Syntheses and Structures of Complexes of α,β-Unsaturated Carbonyl Compounds and the Chiral Rhenium Fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$: Divergent Kinetic and Thermodynamic O=C/C=C and O=C/C≡C Binding Selectivities

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Reactions of the substitution-labile dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ with α,β-unsaturated aldehydes and ketones are described. Acrolein gives a π O=C complex, which cleanly isomerizes in the solid state (100 °C) to a π C=C complex. Crotonaldehyde gives both π and σ O=C complexes (52:48, CH_2Cl_2, room temperature), which convert at 80 °C to a π C=C complex. Methyl vinyl ketone gives a σ O=C complex, which is characterized by NMR at −25 °C. At room temperature, a π C=C complex forms. Other acyclic vinyl ketones behave similarly. Cyclopentenone and cyclohexenone give σ O=C complexes that only partially isomerize to π C=C complexes at 60–90 °C. The acetylenic ketone 4-phenyl-3-butyn-2-one gives a σ O=C complex at −25 °C. At room temperature, a π C≡C complex forms. The crystal structure of a π C=C complex of *trans*-4-hexen-3-one is determined. The NMR, configurational, and conformational properties of the preceding complexes, all of which can exist in several isomeric forms, are analyzed in detail. These data show that, with respect to the rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$, the O=C groups of α,β-unsaturated aldehydes and ketones are the kinetically preferred binding sites, but the C=C or C≡C groups are generally the thermodynamically preferred binding sites.

Chiral transition metal reagents and catalysts are now extensively utilized for the elaboration of achiral monofunctional aldehydes, ketones, and alkenes to optically active organic molecules.[1] As such, increasing attention is being directed at metal-mediated enantioselective syntheses involving either conjugated or unconjugated difunctional substrates.[2] In this context, the rational design and optimization of new transformations can be greatly aided by data on the relative rates and thermodynamics of binding of organic functional groups to Lewis acidic metal centers.

We have undertaken an extensive investigation of complexes of the chiral rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I) with simple monofunctional aliphatic aldehydes,[3] aromatic aldehydes,[4] ketones,[5] esters,[6] alkenes,[7] and alkynes.[8] These studies have generally utilized the substitution-labile dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (1)[9] or related chlorohydrocarbon complexes, which serve as functional equivalents of I. Numerous adducts have been crystallographically characterized, and structures in solution have been probed by NMR techniques. The ligands commonly adopt conformations that allow a high degree of overlap between their acceptor orbitals and the rhenium fragment d orbital HOMO shown in Figure 1.

Hence, we sought to similarly define the binding properties of α,β-unsaturated aldehydes and ketones. Data for a series of representative compounds are described below, and reveal a marked contrast between kinetic and thermodynamic binding affinities of carbonyl and alkene or alkyne groups. However, in order to help analyze the diverse array of coordination modes possible with these difunctional donor ligands, an overview of the structures of complexes of related monofunctional ligands is given first.

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(2) Representative papers: (a) Lee, N. H.; Jacobsen, E. N. *Tetrahedron Lett.* **1991**, *32*, 6533. (b) Xu, D.; Crispino, G. A.; Sharpless, K. B. *J. Am. Chem. Soc.* **1992**, *114*, 7570. (c) Rossiter, B. E.; Swingle, N. M. *Chem. Rev.* **1992**, *92*, 771. (d) Kagan, H. B.; Riant, O. *Chem. Rev.* **1992**, *92*, 1007.

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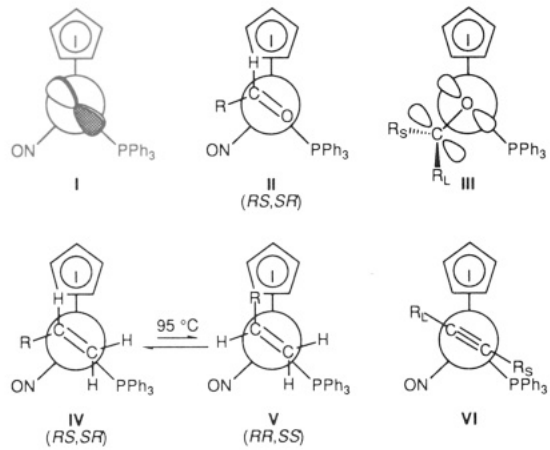


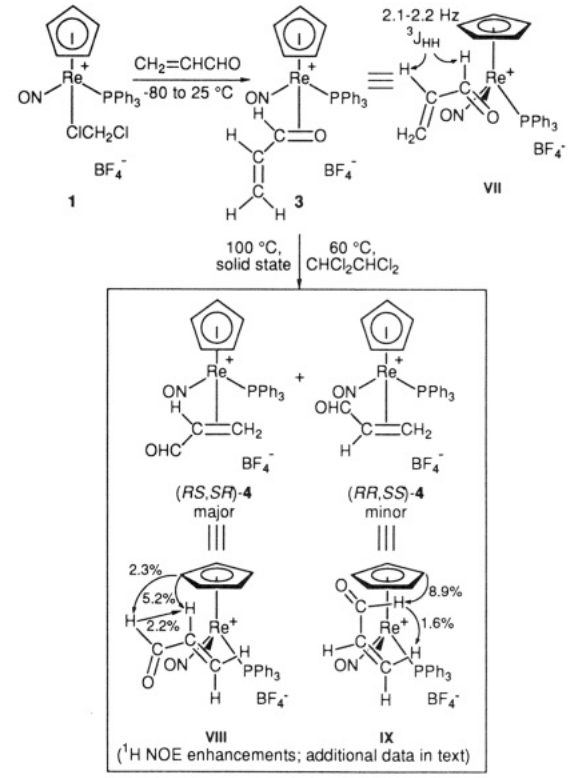
Figure 1. I, d-orbital HOMO of the chiral rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$; II, idealized structures of π-aldehyde complexes of I (more stable diastereomers); III, idealized structures of σ-ketone complexes of I; IV, V, idealized structures of monosubstituted alkene complexes of I; VI, idealized structures of alkyne complexes of I.

Aliphatic aldehydes and **1** react to give π complexes of the idealized structure II (Figure 1).[3] The aldehyde ligands adopt Re–(O⋯C) conformations that place the larger =CHR terminus *anti* to the bulky PPh_3 ligand. Two configurational diastereomers are then possible. These differ in the positions of the alkyl and hydrogen substituents, or the O=C enantioface bound to rhenium. That shown in II, in which the alkyl group is directed away from the larger cyclopentadienyl ligand and *syn* to the small nitrosyl ligand, is greatly preferred thermodynamically (≥99:1).[10,11]

In contrast, most aliphatic and aromatic ketones give σ complexes with the idealized Re–O conformation shown in III.[5] Although quantitative *E*/*Z* O=C geometric isomer ratios are not yet available, methyl alkyl and aryl ketones are believed to give predominantly *E* isomers (large rhenium fragment and small methyl group *cis*).[5a] Aromatic aldehydes give mixtures of π and σ isomers, with equilibria strongly influenced by the electronic properties of aryl substituents, solvent, and temperature.[4] These trends have been analyzed in detail.[4c]

Monosubstituted alkenes and **1** react to give mixtures of the configurational diastereomers IV and V (Figure 1).[7,11] These equilibrate by nondissociative processes in chlorohydrocarbon solvents at 90–100 °C.[7d] Kinetic binding selectivities (ca. 67:33) are lower than thermodynamic binding selectivities (90–99:10–1).[7c] Analogous complexes of symmetrical *cis*- and *trans*-alkenes are detailed in the preceding paper.[7e] Alkyne ligands adopt the idealized Re–(C≡⋯C) conformation shown in VI, despite the fact that one substituent is directed at the bulky PPh_3 ligand.[8] Barriers to Re–(C≡⋯C) rotation are >22 kcal/mol (180 °C).

Scheme I. Binding of Acrolein to the Chiral Lewis Acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I)



Rotamers can be detected with 2-hexyne, in which the C≡C substituents have similar steric demands, but not with terminal alkynes, where the substituent sizes are more biased.

Results

1. Binding of Acrolein: Room Temperature. The dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**1**) was generated from the methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**2**) and $HBF_4\cdot OEt_2$ at −80 °C in CH_2Cl_2 as previously described.[9] Then acrolein was added (3 equiv; Scheme I). Workup gave the light tan π aldehyde complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}O{=}CHCH{=}CH_2)]^+BF_4^-$ (**3**)[12] in 75–89% yields. Complex **3**, and other new compounds isolated below, were characterized by microanalysis and IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy. Full data are given in the Experimental Section, and selected ^1H and ^{13}C NMR chemical shifts are illustrated pictorially in Chart I.

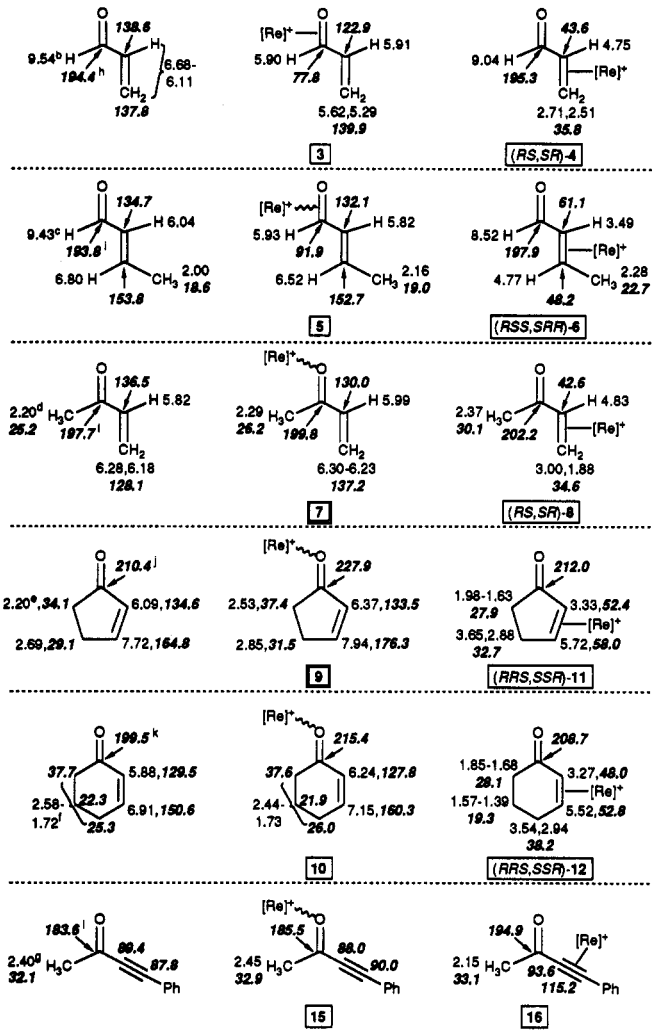
Complex **3** exhibited O=CH ^1H and ^{13}C NMR resonances (δ 5.90; 77.8 ppm) that were considerably upfield from those of free acrolein (δ 9.54; 194.4 ppm), as shown in Chart I. Aliphatic π aldehyde complexes of I display similar chemical shift trends (δ 5.2–5.4; 60–92 ppm).[3] The O=CH ^1H and ^{13}C NMR resonances of aldehyde ligands that give high proportions of σ isomers, such as *p*-methoxybenzaldehyde, are closer to those of free aldehydes (e.g., δ 8.42; 169.1 ppm; 15:85 π/σ, CH_2Cl_2, 26 °C).[4a,c] Similarly, **3** exhibited a PPh_3 ^{31}P NMR resonance (12.1/10.6 ppm, CD_3NO_2/CD_2Cl_2) near the range associated with π aliphatic aldehyde complexes of I (9–11 ppm),[3] and outside of that characteristic of σ ketone complexes (18–19 ppm).[5] As a check, ^{31}P NMR spectra were recorded in

(10) Quantitative π diastereomer ratios are now available for a series of aliphatic aldehyde complexes of I and will be reported shortly: B. Boone, unpublished data, University of Utah. The π diastereomers rapidly equilibrate via σ isomers.[4b]

(11) (a) Rhenium and carbon configurations in π aldehyde and alkene complexes are assigned as previously described.[3a,7e] The rhenium configuration is specified first, followed by those of the =CHR stereocenters. In alkene complexes with two =CHR stereocenters, the configuration of the carbon with the highest Cahn–Ingold–Prelog priority (=CHCO > =CHCH$_2$R) is given first. (b) A synclinal (*sc*) Re–(C⋯C) rotamer is one in which the highest priority substituent on rhenium (η^5-C_5H_5) and the C⋯C centroid (=CHCO) 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 XI/XVI and X/XVII are 45° and 135°, respectively. See section E-5.6, p 24, of *Pure Appl. Chem.* **1976**, *45*, 11.

(12) For the line formulae in this paper, ligand binding sites are specified by the hapticity (η) designation. Thus, O=CH-η^2-CH=CH$_2$ indicates an alkene complex of acrolein.

Chart I. Comparison of ^1H and ^{13}C (Bold and Italicized) NMR Chemical Shifts (ppm) of Free Ligands and $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ ([Re]$^+$) Adducts[a]

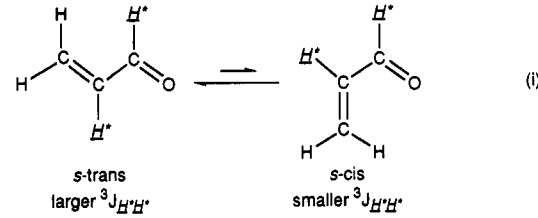


[a] Data for organic compounds are in $CDCl_3$; data for rhenium complexes are in CD_2Cl_2, except for (*RS,SR*)-4 ($CDCl_3$), 3 (CD_3NO_2), and (*RRS,SSR*)-12 (CD_3NO_2). [b] *The Sadtler Standard Spectra*; Sadtler Research Laboratories: Philadelphia, Pennsylvania; Vol. 14, spectrum 9153M. [c] *Ibid*; Vol. 18, spectrum 11669M. [d] *Ibid*; Vol. 14, spectrum 9272M. [e] *Ibid*; Vol. 23, spectrum 14728M. [f] *Ibid*; Vol. 15, spectrum 9880M. [g] *Ibid*; Vol. 21, spectrum 13383M. [h] *The Sadtler Guide to Carbon-13 NMR Spectra*; Simons, W. W., Ed.; Sadtler Research Laboratories: Philadelphia, Pennsylvania, 1983; spectrum 404. [i] *TRC Spectral Data—^{13}C Nuclear Magnetic Resonance*, Thermodynamics Research Center: Texas A&M University, College Station, Texas; spectrum 77. [j] *Ibid*; spectrum 83. [k] Hesse, M.; Meier, H.; Zeeh, B. *Spektroskopische Methoden in der Organischen Chemie*; Verlag: New York, 1987; p149. [l] This ^{13}C NMR spectrum was recorded at 75 MHz in $CDCl_3$ and referenced to TMS at 0.0 ppm.

$CHFCl_2$/acetone between 22 and −120 °C in ca. 20 °C steps. Although π/σ equilibrium ratios can vary greatly over such temperature intervals,[4] the chemical shift changed only slightly (ppm: 10.95, 22 °C; 10.65, −60 °C; 10.88, −120 °C), and no decoalescence phenomena were observed.

Complex **3** also exhibited an IR ν_{NO} absorption (1748 cm^{-1}) in a region characteristic of π aliphatic and aromatic aldehyde complexes of I (1723–1740[3] and 1733–1745[4] cm^{-1}), and distinct from that of σ ketone and aromatic aldehyde complexes (1697–1680[5] and 1701–1692[4] cm^{-1}). With π aromatic aldehyde complexes, it has proved possible to detect as little as 4% of a σ isomer by IR.[4] However, neither a second IR ν_{NO} band nor the $\nu_{C=C}$ absorption that would be expected of either isomer were observed in KBr, CH_2Cl_2, or thin films.

Acyclic α,β-unsaturated carbonyl compounds can exist in either *s-trans* or *s-cis* conformations, as shown in eq i.[13]



(i)

This equilibrium plays an important role in the stereochemistry of addition reactions.[14] We sought to probe this feature in **3** by ^1H difference NOE experiments.[15] However, the chemical shifts of the O=C*H* and O=CH—C*H*= resonances were too close. Nonetheless, the small magnitude of their coupling constant ($^3J_{HH}$ = 2.1–2.2 Hz) suggested, by analogy to literature values[13e] and other data given below, a dominant *s-cis* conformation, as illustrated in VII (Scheme I).

2. Binding of Acrolein: Elevated Temperature. Thermolyses of **3** were investigated next. First, a $CHCl_2$-$CHCl_2$ solution of **3** was kept at 60 °C for 20 h (Scheme I). It became dark, and ^1H NMR spectra gave very broad resonances, suggestive of some paramagnetic product. However, ^{31}P NMR spectra showed the clean conversion to two compounds (58:42).[16] The chemical shifts (10.9, 10.7 ppm) were in a range characteristic of diastereomeric monosubstituted alkene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(RCH{=}CH_2)]^+BF_4^-$.[7a,c,d]

Chromatography gave a sample that could be characterized by ^1H NMR, although at considerable cost in yield (34%). Spectroscopic data showed the isolated product to be a 49:51 mixture of *RS,SR* and *RR,SS* diastereomers of the alkene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}CH\text{-}\eta^2\text{-}CH{=}CH_2)]^+BF_4^-$ (**4**).[11,12] As summarized in Chart I,[13f] now the HC=CH_2 ^1H and ^{13}C NMR resonances (δ 4.75–2.51; 36–44 ppm) were upfield of those of acrolein (δ 6.11–6.88; 138–139 ppm), whereas the O=CH ^1H and ^{13}C NMR resonances (δ 9.04–9.32; 195–201 ppm) were close to those of acrolein (δ 9.54; 194 ppm). The IR ν_{CO} value (1687 cm^{-1}) was less than that of acrolein (1704 cm^{-1}), and the IR ν_{NO} value (1732 cm^{-1}) was greater than those of alkyl-substituted alkene complexes of I (1713–1727 cm^{-1}).[7a,c] The latter trend, which is more pronounced in similar carbonyl-substituted alkene complexes below, indicates lower back-bonding into the nitrosyl ligand, consistent with the expected effect of an electron-withdrawing substituent upon C=C donor and π acceptor properties.

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(15) Neuhaus, D.; Williamson, M. *The Nuclear Overhauser Effect in Structural and Conformational Analyses*; VCH: New York, 1989; Chapter 7. Upon irradiation of the cyclopentadienyl ligand ^1H NMR resonances, all of the compounds studied show 0.2–0.5% enhancements of the PPh_3 ligand *ortho* ^1H NMR resonances. These are not tabulated.

(16) All isomer ratios are normalized to 100, and error limits on each integer are ±2; e.g., 58:42 ≡ 58 ± 2:42 ± 2.

The upfield and downfield C=C ^{13}C NMR resonances (36–37, 43–44 ppm) were assigned to the $=CH_2$ and =CHR carbons by analogy to chemical shift trends previously established in this series of compounds.[7a,c] As a check, the =CHR ^1H resonance of (*RS,SR*)-4 was irradiated. The downfield C=C ^{13}C resonance was decoupled. Of importance to a structural issue below, only the upfield $=CH_2$ resonances exhibited observable phosphorus couplings ($^2J_{CP}$ = 6.4–6.9 Hz). Such couplings are diagnostic of C=C (or C≡C) carbons that are *syn* to the PPh_3 ligand,[7,8] consistent with the Re–(C=C) conformations shown in Newman projections VIII–IX (Scheme I). The $=CH_2$ and =CHR ^1H NMR resonances gave similar phosphorus coupling patterns ($^3J_{HP}$ = 13.7–5.0 Hz vs ≤1.8 Hz).

Attempts to isomerize **3** to **4** in chlorobenzene at 100 °C gave appreciable codecomposition. However, clean solid-state rearrangements have sometimes been observed in this series of compounds.[17] Hence, solid **3** was heated at 100 °C. After 24 h, no **3** remained, and **4** was isolated in 94% yield as a 98:2 mixture of *RS,SR/RR,SS* diastereomers.[18a] Crystallization gave pure (*RS,SR*)-**4**. This experiment implied high thermodynamic C=C enantioface binding selectivity, and analogous data were sought in solution. Thus, samples of (*RS,SR*)-**4** and a 61:39 *RS,SR/RR,SS* mixture (crude, from a preparative reaction prior to chromatography) were kept in $CHCl_2CHCl_2$ at 100 °C. After 17 h, ^{31}P NMR spectra showed only (*RS,SR*)-**4**,[18b] with no sign of any codecomposition. Hence, under these conditions the *RS,SR/RR,SS* equilibrium ratio is >99:<1.

The structure of **4** was further probed by ^1H difference NOE experiments.[15] Irradiation of the cyclopentadienyl resonance of (*RS,SR*)-**4** gave 5.2% and 2.3% enhancements in the O=CH—C*H*= and O=CH resonances, respectively, as depicted in VIII in Scheme I. These values confirmed the diastereomer assignment, as further illustrated by related examples in the preceding paper.[7e] Irradiation of the O=CH resonance gave a 2.2% enhancement in the O=CH—C*H*= resonance, but none in the $=CH_2$ resonances. This suggested a dominant *s-cis* ligand conformation, as shown in VIII. The $^3J_{HH}$ value for the O=CH—CH= linkage was relatively small (3.7 Hz).

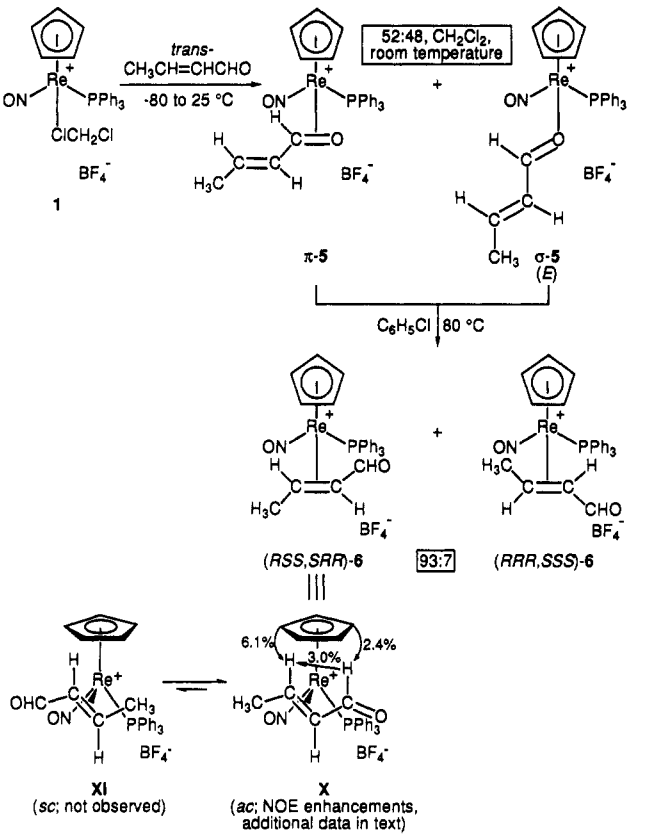
Irradiation of the cyclopentadienyl resonance of (*RR,SS*)-**4** gave a large 8.9% enhancement in the O=CH resonance, as depicted in IX in Scheme I. Irradiation of the O=CH resonance gave 1.6–1.7% enhancements in the *Z* $=CH_2$ and cyclopentadienyl resonances, but none in the O=CH—C*H*= resonance. These data suggest that the *s-trans* ligand conformation is favored, as shown in IX. Accordingly, the $^3J_{HH}$ value for the O=CH—CH= moiety is somewhat higher (5.3 Hz).

3. Binding of Crotonaldehyde. Complex **1** and *trans*-crotonaldehyde were reacted in a procedure analogous to that used for acrolein (Scheme II). Workup gave the carbonyl-bound complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2/\eta^1\text{-}O{=}CHCH{=}CHCH_3)]^+BF_4^-$ (π/σ-**5**) in 83% yield. Complex **5** gave deep brown solutions, and was characterized in a manner identical to **3**, as summarized in Chart I and the experimental section.

Complex **5** exhibited O=CH ^1H and ^{13}C NMR resonances (δ 5.93; 91.9 ppm) that were upfield from those of free *trans*-crotonaldehyde (Chart I). However, the ^{13}C shift was smaller than that of the acrolein ligand in **3**. Furthermore, the ^{31}P NMR resonance (15.3 ppm) was between the regions characteristic of π aldehyde and σ ketone complexes of I. Accordingly, an IR spectrum in CH_2Cl_2 revealed ν_{NO} bands for both π and σ isomers (1734, 1694 cm^{-1}), and quantitative analysis as described earlier gave a 52:48 ratio.[4a,c] The ν_{CO} and $\nu_{C=C}$ absorptions of the σ isomer were also apparent (1629, 1575 cm^{-1}).[4c,19] As observed for aromatic aldehyde complexes of I,[4a,c] the π/σ ratio increased in the more polar medium 1:1 CH_2Cl_2/CH_3NO_2 (73:27), and with a decrease in temperature.[20] Complex **5** also showed a visible absorption characteristic of σ aromatic aldehyde and aromatic ketone complexes of I (432 nm, ε 3200 M^{-1} cm^{-1}; 0.0002 M, CH_2Cl_2, 26 °C).[4c]

Difference ^1H NOE experiments were conducted. Irradiation of the cyclopentadienyl resonance of **5** did not enhance any crotonaldehyde ligand resonances. However, irradiation of the O=CH resonance gave a 6.5% enhancement in the =C*H*CH_3 resonance, but none in the O=CH—C*H*= resonance. This suggests that the *s-trans*-crotonaldehyde ligand conformation dominates, as depicted in the formulae in Scheme II. Accordingly, the O=CH—CH= linkage exhibited a large $^3J_{HH}$ value of 9.3 Hz.[13e,21] There is also the potential for geometric isomers about the O=C bond in σ-**5**. On the basis of the relative sizes of the O=*C* substituents, and the crystal structure

Scheme II. Binding of Crotonaldehyde to the Chiral Lewis Acid I



(17) Roger, C.; Bodner, G. S.; Hatton, W. G.; Gladysz, J. A. *Organometallics* **1991**, *10*, 3266.

(18) (a) Separate thermolyses showed conversions of 44%, 72%, 82%, 87%, 94%, and 100% after 1, 2, 4, 8, 12, and 20 h, respectively, as assayed by ^{31}P NMR. At all stages, the *RS,SR/RR,SS* ratio was ≥98:2. (b) The 61:39 *RS,SR/RR,SS* mixture had converted to 69:31 and 81:19 mixtures after 2 and 8 h, respectively.

(19) The IR ν_{CO} and $\nu_{C=C}$ absorptions of σ-O=C complexes of α,β-unsaturated aldehydes and ketones are assigned on the basis of frequency values ($\nu_{CO} > \nu_{C=C}$) and intensity ($\nu_{CO} > \nu_{C=C}$). A reversed assignment would require that the $\nu_{C=C}$ bands of the free ligands shift negligably or to *higher* frequency upon formation of a σ-O=C adduct of I.

(20) Separate ^{31}P NMR resonances are observed for π-**5** and σ-**5** at −120 °C in $CDFCl_2$ (10.8, 21.2 ppm; 89:11). These coalesce at −60 °C, and full details of the dynamic behavior will be reported separately. A second π isomer was not observed,[4b,10] and as little as 1% would have been detected.

of a σ aromatic aldehyde complex of I,[4a,c] the *E* isomer is presumed to greatly dominate.

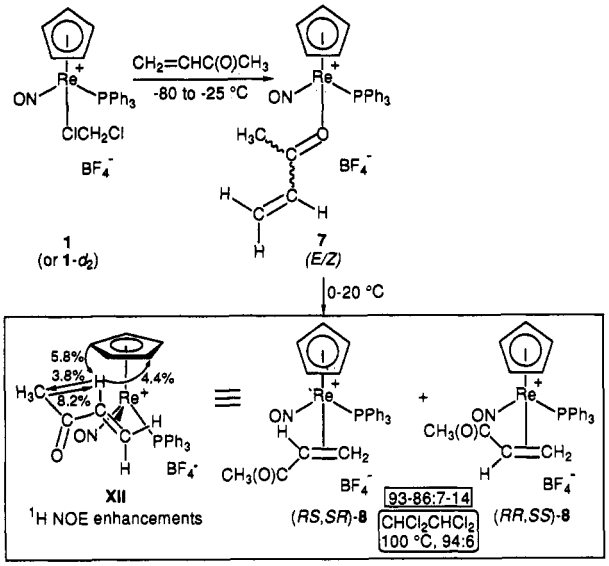
Next, a chlorobenzene suspension of **5** and excess crotonaldehyde was kept at 80 °C (Scheme II). After 30 min, **5** had dissolved. After 18 h, workup gave the alkene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}CH\text{-}\eta^2\text{-}CH{=}CH\text{-}CH_3)]^+BF_4^-$ (**6**) in 78% yield as a 93:7 mixture of *RSS,SRR*/*RRR,SSS* diastereomers.[11,22] Product configurations were assigned by analogy to the corresponding symmetrical *trans*-alkene complexes in the preceding paper, which gave similar diastereomer ratios under comparable conditions,[7e] and from NOE data below. Complex **5** also isomerized to **6** in the solid state (34% conversion, 8 h, 100 °C), without independent decomposition.

Many spectroscopic properties of (*RSS,SRR*)-**6** were similar to those of the acrolein alkene complex **4** (IR ν_{NO}, ν_{CO}: 1740, 1683 cm^{-1}). However, now the O=CH—*C*H= ^{13}C NMR resonance exhibited a larger $^2J_{CP}$ (5.4 Hz) than the =$CHCH_3$ resonance ($w_{1/2}$ = 1.3 Hz), as confirmed by a heteronuclear decoupling experiment. The O=CH—*C*H= ^1H NMR resonance also gave a larger $^3J_{HP}$ than the =*C*HCH_3 resonance (7.6 vs 2.0 Hz). This suggested that (*RSS,SRR*)-**6** preferentially adopted the *ac*[11b] Re–(C$\overline{\cdot\cdot}$C) conformation shown in X (Scheme II), as opposed to the alternative *sc* isomer XI.[23] Thus, the more congested interstice between the cyclopentadienyl and large PPh_3 ligands more readily accommodates the O=CH moiety.

Supporting ^1H NOE data were sought. Irradiation of the cyclopentadienyl resonance of (*RSS,SRR*)-**6** gave 6.1% and 2.4% enhancements in the =*C*HCH_3 and O=CH resonances, as summarized in X. The other crotonaldehyde ligand resonances were unaffected, confirming the *ac* Re–(C$\overline{\cdot\cdot}$C) rotamer assignment. Irradiation of the O=CH resonance gave 3.0% and 0.6% enhancements in the =*C*HCH_3 and cyclopentadienyl resonances. These data further indicate that the *s-trans* ligand conformation dominates, consistent with the O=CH—CH=$^3J_{HH}$ value of 5.8 Hz. Due to the small quantities produced, similar studies of (*RRR,SSS*)-**6** were not pursued.

4. Binding of Methyl Vinyl Ketone. The deuteriodichloromethane complex **1**-d_2 was generated in CD_2Cl_2 in an NMR tube at −80 °C,[9] and methyl vinyl ketone (1.0 equiv) was added (Scheme III). The sample was warmed to −25 °C, and ^1H, ^{13}C, and ^{31}P NMR spectra were recorded. These showed complete conversion to the σ ketone complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(CH_3)CH{=}CH_2)]^+BF_4^-$ (**7**). Complex **7** exhibited a ^{31}P NMR resonance (18.5 ppm) in the region characteristic of σ ketone complexes, and a O=C ^{13}C NMR resonance (199.8 ppm) slightly downfield of that of free methyl vinyl ketone (197.7 ppm; Chart I).[13f] An IR spectrum showed ν_{NO}, ν_{CO}, and $\nu_{C=C}$ absorptions similar to those of σ-**5** (1681 vs, 1617 m, 1550 w cm^{-1}).[19] Since the O=*C* substituents in **7** are of comparable size, appreciable quantities of both *E* and *Z* geometric isomers may be present.

Scheme III. Binding of Methyl Vinyl Ketone to the Chiral Lewis Acid I



The O=C ^{13}C NMR resonance of the corresponding σ acetone complex is 25.9 ppm downfield from that of free acetone.[5a,9] In view of the smaller shift in **7**, we considered the possibility that there might be a small amount of a π isomer present. Hence, **7** was generated by an analogous procedure in $CHFCl_2$, and ^{31}P NMR spectra were recorded at ca. 20 °C intervals between −25 and −140 °C. However, the chemical shift varied only slightly (ppm: 18.57, −25 °C; 18.40, −60 °C; 18.72, −140 °C), and no decoalescence phenomena were observed.

The solution of **7** that had been prepared from **1**-d_2 was gradually warmed (Scheme III). Clean conversion to the alkene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}C(CH_3)\text{-}\eta^2\text{-}CH{=}CH_2)]^+BF_4^-$ (**8**) occurred, as assayed by ^{31}P NMR (0 °C, 60 min, 91:9; 10 °C, 30 min, 78:22; 20 °C, 10 min, 67:33). At all stages, the *RS,SR* diastereomer greatly dominated. Preparative reactions gave **8** in 87–93% yields as 93–86:7–14 mixtures of *RS,SR*/*RR,SS* diastereomers. A $CHCl_2CHCl_2$ solution of a 86:14 *RS,SR*/*RR,SS* mixture was kept at 100 °C. Isomerization gradually occurred to a 94:6 equilibrium mixture (4 h, 87:13; 22 h, 93:7; 30, 38, 45 h, 94:6).

Most spectroscopic properties of **8** (Experimental Section, Chart I) closely resembled those of the acrolein alkene complex **4**. NOE experiments were conducted with (*RS,SR*)-**8** as described for the other complexes above. These gave the enhancements summarized in XII (Scheme III). The patterns confirmed the diastereomer assignment, and indicated a dominant *s-cis* ligand conformation.[24]

5. Binding of Cycloalkenones. The dichloromethane complex **1** was reacted with cyclopentenone and cyclohexenone in procedures analogous to those used for the acyclic substrates above (Scheme IV). Workup gave the red σ-ketone complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}\overline{CCH{=}CH(CH_2)_n})]^+BF_4^-$ (n = 2, 9; 3, 10) in 76–81% yields. Complex **10** displayed a visible absorption at 424 nm (ϵ 4200 M^{-1} cm^{-1}; 0.0002 M, CH_2Cl_2, 26 °C).

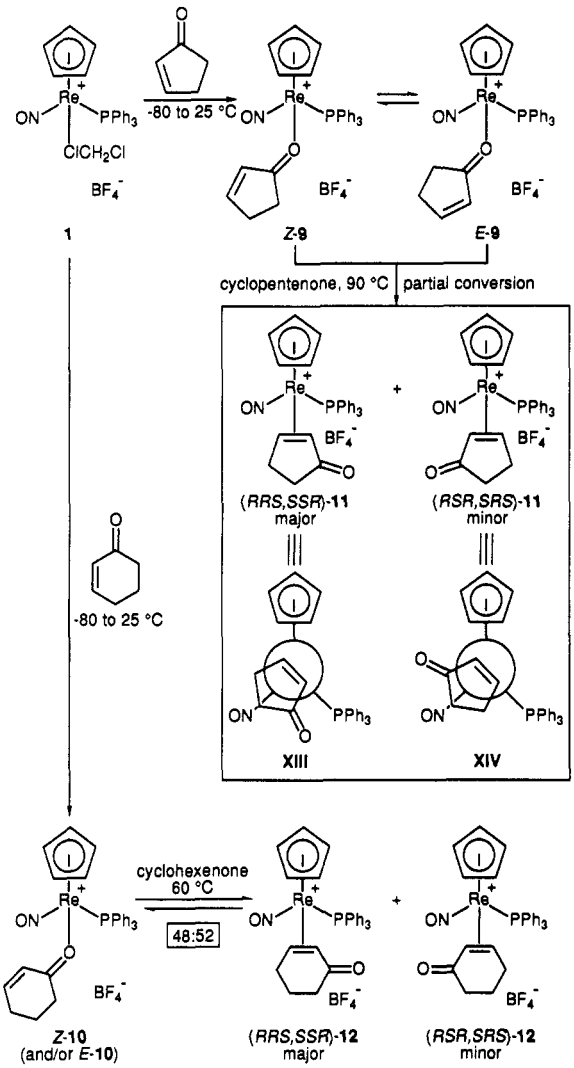
(21) (a) The corresponding "isosteric" *trans*-piperylene π complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}CHCH{=}CHCH_3)]^+BF_4^-$ exhibits an *s-trans* conformation in the solid state and a $^3J_{HH}$ value of 5.0 Hz for the =CH—CH= linkage.[7f] (b) The *trans*-crotonaldehyde imine complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}HN{=}CHCH{=}CHCH_3)]^+X^-$ exists exclusively as a σ isomer and exhibits a $^3J_{HH}$ value of 9.7 Hz: B. Bennett, unpublished data, University of Utah.

(22) The isomerization of **5** to **6** was monitored by ^{31}P NMR in $CHCl_2$-$CHCl_2$, and was found to be faster than that of **3** to **4**. At 24% and 68% conversions (2 h, 40 °C; 2 h, 60 °C), *RSS,SRR*/*RRR,SSS* ratios were 93:7 and 92:8. When the sample was warmed to 85–95 °C, independent thermal decomposition of **6** occurred, but the diastereomer ratios were unaffected.

(23) In order to probe for a small amount of XI in rapid equilibrium with X, ^{31}P NMR spectra of (*RSS,SRR*)-**6** [and (*RRR,SSS*)-**6**] were recorded in CH_2Cl_2 at ca. 20 °C intervals between 24 and −100 °C. The chemical shifts were somewhat temperature dependent (ppm: 3.87, 6.83 (24 °C); 5.16, 7.81 (−100 °C)), but no decoalescence was observed.

(24) The $^3J_{HH}$ couplings employed as qualitative probes of acrolein and *trans*-crotonaldehyde ligand conformations (equation i) are absent in α,β-unsaturated ketones. However, we note for future study that the $^3J_{CH}$ values of O=C(*C*H_2R)—*C*H= linkages are in principle of analogous utility.

Scheme IV. Binding of Cycloalkenones to the Chiral Lewis Acid I



Complexes **9** and **10** exhibited O=C ^{13}C NMR resonances (227.9, 215.4) that were 16–17 ppm downfield from those of the free ligands (Chart I). The ^{31}P NMR resonances and IR ν_{NO} absorptions were in the ranges expected for σ complexes (18.7, 18.2 ppm; 1681, 1683 cm^{-1}), and IR ν_{CO} and $\nu_{C=C}$ bands were apparent (1604, 1605; 1566, 1558 cm^{-1}).[19] The O=C—*CH*= and =*CH*CH_2 ^1H and ^{13}C NMR resonances were assigned on the basis of chemical shift and coupling constant patterns in the free ligands. Both *E* and *Z* O=C geometric isomers are shown for **9** in Scheme IV. However, the C=C group in **10** is depicted as *cis* to the rhenium, analogous to the crystal structures of two iron σ-cyclohexenone complexes.[25-27]

Thermolyses of **9** and **10** were investigated. First, **9** was kept at 90 °C for 8 h in neat cyclopentenone (Scheme IV). Purification of the resulting gum gave the alkene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}\overset{\frown}{C}\text{-}\eta^2\text{-}CH{=}CHCH_2CH_2)]^+BF_4^-$ (**11**) in 16% yield, and as a 93:7 mixture of *RRS,SSR*/*RSR,SRS* diastereomers.[28] However, a ^{31}P NMR spectrum recorded prior to workup showed a 63:37 mixture of diastereomers. Thermolyses conducted in chlorinated solvents gave lower yields. The O=C—*CH*= and =*CH*CH_2 ^1H NMR resonances of (*RRS,SSR*)-**11** could be distinguished based upon their coupling patterns with other protons. Only the former was coupled to phosphorus ($^3J_{HP}$ 6.9 Hz). Hence, as found for the *trans*-crotonaldehyde alkene complex (*RSS,SRR*)-**6**, the O=C—CH= terminus must be *syn* to the PPh_3 ligand, as shown in XIII.

Complex **10** was similarly heated in neat cyclohexenone (60 °C, 13 h). A ^{31}P NMR spectrum showed the formation of a 52:48 mixture of a new compound and **10**. The ratio remained unchanged with additional time. Purification gave the alkene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}\overset{\frown}{C}\text{-}\eta^2\text{-}CH{=}CHCH_2CH_2CH_2)]^+BF_4^-$ (**12**) in 32% yield as a 97:3 mixture of *RRS,SSR*/*RSR,SRS* diastereomers (Scheme IV).[28] However, ^{31}P NMR spectra recorded prior to workup showed 80–83:20–17 mixtures of diastereomers. The spectroscopic properties of (*RRS,SSR*)-**12** were very similar to those of (*RRS,SSR*)-**11**. Attempts to equilibrate the *RRS,SSR*/*RSR,SRS* diastereomers of **11** or **12** in $CHCl_2CHCl_2$ at 100 °C gave rapid decomposition.

When solid samples of **9** or **10** were kept at 100 °C for 20 h, no isomerization or significant amount of decomposition was observed. We suspected that the poor conversions in this series of compounds might be due to equilibrium constraints. Thus, **12** was kept at 60 °C for 8 h in neat cyclohexenone. A 62:38 **12**/**10** mixture formed, as assayed by ^{31}P NMR. A small amount of $O{=}PPh_3$ was also present. Hence, similar mixtures are obtained from either **10** or **12**, and the equilibrium constant is only slightly greater than unity.

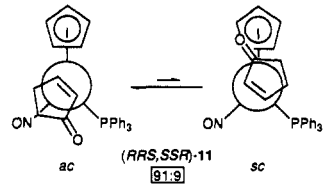
We also sought to determine the relative binding affinities of cyclohexanone and cyclohexenone for the rhenium fragment I. Thus, a $CHCl_2CHCl_2$ solution of the previously reported cyclohexanone complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}\overset{\frown}{C}H_2(CH_2)_4)]^+BF_4^-$ (**14**)[5c] was treated with 1.0 equiv of cyclohexenone (eq ii). Substitution was very slow at room temperature, but occurred readily over the course of 2 h at 46 °C to give a 91:9 **10**/**14** mixture, as assayed by ^{31}P NMR. This ratio was unchanged after an additional hour. Complex **10** was similarly treated with 1.0 equiv of cyclohexanone. A 92:8 **10**/**14** mixture formed.

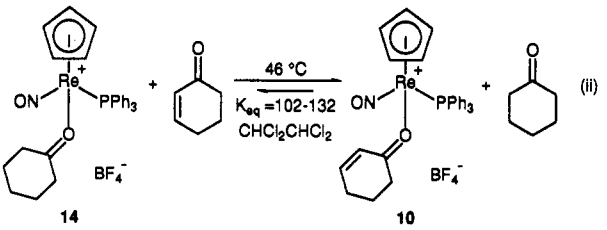
(25) (a) Foxman, B. M.; Klemarczyk, P. T.; Liptrot, R. E.; Rosenblum, M. *J. Organomet. Chem.* **1980**, *187*, 253. (b) For *E*/*Z* isomer ratios of σ adducts of cyclohexenone and BF_3, see Torri, J.; Azzaro, M. *Bull. Soc. Chim. Fr.* **1978**, II-283.

(26) Shambayati, S.; Schreiber, S. L. In *Comprehensive Organic Synthesis*; Trost, B. M., Editor-in-Chief; Fleming, I., Deputy Editor-in-Chief; Schreiber, S. L., Volume Editor; Pergamon: New York, 1991; Vol. 1, Chapter 1.10.

(27) In an attempt to detect *E*/*Z* O=C geometric isomers, ^{31}P and ^{13}C NMR spectra of **9** and **10** were recorded in CD_2Cl_2 at −100 °C. However, no decoalescence was observed.

(28) Additional isomers of **11** and **12**, which differ by ca. 180° rotations about the Re–(C=C) axes from those in Scheme IV, are possible. Analogous equilibria of symmetrical *cis*-alkene complexes of I are characterized in the preceding paper.[7e] Such rotamers usually interconvert with 11–14 kcal/mol barriers and give coalesced NMR spectra at room temperature. No isomers of (*RRS,SSR*)-**12** were detected by ^{31}P NMR in CH_2Cl_2 between 22 and −100 °C, and 2D NMR exchange experiments of the type described in the preceding paper showed no cross peaks between the resonances assigned to (*RRS,SSR*)- and (*RSR,SRS*)-**12**. However, (*RRS,SSR*)-**11** gave *two* ^{31}P NMR resonances in CH_2Cl_2 (3.2/10.2 ppm; 91:9) at room temperature and below. A similar 2D NMR spectrum (acetone-d_6) gave cross peaks, showing that the resonances arise from equilibrating species (5.1/12.8 ppm, 91:9; coalescence between 35 and 40 °C). Hence, they were assigned to *ac*/*sc*[11b] rotamers as shown:





14 10

These data show that the carbonyl group in cyclohexenone is more basic than that in cyclohexanone, and establish a K_{eq} of 102–132 for eq ii.

6. Binding of an Acetylenic Ketone. The deuteriodichloromethane complex **1**-d_2 and 4-phenyl-3-butyn-2-one were combined in an NMR tube at −80 °C (Scheme V). The solution was warmed to −25 °C, and ^1H, ^{13}C, and ^{31}P NMR spectra were recorded. These showed complete conversion to the σ ketone complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(CH_3)C{\equiv}CC_6H_5)]^+BF_4^-$ (**15**). Complex **15** exhibited a O=C ^{13}C NMR resonance ca. 2 ppm downfield of that of the free ketone (Chart I). The C≡C resonances (88.0, 90.0 ppm) were tentatively assigned by analogy to chemical shift trends shown by the σ-enone complexes (C_α, upfield of free ligand; C_β, downfield of free ligand). The ^{31}P NMR resonance was in a region characteristic of σ ketone complexes (19.1 ppm). An IR spectrum showed the expected ν_{NO}, ν_{CO}, and $\nu_{C\equiv C}$ absorptions (1671 vs, 1541 m, 2169 m cm^{-1}).[19]

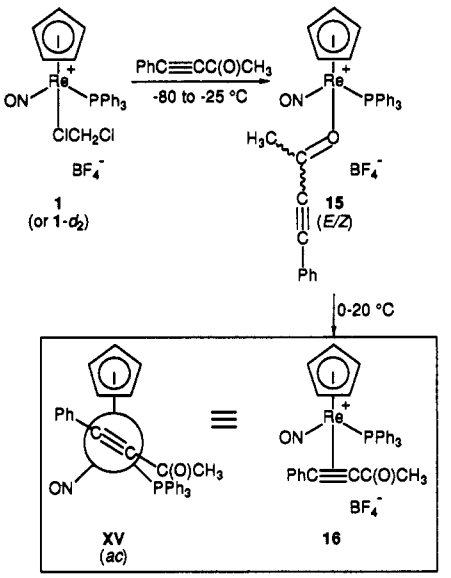
The sample was gradually warmed, and clean conversion to a new compound occurred (−20 °C, 55 min, >99:<1; 0 °C, 38 min, 87:13; 20 °C, 60 min, 23:77). Workup of a preparative reaction gave the alkyne complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}C(CH_3)\text{-}\eta^2\text{-}C{\equiv}CC_6H_5)]^+BF_4^-$ (**16**) in 89% yield. In both experiments the product was homogeneous, suggesting a single Re–(C≡C) rotamer.[8]

The NMR properties of **16** closely matched those of other alkyne complexes of I.[8] Only the upfield C≡C ^{13}C NMR resonance was coupled to phosphorus (93.6 ppm, $^2J_{CP}$ = 12.6 Hz), and was therefore assigned to the carbon *syn* to the PPh_3 ligand. Also, in the corresponding 2-butyne and 3-hexyne complexes, only the propargylic carbons *syn* to the PPh_3 ligand are coupled to phosphorus ($^3J_{CP}$ = 5.7–5.9 Hz).[8a] Since the O=*C*—C≡ resonance in **16** exhibited phosphorus coupling (194.9 ppm, $^3J_{CP}$ = 3.8 Hz), this group was presumed to be *syn* to the PPh_3 ligand, as shown in XV (Scheme V).

The IR ν_{NO} value of **16** (1720–1718 cm^{-1} vs) was somewhat greater than those of alkyl-substituted alkyne complexes of I (1696–1716 cm^{-1}),[8a,b] and the ν_{CO} absorption (1680–1668 cm^{-1} s) was slightly lower than those of the carbonyl-substituted alkene complexes above. A band was also reproducibly observed at 1808–1813 cm^{-1} (m). We suggest that this is associated with the C≡C linkage of the coordinated alkyne. However, it is of lower frequency and greater intensity than usual for $\nu_{C\equiv C}$ absorptions of alkyne complexes. We speculate that these attributes are due to the conjugated O=C group.[29]

7. Binding of Other Acyclic Vinyl Ketones. In order to probe the generality of the preceding data, additional substrates were investigated. First, **1** and ethyl vinyl ketone were combined in a preparative reaction analogous to those given above. Workup gave the alkene complex

Scheme V. Binding of an Acetylenic Ketone to the Chiral Lewis Acid I



$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}C(CH_2CH_3)\text{-}\eta^2\text{-}CH{=}CH_2)]^+BF_4^-$ (**17**) in 70% yield as a 93:7 mixture of *RS,SR*/*RR,SS* diastereomers. The NMR properties of both diastereomers closely matched those of the corresponding methyl vinyl ketone alkene complex **8**.

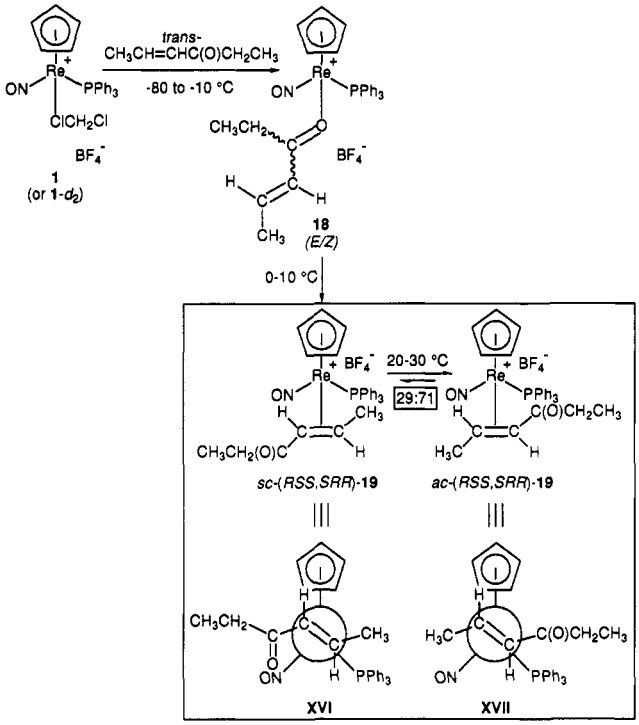
Complex **1**-d_2 and ethyl vinyl ketone were also combined in an NMR tube as described for methyl vinyl ketone. A ^1H NMR spectrum was recorded at −10 °C, and showed complete conversion to a σ ketone complex (δ 5.62, C_5H_5). Rearrangement to **17** occurred over the course of 1 h at 10 °C. In three independent experiments, the *RS,SR* diastereomer greatly dominated (90–95:10–5). However, in one preparative experiment the less stable *RR,SS* diastereomer constituted 67% of the product upon workup (86% total yield). A similar result was also obtained in one NMR experiment with methyl vinyl ketone. Although these observations could not be reproduced, they were not hallucinations: complete NMR data for (*RR,SS*)-**17**, which would otherwise be unattainable, is given in the Experimental Section.[30] Further studies of these potentially significant phenomena are planned, as discussed below.

Complex **1**-d_2 and *trans*-4-hexen-3-one were similarly combined in an NMR tube (Scheme VI). A ^1H NMR spectrum was recorded at −10 °C, and showed complete conversion to the σ ketone complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(CH_2CH_3)CH{=}CHCH_3)]^+BF_4^-$ (**18**; δ 5.60, C_5H_5). Isomerization occurred slowly at 0 °C and more rapidly at 10 °C to give the π alkene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}C(CH_2CH_3)\text{-}\eta^2\text{-}CH{=}CHCH_3)]^+BF_4^-$ (**19**). At 68% conversion, **19** was a 96:4 mixture of two isomers. These were assigned as *sc*/*ac* Re–(C≡C) rotamers of the *RSS,SRR* diastereomer (XVI, XVII; Scheme VI)[11b] based upon NMR data and a crystal structure below. At 90% conversion, the *sc*/*ac* ratio was 86:14. Upon warming to 29 °C, conversion to a 29:71 *sc*/*ac* mixture occurred.[31] The ratio did not change when the sample was cooled. Thus, the less stable rotamer is formed more rapidly.

(29) IR $\nu_{C\equiv C}$ absorptions have been observed at 1763–1805 cm^{-1} in molybdenocene complexes of acetylenic esters. However, intensities were not noted to be greater than those in analogous aliphatic alkyne complexes: (a) Herberich, G. E.; Okuda, J. *Chem. Ber.* **1984**, *117*, 3112. (b) Herberich, G. E.; Englert, U.; Fassbender, W. *J. Organomet. Chem.* **1991**, *420*, 303.

(30) A $CHCl_2CHCl_2$ solution of the batch of **17** that was a 33:67 *RS,SR*/*RR,SS* mixture was kept at 100 °C. Equilibration to a 96:4 mixture gradually occurred over the course of 120 h (2 h, 36:64; 5 h, 45:55; 11 h, 60:40; 22 h, 75:25; 48 h, 87:13; 66 h, 93:7; 98 h, 95:5; 120 h, 96:4; 154 h, 96:4).

Scheme VI. Binding of *trans*-4-Hexen-3-one to the Chiral Lewis Acid I



In preparative reactions, (*RSS,SRR*)-**19** precipitated from CH_2Cl_2/ether in 76–65% yields and as 42–31:58–69 mixtures of *sc*/*ac* isomers. However, crystallization from CH_2ClCH_2Cl/ether at 0 °C reproducibly gave *only* the less stable rotamer as the hemisolvate *sc*-(*RSS,SRR*)-**19**·$(CH_2ClCH_2Cl)_{0.5}$. As expected from the NMR trends established above, the O=C—*CH*= ^{1}H and ^{13}C resonances of *ac*-(*RSS,SRR*)-**19** exhibited larger phosphorus couplings (8.0, 5.9 Hz) than those of *sc*-(*RSS,SRR*)-**19** (<2 Hz). Similarly, the =*CH*CH_3 ^{1}H and ^{13}C resonances of *sc*-(*RSS,SRR*)-**19** exhibited larger phosphorus couplings (10.5, 5.1 Hz) than those of *ac*-(*RSS,SRR*)-**19** (2.1, <2 Hz). Complex (*RSS,SRR*)-**19** slowly decomposed at 70–80 °C in $CHCl_2CHCl_2$ without the appearance of any new diastereomers.

X-ray data were collected on *sc*-(*RSS,SRR*)-**19**·$(CH_2ClCH_2Cl)_{0.5}$ as outlined in Table I. Refinement included the location of the alkene =CH hydrogens, and gave the structures shown in Figure 2. Atomic coordinates and selected bond lengths, bond angles, and torsion angles are summarized in Tables II and III. Figure 2 confirms the assigned structure, and shows that the enone moiety adopts an *s-cis* conformation in the solid state, with C1–C2–C4–O2 and C1–C2–C4–C5 torsion angles of 0(1)° and 179(1)°.

Complex *sc*-(*RSS,SRR*)-**19** adopts a Re–(C=C) conformation similar to that of idealized rotamer XVI. However, as with the analogous *trans*-2-butene complex described in the preceding paper,[7e] some deviation is evident. In XVI, the Re—C=C plane defines angles of 0° and ±90°, respectively, with the Re–P and Re–N bonds. In *sc*-(*RSS,SRR*)-**19**, the corresponding angles are 21.9° and 65.2°. The angle of the Re—C=C plane with that defined by the cyclopentadienyl centroid, rhenium, and C=C centroid is 45° in IV, but 72.1° in *sc*-(*RSS,SRR*)-**19**.[32]

Table I. Summary of Crystallographic Data for the *trans*-4-Hexen-3-one Complex *sc*-(*RSS,SRR*)-19·$(CH_2ClCH_2Cl)_{0.5}$

molecular formula	$C_{30}H_{32}BClF_4NO_2PRe$
molecular weight	778.027
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
cell dimensions	
a, Å	12.623(7)
b, Å	13.944(4)
c, Å	17.861(2)
β, deg	99.747(3)
V, Å^3	3098.72
Z	4
d_{calcd}, g/cm^3 (15 °C)	1.668
d_{obs}, g/cm^3 (23 °C)	1.699
crystal dimensions, mm	0.25 × 0.19 × 0.12
diffractometer	Enraf-Nonius CAD-4
radiation, Å	λ(Cu Kα) = 1.540 56
data collection method	θ–2θ
scan speed, deg/min	variable (1–12)
reflections measured	5707
range/indices (hkl)	0–14, 0–16, –20 to +20
scan range	0.80 + 1.40 tan θ
no. of reflections between stds	1 X-ray h
total no. of unique data	5223
no. of observed data, $I > 3\sigma(I)$	4130
abs coeff (μ), cm^{-1}	91.486
% minimum transmission	69.567
% maximum transmission	99.760
no. of variables	385
$R = \Sigma(\|\|F_o\| - \|F_c\|\|)/\Sigma\|F_o\|$	0.0327
$R_w = \Sigma(\|\|F_o\| - \|F_c\|\|)w^{1/2}/\Sigma\|F_o\|w^{1/2}$	0.0355
goodness of fit	0.806
Δ/σ (max)	0.008
$\Delta\rho$ (max), e/Å^3	0.586

Discussion

1. O=C vs C=C/C≡C Binding. The preceding data clearly establish that the C=C and C≡C functionalities in acrolein, *trans*-crotonaldehyde, methyl vinyl ketone, ethyl vinyl ketone, *trans*-4-hexen-3-one, and 4-phenyl-3-butyn-2-one have higher thermodynamic binding affinities for the rhenium Lewis acid I than the carbonyl groups. However, in all cases the kinetic binding order is opposite, with the carbonyl groups exhibiting greater nucleophilicity. Furthermore, nonconjugated ketoalkenes behave similarly.[33]

We suggest that this rate trend derives from (1) the ability of carbonyl groups to attack electrophiles in a sterically economical fashion through the oxygen atom terminus and (2) the higher energies of the oxygen σ donor orbitals.[34] Transition states involving attack of an entire O=C or C=C π face would be more congested, and utilize lower energy frontier orbitals. This implies that σ O=C adducts of I should always be the kinetic products, even when π O=C isomers are more stable, as for the acrolein complex **3** in Scheme I. Obviously, the mechanism of substitution of the dichloromethane ligand in **1**, which is

(31) The isomerization of a 42:58 *sc*/*ac* mixture to a 29:71 mixture was monitored by ^{1}H NMR in CD_2Cl_2 at 29 °C. These limited data gave rate constants of 1.50 ± 0.05 × 10^{-3} s^{-1} for the conversion of the *sc* to the *ac* rotamer, and 5.9 ± 0.2 × 10^{-4} s^{-1} for the conversion of the *ac* to the *sc* rotamer. For the techniques utilized, see ref 7d (footnote 15) and Capellos, C.; Bielski, B. H. *Kinetic Systems*; Wiley: New York, 1972; Chapter 8.

(32) The crystal structures of *trans*-alkene complexes of I are more fully analyzed in the preceding paper.[7e] The C=C bond length in *sc*-(*RSS,SRR*)-**19** [1.42(1) Å] is identical with those in the corresponding *trans*- and *cis*-2-butene complexes (1.42(2)–1.417(9) Å), and the O=C bond length [1.22(1) Å] is typical of ketones. The C1–H1, C1–C3, C2–H2, and C2–C4 "bend back" angles are 10.3°, 18.1°, 3.4°, and 12.7°, respectively, and the Ibers α, β, and β' angles are 44.8°, 63.8°, and 2.2°. The Re–C2 bond [2.211(8) Å] is shorter than the Re–C1 bond [2.264(7) Å], giving a slippage value[3a,c] of 12%.

(33) Fairfax, E., M.S. Thesis, University of Utah, 1993.

(34) Jorgensen, W. L.; Salem, L. *The Organic Chemist's Book of Orbitals*; Academic Press: New York, 1973; pp 179–184.

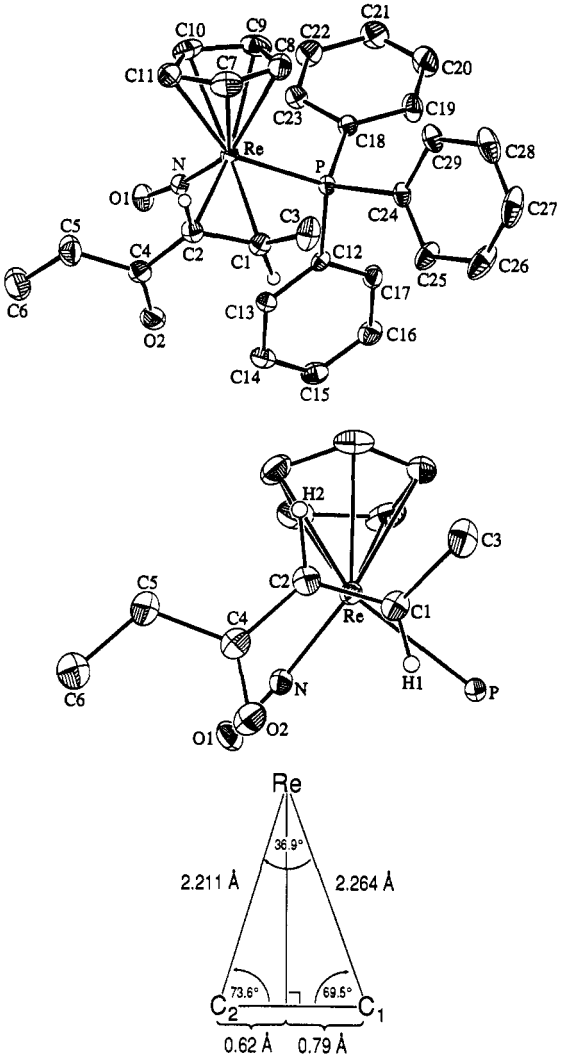


Figure 2. Structure of the cation of the *trans*-4-hexen-3-one complex *sc*-(*RSS,SRR*)-19·$(CH_2ClCH_2Cl)_{0.5}$: top, numbering diagram; middle, Newman-type projection with phenyl rings omitted; bottom, view of Re–C···C plane.

presently under investigation, also bears upon the kinetic binding selectivities. Interestingly, tropone and cyclohexanone react via *associative* processes, and no "indenyl effect" is observed.[35]

As shown in Scheme IV, cycloalkenones do not exhibit as strong a thermodynamic bias toward C=C binding as acyclic analogs. Importantly, however, two other ligands with disubstituted C=C linkages, *trans*-crotonaldehyde and *trans*-4-hexen-3-one, completely isomerize from ketone to alkene adducts (Schemes II and VI). Normally, *cis*-alkenes give more stable metal complexes than *trans*-alkenes. We therefore speculate that some factor stabilizes the σ binding modes of cyclohexenone and cyclopentenone. The rings enforce *s-trans* conformations, and perhaps this enhances the basicity of an oxygen σ donor orbital.[36] In this context, eq ii shows that cyclohexenone has a higher binding affinity for I than cyclohexanone.

We are aware of only one comparable report of divergent kinetic and thermodynamic O=C/C=C binding selectivities. As shown in Scheme VII, Harman and Taube find that the electron-rich d^6 osmium(II) fragment $[Os(NH_3)_5)]^{2+}$ and cyclohexenone react to give a ca. 1:1 mixture of the π O=C and C=C adducts **20** and **21**.[37] However, at 75 °C nearly complete isomerization to the alkene complex **21** occurs. This contrasts with the partial thermal rearrangement of the rhenium σ cyclohexenone complex **10** (Scheme IV).

A theoretical study is planned to probe the origin of the generally greater stability of π C=C and C≡C adducts of I. With Lewis acids derived from first and second-row elements, such as Li^+ or BF_3, σ O=C adducts are more stable.[26] Importantly, such Lewis acids lack high-lying donor orbitals suitable for back-bonding to ligand acceptor orbitals. We therefore suspect that the π donor properties of I (and $[Os(NH_3)_5]^{2+}$), and the C=C/C≡C LUMO coefficients, are important determinants of the equilibria in Schemes I–VII. Finally, tri- and tetrasubstituted alkenes usually give much less stable π complexes than mono- and disubstituted alkenes. Therefore, in some cases the stability order of O=C and C=C adducts may be reversed.

2. Other O=C and C=C Binding Equilibria. The above complexes illustrate a variety of other ligand binding

Table II. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for *sc*-(*RSS,SRR*)-19·$(CH_2ClCH_2Cl)_{0.5}$[a]

atom	*x*	*y*	*z*	*B* (Å²)
Re	0.69647(2)	0.07633(2)	0.73594(1)	2.977(5)
Cl	0.4202(3)	0.5426(2)	0.3895(2)	9.53(8)
P	0.8444(1)	0.1883(1)	0.74051(8)	3.02(3)
F1	0.4227(5)	0.7634(5)	0.0393(4)	11.4(2)
F2	0.5068(6)	0.6926(6)	0.1422(3)	11.9(2)
F3	0.501(1)	0.6296(6)	0.0382(5)	10.5(3)
F4	0.5955(7)	0.7728(8)	0.0808(8)	13.5(4)
O1	0.7486(4)	0.0448(4)	0.9006(2)	5.0(1)
O2	0.8576(4)	–0.1296(4)	0.8152(3)	5.9(1)
N	0.7337(4)	0.0564(4)	0.8339(3)	3.4(1)
C1	0.8078(5)	–0.0153(5)	0.6790(4)	4.1(1)
C2	0.7338(5)	–0.0736(5)	0.7096(4)	4.2(1)
C3	0.7973(7)	–0.0074(6)	0.5919(4)	6.4(2)
C4	0.7662(6)	–0.1301(5)	0.7801(4)	4.6(2)
C5	0.6792(7)	–0.1869(7)	0.8070(5)	6.9(2)
C6	0.7047(8)	–0.2340(8)	0.8808(6)	8.8(3)
C7	0.5515(6)	0.0613(7)	0.6381(5)	6.4(2)
C8	0.5883(6)	0.1532(7)	0.6365(5)	6.7(2)
C9	0.5764(6)	0.1959(6)	0.7059(6)	6.7(2)
C10	0.5293(6)	0.1290(7)	0.7481(5)	6.2(2)
C11	0.5164(6)	0.0457(6)	0.7069(5)	6.3(2)
C12	0.9683(4)	0.1578(5)	0.8057(3)	3.3(1)
C13	0.9817(5)	0.0735(5)	0.8469(3)	3.8(1)
C14	1.0753(6)	0.0567(5)	0.8982(4)	4.9(2)
C15	1.1568(6)	0.1234(6)	0.9083(4)	5.1(2)
C16	1.1451(6)	0.2074(6)	0.8670(4)	5.2(2)
C17	1.0507(5)	0.2249(5)	0.8160(4)	4.4(2)
C18	0.8145(5)	0.3059(4)	0.7761(4)	3.5(1)
C19	0.8472(7)	0.3911(5)	0.7472(5)	5.5(2)
C20	0.8230(8)	0.4787(6)	0.7765(6)	6.8(2)
C21	0.7698(7)	0.4819(6)	0.8373(5)	6.6(2)
C22	0.7389(6)	0.3973(6)	0.8697(5)	5.7(2)
C23	0.7588(6)	0.3102(5)	0.8374(4)	4.2(1)
C24	0.8867(5)	0.2122(5)	0.6503(3)	3.9(1)
C25	0.9796(6)	0.1726(7)	0.6328(4)	5.8(2)
C26	1.0065(7)	0.186(1)	0.5613(4)	8.5(3)
C27	0.9421(8)	0.2406(9)	0.5089(5)	9.2(3)
C28	0.8494(8)	0.2810(7)	0.5250(4)	7.6(2)
C29	0.8202(6)	0.2663(6)	0.5957(4)	5.1(2)
C30	0.5347(9)	0.516(1)	0.4803(7)	11.5(4)
B	0.5105(8)	0.7179(8)	0.0690(5)	6.3(2)
H1	0.121(6)	0.491(6)	0.796(4)	5.0
H2	0.337(6)	0.411(6)	0.833(4)	5.0

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

(35) Dewey, M. A.; Zhou, Y.; Liu, Y.; Gladysz, J. A., submitted for publication in *Organometallics*.

(36) For possibly related phenomena involving Lewis acid adducts of saturated esters and lactones, see: Wiberg, K. B.; Waldron, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 7705.

(37) Harman, W. D.; Schaefer, W. P.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2682.

Table III. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) in *sc*-(*RSS,SRR*)-19-$(CH_2ClCH_2Cl)_{0.5}$

Re–P	2.424(2)	O1–N	1.185(7)
Re–N	1.756(6)	O2–C4	1.22(1)
Re–C1	2.264(7)	C1–C2	1.42(1)
Re–C2	2.211(8)	C1–C3	1.54(1)
Re–C7	2.316(8)	C2–C4	1.48(1)
Re–C8	2.313(9)	C4–C5	1.50(1)
Re–C9	2.255(9)	C5–C6	1.46(1)
Re–C10	2.279(8)	C7–C8	1.36(1)
Re–C11	2.285(8)	C7–C11	1.39(1)
P–C12	1.834(7)	C8–C9	1.41(1)
P–C18	1.821(7)	C9–C10	1.39(1)
P–C24	1.812(7)	C10–C11	1.37(1)
P–Re–N	89.6(2)	Re–C2–C1	73.6(4)
P–Re–C1	81.1(2)	Re–C2–C4	111.1(5)
P–Re–C2	115.2(2)	C1–C2–C4	121.8(7)
N–Re–C1	106.0(3)	O2–C4–C2	122.4(8)
N–Re–C2	91.8(3)	O2–C4–C5	121.4(9)
C1–Re–C2	36.9(3)	C2–C4–C5	116.2(8)
Re–P–C12	116.2(2)	C4–C5–C6	117.8(9)
Re–P–C18	112.8(2)	C8–C7–C11	109.0(9)
Re–P–C24	115.4(2)	C7–C8–C9	106.9(9)
Re–N–O1	173.5(5)	C8–C9–C10	108.2(9)
Re–C1–C2	69.5(4)	C9–C10–C11	107.5(9)
Re–C1–C3	117.3(6)	C7–C11–C10	108.3(9)
C2–C1–C3	118.7(7)		

C3–C1–C2–C4	144(1)
C1–C2–C4–O2	0(1)
C1–C2–C4–C5	179(1)
O2–C4–C5–C6	6(1)
C2–C4–C5–C6	−173(1)

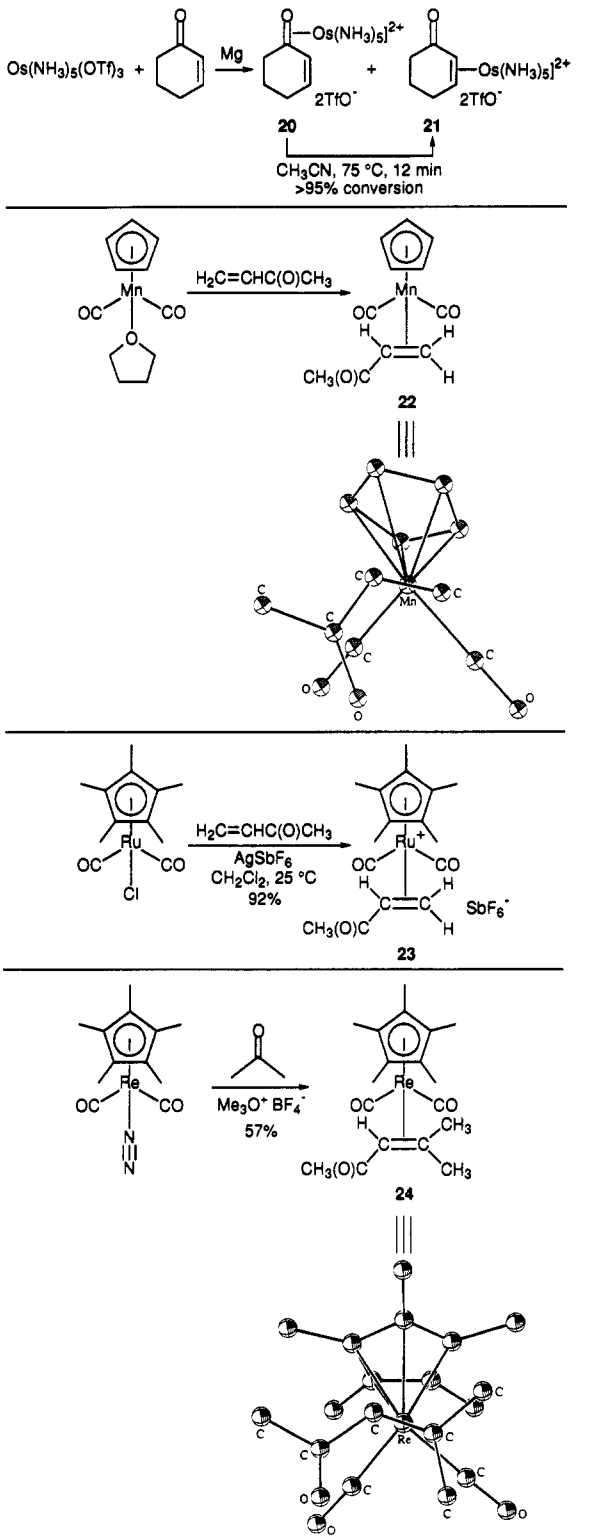
properties. Consider first π/σ O=C linkage isomerism. The acrolein complex **3** exhibits a much higher π/σ equilibrium ratio (>96:<4) than the *trans*-crotonaldehyde complex **5** (52:48) in CH_2Cl_2 at room temperature. The corresponding benzaldehyde and *p*-methyl benzaldehyde complexes show a similar trend (84:16 vs 53:47).[4a,c] As analyzed earlier,[4c] the added methyl donor groups enhance O=C σ basicity and decrease π acidity. Both effects serve to increase the proportions of σ isomers.

As expected from steric and electronic factors discussed previously,[4c,5] only σ isomers of the unsymmetrical ketone complexes **7**, **9**, **10**, **15**, and **18** are detected. Importantly, the O=*C* substituents in acetone and 3-pentanone complexes of I undergo extremely rapid exchange by nondissociative processes ($\Delta G^{\ddagger}$ = 6–7 kcal/mol).[5a,c] Thus, all attempts to observe *E*/*Z* O=C geometric isomers of σ aldehyde and unsymmetrical ketone complexes of I by low-temperature NMR have been unsuccessful.[27] As indicated above, we believe that the *trans*-crotonaldehyde complex σ-**5** should be strongly biased toward an *E* isomer, with the rhenium *cis* to the small hydrogen substituent. We tentatively suggest that *E* isomers of the methyl ketone complexes **7** and **15** may be favored. However, on the basis of the relative sizes of the O=*C* substituents in cycloalkenone complexes **9** and **10** and *trans*-4-hexen-3-one complex **18**, comparable amounts of *E*/*Z* isomers would be predicted.[25b]

As noted in the introduction, π aldehyde complexes of I can exist as two diastereomers that differ in the O=C enantioface bound to rhenium.[4b,10] Our low-temperature NMR spectra of **3** and π-**5**[20] would have revealed as little as 1% of a second isomer. Thus, the thermodynamic enantioface binding selectivities for these ligands are higher than that of benzaldehyde (86:14, CH_2Cl_2), and comparable to those of aliphatic aldehydes.[10] Similarly, the monosubstituted alkene ligands in acrolein complex **4**, methyl vinyl ketone complex **8**, and ethyl vinyl ketone complex **17** exhibit enantioface binding selectivities (>99:<1, 94:6, 96:4[30]) greater than that of styrene (90:10), and close to those of propene, 1-pentene, and allylbenzene (96–97:4–3).[7c] Curiously, the alkene with the smallest C=C substituent, acrolein (O=CH), appears to bind the most selectively, perhaps due to an electronic effect.

The C=C faces of *trans*- and unsymmetrical *cis*-alkenes are also enantiotopic. The alkene ligands in *trans*-crotonaldehyde complex **6** and *trans*-4-hexen-3-one complex **19** appear to exhibit high enantioface binding

Scheme VII. Other Syntheses, Isomerizations, and Structures of Transition Metal Complexes of α,β-Unsaturated Carbonyl Compounds



selectivities (93:7, >99:<1), similar to those of symmetrical *trans*-alkene complexes of I.[7e] However, all preparative conditions give identical mixtures of isomers, so the attainment of equilibrium cannot be directly observed.[22] Nonetheless, isomer ratios remain constant at temperatures where other diastereomeric *trans*-alkene complexes of I interconvert (70–85 °C).[7e] The *cis*-alkene ligands in cycloalkenone complexes **11** and **12** (Scheme IV) also appear to give appreciable enantioface binding selectivities. The direction of equilibrium follows from the relative sizes of the allylic O=C and CH_2 groups. The *RRS,SSR* diastereomers, in which the former is *syn* to the bulky PPh_3 ligand, are favored (see XIII). However, the acquisition of quantitative equilibrium data is complicated by the lower thermal stabilities of these compounds.

In unsymmetrical alkene complexes of I, there is the potential for *sc*/*ac* rotamers[11b] about the Re–(C=C) axis. The $=CH_2$ and =CHR termini of monosubstituted alkenes have greatly differing sizes, and rotamers have never been observed.[7a,c,d] However, small quantities of second rotamers are usually found with *cis*-alkenes, as detailed in the preceding paper[7e] and noted for the cyclopentenone complex (*RRS,SSR*)-**11**.[28] The NMR properties of *trans*-crotonaldehyde complex (*RSS,SRR*)-**6** show that an *ac* rotamer is greatly favored (X, Scheme II).[23] However, the *trans*-4-hexen-3-one complex (*RSS,SRR*)-**19** gives detectable amounts of both *ac* and *sc* rotamers (71:29; XVI and XVII, Scheme VI). In both compounds, the sp^2 hybridized C=C substituent is more readily accommodated in the more congested interstice between the cyclopentadienyl and PPh_3 ligands. However, the difference in effective sizes of the C=C substituents in the former ($O{=}CH \ll CH_3$) is apparently greater than in the latter ($O{=}C(CH_2CH_3) < CH_3$).

3. *s-cis*/*s-trans* Equilibria. It was not an objective of this study to rigorously probe *s-cis*/*s-trans* equilibria of the =CH—CH= and =CR—CH= linkages in the preceding compounds. Furthermore, all of our ^1H NOE and $^3J_{HH}$ data that bear upon this issue are qualitative. There is also a potential complication in the analysis of π complexes. As illustrated by the crystal structure of *sc*-(*RSS,SRR*)-**19** (Figure 2), the ligating atoms pyramidalize.[32] Thus, the limiting *J* values may differ slightly from those of purely sp^2-hybridized model compounds (e.g., equation i).

However, as further exemplified below, both π and σ metal complexes of ligands with =CH—CH= linkages—as well as the free ligands[13e]—appear to give similar $^3J_{HH}$ values in the *s-trans* limit (8.5–9.7 Hz).[21] Thus, subject to the above caveats, we suggest that a $^3J_{HH}$ value of >5.2 Hz indicates a dominant *s-trans* conformation, and a value of <3.8 Hz indicates a dominant *s-cis* conformation. These intuitively plausible "cutoffs" are supported by a considerable amount of independent ^1H NOE data (Schemes I–III and text).

Several interesting relationships emerge from these premises. First, free acrolein, *trans*-crotonaldehyde, and methyl vinyl ketone are known to exist predominantly in *s-trans* conformations, although the energy difference is only ca. 0.5 kcal/mol for the latter.[13a–d] In contrast, the more stable alkene complexes of acrolein ((*RS,SR*)-**4**; VIII, Scheme I) and methyl vinyl ketone ((*RS,SR*)-**8**; XII, Scheme III) preferentially adopt *s-cis* conformations. The *trans*-4-hexen-3-one ligand in *sc*-(*RSS,SRR*)-**19** is oriented analogously in the solid state (XVI, Scheme VI; Figure 2). In all three compounds, the carbonyl C=C substituents are *syn* to the nitrosyl ligands.

However, the less stable alkene complex of acrolein ((*RR,SS*)-**4**; IX, Scheme I) preferentially adopts an *s-trans* conformation—analogous to the free ligand. In this compound, the carbonyl substituent is *syn* to the cyclopentadienyl ligand. The more stable alkene complex of *trans*-crotonaldehyde ((*RSS,SRR*)-**6**; X, Scheme II) also gives mainly an *s-trans* isomer. In this case, the carbonyl substituent occupies a position on the C=C terminus *syn* to the PPh_3 ligand.

Next, consider the oxygen-ligated adducts of I. On the basis of the small $^3J_{HH}$ value, the π acrolein ligand in **3** is strongly biased toward an *s-cis* conformation (VII, Scheme I). Thus, the "isosteric" linkage isomers **3** (VII) and (*RS,SR*)-**4** (VIII) exhibit identical acrolein conformations, as would be intuitively expected. On the basis of the large $^3J_{HH}$ value, and data for the analogous π *trans*-piperylene complex and σ *trans*-crotonaldehyde imine complex,[21] the *trans*-crotonaldehyde ligand in **5** likely adopts *s-trans* conformations in both the π and σ isomers. This implies, curiously, that the acrolein and *trans*-crotonaldehyde conformations in the π O=C complexes **3** and π-**5** may differ. The σ complex of BF_3 and crotonaldehyde is also predominantly an *s-trans* isomer.[39] Due to the facile rearrangement of the σ methyl vinyl ketone complex **7**, NOE experiments were not attempted. However, we suggest that the *E* isomer of **7** adopts mainly an *s-trans* conformation.[40]

The further study and calibration of $^3J_{HH}$ values in compounds with =CH—CH= linkages is clearly needed. However, we believe that they represent greatly underutilized conformational probes.[24] The dominant =CH—CH= and =CR—CH= conformations thus implicated for the preceding compounds will be of particular use in interpreting and formulating transition state models for diastereoselective and enantioselective addition reactions that will be described in the near future.[41]

4. Isomerization Mechanisms. The mechanisms of rearrangement of the O=C complexes of I to C=C/C≡C complexes are of considerable interest. Although additional studies are in progress, it is instructive to frame some key issues at this time. First, analogous isomerizations involving nonconjugated ketoalkene ligands occur largely by nondissociative pathways.[33] Thus, direct migrations of rhenium along the donor orbitals of the O=C—C=C and O=C—C≡C linkages seem most probable.[42] Importantly, in many allene complexes the metal readily migrates from one orthogonal C=C π cloud to the other.[43]

The ketone σ O=C complexes **7**, **15**, and **18** rearrange to C=C or C≡C adducts below room temperature.

(38) For similar reasons, we propose that the diastereomer (*RRR,SSS*)-**6** adopts the Re–(C=C) conformation implied in Scheme II, with the larger C=C substituent (CH_3) on the terminus *anti* to the bulky PPh_3 ligand. However, we presently have no data that directly bear upon this point.

(39) Childs, R. F.; Mulholland, D. L.; Nixon, A. *Can. J. Chem.* **1982**, *60*, 801.

(40) We are unaware of any structural data for σ complexes of Lewis acids and methyl vinyl ketone.

(41) Wang, Y.; Gladysz, J. A., manuscript in preparation.

(42) The isomerizations of O=C complexes **5**, **9**, and **10** proceed in higher yields in the presence of added ligand. However, this does not in itself bear upon the issue of dissociative vs associative mechanisms. For example, the initial steps of many types of independent thermal decomposition pathways should be more readily reversed in the presence of added ligand.

(43) (a) Foxman, B.; Marten, D.; Rosan, A.; Raghu, S.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 2160. (b) Oon, S. M.; Jones, W. M. *Organometallics* **1988**, *7*, 2172.

However, the crotonaldehyde σ/π O=C complex **5** and acrolein π O=C complex **3** isomerize at progressively higher temperatures.[22] In general, π aldehyde ligands have stronger thermodynamic binding affinities than σ ketone ligands for I.[6] Hence, we propose that the faster rearrangements of **7**, **15**, and **18** are principally due to reduced ground state stabilities. However, we also suggest that for all substrates, π O=C complexes are the most probable immediate precursors to C=C or C≡C complexes. Thus, **7**, **15**, and **18** must rearrange by at least a two-step process, whereas the more stable complexes π-**5** and **3** can rearrange by a one-step process.

Although the data cannot be fully interpreted at this time, the kinetic ratios of alkene complex diastereomers and Re–(C⋯C) rotamers also provide important information on isomerization mechanisms. For example, when the acrolein O=C complex **3** rearranges at 60 °C in $CHCl_2$-$CHCl_2$, a *non*equilibrium mixture of *RS*,*SR*/*RR*,*SS* diastereomers of the alkene complex **4** is produced. Importantly, from the ground-state *s-cis* conformation of **3** (VII, Scheme I), direct migration of rhenium to the C=C moiety must give the less stable diastereomer (*RR*,*SS*)-**4**. Similarly, the less stable *sc* rotamer of (*RSS*,*SRR*)-**19** is generated initially. We find this result difficult to rationalize from any π ketone precursor with a Re–(O⋯C) conformation analogous to that of the π aldehyde ligand in II (Figure 1).

However, additional study of the kinetic product distributions for several alkene complexes is needed. For example, isomerizations of the σ O=C complexes of methyl vinyl ketone and ethyl vinyl ketone, which can only be generated *in situ*, in most cases directly give equilibrium mixtures of diastereomers. However, sporadic exceptions have been observed. Perhaps a byproduct, impurity, or excess reagent from the recipes utilized to generate these compounds can catalyze equilibration. Any such phenomenon is of considerable interest in its own right. We have also considered the possibility that C=C substituents that can provide "relay" binding sites—such as aryl and carbonyl groups—might facilitate the passage of metals from one π face to another.[7d] Indeed, Kegley has reported evidence for such processes in molybdenum alkene complexes of acrylate esters.[44] However, the diastereomeric carbonyl-substituted alkene complexes in this paper do not interconvert more rapidly than aliphatic analogs,[7c-e] at least when purified samples are employed.[18b,30]

5. Related Transition Metal Complexes. Numerous metal complexes of α,β-unsaturated aldehydes and ketones have been reported in the literature. A few have been given above,[25a,37] and others that bear upon major themes in our data are as follows. First, Dixneuf has reacted the substitution-labile, d^6 cyclopentadienyl manganese complex $(\eta^5\text{-}C_5H_5)Mn(CO)_2(THF)$ and an extensive series of enals and enones. In all cases, alkene complexes are isolated, as exemplified by the methyl vinyl ketone adduct **22** in Scheme VII.[45] The crystal structure of **22** shows an *s-cis* ligand conformation, identical to that proposed for the corresponding rhenium complex (*RS*,*SR*)-**8**. Interestingly, the acrolein analog of **22** gives a $^3J_{HH}$ value of 7 Hz for the =CH—CH= linkage—suggestive of a predominant *s-trans* conformation.[45a]

Crabtree and Tanke have prepared a similar cationic ruthenium complex of methyl vinyl ketone, $[(\eta^5\text{-}C_5H_5)Ru(CO)_2(O{=}C(CH_3)\text{-}\eta^2\text{-}CH{=}CH_2)]^+SbF_6^-$ (**23**), as shown in Scheme VII.[46] On the basis of our results with ketone ligands, we suggest that σ O=C complexes are precursors to both **22** and **23**. Sutton has discovered an unusual condensation reaction that gives a cyclopentadienyl rhenium alkene complex of 4-methyl-3-penten-2-one (mesityl oxide), $(\eta^5\text{-}C_5H_5)Re(CO)_2(O{=}C(CH_3)\text{-}\eta^2\text{-}CH{=}C(CH_3)_2)$ (**24**), as shown in Scheme VII.[47] In this case at least, a congested *tri*substituted C=C moiety binds preferentially to a methyl ketone group. Also, the crystal structure shows an *s-cis* ligand conformation.

The tungsten σ acrolein complex $[W(CO)_3(NO)(PMe_3)(\eta^1\text{-}O{=}CHCH{=}CH_2)]^+SbF_6^-$ (**25**) has been isolated by Hersh.[48] Faller has prepared related tungsten and molybdenum σ complexes of *trans*-crotonaldehyde and *trans*-cinnamaldehyde, $[(HC(2\text{-}py)_3)M(CO)(NO)_2(\eta^1\text{-}O{=}CHCH{=}CHR)]^{2+}2SbF_6^-$ (**26**).[49] The $^3J_{HH}$ values for the =CH—CH= linkages in **25** and **26** range from 8.5 to 8.9 Hz, suggestive of *s-trans* ligand conformations. Accordingly, the crystal structure of **25** shows an *s-trans* isomer. The ruthenium σ *trans*-cinnamaldehyde complex $[(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)(\eta^1\text{-}O{=}CHCH{=}CHC_6H_5)]^+SbF_6^-$ gives a $^3J_{HH}$ value of 8.4 Hz.[50] Interestingly, the tungsten and molybdenum complexes **26** show no tendency to isomerize to alkene complexes on the time scales of 30–40 min at 80–90 °C.

6. Conclusion. This study has established divergent kinetic and thermodynamic O=C/C=C and O=C/C≡C binding selectivities for complexes of I and a variety of α,β-unsaturated aldehydes and ketones (Schemes I–VI). Although exceptions may be encountered in sterically unusual cases, our results can likely be generalized to a large number of organic substrates and transition metal fragments. This fortuitous ability to control the metal binding site has important implications. For example, a single transition metal fragment can be used to activate either (or both) of two functional groups, depending upon conditions. Furthermore, the locus of enantioselective transformations can be rationally manipulated.

In order to thoroughly characterize the above complexes of I, it was also necessary to probe many other types of equilibria: (1) π/σ linkage isomers in O=C complexes, (2) *E*/*Z* geometric isomers in σ O=C complexes, (3) enantioface binding selectivities (or configurational diastereomers) in π complexes, (4) *sc*/*ac* Re–(X⋯C) rotamers in π complexes, and (5) *s-cis*/*s-trans* conformers in all complexes. Although we were not able to determine *E*/*Z* geometric isomer ratios, in all other cases a substantial body of quantitative or qualitative data was acquired. In retrospect, this clearly would not have been a tractable undertaking if we had not conducted a large number of predecessor studies with simpler monofunctional ligands[3-8]—a strategy that now has an evident payoff, but required approximately 6 years to complete.

We note in closing that eq ii establishes a valuable precedent for the development of catalytic chemistry. Specifically, if a cycloaddition (or comparable process) can be effected with the C=C linkage in **10**, the resulting

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saturated ketone ligand should have a much lower binding affinity for I than cyclohexenone. Thus, as in eq ii, free cyclohexenone should displace the new ligand from I under mild conditions. Organic transformations designed around this potentially general binding trend will be reported in the near future.[41]

Experimental Section[51,52]

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}O{=}CHCH{=}CH_2)]^+BF_4^-$ (3). A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**2**;[53] 0.156 g, 0.279 mmol), CH_2Cl_2 (8 mL), and a stir bar and was cooled to −80 °C. Then $HBF_4{\cdot}OEt_2$ (33 μL, 0.31 mmol) and acrolein (60 μL, 0.90 mmol) were sequentially added with stirring. The cold bath was allowed to gradually warm. After 4 h, the mixture was concentrated under oil-pump vacuum. A tan powder formed, and ether was added to complete the precipitation. The light tan powder was collected by filtration, washed with ether (2 × 5 mL), and dried under oil-pump vacuum to give **3** (0.171 g, 0.249 mmol, 89%). Mp: 107 °C (phase transition to gray solid), 210–217 °C dec. IR (cm^{-1}, KBr): ν_{NO} 1748 vs. Anal. Calcd for $C_{26}H_{24}BF_4NO_2PRe$: C, 45.49; H, 3.52. Found: C, 45.36; H, 3.57.

NMR:[54] ^1H (δ, CD_2Cl_2/CD_3NO_2, TMS/CD_2HNO_2 ref) 7.78–7.44/7.74–7.55 (m, $3C_6H_5$), 5.97/6.13 (s, C_5H_5), 5.91/5.90 (d, J_{HH} = 2.2/2.1, CHO), 5.85/5.91 (m, $=CHCHO$), 5.62/5.62 (d, J_{HH} = 16.4/16.8, $H_ZCH_E{=}$), 5.32/5.29 (d, J_{HH} = 10.0/10.2, $H_ZCH_E{=}$); $^{13}C\{^1H\}$ (ppm, CD_3NO_2, CD_3NO_2 ref, −25 °C) 139.9 (s, $=CH_2$), 134.8 (d, J_{CP} = 10.3, *o*-Ph), 134.0 (d, J_{CP} = 2.7, *p*-Ph), 130.7 (d, J_{CP} = 11.4, *m*-Ph), 128.3 (d, J_{CP} = 59.8, *i*-Ph), 122.9 (s, $=CHCHO$), 100.6 (s, C_5H_5), 77.8 (s, CO);[55] $^{31}P\{^1H\}$ (ppm, CD_2Cl_2/CD_3NO_2) 10.6/12.1 (s).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}CH\text{-}\eta^2\text{-}CH{=}CH_2)]^+BF_4^-$ (4). A. A Schlenk flask was charged with **3** (0.218 g, 0.318 mmol) and a stir bar. Then acrolein (430 μL, 6.36 mmol) and $CHCl_2CHCl_2$ (2 mL) were sequentially added. The suspension was warmed to 60 °C, and became homogeneous. After 20 h, the dark solution was added to ether (30 mL). The resulting light yellow precipitate was collected by filtration and dried under oil-pump vacuum. A ^{31}P NMR spectrum showed two resonances (10.9, 10.7 ppm, $CDCl_3$, 58:42),[16] but the ^1H NMR spectrum was severely broadened. The solid was dissolved in CH_2Cl_2 (1 mL) and chromatographed on a silica column (3 × 15 cm) with 90:10 and then 60:40 CH_2Cl_2/acetone (v/v). Solvent was removed from the product fraction to give an oily solid (0.084 g), which was dissolved in CH_3NO_2 and layered with 50:50 hexane/ether (v/v). Yellow microcrystals formed, which were collected by filtration and dried under oil-pump vaccum to give **4** (0.075 g, 0.109 mmol, 34%) as a 49:51 mixture of *RS,SR*/*RR,SS* diastereomers. Mp: 221–229 °C dec. IR (cm^{-1}, KBr): ν_{NO} 1732 vs, ν_{CO} 1687 s. **B.** A Schlenk flask was charged with **3** (0.062 g, 0.090 mmol). The solid was kept at 100 °C for 24 h. A ^{31}P NMR spectrum of the resulting gray solid showed it to be a 98:2 (*RS,SR*)/(*RR,SS*)-**4** mixture (0.058 g, 0.085 mmol, 94%) of ca. 96% purity. The solid was dissolved in CH_3NO_2 (1 mL) and layered with 50:50 hexane/ether (v/v). Olive-yellow microcrystals formed, which were collected by filtration and dried under oil-pump vacuum to give **4** (0.053 g, 0.077 mmol, 85%) as a >99:<1 mixture of *RS,SR*/*RR,SS* diastereomers. Mp: 218–225 °C dec. Anal. Calcd for $C_{26}H_{24}BF_4NO_2PRe$: C, 45.49; H, 3.52. Found: C, 45.26; H, 3.47.

NMR ($CDCl_3$) (*RS,SR*)-**4**: ^1H (δ, TMS ref) 9.04 (d, J_{HH} = 3.7, CHO), 7.62–7.27 (m, $3C_6H_5$), 5.98 (s, C_5H_5), 4.75 (dddd, J_{HH} = 3.7, 9.3, 10.7, J_{HP} = 1.8, $=CHCHO$),[56] 2.71 (ddd, J_{HH} = 4.8, 10.7, J_{HP} = 10.7, $H_ZCH_E{=}$),[56] 2.51 (ddd, J_{HH} = 4.8, 9.3, J_{HP} = 11.2, $H_ZCH_E{=}$);[56] $^{13}C\{^1H\}$ (ppm, $CDCl_3$ ref) 195.3 (s, CO), 133.2 (d, J_{CP} = 10.1, *o*-Ph), 132.5 (d, J_{CP} = 2.6, *p*-Ph), 129.8 (d, J_{CP} = 11.2, *m*-Ph), 128.8 (d, J_{CP} = 60.9, *i*-Ph), 98.4 (s, C_5H_5), 43.6 (s, $=CHCHO$),[57] 35.8 (d, J_{CP} = 6.4, $=CH_2$); $^{31}P\{^1H\}$ (ppm) 11.1 (s). (*RR,SS*)-**4**: ^1H (δ) 9.32 (d, J_{HH} = 5.3, CHO), 7.62–7.27 (m, $3C_6H_5$), 5.85 (s, C_5H_5), 3.73 (ddd, J_{HH} = 5.3, 8.1, 12.6, $=CHCHO$),[56] 2.97 (ddd, J_{HH} = 5.2, 8.1, J_{HP} = 13.7, $H_ZCH_E{=}$),[56] 2.57 (ddd, J_{HH} = 5.2, 12.6, J_{HP} = 5.0, $H_ECH_Z{=}$);[56] $^{13}C\{^1H\}$ (ppm) 200.8 (s, CO), 133.2 (d, J_{CP} = 10.1, *o*-Ph), 132.7 (d, J_{CP} = 2.1, *p*-Ph), 129.9 (d, J_{CP} = 11.2, *m*-Ph), 128.5 (d, J_{CP} = 60.9, *i*-Ph), 97.9 (s, C_5H_5), 44.2 (s, $=CHCHO$), 36.8 (d, J_{CP} = 6.9, $=CH_2$); $^{31}P\{^1H\}$ (ppm) 10.8 (s).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2/\eta^1\text{-}O{=}CHCH{=}CHCH_3)]^+BF_4^-$ (5). A Schlenk flask was charged with **2** (0.257 g, 0.460 mmol), CH_2Cl_2 (10 mL), and a stir bar and was cooled to −80 °C. Then $HBF_4{\cdot}OEt_2$ (55 μL, 0.51 mmol) was added with stirring. After 20 min, *trans*-crotonaldehyde (114 μL, 1.38 mmol) was added, and the cold bath was allowed to slowly warm to room temperature. After 9 h, the mixture was concentrated and added to ether (40 mL). The resulting brown powder was collected by filtration, washed with ether, and dried under oil-pump vacuum to give **5** (0.267 g, 0.381 mmol, 83%). Mp: 190–195 °C dec. IR (cm^{-1}, thin film): ν_{NO} 1730/1688 (π/σ) vs, ν_{CO} 1629 (σ) m, $\nu_{C=C}$ 1575 (σ) m.[19] Anal. Calcd for $C_{27}H_{26}BF_4NO_2PRe$: C, 46.30; H, 3.74. Found: 46.07; H, 3.73.

NMR (CD_2Cl_2): ^1H (δ, TMS ref) 7.66–7.33 (m, $3C_6H_5$), 6.52 (dq, J_{HH} = 15.4, 7.0, $=CHCH_3$), 5.93 (d, J_{HH} = 9.3, CHO), 5.82 (m, $=CHCHO$), 5.77 (s, C_5H_5), 2.16 (dd, J_{HH} = 1.5, 7.0, CH_3); $^{13}C\{^1H\}$ (ppm, CD_2Cl_2 ref) 152.7 (s, $=CHCH_3$), 133.7 (d, J_{CP} = 10.6, *o*-Ph), 132.5 (d, J_{CP} = 2.6, *p*-Ph), 129.8 (d, J_{CP} = 11.1, *m*-Ph), 129.1 (d, J_{CP} = 57.7, *i*-Ph), 132.1 (s, $=CHCHO$), 96.0 (s, C_5H_5), 91.9 (s, CO), 19.0 (s, CH_3); $^{31}P\{^1H\}$ (ppm) 15.3 (s).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}CH\text{-}\eta^2\text{-}CH{=}CHCH_3)]^+BF_4^-$ (6). A Schlenk flask was charged with **5** (0.093 g, 0.133 mmol), *trans*-crotonaldehyde (110 μL, 1.33 mmol), C_6H_5Cl (5 mL), and a stir bar. The suspension was warmed to 80 °C and after 0.5 h became homogeneous, but ca. 1 h later a new gray precipitate appeared. After 18 h, the mixture was concentrated, and CH_2Cl_2 was added (minimum amount) to give a solution. The solution was added to ether (40 mL) with stirring. The resulting tan powder was collected by filtration and dried under oil-pump vacuum to give **6** (0.073 g, 0.104 mmol, 78%) as a 93:7 mixture of *RSS,SRR*/*RRR,SSS* diastereomers. Mp: 196–200 °C dec. IR (cm^{-1}, thin film): ν_{NO} 1740 vs, ν_{CO} 1683 s. Anal. Calcd for $C_{27}H_{26}BF_4NO_2PRe$: C, 46.30; H, 3.74. Found: 46.07; H, 3.82.

NMR (CD_2Cl_2), (*RSS,SRR*)-**6**: ^1H (δ, TMS ref) 8.52 (d, J_{HH} = 5.8, CHO), 7.70–7.28 (m, $3C_6H_5$), 5.95 (s, C_5H_5), 4.77 (ddq, J_{HH} = 10.7, 6.2, J_{HP} = 2.0, $=CHCH_3$), 3.49 (ddd, J_{HH} = 5.8, 10.7, J_{HP} = 7.6, $=CHCHO$), 2.28 (d, J_{HH} = 6.2, CH_3); $^{13}C\{^1H\}$ (ppm, CD_2Cl_2 ref) 197.9 (d, J_{CP} = 2.6, CO), 133.8 (d, J_{CP} = 10.2, *o*-Ph), 133.1 (d, J_{CP} = 3.2, *p*-Ph), 130.1 (d, J_{CP} = 11.2, *m*-Ph), 129.2 (d, J_{CP} = 60.3, *i*-Ph), 98.1 (s, C_5H_5), 61.1 (d, J_{CP} = 5.4, $=CHCHO$),[57] 48.2 (s, $=CHCH_3$), 22.7 (s, CH_3); $^{31}P\{^1H\}$ (ppm) 3.9 (s). (*RRR,SSS*)-**6** (partial): ^1H (δ) 9.05 (d, J_{HH} = 3.9, CHO), 6.02 (s, C_5H_5), 1.44 (d, J_{HH} = 6.3, CH_3); $^{31}P\{^1H\}$ (ppm) 6.9 (s).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(CH_3)CH{=}CH_2)]^+BF_4^-$ (7). A 5-mm NMR tube was charged with **2** (0.051 g, 0.091 mmol) and CD_2Cl_2 (0.7 mL), capped with a septum, and was cooled to

(51) General procedures were identical with those described in a previous paper.[7c] UV/visible spectra were recorded on a HP-8452A spectrometer. Solvents and reagents were treated as follows: chlorinated solvents, distilled from P_2O_5 or CaH_2; ether, distilled from Na/benzophenone; $HBF_4{\cdot}OEt_2$ (Aldrich), standardized with *N,N*-dimethylaniline (Jablonski, C. R. *Aldrichimica Acta* **1990**, *23*, 58); acrolein (Aldrich), distilled from $CaSO_4$; other organic carbonyl compounds (Aldrich), CD_3NO_2, CH_3CN, and acetone, used as received.

(52) (a) NMR spectra were recorded at ambient probe temperatures on Varian XL-300 spectrometers, unless noted, and referenced as follows: ^1H (δ) $CHDCl_2$ (5.32), CHD_2NO_2 (4.33) or TMS (0.00); ^{13}C (ppm) CD_2Cl_2 (53.8), CD_3NO_2 (62.8), or $CDCl_3$ (77.0); ^{31}P (ppm) external 85% H_3PO_4 (0.0). All coupling constants (*J*) are in Hz. (b) The ^1H NOE difference spectra[15] were acquired as described previously with the following resonance saturation levels: C_5H_5, 90–94%; CH_3 in (*RS,SR*)-**8**, 95%; others, 99–100%. Pu, J.; Peng, T.-S.; Arif, A. M.; Gladysz, J. A. *Organometallics*, **1992**, *11*, 3232.

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(54) Complex **3** is only sparingly soluble in chlorinated solvents. Thus, complete ^{13}C NMR data could only be obtained in the more polar solvent CD_3NO_2.

(55) This resonance was not observed in spectra recorded at room temperature.

(56) This assignment and the coupling constants were verified by a homonuclear decoupling experiment.

(57) This assignment was verified by a heteronuclear decoupling experiment involving the O=CH—C*H*= ^1H resonance.

−80 °C. Then $HBF_4 \cdot OEt_2$ (10.0 μL, 0.093 mmol) was added. After 10 min, methyl vinyl ketone (7.6 μL, 0.091 mmol) was added. The tube was warmed to −25 °C and NMR spectra were recorded. IR (cm^{-1}, thin film): ν_{NO} 1681 vs, ν_{CO} 1617 m, $\nu_{C=C}$ 1550 w.

NMR (CD_2Cl_2, −25 °C): ^1H (δ, $CHDCl_2$ ref) 7.62–7.23 (m, $3C_6H_5$), 6.30–6.23 (m, $=CH_2$), 5.99 (dd, J_{HH} = 9.5, 3.0, =CHCO), 5.70 (s, C_5H_5), 2.29 (s, CH_3); $^{13}C\{^1H\}$ (ppm, CD_2Cl_2 ref) 199.8 (s, CO), 137.2 (s, $=CH_2$), 133.6 (d, J_{CP} = 11.0, *o*-Ph), 131.9 (d, J_{CP} = 2.5, *p*-Ph), 130.5 (d, J_{CP} = 56.2, *i*-Ph), 130.0 (s, =*C*HCO), 129.5 (d, J_{CP} = 10.9, *m*-Ph), 93.3 (s, C_5H_5), 26.2 (s, CH_3); $^{31}P\{^1H\}$ (ppm) 18.5 (s).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}C(CH_3)\text{-}\eta^2\text{-}CH{=}CH_2)]^+BF_4^-$ (8). A Schlenk flask was charged with **2** (0.117 g, 0.210 mmol), CH_2Cl_2 (5 mL), and a stir bar and was cooled to −80 °C. Then $HBF_4 \cdot OEt_2$ (24 μL, 0.22 mmol) was added with stirring. After 10 min, methyl vinyl ketone (87 μL, 1.046 mmol) was added. The cold bath was allowed to slowly warm to room temperature. After 24 h, a yellow precipitate had formed. The solvent was removed by rotary evaporation, and the residue was dissolved in CH_3CN. The solution was added to ether. The resulting beige powder was collected by filtration and dried under oil-pump vacuum to give **8** (0.128 g, 0.183 mmol, 87%) as a 93:7 mixture of *RS,SR*/*RR,SS* diastereomers. Mp: 249–258 °C dec. IR (cm^{-1}, thin film): ν_{NO} 1743 vs, ν_{CO} 1688 s. Anal. Calcd for $C_{27}H_{26}BF_4NO_2PRe$: C, 46.30; H, 3.74. Found: 46.44; H, 3.73.

NMR (CD_2Cl_2) (*RS,SR*)-**8**: ^1H (δ, $CHDCl_2$ ref) 7.68–7.34 (m, $3C_6H_5$), 5.93 (d, J_{CP} = 0.7, C_5H_5), 4.83 (ddd, J_{HH} = 10.8, 9.3, J_{HP} = 1.9, =CHCO), 3.00 (ddd, J_{HH} = 10.8, 4.8, J_{HP} = 11.7, H_ZCH_E=), 2.37 (s, CH_3), 1.88 (ddd, J_{HH} = 9.3, 4.8, J_{HP} = 6.4, H_ZCH_E=); $^{13}C\{^1H\}$ (ppm, CD_2Cl_2 ref) 202.2 (s, CO), 133.6 (d, J_{CP} = 10.2, *o*-Ph), 132.8 (d, J_{CP} = 2.1, *p*-Ph), 130.0 (d, J_{CP} = 11.3, *m*-Ph), 98.3 (s, C_5H_5), 42.6 (s, =CHCO), 34.6 (d, J_{CP} = 6.6, $=CH_2$), 30.1 (s, CH_3);[58] $^{31}P\{^1H\}$ (ppm) 12.2 (s). (*RR,SS*)-**8**: ^1H (δ) 5.66 (d, J_{CP} = 0.9, C_5H_5), 3.82 (dd, J_{HH} = 12.5, 8.2, =CHCO), 2.85 (ddd, J_{HH} = 8.2, 4.6, J_{HP} = 14.3, H_ZCH_E=), 2.59 (s, CH_3), 2.29 (ddd, J_{HH} = 12.5, 4.6; J_{HP} = 4.4, H_ZCH_E=); $^{13}C\{^1H\}$ (ppm) 208.0 (s, CO), 133.5 (d, J_{CP} = 10.0, *o*-Ph), 133.1 (d, J_{CP} = 2.4, *p*-Ph), 130.2 (d, J_{CP} = 10.6, *m*-Ph), 99.5 (s, C_5H_5), 43.5 (s, =*C*HCO), 36.9 (d, J_{CP} = 7.3, $=CH_2$), 32.0 (s, CH_3);[58] $^{31}P\{^1H\}$ (ppm) 11.0 (s).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}\overline{CCH{=}CHCH_2CH_2})]^+BF_4^-$ (9). A Schlenk flask was charged with **2** (0.081 g, 0.145 mmol), CH_2Cl_2 (5 mL), and a stir bar and was cooled to −80 °C. Then $HBF_4 \cdot OEt_2$ (17.0 μL, 0.157 mmol) was added with stirring. After 10 min, cyclopentenone (120 μL, 1.430 mmol) was added, and the cold bath was allowed to slowly warm to room temperature. After 4.5 h, the solution was concentrated and added to ether (40 mL). The resulting red powder was collected by filtration and dried under oil-pump vacuum to give **9** (0.078 g, 0.110 mmol, 76%). Mp: 182–189 °C dec. IR (cm^{-1}, thin film): ν_{NO} 1681 vs, ν_{CO} 1604 s, $\nu_{C=C}$ 1566 m. Anal. Calcd for $C_{28}H_{26}BF_4NO_2PRe$: C, 47.20; H, 3.68. Found: C, 46.98; H, 3.73.

NMR (CD_2Cl_2): ^1H (δ, TMS ref) 7.65–7.30 (m, $3C_6H_5$), 7.94 (dt, J_{HH} = 5.6, 2.5, =*CH*CH_2), 6.37 (dt, J_{HH} = 5.6, 2.0, =CHCO), 5.61 (s, C_5H_5), 2.85 (m, 2H), 2.53 (m, 2H); $^{13}C\{^1H\}$ (ppm, TMS ref) 227.9 (s, CO), 176.3 (s, =*C*HCH_2), 133.9 (d, J_{CP} = 11.0, *o*-Ph), 133.5 (s, =*C*HCO), 131.9 (d, J_{CP} = 2.5, *p*-Ph), 131.6 (d, J_{CP} = 55.3, *i*-Ph), 129.6 (d, J_{CP} = 10.7, *m*-Ph), 92.8 (d, J_{CP} = 1.5, C_5H_5), 37.4 (s, CH_2CO). 31.5 (s, =CH*C*H_2); $^{31}P\{^1H\}$ (ppm) 18.7 (s).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}\overline{CCH{=}CHCH_2\text{-}CH_2CH_2})]^+BF_4^-$ (10). Complex **2** (0.572 g, 1.025 mmol), CH_2Cl_2 (40 mL), $HBF_4 \cdot OEt_2$ (140 μL, 1.30 mmol), and cyclohexenone (310 μL, 3.11 mmol) were combined in a procedure similar to that given for **9**. After 3.5 h, solvent was removed under oil-pump vacuum, and the residue was dissolved in CH_2Cl_2. The solution was added to ether. The resulting red powder was collected by filtration and dried under oil-pump vacuum to give **10** (0.605 g, 0.833 mmol, 81%). Mp: 179–187 °C dec. IR (cm^{-1}, thin film/KBr): ν_{NO} 1683/1676 vs, ν_{CO} 1605/1601 s, $\nu_{C=C}$ 1558/1555 s. Anal. Calcd for $C_{29}H_{28}BF_4NO_2PRe$: C, 47.94; H, 3.88. Found: C, 48.07; H, 4.10.

(58) The *ipso* PPh_3 resonance was obscured.

NMR (CD_2Cl_2): ^1H (δ, TMS ref) 7.58–7.28 (m, $3C_6H_5$), 7.15 (dt, J_{HH} = 10.1, 4.2, =*CH*CH_2), 6.24 (dt, J_{HH} = 10.1, 1.6, =CHCO), 5.60 (s, C_5H_5), 2.44 (m, 4H), 1.73 (m, 2H); $^{13}C\{^1H\}$ (ppm, TMS ref) 215.4 (s, CO), 160.3 (s, =*C*HCH_2), 133.7 (d, J_{CP} = 11.1, *o*-Ph), 131.8 (d, J_{CP} = 2.4, *p*-Ph), 131.4 (d, J_{CP} = 57.0, *i*-Ph), 129.5 (d, J_{CP} = 11.2, *m*-Ph), 127.8 (s, =*C*HCO), 93.0 (d, J_{CP} = 1.9, C_5H_5), 37.6 (s, CH_2CO), 26.0 (s, CH_2), 21.9 (s, =CH*C*H_2); $^{31}P\{^1H\}$ (ppm) 18.2 (s).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}\overline{C\text{-}\eta^2\text{-}CH{=}CHCH_2CH_2})]^+BF_4^-$ (11). A Schlenk flask was charged with **9** (0.344 g, 0.483 mmol) and a stir bar. Then cyclopentenone (1.5 mL, 18 mmol) was added. The solution was kept at 90 °C for 8 h. The resulting sticky gel was dissolved in CH_2Cl_2 (1 mL), and a ^{31}P NMR spectrum showed resonances at 10.2, 3.2, and 2.7 ppm (ca. 4:59:37).[28] The solution was added to ether (40 mL), and the resulting orange precipitate was collected by filtration and dissolved in CH_2Cl_2 (1 mL). The solution was chromatographed on a silica column (3 × 15 cm) that was eluted with 80:20 CH_2Cl_2/acetone (v/v) to remove byproducts and then 60:40 CH_2Cl_2/acetone to remove the orange product band. The orange fractions were taken to dryness and dissolved in CH_2Cl_2 (2 mL). Ether was added dropwise until a cloud point was reached, and then CH_2Cl_2 was added dropwise until a clear point was reached. The solution was transferred to an open flask and allowed to concentrate by evaporation. After 48 h, the resulting yellow needles were collected by filtration and dried under oil-pump vacuum to give **11** (0.055 g, 0.077 mmol, 16%) as a 93:7 mixture of *RRS,SSR*/*RSR,SRS* diastereomers.[28] Mp: 169–175 dec. IR (cm^{-1}, KBr): ν_{NO} 1730 vs, ν_{CO} 1714 vs. Anal. Calcd for $C_{28}H_{26}BF_4NO_2PRe$: C, 47.20; H, 3.68. Found: C, 47.09; H, 3.71.

NMR (CD_2Cl_2) (*RRS,SSR*)-**11**: ^1H (δ, TMS ref) 7.60–7.45 (m, $3C_6H_5$), 5.87/5.85 (2 s, *ac*/*sc* C_5H_5, 91:9), 5.72 (m, =*CH*CHH'),[56] 3.65 (m, =CHC*H*H'), 3.33 (dd, J_{HH} = 6.9, J_{HP} = 6.9, =CHCO),[56] 2.88 (dd, J_{HH} = 8.4, 16.2, =CHCH*H*'),[56] 1.98–1.63 (m, CH_2CO); $^{13}C\{^1H\}$ (ppm, CD_2Cl_2 ref) 212.0 (s, CO), 133.5 (d, J_{CP} = 10.1, *o*-Ph), 132.6 (d, J_{CP} = 2.7, *p*-Ph), 130.2 (d, J_{CP} = 55.5, *i*-Ph), 129.9 (d, J_{CP} = 11.2, *m*-Ph), 99.5/99.0 (2 s, *ac*/*sc* C_5H_5), 58.0 (s, =*C*HCH_2), 52.4 (d, J_{CP} = 4.8, =*C*HCO), 32.7 (s, =CH*C*H_2), 27.9 (s, CH_2CO); $^{31}P\{^1H\}$ (ppm) 3.2/10.2 (2 s, 91:9, *ac*/*sc*). (*RSR,SRS*)-**11** (partial): $^{31}P\{^1H\}$ (ppm) 2.7 (s).

$[(\eta^2\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}\overline{C\text{-}\eta^2\text{-}CH{=}CHCH_2\text{-}CH_2CH_2})]^+BF_4^-$ (12). A Schlenk flask was charged with **10** (0.215 g, 0.296 mmol) and a stir bar. Then cyclohexenone (1.5 mL, 15 mmol) was added. The solution was kept at 60 °C for 13 h. Then CH_2Cl_2 (2 mL) and ether (dropwise) were sequentially added. A black solid formed (unreacted **10** remains soluble), and the supernatant was removed by pipet. The solid was washed with ether and dissolved in CH_2Cl_2. Ether was added dropwise, and solvent was removed from the resulting precipitate by pipet. The solid was washed with ether and dissolved in CH_3NO_2, and the solution was layered with ether. After 24 h, the resulting gray microcrystals were collected by filtration and dried under oil-pump vacuum to give **12** (0.068 g, 0.094 mmol, 32%) as a 97:3 mixture of *RRS,SSR*/*RSR,SRS* diastereomers. Mp: 174–186 °C dec. IR (cm^{-1}, KBr): ν_{NO} 1720 vs, ν_{CO} 1679 s. Anal. Calcd for $C_{29}H_{28}BF_4NO_2PRe$: C, 47.94, H, 3.88. Found: C, 47.35, H, 3.93.

NMR (CD_3NO_2) (*RRS,SSR*)-**12**: ^1H (δ, CHD_2NO_2 ref) 7.75–7.55 (m, $3C_6H_5$), 5.89 (d, J_{HP} = 0.7, C_5H_5), 5.52 (m, =*CH*CHH'),[56] 3.54 (m, =CHC*H*H'), 3.27 (dd, J_{HH} = 9.6, J_{HP} = 4.8, =CHCO),[56] 2.94 (v br d, J_{HH} = 16.8, =CHCH*H*'),[56] 1.85–1.68 (m, CH_2CO), 1.57–1.39 (m, CH_2CH_2CO); $^{13}C\{^1H\}$ (ppm, CD_3NO_2 ref) 208.7 (s, CO), 134.8 (d, J_{CP} = 10.1, *o*-Ph), 133.3 (d, J_{CP} = 2.3, *p*-Ph), 131.7 (d, J_{CP} = 58.6, *i*-Ph), 130.5 (d, J_{CP} = 11.2, *m*-Ph), 100.8 (s, C_5H_5), 52.8 (s, =*C*HCH_2), 48.0 (d, J_{CP} = 5.5, =*C*HCO), 38.2 (s, =*C*CH_2), 28.1 (s, CH_2CO), 19.3 (s, CH_2CH_2CO); $^{31}P\{^1H\}$ (ppm, CD_3NO_2) 6.2 (s). (*RSR,SRS*)-**12** (partial): ^1H (δ) 5.92 (d, J_{CP} = 0.9 Hz, C_5H_5); $^{13}C\{^1H\}$ (ppm) 100.7 (s, C_5H_5); $^{31}P\{^1H\}$ (ppm) 7.6 (s).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}C(CH_3)C{\equiv}CC_6H_5)]^+BF_4^-$ (15). A 5-mm NMR tube was charged with **2** (0.045 g, 0.081 mmol) and CD_2Cl_2 (0.7 mL), capped with a septum, and cooled to −80 °C. Then $HBF_4 \cdot OEt_2$ (12.0 μL, 0.111 mmol) was added.

After 10 min, 4-phenyl-3-butyn-2-one (12 μL, 0.082 mmol) was added. The tube was warmed to −25 °C and NMR spectra were recorded. IR (cm^{-1}, thin film): ν_{NO} 1671 vs, ν_{CO} 1541 m, $\nu_{C\equiv C}$ 2169 m.

NMR (−25 °C, CD_2Cl_2): ^1H (δ, $CHDCl_2$ ref) 7.62–7.24 (m, $4C_6H_5$), 5.70 (s, C_5H_5), 2.45 (s, CH_3); $^{13}C\{^1H\}$ (ppm, CD_2Cl_2 ref) 185.5 (d, J_{CP} = 1.5, CO), 133.7 (d, J_{CP} = 11.0, *o*-PPh), 133.5 (d, J_{CP} = 55.3, *i*-PPh), 131.6 (d, J_{CP} = 2.1, *p*-PPh), 129.4 (d, J_{CP} = 11.0, *m*-PPh), 133.1 (s, C*Ph*), 131.0 (s, C*Ph*), 128.8 (s, C*Ph*), 119.6 (s, C*Ph*), 93.8 (s, C_5H_5), 90.0 (s, C≡CPh), 88.0 (s, *C*≡CPh), 32.9 (s, CH_3); $^{31}P\{^1H\}$ (ppm) 19.1 (s).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}C(CH_3)\text{-}\eta^2\text{-}C{\equiv}CC_6H_5)]^+BF_4^-$ (16). Complex **2** (0.303 g, 0.542 mmol), CH_2Cl_2 (12 mL), $HBF_4{\cdot}OEt_2$ (83 μL, 0.57 mmol), and 4-phenyl-3-butyn-2-one (237 μL, 1.63 mmol) were combined in a procedure similar to that given for **9**. After 3.5 h, solvent was removed under oil-pump vacuum, and the residue was dissolved in CH_2Cl_2. Ether was then added by vapor diffusion. The resulting yellow powder was collected by filtration and dried under oil-pump vacuum to give **16** (0.373 g, 0.481 mmol, 89%). A sample was crystallized from CH_2Cl_2/ether to give **16**·$(CH_2Cl_2)_{0.75}$ as yellow needles. Mp: 141–144 °C dec. IR (cm^{-1}, thin film/KBr): ν_{NO} 1720/1718 vs, ν_{CO} 1680/1668 s, $\nu_{C\equiv C}$ 1808/1813 m. Anal. Calcd for $C_{33}H_{28}BF_4NO_2PRe{\cdot}(CH_2Cl_2)_{0.75}$: C, 48.29; H, 3.54; Cl, 6.34. Found: C, 48.33; H, 3.72; Cl, 6.67.

NMR (CD_2Cl_2): ^1H (δ, TMS ref) 7.78–7.27 (m, $4C_6H_5$), 5.98 (s, C_5H_5), 2.15 (s, CH_3); $^{13}C\{^1H\}$ NMR (ppm, TMS ref) 194.9 (d, J_{CP} = 3.8, CO), 131.8 (s, C*Ph*), 131.6 (s, C*Ph*), 129.8 (s, C*Ph*), 100.5 (s, C_5H_5), 115.2 (s, C≡C *anti* to PPh_3), 93.6 (d, J_{CP} = 12.6, C≡C *syn* to PPh_3), 33.1 (s, CH_3);[59] $^{31}P\{^1H\}$ NMR (ppm) 12.0 (s).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}C(CH_2CH_3)\text{-}\eta^2\text{-}CH{=}CH_2)]^+BF_4^-$ (17). Complex **2** (0.086 g, 0.155 mmol), CH_2Cl_2 (1.5 mL), $HBF_4{\cdot}OEt_2$ (16.7 μL, 0.155 mmol), and ethyl vinyl ketone (31 μL, 0.31 mmol) were combined in a procedure similar to that given for **9**. After 6 h, the mixture was added to ether (30 mL). The resulting tan powder was collected by filtration, washed with ether (3 × 5 mL), and dried under oil-pump vacuum to give **17** (0.074 g, 0.109 mmol, 70%) as a 93:7 mixture of *RS,SR*/*RR,SS* diastereomers. Mp: 224–233 °C dec. IR (cm^{-1}, thin film): ν_{NO} 1741 vs, ν_{CO} 1686 s. Anal. Calcd for $C_{28}H_{28}BF_4NO_2PRe$: C, 47.07; H, 3.95. Found: C, 46.95; H, 3.95.

NMR (CD_2Cl_2) (*RS,SR*)-**17**: ^1H (δ, $CHDCl_2$ ref) 7.72–7.34 (m, $3C_6H_5$), 5.92 (s, C_5H_5), 4.79 (ddd, J_{HH} = 9.4, 11.2, J_{HP} = 2.0, =CHCO), 3.03 (ddd, J_{HH} = 11.2, 4.4, J_{HP} = 11.1, H_ZCH_E=), 2.88 (dq, J_{HH} = 18.2, 7.2, COC*H*H′), 2.75 (dq, J_{HH} = 18.2, 7.2, COCH*H*′), 1.82 (ddd, J_{HH} = 9.4, 4.4, J_{HP} = 6.0, H_ZCH_E=), 1.11 (dd, J_{HH} = 7.2, 7.2, CH_3); $^{13}C\{^1H\}$ (ppm, CD_2Cl_2 ref) 205.3 (s, CO), 133.5 (d, J_{CP} = 9.5, *o*-Ph), 133.1 (d, J_{CP} = 2.6, *p*-Ph), 130.2 (d, J_{CP} = 11.6, *m*-Ph), 129.2 (d, J_{CP} = 59.1, *i*-Ph), 98.3 (s, C_5H_5), 42.0 (s, =*C*HCO), 36.5 (s, CO*C*H_2), 34.7 (d, J_{CP} = 6.2, =CH_2), 8.1 (s, CH_3);[58] $^{31}P\{^1H\}$ (ppm) 12.3 (s). (*RR,SS*)-**17**: ^1H (δ) 7.72–7.34 (m, $3C_6H_5$), 5.65 (d, J_{HP} = 0.6, C_5H_5), 3.83 (ddd, J_{HH} = 12.7, 8.0, J_{HP} = 1.5, =CHCO), 3.03 (dq, J_{HH} = 18.6, 7.2, COC*H*H′), 2.91 (dq, J_{HH} = 18.6, 7.2, COCH*H*′), 2.85 (ddd, J_{HH} = 4.0, 8.0, J_{HP} = 17.1, H_ZH_E=), 2.34 (ddd, J_{HH} = 12.7, 4.0, J_{HP} = 4.5, H_ZCH_E=), 1.22 (dd, J_{HH} = 7.2, 7.2, CH_3); $^{13}C\{^1H\}$ (ppm) 210.9 (s, CO), 133.5 (d, J_{CP} = 9.8, *o*-Ph), 133.1 (d, J_{CP} = 3.0, *p*-Ph), 130.2 (d, J_{CP} = 11.0, *m*-Ph), 129.2 (d, J_{CP} = 60.1, *i*-Ph), 99.3 (s, C_5H_5), 42.8 (s, =*C*HCO), 37.9 (s, CO*C*H_2), 36.9 (d, J_{CP} = 7.3, =CH_2), 8.1 (s, CH_3); $^{31}P\{^1H\}$ (ppm) 11.1 (s).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}C(CH_2CH_3)\text{-}\eta^2\text{-}CH{=}CH\text{-}CH_3)]^+BF_4^-$ (19). Complex **2** (0.370 g, 0.662 mmol), CH_2Cl_2 (20 mL), $HBF_4{\cdot}OEt_2$ (130 μL, 0.813 mmol), and *trans*-4-hexen-3-one (300 μL, 2.62 mmol) were combined in a procedure similar to that given for **9**. After 16 h, solvent was removed under oil-pump vacuum, and the residue was dissolved in CH_2Cl_2. Ether was added, and the resulting pale yellow solid was collected by filtration and dried under oil-pump vacuum to give (*RSS,SRR*)-**19** (0.312 g, 0.428 mmol, 76%) as a 42–31:58–69 *sc*/*ac*[11b] mixture. Mp: 185–194 °C dec. IR (cm^{-1}, KBr/thin film): ν_{NO} 1748–1742/1743–1738 vs, ν_{CO} 1690–1682/1685–1682 s. Anal. Calcd for $C_{29}H_{30}BF_4NO_2PRe$: C, 47.81; H, 4.15. Found: C, 47.59; H, 4.17.

NMR (CD_2Cl_2) *sc*-(*RSS,SRR*)-**19**: ^1H (δ, $CHDCl_2$ ref) 7.74–7.22 (m, $3C_6H_5$), 5.96 (s, C_5H_5), 4.87 (d, J_{HH} = 10.6, =CHCO), 3.78 (ddq, J_{HH} = 6.5, 10.6; J_{HP} = 10.5, =C*H*CH$_3$), 2.87 (dq, J_{HH} = 18.0, 7.2, COC*H*H′), 2.74 (dq, J_{HH} = 18.0, 7.2, COCH*H*′), 1.14 (dd, J_{HH} = 7.2, 7.2, CH_2CH_3), 1.05 (d, J_{HH} = 6.5, =CHCH_3); $^{13}C\{^1H\}$ (ppm, CD_2Cl_2 ref) 205.6 (s, CO), 133.6 (d, J_{CP} = 10.0, *o*-Ph), 132.8 (d, J_{CP} = 2.4, *p*-Ph), 132.5 (d, J_{CP} = 60.4, *i*-Ph), 130.1 (d, J_{CP} = 11.1, *m*-Ph), 98.8 (s, C_5H_5), 49.1 (d, J_{CP} = 5.1, =*C*HCH$_3$), 47.0 (s, =*C*HCO), 36.5 (s, CO*C*H_2), 20.1 (s, =CH*C*H$_3$), 8.0 (s, CH_2CH_3); $^{31}P\{^1H\}$ (ppm) 8.4 (s). *ac*-(*RSS,SRR*)-**19**: ^1H (δ) 7.74–7.22 (m, $3C_6H_5$), 5.91 (s, C_5H_5), 4.61 (ddq, J_{HH} = 10.5, 6.3, J_{HP} = 2.1, =C*H*CH$_3$), 3.62 (dd, J_{HH} = 10.5, J_{HP} = 8.0, =CHCO), 2.34 (d, J_{HH} = 6.3, =CHC*H*$_3$), 2.13 (dq, J_{HH} = 18.8, 7.1, COC*H*H′), 1.36 (dq, J_{HH} = 18.8, 7.1, COCH*H*′), 0.72 (dd, J_{HH} = 7.1, 7.1, CH_2CH_3); $^{13}C\{^1H\}$ (ppm) 211.3 (s, CO), 133.1 (d, J_{CP} = 10.2, *o*-Ph), 132.2 (d, J_{CP} = 2.6, *p*-Ph), 129.9 (d, J_{CP} = 11.4, *m*-Ph), 128.1 (d, J_{CP} = 59.7, *i*-Ph), 98.8 (s, C_5H_5), 61.7 (d, J_{CP} = 5.9, =*C*HCO), 51.0 (s, =*C*HCH$_3$), 36.2 (s, CO*C*H_2), 23.8 (s, =CH*C*H$_3$), 8.0 (s, CH_2CH_3); $^{31}P\{^1H\}$ (ppm) 4.3 (s).

Relative Binding Affinities of Cyclohexenone and Cyclohexanone. The following experiment is representative. A 5-mm NMR tube was charged with $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}O{=}\overline{CCH_2(CH_2)_4})]^+BF_4^-$ (14;[5c] 0.0167 g, 0.023 mmol) and capped with a septum. Then $CHCl_2CHCl_2$ (0.6 mL) and cyclohexenone (87 μL, solution of 0.0507 g in $CHCl_2CHCl_2$, prepared in a 2.000 ± 0.015 mL volumetric flask; 0.023 mmol) were sequentially added. The tube was placed in a 46 °C oil bath, and after 3 h was transferred to an ambient temperature NMR probe. The **14**/**10** ratio was assayed by ^{31}P NMR (17.6/17.9 ppm).

Crystal Structure of *sc*-(*RSS,SRR*)-19·$(CH_2ClCH_2Cl)_{0.5}$. A yellow rectangular prism was grown by diffusion of ether vapor into a 0 °C CH_2ClCH_2Cl solution of (*RSS,SRR*)-**19**. A ^1H NMR spectrum verified the formation of a hemisolvate (δ, CD_2Cl_2: 5.94). Data were collected on an Enraf-Nonius CAD4 diffractometer as summarized in Table I. Cell constants were obtained from 25 reflections with $20° < 2\theta < 33°$. The space group was determined from systematic absences ($0k0\ k = 2n$, $h0l\ l = 2n$) and subsequent least-squares refinement. Lorentz, polarization, and empirical absorption (Ψ scans) corrections were applied. The structure, in which the hemisolvate occupied an inversion center, was solved by standard heavy-atom techniques with the SDP/VAX package.[60] Non-hydrogen atoms were refined with anisotropic thermal parameters, and H1 and H2 were located from the final difference Fourier map. Other hydrogen atom positions were calculated and added to the structure factor calculations but were not refined. Scattering factors, and Δ*f*′ and Δ*f*″ values, were taken from the literature.[61]

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Supplementary Material Available: A table of anisotropic thermal parameters for *sc*-(*RSS,SRR*)-19·$(CH_2ClCH_2Cl)_{0.5}$ (1 page). Ordering information is given on any current masthead page.

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(59) Several sets of PPh_3 ^{13}C NMR resonances were observed, as previously found in related alkyne complexes and attributed to restricted Re–P and/or P–C bond rotation.[8] Partial data: 135.1 (d, J_{CP} = 11.1), 134.5 (d, J_{CP} = 11.4), 132.2 (d, J_{CP} = 9.8), 129.1 (d, J_{CP} = 12.2), and other broadened resonances.

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