyl (*Z*)-α-acetamidocinnamate ligand (*Scheme 4*) [2a]. Binding selectivities depend slightly upon temperature and are higher for other chiral chelating diphosphines. Complexes analogous to **8** are intermediates in a large and extensively studied class of highly enantioselective Rh^{I}-catalyzed hydrogenations. Interestingly, the *less* stable diastereoisomer is always more reactive.

Finally, the binding of monosubstituted alkenes to various chiral Pt^{II} fragments has also been studied [11]. However, most diastereoselectivities obtained to date are modest. *E.g.*, *Boucher* and *Bosnich* characterized a series of optically active sulfoxide complexes *cis*-[Pt(Cl)$_2${ArS(O)Me}(CH_2=CHR)] (**9**; *Scheme 4*) [11a]. As would be expected, 3-methylbut-1-ene (R=i-Pr) exhibits a larger enantioface-binding selectivity than but-1-ene. However, as with **7**, propene binds preferentially by the opposite enantioface. Also, styrene exhibits a higher binding selectivity than aliphatic alkenes. Enhanced styrene-binding selectivity is also observed in the related complexes **10** (*Scheme 4*) [11b], but electron-withdrawing and electron-donating *para*-substituents both give lower selectivities. Very recently, high binding selectivities were found for allylic alcohols in related compounds [11d].

Conclusion. – The rhenium *Lewis* acid **I** is, to our knowledge, the only chiral transition-metal fragment that gives both high enantioface-binding selectivities for simple monosubstituted alkenes and isolable, readily characterized adducts. In constrast to most of the complexes shown in *Scheme 4*, the direction and magnitude of equilibria are easily rationalized from simple stereoelectronic considerations. The structural models developed (*Fig. 1* and *Scheme 2*) are supported by a variety of NMR and crystallographic experiments [12] [16].

Many synthetic applications can be envisioned for such a marked and general chiral recognition phenomenon. In this context, it should be emphasized that alkene complexes **1** are easily accessed in enantiomerically pure form and that diastereoisomer equilibrations occur with essentially complete retention of configuration at the Re-atom [12]. In work to date, we find that Me_2CuLi adds regiospecifically to the more substituted C-atom of **1** and from a direction *anti* to the Re-atom to give secondary alkyl complexes [Re{RCH(Me)CH_2}(η^5–C_5H_5)(NO)(PPh_3)] in > 99% diastereoisomeric (and > 97% enantiomeric) excesses [29]. Studies involving oxidants, basic reagents [30], and other nucleophiles are in progress.

In conclusion, this study has provided thermodynamic enantioface-binding selectivities for the first rationally designed and highly discriminating receptor for monosubstituted alkenes. Future papers will describe the unusual mechanism by which equilibrium is reached [17].

Experimental Part

General. Solvents were purified as follows: Et_2O and THF, distilled from Na/benzophenone; hexanes, distilled from Na; CH_2Cl_2 and PhCl, distilled from P_2O_5; $CDCl_3$, vacuum transferred from CaH_2; CD_2ClCD_2Cl, used as received. Reagents were obtained as follows: alkenes from *Matheson*, *Alfa*, or *Aldrich*, used as received; $HBF_4 \cdot OEt_2$ from *Aldrich*, standardized as reported previously [13]. All reactions were carried out under a dry N_2 atmosphere. M.p.: in evacuated capillaries without thermometer calibration. IR Spectra (cm^{-1}): *Mattson-Polaris-FT* spectrometer. NMR Spectra: *Varian-XL-300* spectrometers; at r.t. unless noted; ^1H referenced to internal $SiMe_4$ (δ 0.00), ^{13}C to $CDCl_3$ (77.0 ppm), and ^{31}P to external 85% H_3PO_4 (0.00 ppm); all coupling constants *J* in

Hz. MS ($^m/_z$ (rel. intensity)): *VG-Micromass-7050-E* double-focusing high-resolution instrument. Microanalyses were conducted by *Atlantic Microlab, Inc.*

(Cyclopentadienyl)(propene)nitrosyl(triphenylphosphine)rhenium(I) Tetrafluoroborate ([Re(η^5–C_5H_5)-(CH_2=CHMe)(NO)(PPh_3)]$^+BF_4^-$; **1a**). To a mixture of [Re(Me)(η^5–C_5H_5)(NO)(PPh_3)] (**11**; 0.056 g, 0.100 mmol) [31] and CH_2Cl_2 (3 ml) in a *Schlenk* flask (capped with a septum secured with copper wire) cooled to −80°, $HBF_4 \cdot Et_2O$ (12 µl, 0.110 mmol) was added with stirring. After 15 min, excess propene was condensed into the flask. After 30 min, the cold bath was removed and the soln. stirred for 18 h. The mixture was filtered into hexane (50 ml) and the resulting tan powder collected by filtration, washed with pentane (2 × 3 ml), and dried *in vacuo*: **1a** (0.064 g, 95%), (*RS,SR*)/(*RR,SS*) [12b][6]. A procedure reported earlier required a pressure apparatus [12b].

(Cyclopentadienyl)(3-methylbut-1-ene)nitrosyl(triphenylphosphine)rhenium(I) Tetrafluoroborate ([Re(η^5–C_5H_5){CH_2=CH(i-Pr)}(NO)(PPh_3)]$^+BF_4^-$; **1e**). To **11** (0.056 g, 0.100 mmol) and CH_2Cl_2 (0.5 ml) in a 5-mm NMR tube at −80°, $HBF_4 \cdot Et_2O$ (12 µl, 0.110 mmol) was added. The tube was shaken and quickly transferred to a −78° NMR probe to verify the formation of [Re(η^5–C_5H_5)(CH_2Cl_2)(NO)(PPh_3)]$^+BF_4^-$ (**2**) [13]. Then 3-methylbut-1-ene (0.11 ml, 1.0 mmol) was added and the tube returned to the probe. The reaction was monitored by ^{31}P-NMR as the probe was warmed from −78 to 20°. Complex **1e** began to form at −20°. The sample was kept at r.t. for 2 days and then filtered through glass microfibers, which were rinsed with CH_2Cl_2 (1 ml). Hexane (5 ml) was added to the filtrate and the resulting brown powder collected by filtration: crude **1e** (0.069 g, 99%), (*RS,SR*)/(*RR,SS*) (64 ± 2):(36 ± 2). The powder was chromatographed (15 × 1.3 cm, silica gel, acetone/CH_2Cl_2 5:95 (*v/v*))[4]: **1e** (0.041 g, 59%), (*RS,SR*)/(*RR,SS*) (67 ± 2):(33 ± 2)[7]. M.p. 125–128° (dec.). IR (film): 1719*vs* (NO). ^{1}H-NMR ($CDCl_3$): (*RS,SR*)-**1e**: 7.60–7.20 (*m*, PPh_3); 5.78 (*s*, C_5H_5); 4.29 (*m*, CHR); 2.40 (*ddd*, *J*(H,H) = 4.2, 11.1, *J*(H,P) = 11.1, H_{trans} to H); 2.31 (*ddd*, *J*(H,H) = 4.2, 9.7, *J*(H,P) = 6.3, H_{cis} to H); 1.50 (*m*, $(CH_3)_2CH$); 1.22 (*d*, *J*(H,H) = 6.6, 3 H, CH_3CH); 1.19 (*d*, *J*(H,H) = 6.5, 3 H, C′H_3CH; (*RR,SS*)-**1e** (partial data): 5.73 (*s*, C_5H_5); 1.32 (*d*, *J*(H,H) = 6.6, 3 H, CH_3CH; 1.28 (*d*, *J*(H,H) = 6.5, 3 H, C′H_3CH). ^{13}C-NMR: (*RS,SR*)-**1e**: 133.0 (*d*, *J*(C,P) = 9.9, C_o); 132.1 (*s*, C_p); 130.2 (C_{ipso})[8]); 129.5 (*d*, *J*(C,P) = 10.9, C_m); 96.8 (*s*, C_5H_5); 59.8 (*s*, CH_2=CHR); 37.4 (*s*, $(CH_3)_2CH$); 36.5 (*d*, *J*(C,P) = 4.9, CH_2=CHR); 28.3, 23.5 (2*s*, $(CH_3)_2CH$); (*RS,RS*)-**1e**: 97.0 (*s*, C_5H_5); 67.4 (*s*, CH_2=CHR); 36.5 (*s*, $(CH_3)_2CH$); 34.1 (br. *s*, CH_2=CHR); 29.8, 23.4 (2*s*, $(CH_3)_2CH$). ^{31}P-NMR: (*RS,SR*)-**1e**: 11.2 (*s*); (*RR,SS*)-**1e**: 12.5 (*s*). MS[9]): 614 (20, M^+), 544 (100, $[M - C_5H_{10}]^+$). Anal. calc. for $C_{28}H_{30}BF_4NOPRe$: C 48.01, H 4.32, N 2.00; found: C 47.93, H 4.31, N 2.07.

(Cyclopentadienyl)(3,3-dimethylbut-1-ene)nitrosyl(triphenylphosphine)rhenium(I) Tetrafluoroborate ([Re-(η^5–C_5H_5){CH_2=CH(*t*-Bu)}(NO)(PPh_3)]$^+BF_4^-$; **1f**). To **11** (0.140 g, 0.250 mmol) and CH_2Cl_2 (0.5 ml; *Schlenk* flask) at −80°, $HBF_4 \cdot Et_2O$ (27 µl, 0.250 mmol) was added with stirring. After 15 min, 2,2-dimethylbut-1-ene (0.258 ml, 2.000 mmol) was added. The cold bath was removed and the mixture stirred at r.t. for 12 h. A tan powder formed, which was collected by filtration to give [Re(η^5–C_5H_5)(NO)(PPh_3)]$_2$(μ–Cl)]$^+BF_4^-$ (**4**; 0.031 g, 21%). Et_2O (5 ml) was added to the filtrate and the resulting brown powder collected by filtration: crude **1f** (0.130 g, 73%), (*RS,SR*)/(*RR,SS*) (84 ± 2):(16 ± 2), which contained detectable amounts of **4** and other impurities. The powder was dissolved in THF (5 ml), and hexane (30 ml) was added. The resulting precipitate was collected by filtration and dried *in vacuo*: **1f** (0.120 g, 67%), (*RS,SR*)/(*RR,SS*) (84 ± 2):(16 ± 2). M.p. 122–124° (dec.). IR (film): 1713*vs* (NO). ^{1}H-NMR ($CDCl_3$): (*RS,SR*)-**1f**: 7.72–7.30 (*m*, PPh_3); 5.81 (*s*, C_5H_5); 4.55 (*dd*, *J*(H,H) = 11.2, 12.0, CHR); 2.48 (*ddd*, *J*(H,H) = 3.8, 11.2, *J*(H,P) = 7.7, H_{cis} to H); 2.34 (*ddd*, *J*(H,H) = 3.8, 12.0, *J*(H,P) = 13.3, H_{trans} to H); 0.99 (*s*, *t*-Bu); (*RR,SS*)-**1f** (partial data): 5.70 (*s*, C_5H_5). ^{13}C-NMR: (*RS,SR*)-**1f**: 133.1 (*d*, *J*(C,P) = 9.8, C_o); 132.2 (*s*, C_p); 130.1 (C_{ipso})[8]); 129.5 (*d*, *J*(C,P) = 11.0, C_m); 97.0 (*s*, C_5H_5); 65.7 (*s*, CH_2=CHR); 37.5 (*s*, $(CH_3)_3C$); 33.9 (*d*, *J*(C,P) = 5.1, CH_2 = CHR); 30.7 (*s*, $(CH_3)_3$C); (*RR,SS*)-**1f** (partial data): 98.1 (*s*, C_5H_5); 65.5 (*s*, CH_2=CHR); 37.7 (*s*, $(CH_3)_3C$); 34.1 (*d*, *J*(C,P) = 3.5, CH_2 = CHR); 31.1 (*s*, $(CH_3)_3$C). ^{31}P-NMR: (*RS,SR*)-**1f**: 9.0 (*s*); (*RR,SS*)-**1f**: 9.3 (*s*). MS[9]): 628 (20, M^+), 544 (100, $[M - C_6H_{12}]^+$). Anal. calc. for $C_{29}H_{32}BF_4NOPRe$: C 48.75, H 4.51, N 1.96; found: C 48.72, H 4.47, N 2.01.

(Cyclopentadienyl)nitrosyl[(trimethylsilyl)ethene](triphenylphosphine)rhenium(I) Tetrafluoroborate ([Re-(η^5–C_5H_5)(CH_2=CHSiMe$_3$)(NO)(PPh_3)]$^+BF_4^-$; **1g**). *a*) Complex **11** (0.056 g, 0.100 mmol), CH_2Cl_2 (1.0 ml), $HBF_4 \cdot Et_2O$ (12 µl, 0.110 mmol), and (trimethylsilyl)ethene (0.077 ml, 0.500 mmol) were combined at −80° in a procedure analogous to that given for **1f**. The mixture was kept at r.t. for 48 h. An identical workup gave **4** (0.020 g, 33%) and **1g** (0.046 g, 63%), (*RS,SR*)/(*RR,SS*) (69 ± 2):(31 ± 2). M.p. 132–135° (dec.). IR (film): 1711*vs* (NO).

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[6]) The IR and ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were identical with those of an authentic sample.

[7]) An identical yield and diastereoisomer ratio was obtained when this reaction was conducted on a 0.50 mmol scale in a *Schlenk* flask.

[8]) One line of the *d* is obscured.

[9]) Conditions: FAB, pos. mode, 5 kV, Ar, 3-nitrobenzyl alcohol/$CHCl_3$ matrix, ^{187}Re.

MS[8]): 644 (65, M^+), 544 (100, $[M - C_5H_{12}Si]^+$). Anal. calc. for $C_{28}H_{32}BF_4NOPReSi$: C 46.03, H 4.41, N 1.92; found: C 45.80, H 4.35, N 1.89.

b) A sample of **1g** was prepared as above (0.074 g, 0.102 mmol) and chromatographed [12b] (silica gel, 15 × 1.3 cm, acetone/CH_2Cl_2 4:96 (*v*/*v*)): pure (*RR,SS*)-**1g** (0.013 g, 17%), (*RS,SR*)-**1g** (0.025 g, 33%), and a (38 ± 2):(62 ± 2) mixture (*RS,SR*)/(*RR,SS*)-**1g** (0.011 g, 15%) were obtained by combining fractions.

(*RS,SR*)-**1g**: ^{1}H-NMR ($CDCl_3$): 7.62–7.20 (*m*, PPh_3); 5.82 (*s*, C_5H_5); 3.04 (*dd*, *J*(H,H) = 13.5, 14.2, CHR); 2.77 (*ddd*, *J*(H,H) = 2.2, 13.5, *J*(H,P) = 7.6, H_{cis} to H); 2.37 (*ddd*, *J*(H,H) = 2.2, 14.2, *J*(H,P) = 9.8, H_{trans} to H); −0.02 (*s*, 3 CH_3). ^{13}C-NMR: 133.1 (*d*, *J*(C,P) = 9.8, C_o); 132.1 (*s*, C_p); 129.6 (*d*, *J*(C,P) = 57.7, C_{ipso}); 129.4 (*d*, *J*(C,P) = 11.0, C_m); 97.2 (*s*, C_5H_5); 42.7 (*d*, *J*(C,P) = 5.1, CH_2=CHR); 35.3 (*s*, CH_2=*C*HR); −0.1 (*s*, 3 CH_3). ^{31}P-NMR: 9.1 (*s*).

(*RR,SS*)-**1g**: ^{1}H-NMR ($CDCl_3$): 7.62–7.00 (*m*, PPh_3); 5.86 (*s*, C_5H_5); 3.12 (*ddd*, *J*(H,H) = 10.7, 15.6, *J*(H,P) = 2.9, CH_2=C*H*R); 1.67, 1.60 (*m*, CH_2=CHR); 0.25 (*s*, 3 CH_3). ^{13}C-NMR: 132.9 (*d*, *J*(C,P) = 10.0, C_o); 132.3 (*s*, C_p); 129.7 (*d*, *J*(C,P) = 11.2, C_m); 129.1 (*d*, *J*(C,P) = 45.6, C_{ipso}); 95.9 (*s*, C_5H_5); 37.4 (*d*, *J*(C,P) = 5.1, CH_2=CHR; 31.3 (*s*, CH_2=*C*HR); 0.6 (*s*, 3 CH_3). ^{31}P-NMR: 11.6 (*s*).

Syntheses of **1** *from a Chlorobenzene Complex*. a) *At −45° to r.t.* To **11** (0.056 g, 0.100 mmol) and PhCl (3 ml), at −45° (MeCN/CO_2 bath), $HBF_4 \cdot Et_2O$ (12 µl, 0.110 mmol) was added with stirring to generate $[Re(\eta^5\text{-}C_5H_5)(C_6H_5Cl)(NO)(PPh_3)]^+BF_4^-$ (**3**) [14]. After 15 min, excess propene was condensed into the flask. After 30 min, the cold bath was removed. After 20 h, the mixture was filtered into hexane (50 ml). The resulting tan powder was collected by filtration, washed with pentane (2 × 3 ml), and dried *in vacuo* to give **1a** (0.061 g, 90%), (*RS,SR*)/(*RR,SS*) (68 ± 2):(32 ± 2) [12b][6]).

Complex **11** (0.224 g, 0.400 mmol), PhCl (4 ml), $HBF_4 \cdot Et_2O$ (47 µl, 0.440 mmol), and pent-1-ene (0.220 ml, 2.000 mmol) were reacted as described above. An identical workup gave **1b** (0.226 g, 95%), (*RS,SR*)/(*RR,SS*) (67 ± 2):(33 ± 2) [12b][6]).

Complex **1c** (0.068 g, 90%; (*RS,SR*)/(*RR,SS*) (67 ● 2):(33 ± 2)) [12b][6]) was similarly prepared from **11** (0.056 g, 0.100 mmol), PhCl (2 ml), $HBF_4 \cdot Et_2O$ (12 µl, 0.110 mmol), and allylbenzene (0.066 ml, 0.500 mmol). Anal. calc. for $C_{32}H_{30}BF_4NOPRe$: C 51.34, H 4.04, N 1.87; found: C 51.30, H 4.06, N 1.87.

Complex **1d** (0.345 g, 94%; (*RS,SR*)/(*RR,SS*) (80 ± 2):(20 ± 2)) [12b][6]) was similarly prepared from **11** (0.279 g, 0.500 mmol), PhCl (5 ml), $HBF_4 \cdot Et_2O$ (54 µl, 0.500 mmol), and styrene (0.287 ml, 2.500 mmol).

Complex **1e** (0.070 g, 99%; (*RS,SR*)/(*RR,SS*) (62 ± 2):(38 ± 2)) was similarly prepared from **11** (0.056 g, 0.100 mmol), PhCl (0.5 ml), $HBF_4 \cdot Et_2O$ (11.8 µl, 0.110 mmol), and 3-methylbut-1-ene (0.22 ml, 2.0 mmol).

Complex **1f** (0.146 g, 82%; (*RS,SR*)/(*RR,SS*) (96 ± 2):(4 ± 2)) was similarly prepared from **11** (0.140 g, 0.250 mmol), PhCl (1.0 ml), $HBF_4 \cdot Et_2O$ (27 µl, 0.250 mmol), and 3,3-dimethylbut-1-ene (0.258 ml, 2.000 mmol). The sample contained a trace impurity (^{1}H-NMR ($CDCl_3$): 5.30 (*s*)).

Complex **1g** (0.134 g, 92%; (*RS,SR*)/(*RR,SS*) (69 ± 2):(31 ± 2)) was similarly prepared from **11** (0.112 g, 0.200 mmol), PhCl (2.0 ml), $HBF_4 \cdot Et_2O$ (24 µl, 0.220 mmol), and (trimethylsilyl)ethene (0.154 ml, 1.000 mmol).

b) *At Higher Temperatures*. Complex **11** (0.056 g, 0.100 mmol), PhCl (3 ml), $HBF_4 \cdot Et_2O$ (12 µl, 0.110 mmol), and excess propene were combined at −45° as in *Exper. a*. The sample was immersed in a 100° bath for 30 h. An identical workup gave **1a** (0.064 g, 95%; (*RS,SR*)/(*RR,SS*) (96 ± 2):(4 ± 2)).

Equilibration of Diastereoisomers of **1**. a) *NMR-Scale Reactions*. A series of 5-mm NMR tubes was charged with clear homogeneous solns. of **1a–g** (0.003–0.005 mmol) in PhCl (0.6 ml). The samples were freeze/pump/thaw-degassed, transferred to a 100° bath, and periodically monitored by ^{1}H-NMR (data, see *Table 1*). When constant (*RS,SR*)/(*RR,SS*) ratios were obtained, the solns, were filtered into hexane (20 ml). The resulting tan powders were collected by filtration and extracted with CH_2Cl_2. Solvents were evaporated to give equilibrated **1**. Mass recoveries and (*RS,SR*)/(*RR,SS*) ratios are summarized in *Table 1*.

b) *Preparative Reactions*. A mixture of *e.g.*, **1a** (0.064 g, 0.095 mmol; (*RS,SR*)/(*RR,SS*) (67 ± 2):(33 ± 2)) and PhCl (3 ml) was freeze/pump/thaw-degassed and transferred to a 100° bath. After 36 h, the soln. was poured into hexane (30 ml). The resulting tan powder was collected by filtration to give **1a** (0.060 g, 94%), (*RS,SR*)/(*RR,SS*) (96 ± 2):(4 ± 2). Other data: *Table 2*.

c) *Starting from (* RR,SS*)-***1***.* A soln. of (*RR,SS*)-**1g** (7.3 mg, 0.010 mmol) and CD_2ClCD_2Cl (0.3 ml) in a 5-mm NMR tube was transferred to a 95° bath. After 24 h, the ^{1}H-NMR showed only (*RS,SR*)-**1g**. The soln. was added to hexane (5 ml). The resulting yellowish powder was collected by filtration to give (*RS,SR*)-**1g** (7.3 mg, > 99%).

Crystal Structure of (RS,SR *)-***1e***.* An amber block of (*RS,SR*)-**1e** (from reaction of **3** and 3-methylbut-1-ene at 95°, PhCl) was submitted to data collection on a *Enraf-Nonius-CAD4* diffractometer (see *Table 3*). Cell contants were obtained from 25 reflections with 15° < 2θ < 30°. The space group was determined from systematic absences ($h0l$ $l = 2n$, $0k0$ $k = 2n$) and subsequent least-squares refinement. *Lorentz*, polarization, and empirical absorption

(ψ scans) corrections were applied to the data. Intensities of equivalent reflections were averaged. The structure was solved by standard heavy-atom techniques with the SDP/VAX package [32]. Non-H-atoms were refined with anisotropic thermal parameters. H-Atoms H(1) to H(7) were located and added to the structure factor calculations but were not refined. Scattering factors and $\Delta f'$ and $\Delta f''$ values were taken from the literature [33].

Tables of atomic coordinates, anisotropic thermal parameters, and calculated and observed structure factors are available from the author and were deposited at the *Cambridge Crystallographic Data Center*.

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