Synthesis, Structure, and Reactivity of η^2-1,3-Diene and Enyne Complexes of the Chiral Rhenium Lewis Acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$: Ozonolysis within a Metal Coordination Sphere

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Reaction of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ (1) and *trans*-piperylene at room temperature (RT) gives $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}CHCH{=}CHCH_3)]^+BF_4^-$ (**2a**; 72%) as a 63:37 mixture of *RS,SR*/*RR,SS* diastereomers. At 95 °C, (89–90):(11–10) mixtures are obtained (84–88%). No linkage isomers with coordinated $CH{=}CHCH_3$ moieties are observed. Reaction of 1 and isoprene (RT) gives $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHC(CH_3){=}CH_2)]^+BF_4^-$ (90%) as a 65:15:7:13 mixture of isomers. At 95 °C, 95:2:1:2 mixtures are obtained (>99%). The major products have coordinated $H_2C{=}CH$ moieties ((*RS,SR*)/(*RR,SS*)-**2b**); the minor products have coordinated $C(CH_3){=}CH_2$ moieties. Reactions of 1 or the corresponding dichloromethane complex and vinylacetylene (RT) give (7–17):(9–35):(61–44):(23–4) mixtures of the *RS,SR* and *RR,SS* diastereomers of alkene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}CHC{\equiv}CH)]^+BF_4^-$ and the *sc* and *ac* Re—(C=C) rotamers of alkyne complex $[(\eta^5\text{-}C_5H_5)Re(NO)PPh_3)(H_2C{=}CH\text{-}\eta^2\text{-}C{\equiv}CH)]^+BF_4^-$. Ozonolyses of **2a** and **2b** cleave the free C=C moieties to give alkene complexes of acrolein and methyl vinyl ketone (79–73%). The crystal structure of (*RS,SR*)-**2a** shows an *s-trans* diene conformation. Other structural features of the preceding compounds are analyzed. Rationales for the kinetic and thermodynamic binding selectivities are given.

Metal-catalyzed reactions of 1,3-dienes see extensive use in both commodity chemical processes, such as the hydrocyanation of butadiene,[1] and fine chemical synthesis, such as Diels–Alder and epoxidation reactions.[2,3] Although numerous η^4-1,3-diene complexes are known,[4] η^2-1,3-diene complexes have received much less attention.[5] Unsymmetrically substituted ligands can give linkage isomers or regioisomers and a complex array of other bonding equilibria. However, only a few studies of binding selectivities have appeared.[5a]

Over the last 7 years, we have systematically investigated complexes of the chiral rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**) and simple monofunctional ligands. We have sought to define fundamental binding modes and develop applications of this auxiliary in asymmetric organic synthesis. Most recently, we have begun to characterize adducts of **I** and difunctional ligands such as 1,2-dienes (allenes),[6] nonconjugated α,ω-dienes,[7] and α,β-unsaturated aldehydes and ketones.[8] One objective has been to acquire a detailed picture of the binding modes of ligands with X=C—C=X′ or X=C—C≡X′ moieties—species that play pivotal roles in organic synthesis—including kinetic and thermodynamic selectivities. Hence, we set out to prepare and study complexes of **I** and 1,3-dienes or enynes.

In this paper, we report (1) syntheses of *trans*-piperylene, isoprene, and vinylacetylene complexes of **I**, (2) characterization of the resulting linkage, configurational, and conformational isomers by crystallography and NMR, (3) binding selectivity data, and (4) ozonolyses that give alkene complexes of 1,3-enals and enones in high yields. In order to help analyze the data that follow, relevant properties of related monosubstituted alkene complexes are summarized first.[9]

The fragment **I** possesses the high-lying d donor orbital shown in Scheme I. Accordingly, monosubstituted alkene ligands adopt Re—(C=C) conformations as depicted in the idealized structures **II** and **III**, in which the larger =CHR termini are *anti* to the bulky PPh_3 ligand. Adducts **II** and **III** are configurational diastereomers that differ in the C=C enantioface bound to rhenium. They are normally generated as ca. 2:1 mixtures from substitution-labile chlorohydrocarbon complexes of the formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClR)]^+BF_4^-$.[10] However, they equilibrate by nondissociative mechanisms in chlorohy-

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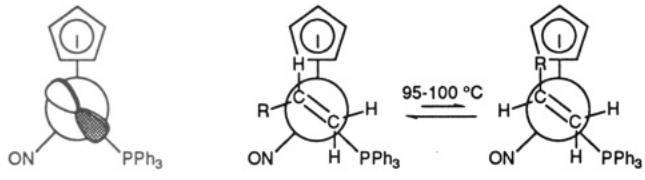
Scheme I. d-Orbital HOMO of the Chiral Rhenium Fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I) and Idealized Structures of Diastereomeric Monosubstituted Alkenes Complexes of I (II and III)



R	II : III
CH_3	96 : 4
$CH_2CH_2CH_3$	97 : 3
$CH(CH_3)_2$	>99 : <1
$C(CH_3)_3$	>99 : <1
C_6H_5	90 : 10

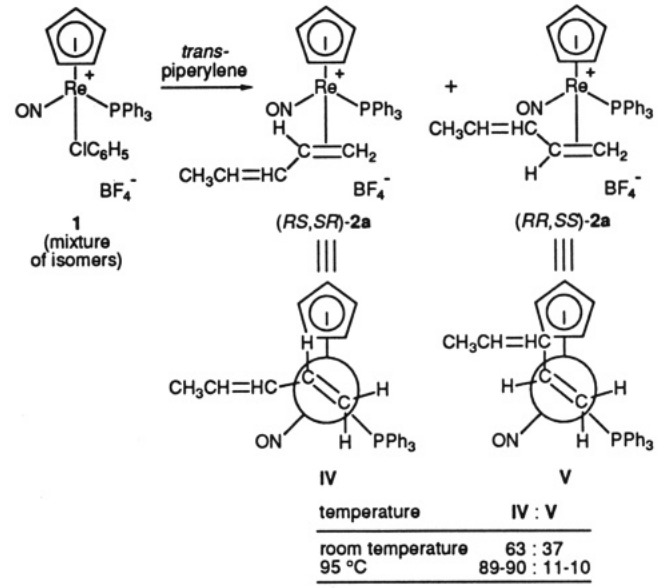
drocarbon solvents at 95-100 °C, giving ≥96:4 **II**/**III** mixtures when R = alkyl or a 90:10 mixture when R = phenyl (Scheme I).[9b,c] Thus, thermodynamic binding selectivities are much higher than kinetic binding selectivities. The lower stability of **III** arises from steric interactions between the =CHR substituent and cyclopentadienyl ligand. Analogous studies have been conducted with *cis*/*trans* and geminal disubstituted alkenes[11] and alkynes.[12]

Results

1. Binding of *trans*-Piperylene. Monosubstituted alkenes react much more rapidly than *trans*-disubstituted alkenes with functional equivalents of **I**.[9,11b] Thus, *trans*-piperylene was expected to bind exclusively through the H_2C=CH moiety. The chlorobenzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ (**I**) was generated in chlorobenzene at −45 °C in an NMR tube as described earlier.[10b] Then, *trans*-piperlyene was added (5 equiv). The sample was warmed and monitored by ^{31}P NMR. After 2 h at room temperature, the *trans*-piperylene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C$=$CHCH$=$CHCH_3)]^+BF_4^-$ (**2a**)[13] had formed in quantitative yield as a 61:39[14] mixture of *RS,SR*/*RR,SS*[15] diastereomers. Workup gave (*RS,SR*)/(*RR,SS*)-**2a** (63:37) in 72% yield (Scheme II). No evidence for linkage isomers with coordinated CH=$CHCH_3$ moieties was observed.

The preceding reaction was repeated, and the NMR probe was warmed to 95 °C to effect equilibration.[9b,c] However, some **2a** precipitated and was harvested in two crops (5 h, 38%, 88:12, *RS,SR*/*RR,SS*; 19 h, 50%, 94:6 *RS,SR*/*RR,SS*). Although these data suggest that the less soluble *RS,SR* diastereomer is more stable, homogeneous isomerization conditions were sought. Thus, **1** and *trans*-piperylene were reacted preparatively at higher dilution. After 36 h at 95 °C, workup gave **2a** in 84% yield as a 89:11 mixture of *RS,SR*/*RR,SS* diastereomers (Scheme II). Also, a partially equilibrated sample of **2a** was isolated (78:22 *RS,SR*/*RR,SS*) and redissolved in chlorobenzene (ca. 0.01 M). After 36 h at 95 °C, workup gave **2a** in 88% yield as a 90:10 mixture of *RS,SR*/*RR,SS* diastereomers. The two preceding reactions were repeated, and identical results were obtained. Thus, the thermodynamic enantioface binding selectivity of *trans*-piperylene is similar to that of styrene (90:10) and lower than those of alkenes with unbranched aliphatic substituents ((96–97):(4–3)).[9b]

Scheme II. Binding of *trans*-Piperylene to the Chiral Lewis Acid I



temperature	IV : V
room temperature	63 : 37
95 °C	89-90 : 11-10

The (63–90):(37–10) mixtures of *RS,SR*/*RR,SS* diastereomers were characterized by microanalysis and IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy, as summarized in the Experimental Section. Configurations were assigned upon the basis of chemical shift trends established earlier[9] and a crystal structure below. The ^1H and ^{13}C NMR signals of the coordinated HC=CH_2 moiety were upfield of those of the free alkene, as commonly observed in this series of compounds[9a,b,11] and illustrated pictorially in Chart I. The =CH_2 ^1H and ^{13}C resonances of both diastereomers were coupled to the PPh_3 phosphorus ($^3J_{HP}$ = 4.0–13.2 Hz, $^2J_{CP}$ = 4.1 Hz). As previously analyzed, this is diagnostic of Re—(C.‥C) conformations that place the smaller =CH_2 termini *syn* to the bulky PPh_3 ligand, as shown in **IV** and **V** (Scheme II).[6-9]

2. Binding of Isoprene. Both monosubstituted and 1,1-disubstituted alkenes readily react with the chlorobenzene complex **1**.[9,11c] Thus, as sketched in Scheme III, up to four complexes of **I** and isoprene were anticipated—*RS,SR* and *RR,SS* diastereomers of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C$=$CHC(CH_3)$=$CH_2)]^+BF_4^-$ (**2b**)[13] and the linkage isomer $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C$=$CH\text{-}\eta^2\text{-}(CH_3)C$=$CH_2)]^+BF_4^-$ (**2b′**). Complex **1** and isoprene (5 equiv) were combined at −45 °C, and the sample was warmed to room temperature. A ^{31}P NMR spectrum of an aliquot showed the reaction to be complete, and workup gave a 65:15:7:13 mixture of **2b,b′** isomers in 90% yield (^1H NMR ($CDCl_3$): δ 5.81, 5.57, 5.69, 5.60; **4s**, C_5H_5). A minor impurity was evident (δ 5.42), and chromatography

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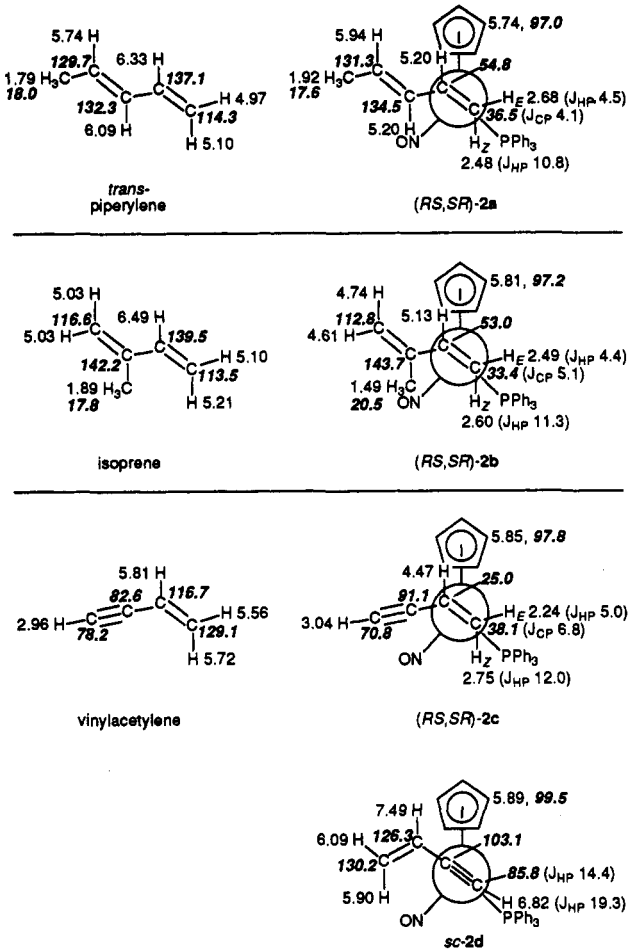
(13) For the line formulas in this paper, ligand binding sites are specified by the hapticity (η) designation. Thus, H_2C=CH-η^2-CH=$CHCH_3$ would denote a π-complex of the CH=$CHCH_3$ moiety in *trans*-piperylene. For convenience, the *trans* designation is omitted for coordinated piperylene.

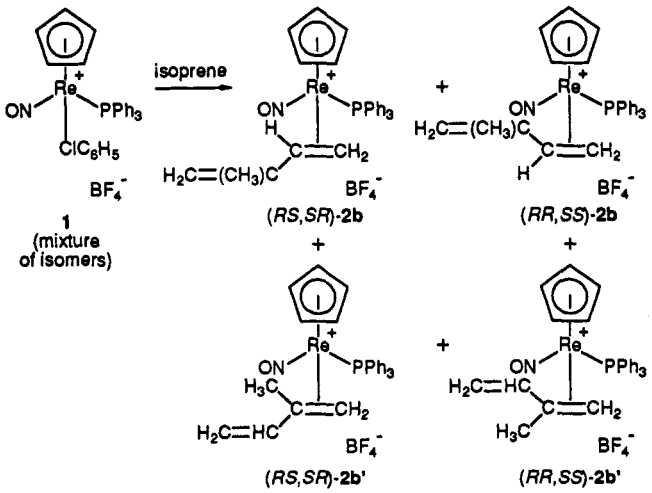
(14) All isomer ratios are normalized to 100, and error limits on each integer are ±2; e.g., 61:39 ≡ (61 ± 2):(39 ± 2).

(15) The absolute configurations of the rhenium and carbon stereocenters are specified as described previously.[9a]

Chart I. Comparison of ^1H (Plain Type) and ^{13}C (Boldface and Italic Type) NMR Chemical Shifts (ppm) of Free Ligands and Selected $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ Adducts ($CDCl_3$, Ambient Probe Temperature)



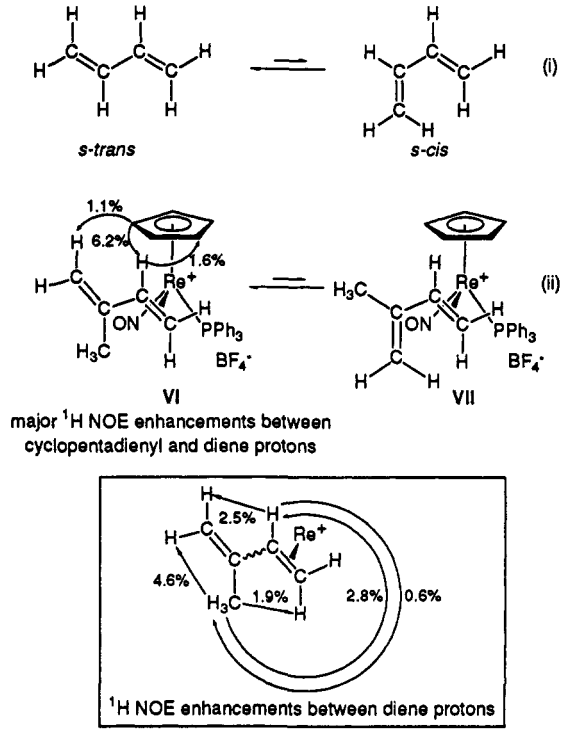
Scheme III. Binding of Isoprene to the Chiral Lewis Acid I



temperature	time (h)	(*RS,SR*)-**2b** : (*RR,SS*)-**2b** / (*RS,SR*)-**2b'** : (*RR,SS*)-**2b'**
room temperature	12	65 : 15 / 7 : 13
95 °C	12	90 : 3 / 2 : 5
95 °C	20-40	95 : 2 / 1 : 2

gave a spectroscopically pure 59:17:8:16 mixture (75% recovery). A $CDCl_3$ solution of this sample was kept at

Scheme IV. *s-trans/s-cis* Equilibria in Free and Coordinated Dienes



room temperature for 24 h. The isomer ratios were unchanged.

A chlorobenzene solution of **2b,b'** was kept at 95 °C for 20 h. The sample was recovered in quantitative yield as a 95:2:1:2 mixture of isomers. Thus, the three minor isomers can equilibrate with the major isomer. The sample was redissolved in chlorobenzene-d_5 and kept at 95 °C for another 20 h. A ^1H NMR spectrum showed no change in the isomer ratio. Finally, a high-temperature preparative reaction of **1** and isoprene (−45 °C, then 95 °C, 12 h) gave **2b,b'** in 86% yield as a 90:3:2:5 mixture of isomers. Complexes **2b,b'** were characterized analogously to **2a** (Experimental Section), although only partial NMR assignments could be made for the minor isomers.

The ^1H NMR spectrum of the major isomer showed two $=CH_2$ resonances (δ 2.60, 2.49) that were shifted markedly upfield from those of the free ligand. These were coupled to phosphorus ($^3J_{HP}$ = 11.3, 4.4 Hz) as well as the $=CHR$ ^1H resonance (δ 5.13; $^3J_{HH}$ = 10.3, 10.3 Hz). Hence, a coordinated $H_2C{=}CH$ moiety was evident. Next, a ^1H difference NOE experiment was conducted.[16] Irradiation of the cyclopentadienyl resonance gave a 6.2% enhancement in the $=CHR$ resonance, as illustrated in Scheme IV, eq ii. This value is characteristic of *RS,SR* diastereomers of monosubstituted alkene complexes of **I**.[6,8,9a,11] On the basis of these data and the stability trends in Scheme I, the major isomer was assigned as (*RS,SR*)-**2b**.

The remaining **2b,b'** isomers were assigned as follows. First, the δ 5.57 cyclopentadienyl ^1H resonance was attributed to (*RR,SS*)-**2b** on the basis of ozonolyses described below. Thus, the enantioface binding selectivity for the $H_2C{=}CH$ moiety is 95:2 (≡98:2),[14] or slightly lower than that of isopropylethylene (>99:<1).[9b] The δ 5.69 and 5.60 resonances were assigned to diastereomers of **2b'**. A

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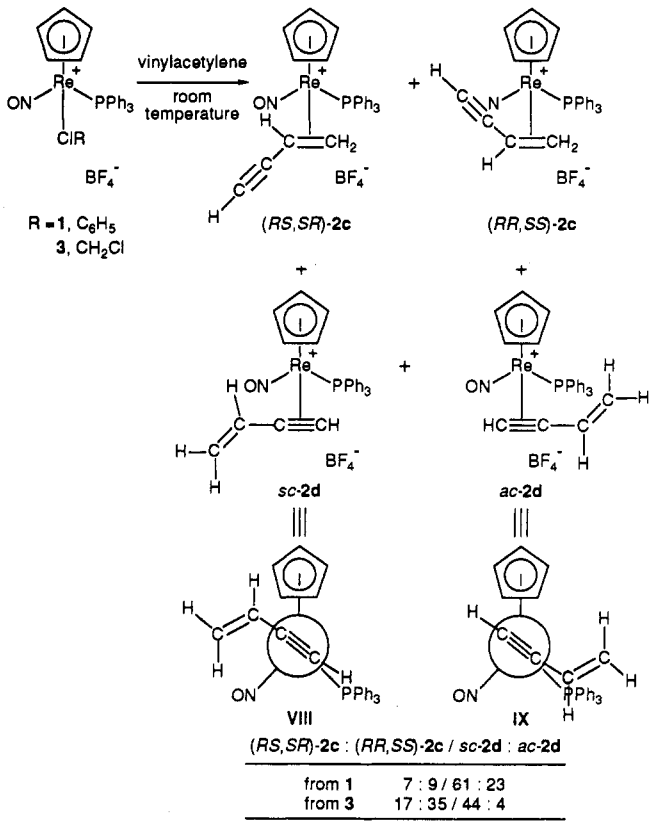
Scheme V. Binding of Vinylacetylene to the Chiral Lewis Acid I



related 1,1-disubstituted alkene ligand, α-methylstyrene, gives a slight thermodynamic preference for the (*RR,SS*) isomer, in which the phenyl group is *syn* to the cyclopentadienyl ligand.[11c] Thus, the dominant δ 5.60 isomer was tentatively assigned as (*RR,SS*)-**2b′**, in which the vinyl group is *syn* to the cyclopentadienyl ligand.

3. Binding of Vinylacetylene. Although terminal alkynes are sterically less encumbered than monosubstituted alkenes, they appear to be less reactive toward **1** or the related dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**3**).[12] Thus, **1** and the simplest enyne, vinylacetylene, were combined in an NMR tube at −45 °C (Scheme V). The sample was warmed and monitored by ^{31}P NMR. Diastereomers of the alkene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}CHC{\equiv}CH)]^+BF_4^-$ (**2c**) slowly formed at −45 °C (11.6, 10.7 ppm). However, the major product was the alkyne complex *sc*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH\text{-}\eta^2\text{-}C{\equiv}CH)]^+BF_4^-$ (*sc*-**2d**), as indicated by a characteristic resonance at 15.8 ppm.[12] A fourth resonance (17.1 ppm) was provisionally assigned to a Re—(C≡C) rotamer, *ac*-**2d**.[17] Reaction was complete at 20 °C. However, some product precipitated. The chlorobenzene solvent was replaced by dichloromethane, and a ^{31}P NMR spectrum indicated a final (*RS,SR*)-**2c**/(*RR,SS*)-**2c**/*sc*-**2d**/*ac*-**2d** ratio of 7:9:61:23 (12.0, 10.1, 15.3, 16.2 ppm). Byproducts were also evident (15.0, 14.6 ppm), but further purification by chromatography or crystallization was not successful.

We sought binding selectivity data under homogeneous conditions. Thus, a dichloromethane solution of **3** was similarly treated with vinylacetylene at −80 °C. The sample was warmed and monitored by ^{31}P NMR. Complexes **2c,d** slowly formed at −30 °C. Reaction occurred rapidly at 20 °C to give a 20:32:43:5 (*RS,SR*)-**2c**/(*RR,SS*)-**2c**/*sc*-**2d**/*ac*-**2d** mixture. Workup gave an analytically pure 17:35:44:4 mixture in 66% yield, which was characterized analogously to **2a,b**. The ≡CH ^{13}C resonance of *sc*-**2d** (85.8 ppm) was assigned on the basis of a proton-coupled spectrum ($^1J_{CH}$ = 235.2 Hz). The ≡CH ^{13}C and ^1H resonances were both strongly coupled to phosphorus ($^2J_{CP}$ = 14.4 Hz, $^3J_{HP}$ = 19.3 Hz), diagnostic of Re—(C≡C) conformations with ≡CH termini *syn* to the PPh_3 ligand.[12]

As shown in Chart I, the =*C*HR ^1H and ^{13}C NMR resonances of *free* vinylacetylene are ca. 0.5 and 20 ppm upfield, respectively, of those of the corresponding dienes. This arises from the well-established shielding effect of the C≡C group.[18] Parallel trends are evident in the rhenium complexes. One consequence is that the =CHR ^{13}C resonances of (*RS,SR*)/(*RR,SS*)-**2c** are 13.1–10.6 ppm upfield from the $=CH_2$ resonances. Other monosubstituted alkene complexes of **I** show an opposite chemical shift trend.

A chlorobenzene solution of the 17:35:44:4 (*RS,SR*)-**2c**/(*RR,SS*)-**2c**/*sc*-**2d**/*ac*-**2d** mixture was heated in an NMR probe. A ^{31}P spectrum showed a broadened (*RR,SS*)-**2c** resonance (10.1 ppm), but no other significant change below 80 °C. At 85 °C, two new peaks appeared (17.4, 17.8 ppm; ca. 50:50). These were tentatively assigned to Re=C geometric isomers of the vinylvinylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=C{=}CHCH{=}CH_2)]^+BF_4^-$—a well-known type of rearrangement previously observed with other terminal alkyne complexes of **I**.[12a,b,19] However, numerous decomposition products subsequently formed. When chlorobenzene solutions of **2c,d** were exposed to air, the free C≡C moiety in **2c** hydrated over the course of 12 h to give the known methyl vinyl ketone alkene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}C(CH_3)\text{-}\eta^2\text{-}HC{=}CH_2)]^+BF_4^-$ (**4b**).[8]

4. Additional Structural Data. Conjugated dienes can adopt either *s-trans* or *s-cis* conformations, as shown in Scheme IV, eq i.[20] Such equilibria play key roles in the stereochemistry of many reactions. Thus, we sought to further probe the structures of the above 1,3-diene complexes. First, X-ray data were collected on (*RS,SR*)-**2a**, as summarized in Table I. Refinement gave the structures shown in Figure 1, in accord with the config-

(17) (a) Alkyne ligands do not readily rotate about the Re—(C≡C) axis in this series of compounds (ΔG^*(180 °C) ≥ 22 kcal/mol).[12a] Hence, rotamers are possible and have been observed for a 2-hexyne complex.[12a] However, rotamers were not detected with *tert*-butylacetylene,[12a] phenylacetylene,[12b] and methylacetylene complexes.[12c] (b) A synclinal (*sc*) Re—(C≡C) rotamer is one in which the highest priority substituent on rhenium ($\eta^5\text{-}C_5H_5$) and the C≡C centroid (≡CR) define a 60 ± 30° torsion angle. An anticlinal (*ac*) conformer is one in which the highest priority substituents define a 120 ± 30° torsion angle. The torsion angles in idealized structures **VIII** and **IX** are 45 and 135°, respectively. See section E-5.6, p 24, of: *Pure Appl. Chem.* **1976**, *45*, 11. (c) We emphasize that our assignment of *ac*-**2d** is provisional and is based solely upon ^{31}P NMR and cyclopentadienyl ^1H and ^{13}C NMR chemical shifts. Due to the small quantities produced, other more diagnostic resonances and couplings could not be detected. In view of the small size of the vinyl C≡C substituent, it is plausible that rotamers of **2d** might be observed, but not other terminal alkyne complexes of **I**.

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(20) (a) Compton, D. A. C.; George, W. O.; Maddams, W. F. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1666 and references therein. (b) Wiberg, K. B.; Rablen, P. R.; Marquez, M. *J. Am. Chem. Soc.* **1992**, *114*, 8654 and references therein.

Table I. Summary of Crystallographic Data for the *trans*-Piperylene Complex (*RS,SR*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}CHCH{=}CHCH_3)]^+BF_4^-$ ((*RS,SR*)-2a)

mol formula	$C_{28}H_{28}BF_4NOPRe$
fw	698.52
cryst syst	monoclinic
space group	*C*2/*c*
cell dimens	
a, Å	18.896(3)
b, Å	19.593(2)
c, Å	14.818(1)
β, deg	93.88(1)
V, Å^3	5473.67
Z	8
d_{calc}, g/cm^3 (15 °C)	1.695
d_{obs}, g/cm^3 (22 °C)	1.678
crystal dimens, mm	0.18 × 0.13 × 0.11
diffractometer	Enraf-Nonius CAD-4
radiation, Å	λ(Cu Kα) = 1.540 56
data collecn method	θ–2θ
scan speed, deg/min	variable
range/indices (*hkl*)	0 to 22, 0 to 22, −17 to +17
scan range	0.8 + 0.14 tan θ
no. of rflns between stds	1 X-ray h
total no. of unique data	4993
no. of obsd data, $I > 3\sigma(I)$	4794
abs coeff (μ), cm^{-1}	93.51
min transmissn, %	62.19
max transmissn, %	99.20
no. of variables	335
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0492
$R_w = \sum(\|\|F_o\| - \|F_c\|\|)w^{1/2}/\sum\|F_o\|w^{1/2}$	0.0505
goodness of fit	1.0442
Δ/σ (max)	0.017
$\Delta\rho$(max), e/Å^3	1.416 (0.992 Å from Re)

urational and conformational assignments made above. Atomic coordinates and selected bond lengths, bond angles, and torsion angles are listed in Tables II and III.

Figure 1 shows that the *trans*-piperylene ligand adopts an *s-trans* conformation in the solid state. However, the C1–C2–C3–C4 torsion angle (152°) indicates that the diene moiety deviates slightly from planarity. Furthermore, C3 was removed from the π-nodal plane of the free alkene. In order to quantify this feature, a plane was defined that contained C1 and C2 and was perpendicular to the Re—C$_{\cdot\cdot}$C plane. The angle of the C2–C3 bond with this plane was 11°. The more informative but derivationally more complex α, β, and β' angles used by Ibers were also calculated (73, 53, 56°).[21]

Figure 1 also shows that (*RS,SR*)-**2a** adopts a Re—(C$_{\cdot\cdot}$C) conformation in which the ligand is rotated slightly counterclockwise from those in the idealized structures **II** or **IV**. This feature can be quantified in several ways. For example, the Re—C$_{\cdot\cdot}$C plane and Re—P and Re—N bonds define angles of 0 and 90°, respectively, in **II** or **IV**. In (*RS,SR*)-**2a**, the corresponding angles are 18 and 69°. Alternatively, the angle of the Re—C$_{\cdot\cdot}$C plane with the plane defined by the cyclopentadienyl centroid, rhenium, and C$_{\cdot\cdot}$C centroid is 45° in **II** or **IV** and 69° in (*RS,SR*)-**2a**. These deviations move C2 further away from, and bring C1 closer to, the cyclopentadienyl ligand.

Analogous 1,3-enal and enone complexes of **I** are also capable of *s-trans*/*s-cis* isomerism. In previous work,[8] we suggested a correlation between solution conformation and the NMR $^3J_{HH}$ values of the =CHCH= moieties (>5.2 Hz, *s-trans* dominant; <3.8 Hz, *s-cis* dominant). However,

(21) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33.

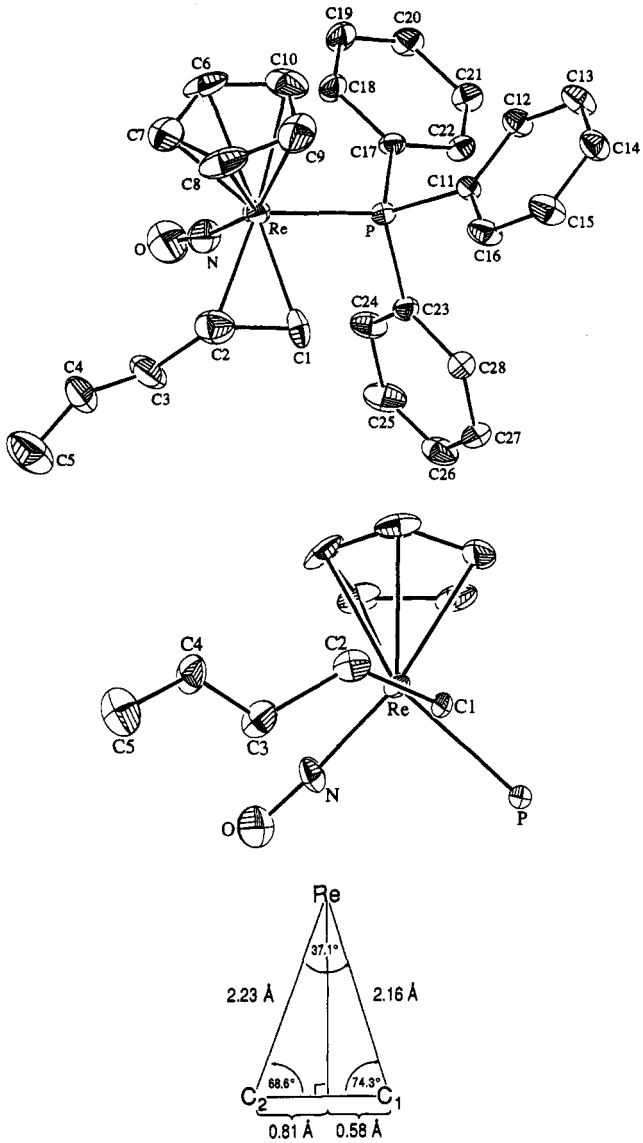


Figure 1. Structure of the cation of the *trans*-piperylene complex (*RS,SR*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}CHCH{=}CHCH_3)]^+BF_4^-$ (**2a**): (top) numbering diagram; (middle) Newman-type projection with phenyl rings omitted; (bottom) view of the Re—C$_{\cdot\cdot}$C plane.

the =CHCH= ^{1}H resonances of (*RS,SR*)-**2a** overlapped and could not be resolved by homonuclear decoupling or at 500 MHz. Thus, this criterion could not be applied. Further, the overlapping =CHCH= ^{1}H resonances precluded difference NOE experiments.

Hence, additional ^{1}H difference NOE experiments were conducted with (*SR,RS*)-**2b**, as summarized in Scheme IV, eq ii. Irradiation of the cyclopentadienyl resonance as described above also gave a 1.1% enhancement in one =CH resonance of the free C(CH$_3$)=CH$_2$ moiety (δ 4.74). This was assigned to the proton *cis* to the bound H$_2$C=CH moiety and suggested a dominant *s-trans* ligand conformation, as in the idealized structure **VI**. As a check, the =C*H*R resonance (δ 5.13) was irradiated. This gave 1.6% and 2.5% enhancements in the cyclopentadienyl and δ 4.74 =CH$_2$ resonances, respectively. However, a 0.6% enhancement in the CH$_3$ resonance was also observed, which cannot be explained by **VI**. Thus, the CH$_3$ resonance was irradiated. This gave a 2.8% enhancement in the =C*H*R resonance and others depicted in Scheme IV. The 0.6% and 2.8% enhancements suggest either that

Table II. Atomic Coordinates and Equivalent Isotropic Parameters for Non-Hydrogen Atoms in (*RS,SR*)-2a[a]

atom	*x*	*y*	*z*	*B* (Å²)
Re	0.32163(2)	0.42791(3)	0.09788(3)	4.431(9)
P	0.2024(1)	0.4494(1)	0.1373(2)	3.52(5)
O	0.2940(6)	0.2823(6)	0.0898(8)	11.1(3)
N	0.3017(6)	0.3398(5)	0.0867(7)	7.0(3)
C1	0.2815(5)	0.4692(5)	−0.0306(8)	5.6(2)
C2	0.3433(7)	0.4337(8)	−0.0481(9)	8.0(4)
C3	0.3467(8)	0.3619(9)	−0.0943(9)	10.0(4)
C4	0.4009(8)	0.3468(8)	−0.1395(9)	9.5(4)
C5	0.403(1)	0.298(1)	−0.204(1)	12.2(6)
C6	0.4007(6)	0.4203(9)	0.2211(8)	8.7(4)
C7	0.4398(5)	0.431(1)	0.1466(9)	10.0(4)
C8	0.4217(7)	0.4941(8)	0.1121(9)	9.1(4)
C9	0.3731(7)	0.5231(7)	0.162(1)	9.1(4)
C10	0.3601(7)	0.4787(9)	0.2310(9)	9.1(4)
C11	0.1886(5)	0.5391(5)	0.1622(6)	3.9(2)
C12	0.1692(5)	0.5600(5)	0.2456(6)	4.8(2)
C13	0.1639(7)	0.6287(6)	0.2658(7)	6.1(3)
C14	0.1744(6)	0.6768(6)	0.2028(8)	5.8(3)
C15	0.1939(8)	0.6580(6)	0.1205(7)	6.7(3)
C16	0.2001(7)	0.5891(6)	0.0991(7)	5.9(3)
C17	0.1745(5)	0.4045(5)	0.2366(6)	3.9(2)
C18	0.2197(5)	0.3647(6)	0.2908(6)	5.1(2)
C19	0.1958(6)	0.3300(6)	0.3644(7)	5.8(3)
C20	0.1263(6)	0.3338(5)	0.3840(6)	5.3(2)
C21	0.0805(5)	0.3734(6)	0.3307(7)	5.0(2)
C22	0.1036(5)	0.4085(5)	0.2577(6)	4.3(2)
C23	0.1337(4)	0.4228(5)	0.0523(6)	4.1(2)
C24	0.1163(6)	0.3549(6)	0.0473(7)	5.6(3)
C25	0.0629(7)	0.3312(7)	−0.0151(8)	7.4(3)
C26	0.0269(6)	0.3763(7)	−0.0709(7)	7.2(3)
C27	0.0449(6)	0.4432(7)	−0.0669(7)	7.5(3)
C28	0.0976(6)	0.4685(6)	−0.0063(7)	5.4(3)
B	0.5951(8)	0.3380(7)	0.0374(9)	6.1(3)
F1	0.593(1)	0.3074(6)	0.1096(9)	20.9(7)
F2	0.5465(7)	0.321(1)	−0.005(1)	20.7(7)
F3	0.5951(8)	0.4015(5)	0.0540(7)	17.7(4)
F4	0.6454(7)	0.3181(7)	−0.009(1)	20.4(5)

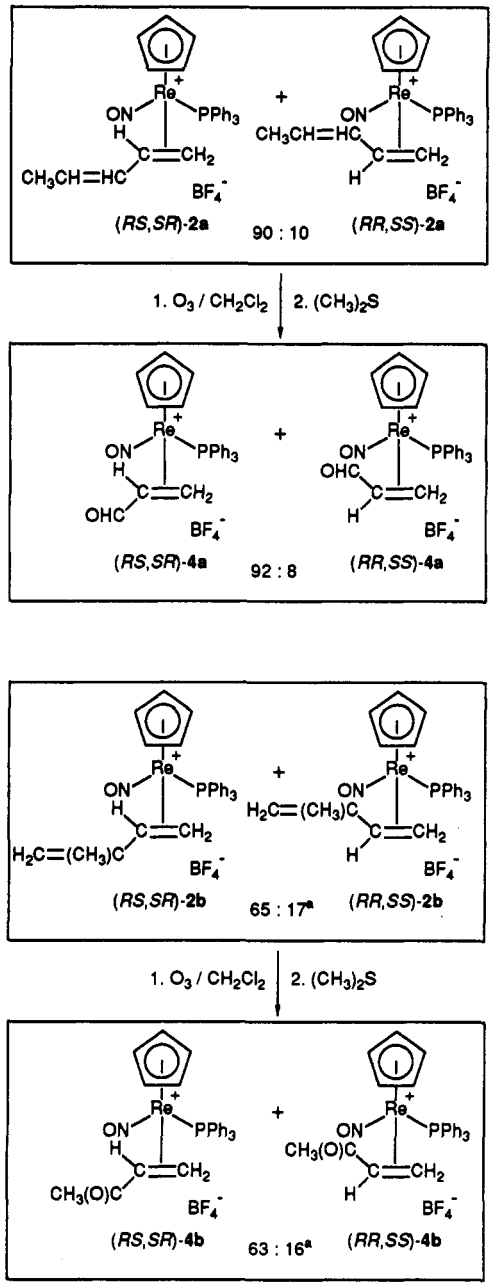
[a] Atoms refined anisotropically are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table III. Key Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) in (*RS,SR*)-2a

Re–P	2.403(2)	Re–N	1.77(1)
Re–C1	2.16(1)	Re–C2	2.23(1)
Re–C6	2.29(1)	Re–C7	2.30(1)
Re–C8	2.29(1)	Re–C9	2.28(1)
Re–C10	2.28(1)	N–O	1.14(1)
P–C11	1.818(9)	P–C17	1.822(9)
P–C23	1.822(9)	C1–C2	1.40(2)
C2–C3	1.57(2)	C3–C4	1.30(2)
C4–C5	1.35(2)	C6–C7	1.39(2)
C6–C10	1.39(2)	C7–C8	1.37(2)
C8–C9	1.35(2)	C9–C10	1.37(2)
P–Re–N	89.8(4)	P–Re–C1	82.5(2)
P–Re–C2	117.6(4)	N–Re–C1	102.9(4)
N–Re–C2	90.6(5)	C1–Re–C2	37.1(4)
Re–P–C11	111.6(3)	Re–P–C17	116.0(3)
Re–P–C23	114.7(3)	Re–N–O	171(1)
Re–C1–C2	74.3(8)	Re–C2–C1	68.6(7)
Re–C2–C3	113(1)	C1–C2–C3	126(1)
C2–C3–C4	119(2)	C3–C4–C5	126(1)
C7–C6–C10	107(2)	C6–C7–C8	107(2)
C7–C8–C9	110(2)	C8–C9–C10	108(2)
C6–C10–C9	108(1)		
Re–C1–C2–C3	104(1)	Re–C2–C3–C4	−129(1)
C1–C2–C3–C4	152(1)	C2–C3–C4–C5	−159(2)
P–Re–C1–C2	−162(1)	P–Re–C2–C1	21(1)
N–Re–C1–C2	−73(1)	N–Re–C2–C1	111(1)

some *s-cis* conformer **VII** is present or that the *s-trans* conformer has a =CHRC= linkage much more twisted than that in **VI**.

Scheme VI. Ozonolyses of Diene Complexes of I



[a] Linkage isomers also present; see text.

5. Ozonolyses of Diene Complexes. One original motivation for this study was the development of convenient syntheses of adducts of **I** and the C=C moieties of 1,3-enals. Although this objective was later rendered moot by other methodology,[8] oxidative cleavages of the preceding 1,3-diene complexes were investigated and afforded the first practical routes to these compounds. Thus, a 90:10 (*RS,SR*)/(*RR,SS*)-**2a** mixture was treated with ozone (Scheme VI). Standard workup with $(CH_3)_2S$ gave a 92:8 mixture of the *RS,SR* and *RR,SS* diastereomers of the acrolein alkene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}CH\text{-}\eta^2\text{-}CH{=}CH_2)]^+BF_4^-$ (**4a**) in 79% yield. An analogous reaction of a 75:25 (*RS,SR*)-/(*RR,SS*)-**2a** mixture gave a 78:22 (*RS,SR*)-/(*RR,SS*)-**4a** mixture (70%). The full characterization of these products is supplied elsewhere.[8]

Similarly, ozonolysis of a 65:17:6:12 mixture of (*RS,SR*)-**2b**, (*RR,SS*)-**2b**, and the two **2b'** diastereomers gave a 63:16:9:13 mixture of oxidation products in 73% yield. On

the basis of NMR ($^1H/^{31}P$) and IR spectra, the two major products were assigned as the previously reported *RS,SR* and *RR,SS* diastereomers of the methyl vinyl ketone alkene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}C(CH_3)\text{-}\eta^2\text{-}CH{=}CH_2)]^+BF_4^-$ (**4b**, Scheme VI).[8] The two minor products were provisionally assigned as diastereomers of the new methacrolein alkene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}CH\text{-}\eta^2\text{-}C(CH_3){=}CH_2)]^+BF_4^-$ (**4b'**). An analogous ozonolysis of a 90:2:5:3 reactant mixture gave a 90:2:5:3 product mixture. Thus, all of the preceding reactions proceed with retention of configuration at the rhenium and carbon stereocenters.

Discussion

1. Linkage Isomerism. Schemes II, III, and V establish the following kinetic binding selectivity order for reactions of **1** or **3** with 1,3-dienes or enynes: terminal C≡C ≥ monosubstituted C=C > geminally disubstituted C=C > *trans*-disubstituted C=C. Whereas the C≡C moiety of vinylacetylene reacts preferentially with **1**, the C≡C and C=C moieties react at comparable rates with **3**. Complexes **1** and **3** have also been found to give somewhat different kinetic ratios of *RS,SR*/*RR,SS* diastereomers with *tert*-butylethylene,[9b] and possible rationales have been discussed. Importantly, the dichloromethane ligand in **3** has been shown to undergo *associative* substitution by ketone nucleophiles.[22]

The above data also establish a parallel and more pronounced thermodynamic binding order for the C=C moieties. This trend has abundant precedent in organometallic complexes,[23] and likely reasons for the lower kinetic differentiation have been previously analyzed.[9b] However, the isomerization of the enyne ligand in **2d** to a vinylvinylidene ligand precludes determination of the relative thermodynamic binding affinity of the terminal C≡C moiety. However, enynes with internal C≡C groups could be used as alternative probes.

Other researchers have noted complementary trends. For example, Nicholas has reported reactions of the substitution-labile iron isobutylene complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(H_2C{=}C(CH_3)_2)]^+BF_4^-$ with conjugated and nonconjugated polyenes.[5a] He found that *trans*-piperylene binds exclusively through the $H_2C{=}CH$ moiety and that terminal alkenes were more reactive than internal alkynes. Similar iron η^2-1,3-diene complexes have been accessed by hydride abstraction reactions.[5d,e] Werner has observed that vinylacetylene and $[Rh(Cl)(P(i\text{-}Pr)_3)_2]_n$ react to give a square-planar rhodium π-alkyne complex.[24] Isomerization to a vinylvinylidene complex subsequently occurred. Similar reactions of vinylacetylenes have been described by Dixneuf.[25]

2. Structural Properties. Surprisingly, a search of the Cambridge Structural Database did not locate any η^2-1,3-diene complexes. Thus, (*RS,SR*)-**2a** is the first compound of this type to be structurally characterized. As expected, the carbon–carbon bond of the coordinated C=C moiety (1.40(2) Å) is longer than that of the uncoordinated C=C moiety (1.30(2) Å). We were unable to find any structural data for free *trans*-piperylene. However, the C=C bond length in 1,3-butadiene is 1.348(1) Å.[26]

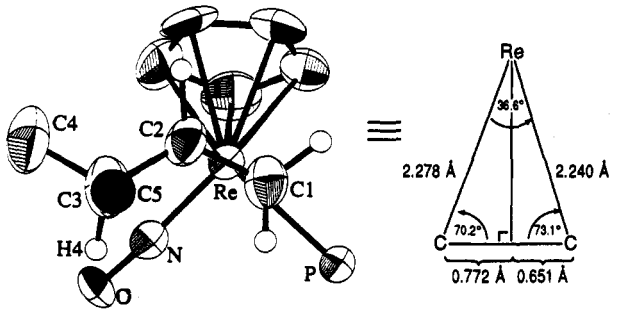


Figure 2. Selected structural features of the isopropylethylene complex (*RS,SR*)-**5**.

We have previously reported the crystal structures of numerous alkene complexes of **I**.[6,8,9,11] Of these, the isopropylethylene complex (*RS,SR*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH(CH_3)_2)]^+BF_4^-$ ((*RS,SR*)-**5**) is the most closely related to (*RS,SR*)-**2a** (Figure 2). In (*RS,SR*)-**5**, the angles of the Re–P and Re–N bonds with the Re—C=C plane are 15 and 71°, or close to the 18 and 69° in (*RS,SR*)-**2a**. Also, the angle of the =C—R bond with the plane perpendicular to the Re—C=C plane is 16°, as opposed to 11° in (*RS,SR*)-**2a**. However, the Re—C= bonds in (*RS,SR*)-**2a** (2.23(1), 2.16(1) Å) are shorter than those in (*RS,SR*)-**5** (2.278(7), 2.240(7) Å). Although the bulkier isopropyl substituent in (*RS,SR*)-**5** may contribute to this trend, we suggest that an electronic effect dominates. Simple Hückel MO theory predicts that 1,3-dienes should be stronger π donors *and* stronger π acceptors than monoalkenes. The enhanced frontier orbital interactions should bring the rhenium and C=C moiety closer together.

Finally, the Re–C1 bond in (*RS,SR*)-**2a** (2.16(1) Å) is shorter than the Re–C2 bond (2.23(1) Å). Similarly, the Re–C1–C2 angle (74.3(8)°) is larger than the Re–C2–C1 angle (68.6(7)°). This indicates that the C=C group is not bound symmetrically. Rather, the rhenium has "slipped" toward the unsubstituted $=CH_2$ terminus. Although π-aldehyde complexes of **I** exhibit an even greater degree of rhenium slippage toward the oxygen terminus,[27] this constitutes the largest distortion found in an alkene complex of **I** to date.

3. Other Bonding Equilibria. Figure 1 establishes an *s-trans* conformation for the *trans*-piperylene ligand in (*RS,SR*)-**2a** in the solid state. The NOE data in Scheme IV establish a dominant *s-trans* conformation for the isoprene ligand in (*RS,SR*)-**2b** in solution. Free butadiene and isoprene give *s-trans*/*s-cis* equilibrium mixtures of ca. 97:3 and 89:11 at ambient temperatures (gas phase).[20a] Thus, the complexes and free ligands exhibit similar conformational preferences. However, some 1,3-enal and enone adducts of **I** appear to adopt different conformations than the free ligands.[8]

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As noted above, *trans*-piperylene and styrene give lower thermodynamic enantioface binding selectivities (90:10) than propene or 1-pentene ((96–97):(3–4); Scheme I). However, the crystal structure of (*RS,SR*)-**2a** shows shortened rhenium–carbon distances, which should enhance chiral recognition. We therefore propose that the decreased *trans*-piperylene and styrene binding selectivities are due to the smaller effective sizes of their sp^2-hybridized, 1-propenyl and phenyl HC=CH_2 substituents. Other equilibria have been reported in which phenyl groups appear sterically smaller than methyl groups.[28,29] Further, of the two diastereomers of the corresponding α-methylstyrene complex, the one in which the phenyl group is *syn* to the cyclopentadienyl ligand is slightly more stable than that with the methyl group *syn* to the cyclopentadienyl ligand.[11c]

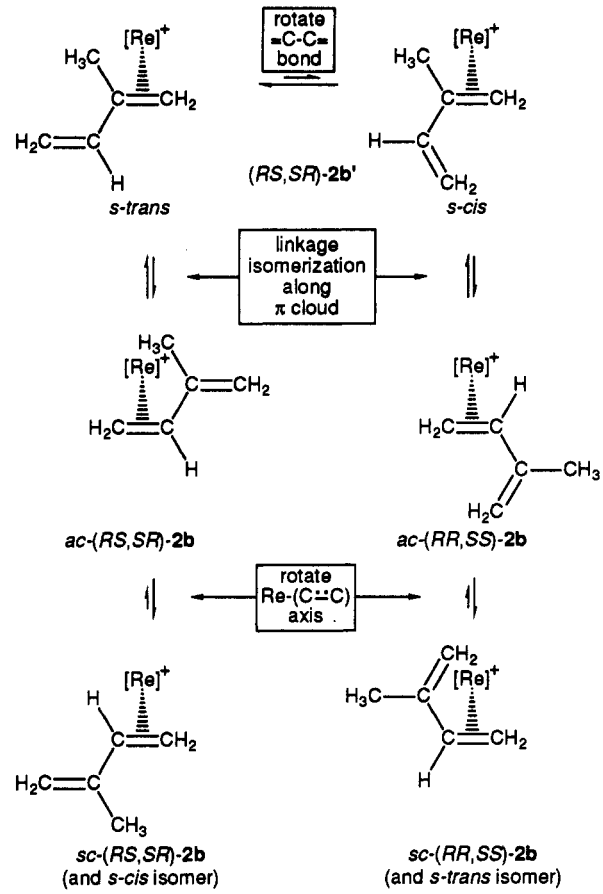
As would be intuitively expected, when the unbranched, 1-propenyl substituent in *trans*-piperylene is replaced by the α-branched, isopropenyl substituent in isoprene, the enantioface binding selectivity increases to 98:2. However, consistent with the preceding analysis, isopropylethylene gives an even higher equilibrium binding ratio (>99:<1). Thus, an isopropenyl group exhibits a smaller effective size than an isopropyl group.

We have previously shown that diastereomeric *mono*alkene complexes of **I** equilibrate via nondissociative pathways.[9c] Evidence was acquired for intermediate C–H "σ-bond" complexes. We presume that analogous mechanisms can operate with 1,3-diene complexes **2a,b**. However, additional possibilities exist. For example, linkage isomers **2b′** and **2b** could plausibly interconvert by a nondissociative migration of rhenium along the diene π-cloud. As shown schematically in Scheme VII, this would allow a given diastereomer of **2b′** to be transformed to *either* diastereomer of **2b**, depending upon whether the diene conformation is *s-trans* or *s-cis*. Significantly, all four **2b,b′** isomers appear to interconvert at comparable rates. On the other hand, the *RS,SR*/*RR,SS* diastereomers of **2a,b** do not equilibrate more rapidly than those of monosubstituted monoalkene complexes of **I**—for which the possibilities in Scheme VII do not exist. Hence, the study of additional complexes, such as adducts of the labeled 1,3-diene H_2C=CHCH=CD_2, will be required to resolve these mechanistic issues.

4. Analecta. It is in our view remarkable that low-oxidation-state organometallic complexes such as **2a,b** are stable toward ozonolysis conditions (Scheme VI). We are not aware of other reports of alkene ozonolyses within metal coordination spheres, except for ferrocene derivatives.[30] Although protocols for selective ozonolyses of dienes have been developed,[31] transition-metal fragments such as **I** would seemingly have potential as protecting groups, conferring additional design flexibility. We have not yet developed general methods for the removal of alkene ligands from **I**. However, deprotection conditions are available for related complexes.[32]

In summary, this study has provided quantitative or qualitative data on linkage isomerism, kinetic and thermodynamic enantioface binding selectivities (configurational diastereomerism), and *s-trans*/*s-cis* conformational isomers for complexes of the rhenium Lewis acid **I** and 1,3-dienes and enynes. Future papers in this series will provide similar data for complexes of **I** and unsymmetrically disubstituted alkenes[11c] and ligands of the formula O=C(X)(X)C=O.[33] Finally, as foreshadowed by Scheme VI, the reaction chemistry of these compounds, which are readily available in enantiomerically pure form[9] and capable of highly regioselective and diastereoselective nucleophilic additions,[34] will also be developed in future reports.

Scheme VII. Possible Relationship between Linkage Isomerization and Equilibration of Configurational Diastereomers



Experimental Section[35]

[(η^5-C_5H_5)Re(NO)(PPh_3)(η^2-H_2C=CHCH=$CHCH_3$)]$^+$-BF_4^- (2a). A.[13] A 5-mm NMR tube was charged with (η^5-C_5H_5)-Re(NO)(PPh_3)(CH_3) (**6**; 0.056 g, 0.10 mmol)[36] and C_6H_5Cl (1.0 mL), capped with a septum, and cooled to −45 °C (CH_3CN/CO_2 bath). Then, HBF_4·OEt_2 (11.8 μL, 0.110 mmol) was added. The

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(35) General procedures were identical with those described in the previous paper.[9b] Dienes (Aldrich) were used without purification. NMR spectra were recorded in $CDCl_3$ at ambient probe temperature and referenced to $Si(CH_3)_4$ (^{1}H, δ 0.00), $CDCl_3$ (^{13}C, 77.0 ppm), or external 85% H_3PO_4 (^{31}P, 0.00 ppm) unless noted. All coupling constants (*J*) are in Hz. The ^{1}H NOE difference spectra[16] were acquired as described previously with the following resonance saturation levels: C_5H_5, 98%; CH_3, 82%; =CHR, 70%.[6]
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tube was shaken and kept at −45 °C for 15 min to generate $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$.[10b] *trans*-Piperylene (0.050 mL, 0.50 mmol) was added. The tube was transferred to an ambient-temperature NMR probe, and ^{31}P spectra were recorded. After 2 h, reaction was complete (61:39 *RS,SR/RR,SS*, 10.8/10.4 ppm).[14,15] The mixture was added dropwise to ether (30 mL), and the resulting precipitate was collected by filtration, washed with pentane (2 × 3 mL), and dried *in vacuo* to give **2a** (0.050 g, 0.072 mmol, 72%; 63:37 *RS,SR/RR,SS*) as a tan powder. Anal. Calcd for $C_{28}H_{28}BF_4NOPRe$: C, 48.15; H, 4.04; N, 2.01. Found: C, 47.86; H, 3.95; N, 1.98. IR (cm^{-1}, thin film): ν_{NO} 1722 vs; $\nu_{C=C}$ 1652 w. MS:[37] 612 (M^+, 63%), 544 ($M^+ - C_5H_8$, 100%).

B. Procedure A was repeated on an identical scale, except that the tube was kept in a 95 °C probe for 5 h. Yellow prisms formed. The sample was cooled to room temperature, and the prisms were collected by filtration to give **2a** (0.026 g, 0.038 mmol, 38%; 88:12 *RS,SR/RR,SS*), mp 222–223 °C dec. Anal. Found: C, 48.26; H, 4.05; N, 1.95. The filtrate (40:60 *RS,SR/RR,SS*) was kept at 95 °C for another 19 h. Workup as in procedure A gave a second crop of **2a** (0.035 g, 0.050 mmol, 50%; 94:6 *RS,SR/RR,SS*) for a total yield of 88% (0.061 g, 0.088 mmol).

C. Procedure B was repeated in a Schlenk flask on an identical scale, except that 5 mL of C_6H_5Cl was employed to avoid crystallization. After 36 h at 95 °C, workup as in procedure A gave **2a** (0.059 g, 0.084 mmol, 84%; 89:11 *RS,SR/RR,SS*).

NMR for (*RS,SR*)-**2a**:[35] ^1H (δ) 7.60–7.28 (m, PPh_3), 5.94 (m, J_{HH} = 14.0, 6.9,[38] CH_3CH=), 5.22–5.18 (2m, =CHCH=), 5.74 (s, C_5H_5), 2.68 (ddd, J_{HH} = 4.5, 9.0, J_{HP} = 4.5, $=CH_E$), 2.48 (ddd, J_{HH} = 4.5, 10.8, J_{HP} = 10.8, $=CH_Z$), 1.92 (d, J_{HH} = 6.5, CH_3); $^{13}C\{^1H\}$ (ppm) 134.5 (s, CH_3CH=*C*H), 131.3 (s, CH_3C=),[39] 133.1 (d, J_{CP} = 9.8, *o*-Ph), 132.2 (s, *p*-Ph), 130.2 (d, J_{CP} = 58.8, *i*-Ph), 129.6 (d, J_{CP} = 10.9, *m*-Ph), 97.0 (s, C_5H_5), 54.8 (s, *C*=CH_2), 36.5 (d, J_{CP} = 4.1, =CH_2), 17.6 (s, CH_3); $^{31}P\{^1H\}$ (ppm) 10.8 (s). NMR for (*RR,SS*)-**2a** (partial): ^1H (δ) 5.62 (s, C_5H_5), 4.17 (m, *CH*=CH_2), 2.91 (ddd, J_{HH} = 4.0, 8.6, J_{HP} = 13.2, $=CH_E$), 2.40 (ddd, J_{HH} = 4.0, 13.2, J_{HP} = 4.0, $=CH_Z$), 2.04 (d, J_{HH} = 6.8, CH_3); $^{13}C\{^1H\}$ (ppm) 134.2/130.0 (s, CH_3C=*C*), 98.9 (s, C_5H_5), 56.3 (s, *C*=CH_2), 35.7 (d, J_{CP} = 4.1, =CH_2), 17.8 (s, CH_3); $^{31}P\{^1H\}$ (ppm) 10.6 (s).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHC(CH_3){=}CH_2)]^+BF_4^-$ (2b,b′). A. A Schlenk flask was charged with **6** (0.056 g, 0.10 mmol), C_6H_5Cl (1.0 ml), and a stirbar and cooled to −45 °C. Then, $HBF_4{\cdot}OEt_2$ (11.8 μL, 0.110 mmol) was added with stirring. After 15 min, isoprene (0.050 mL, 0.50 mmol) was added, and the cold bath was removed. After 12 h, workup as in procedure A for **2a** gave **2b,b′** (0.063 g, 0.090 mmol, 90%) as a 65:15:7:13 mixture of isomers (data given in the text). Column chromatography (silica, 15 × 1.3 cm, 5:95 v/v acetone/CH_2Cl_2) gave **2b,b′** (0.047 g, 0.068 mmol, 68%) as a yellow powder and a 59:17:8:16 mixture of isomers.

B. A Schlenk flask was charged with the preceding sample (0.036 g, 0.047 mmol) and C_6H_5Cl (3 mL). The solution was stirred at 95 °C for 20 h. Workup as in procedure A for **2a** gave **2b,b′** (0.036 g, 0.047 mmol, >99%) as a 95:2:1:2 mixture of isomers. Anal. Calcd for $C_{28}H_{28}BF_4NOPRe$: C, 48.15; H, 4.04. Found: C, 47.65; H, 3.98.

C. Procedure A was repeated on an identical scale. The mixture was warmed to room temperature and then kept at 95 °C for 12 h. Workup as in procedure A for **2a** gave **2b,b′** (59.9 mg, 0.086 mmol, 86%) as a tan powder and a 90:3:2:5 mixture of isomers, mp 203–205 °C. IR (cm^{-1}, thin film): ν_{NO} 1723 vs; $\nu_{C=C}$ 1650 w. MS:[37] 612 (M^+, 74%), 544 ($M^+ - C_5H_8$, 100%).

NMR for (*RS,SR*)-**2b**:[35] ^1H (δ) 7.60–7.28 (m, PPh_3), 5.81 (s, C_5H_5), 5.13 (dd, J_{HH} = 10.3, 10.3, =CHR), 4.74 (s, $H_3CC{=}CH_ZH_E$),[40] 4.61 (s, $H_3CC{=}CH_ZH_E$), 2.60 (ddd, J_{HH} = 4.4, 10.3, J_{HP} = 11.3, $CH{=}CH_ZH_E$), 2.49 (ddd, J_{HH} = 4.4, 10.3, J_{HP} = 4.4, $CH{=}CH_ZH_E$), 1.49 (s, CH_3); $^{13}C\{^1H\}$ (ppm) 143.7 (s, $=CCH_3$), 133.1 (d, J_{CP} = 10.2, *o*-Ph), 132.2 (s, *p*-Ph), 130.3 (*i*-Ph),[41] 129.5 (d, J_{CP} = 11.1, *m*-Ph), 112.8 (s, $H_3CC{=}CH_2$), 97.2 (s, C_5H_5), 53.0 (s, =CHR), 33.4 (d, J_{CP} = 5.1, $CH{=}CH_2$), 20.5 (s, CH_3); $^{31}P\{^1H\}$ (ppm) 11.3 (s). NMR for other isomers (partial): ^1H (δ) 5.69/5.60/5.57 (3s, 8:16:17, C_5H_5), 2.28/2.08/1.85 (3s, CH_3); $^{13}C\{^1H\}$ (ppm) 145.9/144.7/144.2 (3s, =CR/free), 115.4/113.8/113.1 (3s, $=CH_2$/free), 99.6/99.3/98.5 (3s, C_5H_5), 70.1/69.5/55.7 (3s, =CR/bound), 45.3/44.4/31.5 (d/d/br s, J_{CP} = 5.6/5.3, $=CH_2$/bound), 26.3/26.0/22.5 (3s, CH_3); $^{31}P\{^1H\}$ (ppm) 11.0/9.5/9.4 (s).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHC{\equiv}CH)]^+BF_4^-$ (2c,d). A 5-mm NMR tube was charged with **6** (0.056 g, 0.10 mmol) and CH_2Cl_2 (0.6 mL), capped with a septum, and cooled to −80 °C. Then, $HBF_4{\cdot}OEt_2$ (10.8 μL, 0.100 mmol) was added. The sample was kept at −80 °C for 15 min to generate $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$.[10a] Excess vinylacetylene[42] was condensed into the tube, which was transferred to a −80 °C NMR probe. The probe was gradually warmed, and ^{31}P NMR spectra were recorded. Complexes **2c,d** began to form slowly at −30 °C. Reaction was complete at 20 °C to give a 20:32:43:5 mixture of isomers (data given in the text). Workup as in procedure A for **2a** gave **2c,d** (0.045 g, 0.066 mmol, 66%) as a tan powder and a 17:35:44:4 mixture of isomers, dec pt 116–121 °C. IR (cm^{-1}, thin film): ν_{NO} 1716, 1722 vs; $\nu_{C\equiv C}$ 2016 w. Anal. Calcd for $C_{27}H_{24}BF_4NOPRe$: C, 47.52; H, 3.54. Found: C, 47.46; H, 3.55.

NMR (CD_2Cl_2) for (*RS,SR*)-**2c**: ^1H (δ, $CHDCl_2$ reference) 7.68–7.24 (m, PPh_3), 5.85 (s, C_5H_5), 4.47 (m, =CHR), 3.04 (d, J_{HH} = 2.1, $\equiv CH$), 2.75 (ddd, J_{HH} = 4.9, 10.5, J_{HP} = 12.0, $=CH_Z$), 2.24 (ddd, J_{HH} = 4.9, 9.9, J_{HP} = 5.0, $=CH_E$); $^{13}C\{^1H\}$ (ppm, CD_2Cl_2 reference) 133.5 (d, J_{CP} = 9.9, *o*-Ph), 133.0 (s, *p*-Ph), 130.2 (d, J_{CP} = 11.2, *m*-Ph),[41] 97.8 (s, C_5H_5), 91.1 (s, $\equiv$CR), 70.8 (s, $\equiv$CH), 38.1 (d, J_{CP} = 6.8, $=CH_2$), 25.0 (s, =CHR); ^{13}C (ppm, partial) 70.8 (br d, J_{CH} = 251.4, $\equiv$CH), 38.1 (dt, J_{CP} = 6.8, J_{CH} = 160.0, $=CH_2$), 25.0 (d, J_{CH} = 167.0, =CHR); $^{31}P\{^1H\}$ (ppm) 11.8 (s). NMR for (*RR,SS*)-**2c**: ^1H (δ) 7.68–7.24 (m, PPh_3), 5.77 (s, C_5H_5), 3.53 (m, =CHR), 2.91 (ddd, J_{HH} = 4.5, 9.3, J_{HP} = 13.8, $=CH_E$), 2.66 (d, J_{HH} = 2.3, $\equiv CH$), 2.15 (ddd, J_{HH} = 4.5, 12.6, J_{HP} = 4.5, $=CH_Z$); $^{13}C\{^1H\}$ (ppm) 133.5 (d, J_{CP} = 9.9, *o*-Ph), 133.0 (s, *p*-Ph), 130.2 (d, J_{CP} = 11.2 *m*-Ph),[41] 101.8 (s, C_5H_5), 100.1 (s, $\equiv$CR), 74.3 (s, $\equiv$CH), 38.4 (d, J_{CP} = 6.4, $=CH_2$), 27.8 (s, =CHR); ^{13}C (ppm, partial) 74.3 (br d, J_{CH} = 253.3, $\equiv$CH), 38.4 (dt, J_{CP} = 6.4, J_{CH} = 161.5, $=CH_2$), 27.8 (d, J_{CH} = 165.1, =CHR); $^{31}P\{^1H\}$ (ppm) 10.0 (s). NMR for (*sc*)-**2d**: ^1H (δ) 7.68–7.24 (m, PPh_3), 7.49 (dddd, J_{HH} = 1.5, 10.2, 16.8, J_{HP} = 0.7, =CHR), 6.82 (dd, J_{HH} = 1.5, J_{HP} = 19.3, $\equiv$CH), 6.09 (d, J_{HH} = 10.2, $=CH_E$), 5.90 (d, J_{HH} = 16.8, $=CH_Z$), 5.89 (s, C_5H_5); $^{13}C\{^1H\}$ (ppm) 133.15 (d, J_{CP} = 9.9, *o*-Ph), 133.0 (s, *p*-Ph), 130.2 (d, J_{CP} = 11.2, *m*-Ph),[41] 130.2 (s, $=CH_2$), 126.3 (s, =CH), 103.1 (s, $\equiv$CR), 99.5 (s, C_5H_5), 85.8 (d, J_{CP} = 14.4, $\equiv$CH); ^{13}C (ppm, partial) 130.2 (br t, J_{CH} = 162.2, $=CH_2$), 126.3 (d, J_{CH} = 165.6, =CH), 103.1 (s, $\equiv$CR), 85.8 (dd, J_{CP} = 14.4, J_{CH} = 235.2, $\equiv$CH); $^{31}P\{^1H\}$ (ppm) 15.4 (s).

Ozonolyses. A. A Schlenk flask was charged with **2a** (0.037 g, 0.053 mmol; 90:10 *RS,SR/RR,SS*), CH_2Cl_2 (2 mL) and a stirbar and cooled to −80 °C. An O_3 stream (Polymetrics Model T-816 generator; 8 psi O_2, 100 V, 2.00 L/min) was passed through the solution with stirring. The effluent was passed through an aqueous KI solution. When I_2 formed, the O_3 was replaced by a N_2 stream. After 10 min, $(CH_3)_2S$ (0.4 mL) was added. After 2 h, the solution was warmed to room temperature and was then added to ether (30 mL). Solvent was removed from the resulting light yellow solid by pipet. The solid was washed with ether and dried *in vacuo* to give the acrolein alkene complex $[(\eta^5\text{-}C_5H_5)$

(37) Conditions: (+)-FAB, 5 kV, Ar, 3-nitrobenzyl alcohol/$CHCl_3$ matrix, units *m/z* (relative intensity), ^{187}Re.

(38) The *J* values were determined by a homonuclear decoupling experiment.

(39) This assigment was verified by a heteronuclear decoupling experiment involving the CH_3CH= ^1H resonance.

(40) This assignment was verified by a ^1H NOE difference experiment involving the $H_2C{=}CHR$ resonance.

(41) The *ipso* carbon was not located, or one line of the doublet was obscured.

(42) Prepared as reported by: Verkruijsse, H. D.; Brandsma, L. *Synth. Commun.* **1990**, *20*, 3355. NMR (CD_2Cl_2): ^1H (δ) 5.81 (ddd, J_{HH} = 1.8, 9.9, 17.7, =CHC), 5.72 (dd, J_{HH} = 3.6, 17.7, $=CH_Z$), 5.56 (ddd, J_{HH} = 1.0, 3.6, 9.6, $=CH_E$), 2.96 (dd, J_{HH} = 1.0, 1.8, $\equiv$CH); ^{13}C (ppm) 129.1 (t, $^1J_{CH}$ = 159.7, $=CH_2$), 116.7 (d, $^1J_{CH}$ = 167.5, =CHR), 82.6 (d, $^2J_{CH}$ = 50.0, $\equiv$CR), 78.2 (d, $^1J_{CH}$ = 249.0, $\equiv$CH).

$Re(NO)(PPh_3)(O{=}CH\text{-}\eta^2\text{-}CH{=}CH_2)]^+BF_4^-$ (**4a**; 0.029 g, 0.042 mmol, 79%; 92:8 *RS,SR/RR,SS*).[8,43]

B. A 65:17:6:12 mixture of **2b,b'** isomers (0.049 g, 0.070 mmol) and O_3 were reacted in a procedure analogous to that given for **2a**. An identical workup gave a 63:16:9:13 mixture of alkene complexes (0.036 g, 0.051 mmol, 73%; ^1H NMR (δ CD_2Cl_2) 5.94, 5.66, 5.84, 5.80), the first two of which were identified by IR and $^1H/^{31}P$ NMR as the known methyl vinyl ketone complexes (*RS,SR*)-/(*RR,SS*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}C(CH_3)\text{-}\eta^2\text{-}CH{=}CH_2)]^+BF_4^-$ (**4b**).[8,43]

Crystallography. Data were collected on a yellow prism of (*RS,SR*)-**2a** as summarized in Table I. Cell constants were obtained from 25 reflections with $20° < 2\theta < 28°$. The space group was determined from systematic absences (hkl, $h + k = 2n$; $h0l$, $l = 2n$; $0k0$, $k = 2n$) and subsequent least-squares refinement. Standard reflections showed 5.0% decay during data collection. Lorentz, polarization, empirical absorption (ψ scans), and anisotropic decay corrections were applied. Intensities of equivalent reflections were averaged. The structure was solved by standard heavy-atom techniques with the SDP/VAX package.[44] Nonhydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated 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.[45]

(43) The IR and ^1H and ^{31}P NMR spectra were identical with those of an authentic sample.

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Supplementary Material Available: A table of anisotropic thermal parameters for (*RS,SR*)-**2a** (1 page). Ordering information is given on any current masthead page.

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