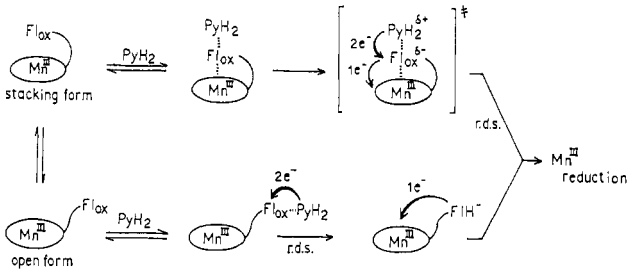
Scheme VI



factors.[46] For the flavin-linked porphyrins the one-electron redox potentials are not correlated to the log k^{2nd}, but we assume that geometrical factors play an important role. The methylene chain length considerably affects the chemical shifts in the ^1H NMR spectra, which reflect the geometry of the flavin-linked porphyrin. In kinetic studies, we used the polar and protic solvent ethanol for practical reasons. In this solvent the flavin moiety is probably partly solvated, and the stability of the stacked conformation decreases with an increase of the flexible methylene chain length. The intermediate state clearly reflects the initial conformation. $Fl_{ox}C_1(TPP)Mn^{III}Cl$, which has little freedom around the methylene spacer, is in a more folded conformation than **1b** and **1c**, and the reaction should proceed via a ternary complex $[PyH_2\cdots Fl_{ox}\cdots(TPP)Mn^{III+}]$. It has been well-known that the redox reaction between flavin and a 1,4-dihydropyridine proceeds via a preequilibrium charge-transfer-type complex $[PyH_2\cdots Fl_{ox}]$.[46] In the proposed ternary complex, one electron can be rapidly transferred to the near manganese(III) porphyrin. The reaction of **1b**, **1c**, **1d**, and **1e** proceeds only partly via this ternary complex and mostly via its open form. The proposed reaction mechanism is summarized in Scheme VI.

Conclusion. Novel flavin-linked porphyrins have been synthesized. The key step, the condensation of the flavin carboxylic acid and the *o*-NH_2TPPH_2, which was carried out via the flavin acid chloride, proceeds in good yield. Spectrophotometric studies revealed that the flavin and the porphyrin moieties are in close proximity in the all-oxidized form. Electrochemical studies suggest an interaction of the chromophores in redox reactions. Especially, the potentials of the $Fl_{ox}/Fl^{\bullet-}$ and $Fl^{\bullet-}/Fl^{2-}$ couples are significantly shifted to more positive values. The flavin-catalyzed 2e/1e electron-transfer reactions between NADH model compounds and $(TPP)Mn^{III}Cl$ were investigated in intermolecular systems (Fl_{ox} + PyH_2 + $(TPP)Mn^{III}Cl$) as well as in intramolecular systems ($Fl_{ox}C_n(TPP)Mn^{III}Cl$ + PyH_2). Reaction rates were accelerated by the intramolecular effect, and this acceleration was strongly affected by the methylene spacer length and the linking position.

Synthesis, Structure, and Alkylation of Chiral Vinylrhenium Complexes (η^5-C_5H_5)Re(NO)(PPh_3)(CX=CHR) (X = H, OCH_3). A Mechanistic Study of 1,3-Asymmetric Induction from Rhenium to Carbon

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Abstract: Reaction of alkylidene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH_2R)]^+PF_6^-$ (**1**-PF_6^-; **a**, R = H; **b**, R = CH_3; **c**, R = $CH_2CH_2CH_3$; **d**, R = $CH_2C_6H_5$) with DBU or *t*-BuO^-K^+ gives vinyl complexes (*E*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH=CHR) ((*E*)-**2a-d**; 72-86%). Complexes (*E*)-**2b-d** equilibrate to 84-92:16-8 *E*/*Z* mixtures in solution. Complex (*E*)-**2b** reacts with CF_3SO_3H and CH_3OSO_2F to give ethylidene complex **1b**-$CF_3SO_3^-$ and isobutylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH(CH_3)_2)]^+FSO_3^-$ (**3**-FSO_3^-; ca. 65%) and with CF_3SO_3D and CD_3OSO_2F to give mainly (*SR,RS*)-**1b**-β-*d*-$CF_3SO_3^-$ and (*SS,RR*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH(CH_3)(CD_3))]^+FSO_3^-$. However, experimental problems hinder quantification of the 1,3-asymmetric induction. Reaction of **3**-FSO_3^- and *t*-BuO^-K^+ gives isobutenyl complex (η^5-C_5H_5)Re(NO)(PPh_3)(CH=$C(CH_3)_2$) (**4**, 60% from **2b**), which in turn reacts with CH_3OSO_2F to give neopentylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CH(CH_3)_3)]^+FSO_3^-$ (90%). Complex **2a** and $Ph_3C^+PF_6^-$ react to give alkylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH_2CPh_3)]^+PF_6^-$ (81%), which in turn reacts with *t*-BuO^-K^+ to give vinyl complex (*E*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH=CHCPh$_3$) (74%). Reactions of methoxycarbene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=C(OCH_3)CH_2R)]^+PF_6^-$ with NaH or DBU give α-methoxyvinyl complexes (*Z*)-(η^5-C_5H_5)Re(NO)(PPh_3)(C(OCH_3)=CHR) ((*Z*)-**10a,b,d,e** (R = C_6H_5)) in high yields. These are more nucleophilic than (*E*)-**2a-d** and react with alkyl iodides R'I to give methoxycarbene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=C(OCH_3)CHRR')]^+I^-$ that readily demethylate to acyl complexes (η^5-C_5H_5)Re(NO)(PPh_3)(COCHRR'). Thus, (*Z*)-**10b** and $C_6H_5CH_2Br$ react to give (*SR,RS*)-(η^5-C_5H_5)Re(NO)(PPh_3)(COCH(CH_3)($CH_2C_6H_5$)) ((*SR,RS*)-**13**; 71%), and (*Z*)-**10d** and CH_3I react to give (*SS,RR*)-**13** (88%; both diastereomers of ≥98% purity). Crystal structures of (*E*)-**2d** and (*Z*)-**10d** and extended Hückel MO calculations on Re-C_α rotamers of (η^5-C_5H_5)Re(NO)(PH_3)(CX=CH_2) (X = H, OH) are also described. Data are consistent with the following model for 1,3-asymmetric induction: electrophiles attack a Re-C_α rotamer with the ON-Re-C_α-C_β torsion angle (θ) close to 0° and on the C=C face opposite the bulky PPh_3 ligand.

Transition-metal complexes containing vinyl, or alkenyl, ligands, $L_nMCR{=}CR'R''$, have been known for some time and extensively studied.[3-8] However, as suggested by the paucity of review literature,[8] only recently have they attracted attention as a class

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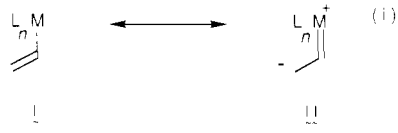
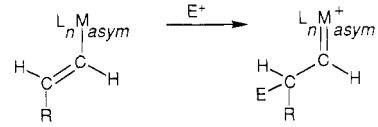
of compounds per se. This interest derives in part from the fundamental importance of substituent effects upon C=C double-bond properties and reactivity. For example, numerous synthetically useful organic reactions require appropriate C=C polarization. Since there are many L_nM systems that are electron donating, electron withdrawing, and chiral, metal substituents should enable a variety of useful modifications of C=C double-bond properties. Furthermore, the study of isolable vinyl complexes can afford insight into processes in which they are reactive intermediates, such as metal-catalyzed coupling reactions of vinyl halides and triflates[9] and acetylene hydrogenations.[10]

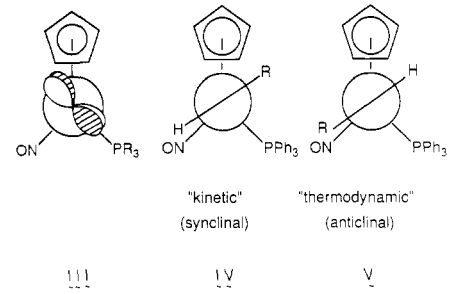
Vinyl complexes of electron-donating or electron-"rich" metals should have two important resonance contributors, I and II, as shown in eq i. Such vinyl complexes should, like enamines,[11] be nucleophilic at C_β and thus reactive toward electrophiles. De-



protonated chiral imines, $RCH{=}C(R')\ddot{N}R_{asym}]^-$, and related compounds have been shown to undergo efficient C_β asymmetric alkylation.[12] It occurred to us that attack of an electrophile E^+ upon a chiral vinyl complex, $L_nMCH{=}CHR$ (M = chiral metal) could give an alkylidene complex $L_nM^+{=}CHCHRE$ in which the new C_β chiral center CHRE might be formed with appreciable 1,3-asymmetric induction (eq ii).



Chiral rhenium complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^{n+}$ undergo a number of remarkably stereospecific ligand-based transformations[13-18] and are easily obtained in optically pure form.[19] Furthermore, the $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)^+$ fragment has a high-lying rhenium-centered d orbital HOMO, shown in III, and hence is a powerful π-donor substituent.[13a,d] Accordingly,



we set out to synthesize and probe the reactivity of chiral vinylrhenium complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CX{=}CHR)$. In this paper, we describe (1) the facile, high-yield synthesis of vinyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CX{=}CHR)$ by deprotonation of alkylidene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CXCH_2R)]^+PF_6^-$, (2) X-ray crystal structures of two vinyl complexes and an extended Hückel MO analysis of the Re–C_α conformations found, (3) reactions of these vinyl complexes with a variety of alkylating agents in which efficient 1,3-asymmetric induction occurs, and (4) a mechanistic model for the 1,3-asymmetric induction. A portion of this study has been communicated.[20]

Results

1. Synthesis of Vinyl Complexes (*E*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH{=}CHR)$. Ethylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH_3)]^+PF_6^-$ (**1a**-PF_6^-)[13c] exists as a (90 ± 2):(10 ± 2) equilibrium mixture of *ac*/*sc* Re=C geometric isomers,[21-23]

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(21) In synclinal (*sc*) Re=C_α isomers, the highest priority[22] ligands on Re ($\eta^5\text{-}C_5H_5$) and C_α (R) define a 60 ± 30° torsion angle; in anticlinal (*ac*) isomers, the highest priority ligands define a 120 ± 30° torsion angle: *Pure Appl. Chem.* **1976**, *45*, 11; see section E-5.6, p 24.

(22) Absolute configurations are assigned according to the Baird/Sloan modification of the Cahn–Ingold–Prelog priority rules. The $\eta^5\text{-}C_5H_5$ ligand is considered to be a pseudoatom of atomic number 30, which gives the following sequence: $\eta^5\text{-}C_5H_5$ > PPh_3 > NO > COR, =CXR, C(X)=CRR. Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598. Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1.

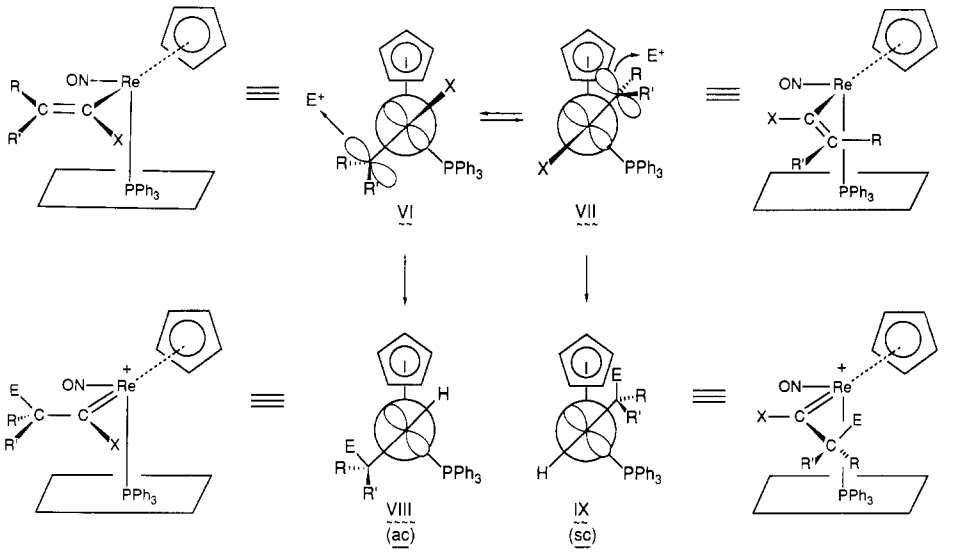
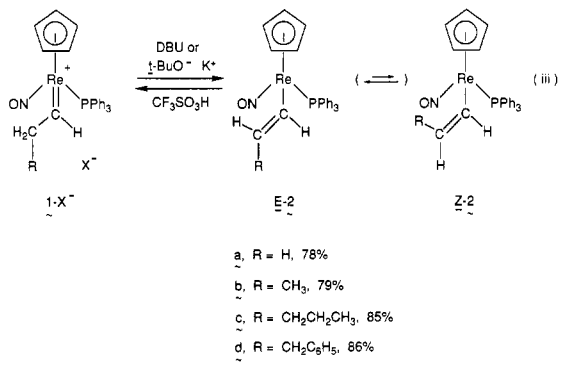


Figure 1. Analysis of the mechanism of 1,3-asymmetric induction in electrophilic attack upon vinyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CX{=}CRR')$.

the general structures of which are given in Newman projections IV and V. Note that the alkylidene ligand adopts conformations that maximize overlap of the C_α acceptor p orbital with the d orbital HOMO shown in III and that the alkyl substituent of the less stable isomer resides between the bulky PPh_3 and medium-sized $\eta^5\text{-}C_5H_5$ ligands. Also, these complexes are octahedral, with the $\eta^5\text{-}C_5H_5$ ligand occupying three coordination sites, so the ON–Re–PPh_3 bond angle is close to 90°.

Reaction of ethylidene complex **1a**-PF_6^- with the base DBU[23c] gave ethenyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH{=}CH_2)$ (**2a**) in 78% yield after workup (eq iii). Propylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH_2CH_3)]^+PF_6^-$ (**1b**-PF_6^-) and pentylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH_2CH_2CH_2CH_3)]^+PF_6^-$ (**1c**-PF_6^-), also ca. 90:10 equilibrium mixtures of *ac*/*sc* Re=C geometric isomers,[13b] similarly gave propenyl complex (*E*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH{=}CHCH_3)$ ((*E*)-**2b**) and pentenyl complex (*E*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH{=}CHCH_2CH_2CH_3)$ ((*E*)-**2c**) in 79% and 85% yields after CH_2Cl_2/hexanes recrystallization. Importantly, these compounds crystallized as >97:3 mixtures of *E*/*Z* C=C geometric isomers. However, (*E*)-**2b** and (*E*)-**2c** equilibrated to (84 ± 2):(16 ± 2) and (92 ± 2):(8 ± 2) *E*/*Z* mixtures, respectively, over the course of 3 h at 25 °C in $CDCl_3$. The deprotonation of **2a–c** could also be effected with *t*-BuO^-K^+ in comparable yields.



a, R = H, 78%
b, R = CH_3, 79%
c, R = $CH_2CH_2CH_3$, 85%
d, R = $CH_2C_6H_5$, 86%

Complexes **2a–c** (and all other vinyl complexes) were characterized by ^1H, ^{13}C, and ^{31}P NMR (Table I) and by IR, mass spectrometry, and microanalysis (Experimental Section). The ^1H NMR chemical shifts of the $\eta^5\text{-}C_5H_5$ ligands (Table I) and the IR $\nu_{N\equiv O}$ (KBr, 1641 cm^{-1}) were characteristic of neutral $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)$ complexes but were slightly shifted in a "cationic direction" from those found in alkyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2R)$ (^1H NMR δ 4.89–4.92, C_5H_5; IR $\nu_{N\equiv O}$ 1614–1624 cm^{-1}).[13b] The ^1H NMR spectra showed the C_β vinyl protons to be *upfield* of those of the C_α vinyl protons (Table I), as found with other alkenes bearing electron-donating substituents.[24a] A ^1H-coupled ^{13}C NMR spectrum showed the C_α ^{13}C NMR resonance in ethenyl complex **2a** to be *downfield* of the C_β resonance. However, for C_β-substituted vinyl complexes such as **2b** and **2c**, C_α was found upfield of C_β. In all cases, $J_{C_\alpha P}$ was significantly greater than $J_{C_\beta P}$ (Table I). The *E*/*Z* assignments were based upon the magnitude of $J_{H_\alpha H_\beta}$[24b] and were confirmed in one case (below) by an X-ray crystal structure.

The new alkylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH_2CH_2C_6H_5)]^+PF_6^-$ (**1d**-PF_6^-) was prepared in 90% yield from alkyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_2CH_2C_6H_5)$[25] and $Ph_3C^+PF_6^-$. When this reaction was monitored by ^1H and ^{31}P NMR at −78 °C, exclusive formation of the less stable product Re=C isomer, *sc*-**1d**-PF_6^-, was observed as expected.[13] When the solution was warmed to room temperature, isomerization to a (90 ± 2):(10 ± 2) equilibrium mixture of *ac*-**1d**-PF_6^-/*sc*-**1d**-PF_6^- occurred. A control experiment, of importance below, showed that this isomerization was not catalyzed by CF_3SO_3H (0.1 equiv, −78 °C, 1 h). Reaction of **1d**-PF_6^- with DBU as above gave, after CH_2Cl_2/hexanes recrystallization, solvated phenylpropenyl complex (*E*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH{=}CHCH_2C_6H_5)\cdot CH_2Cl_2$ ((*E*)-**2d**·CH_2Cl_2, 86%; eq iii). Over the course of 3 h at 25 °C in $CDCl_3$, (*E*)-**2d** equilibrated to a (92 ± 2):(8 ± 2) *E*/*Z* mixture.

2. Reactions of Vinyl Complexes (*E*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH{=}CHR)$. 1,3-Asymmetric Induction. Reactions of vinyl complexes **2a–d** with 1.1 equiv of CF_3SO_3H in CD_2Cl_2 were monitored by ^1H NMR at −78 °C. Alkylidene complexes **1a–d**-$CF_3SO_3^-$ rapidly formed (<4 min; eq iii) in spectroscopically quantitative yields as (71 ± 2):(29 ± 2), (90 ± 2):(10 ± 2), (88 ± 2):(12 ± 2), and (90 ± 2):(10 ± 2) mixtures of *ac*/*sc* Re=C isomers, respectively. As will be rationalized in the Discussion, the *ac* and *sc* isomers are visualized as arising from transition states VI and VII in Figure 1.

Interestingly, addition of 1.03 equiv of $CHCl_2CO_2H$ ($pK_a(H_2O)$ = 1.29)[26] to propenyl complex (*E*)-**2b** in CD_2Cl_2 at −68 °C gave a (66 ± 2):(34 ± 2) equilibrium mixture of **1b**-$CHCl_2CO_2^-$ ((90

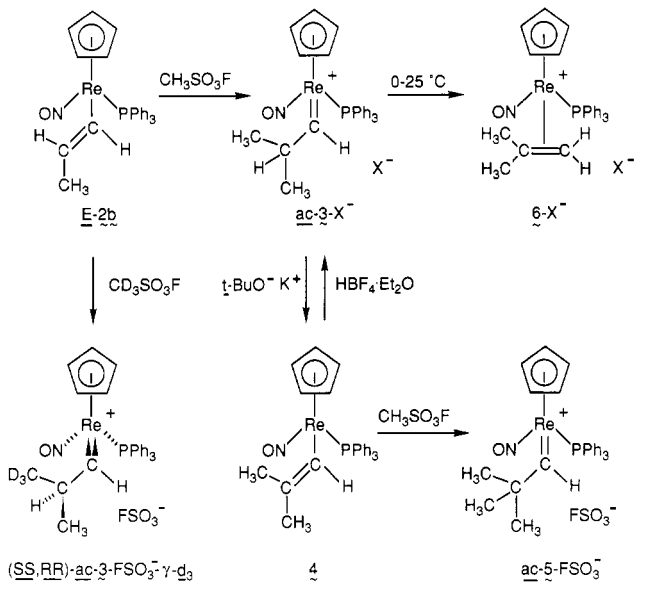
(23) Additional nomenclature conventions are as follows: (a) Compounds not specified as specific geometric isomers (Re=C, *ac*/*sc*; C=C, *E*/*Z*) are equilibrium mixtures of isomers. (b) In complexes with more than one chiral center, the rhenium configuration is specified first. (c) DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

(24) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981; (a) Appendix d, p 227; (b) Appendix f, p 235.

(25) Buhro, W. E.; Wong, A.; Merrifield, J. H.; Lin, G.-Y.; Constable, A. G.; Gladysz, J. A. *Organometallics* **1983**, *2*, 1852.

(26) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper and Row: New York, 1981; p 274.

Scheme I. Formation and Reactions of Isobutylidene Complex *ac*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH(CH_3)_2)]^+X^-$ (*ac*-**3**-X^-)



± 2):(10 ± 2) *ac*/*sc*) and **2b** ((82 ± 2):(18 ± 2) *E*/*Z*). Thus, the β-hydrogens of propylidene complex **1b** are acidic enough to be appreciably abstracted by the weak base $CHCl_2CO_2^-$. Casey has previously shown that, in THF, neutral Fischer-type carbene complexes such as $(CO)_5Cr{=}C(OCH_3)CH_3$ have H_β acidities comparable to the OH acidities of phenols.[27]

When propenyl complex (*E*)-**2b** was treated with 0.25 equiv of $CHCl_2CO_2H$ in CD_2Cl_2 at ≤−75 °C, equilibration to a (84 ± 2):(16 ± 2) (*E*)-**2b**/(*Z*)-**2b** mixture (as well as partial protonation to **1b**-$CHCl_2CO_2^-$) immediately occurred. Hence, the *E*/*Z* isomerization of **2b** is catalyzed by mild acids. When (*E*)-**2b** was similarly treated with 0.25 equiv of the strong acid CF_3SO_3H, partial protonation to **1b**-$CF_3SO_3^-$ occurred *without* starting material *E*/*Z* equilibration.

The feasibility of effecting 1,3-asymmetric induction by electrophilic attack upon propenyl complex (*E*)-**2b** was investigated. Reaction of (*E*)-**2b** with 1.03 equiv of CF_3SO_3D in CD_2Cl_2 was monitored by ^1H NMR at −75 °C. Propylidene complexes *ac*-**1b**-β-d_x-$CF_3SO_3^-$ and *sc*-**1b**-β-d_x-$CF_3SO_3^-$ formed in a (87 ± 2):(13 ± 2) ratio. The areas of the two diastereotopic H_β resonances of *ac*-**1b**-β-d_1-$CF_3SO_3^-$ indicated a (76 ± 5):(24 ± 5) ratio of diastereomers. However, analysis was complicated by the presence of the other Re=C geometric isomer, *sc*-**1b**-β-d_1-CF_3SO_3, and some dideuteriated product, **1b**-β-d_2-$CF_3SO_3^-$ (ca. 20%; measured by integration). Hence, we sought to assay for 1,3-asymmetric induction via a carbon–carbon bond-forming reaction.

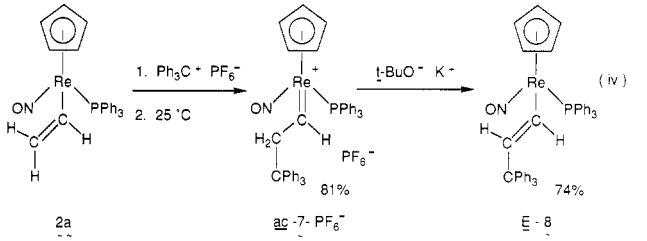
Reaction of propenyl complex (*E*)-**2b** with 10 equiv of CH_3OSO_2F at −25 °C gave, after careful workup, isobutylidene complex *ac*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH(CH_3)_2)]^+FSO_3^-$ (*ac*-**3**-FSO_3^-) as a thermally unstable oil of ca. 95% purity by ^1H NMR (Scheme I). Experiments conducted in the presence of an internal standard indicated a yield of ≥65%. Only one Re=C geometric isomer was detected, and the two diastereotopic methyl groups exhibited different ^1H and ^{13}C NMR resonances.

Spectroscopically pure isobutylidene complex **3**-BF_4^- could be generated via a two-step procedure (Scheme I). First, treatment of crude *ac*-**3**-FSO_3^- with *t*-BuO^-K^+/*t*-BuOH gave stable isobutenyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH{=}C(CH_3)_2)$ (**4**) in 60% overall yield from (*E*)-**2b**. This deprotonation could also be effected with DBU. Reaction of **4** with $HBF_4{\cdot}Et_2O$ at −78 °C cleanly gave **3**-BF_4^- as a (90 ± 2):(10 ± 2) mixture of *ac* and *sc* Re=C isomers. Isobutenyl complex **4** also readily reacted with CH_3OSO_2F. Neopentylidene complex *ac*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHC(CH_3)_3)]^+FSO_3^-$ (*ac*-**5**-FSO_3^-) was subsequently isolated in 90% yield (Scheme I). Only one Re=C isomer was detected.

Two factors complicated the preparation of isobutylidene complex *ac*-**3** from (*E*)-**2b**. First, as in enolate and enamine chemistry,[4d,11,28] polyalkylation/proton transfer side reactions occurred under all but the most careful conditions. This was best illustrated by the ^1H NMR monitored reaction of ethenyl complex **2a** with 1.0 equiv of CH_3OSO_2F in CD_2Cl_2, which gave (between 2 and 22 °C) ethylidene complex **1b**-FSO_3^-, propenyl complex (*E*)-**2b**, isobutylidene complex *ac*-**3**-FSO_3^-, isobutenyl complex **4**, and neopentylidene complex *ac*-**5** (identified by the ^1H NMR chemical shifts of the CH_3, =CHR, and η^5-C_5H_5 resonances), as well as other products. Second, when isobutylidene complex *ac*-**3**-FSO_3^- was warmed to between 0 and 25 °C, it underwent clean rearrangement to isobutylene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}C(CH_3)_2)]^+FSO_3^-$ (**6**-FSO_3^-; Scheme I). This chemistry will be described in a separate publication.[29]

The methylation of propenyl complex (*E*)-**2b** was reexamined with 10 equiv of CD_3OSO_2F in CD_2Cl_2 at −25 °C. Initial equilibration, presumably due to traces of acid, of the starting material to a (84 ± 2):(16 ± 2) (*E*)-**2b**/(*Z*)-**2b** mixture was observed. Methylation occurred over the course of ca. 20 min at −25 °C. Integration of the diastereotopic CH_3 ^1H NMR resonances of the resulting isobutylidene complex *ac*-**3**-γ-d_3-FSO_3^- indicated a (92 ± 2):(8 ± 2) ratio of diastereomers. Hence, both protonation and alkylation of (*E*)-**2b** occur with appreciable 1,3-asymmetric induction. The configurations of the major diastereomers (see Scheme I) were assigned as described in the Discussion.

The reaction of ethenyl complex **2a** with $Ph_3C^+PF_6^-$ was briefly examined in hopes of effecting α-hydride abstraction to give the vinylidene complex[14] $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=C{=}CH_2)]^+PF_6^-$ or β-hydride abstraction to give the unknown acetylene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(HC{\equiv}CH)]^+PF_6^-$. Instead, clean alkylation to give alkylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH_2CPh_3)]^+PF_6^-$ (**7**-PF_6^-) occurred (eq iv).



When this reaction was monitored by ^1H NMR at −71 °C, a (76 ± 2):(24 ± 2) ratio of two Re=C geometric isomers, *ac*-**7**-PF_6^- and *sc*-**7**-PF_6^-, was noted. Product crystallized from CH_2Cl_2/hexane as a solvate of the more stable isomer, *ac*-**7**-$PF_6^-{\cdot}CH_2Cl_2$ (81%). Reaction of **7**-PF_6^- and *t*-BuO^-K^+ gave vinyl complex (*E*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH{=}CHCPh_3)$ ((*E*)-**8**, 74%), which was a single C=C isomer both in solution and as a solid.

3. Syntheses of α-Methoxyvinyl Complexes (*Z*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(OCH_3){=}CHR)$. We sought vinyl complexes that would be more reactive toward alkylating agents than those above and whose alkylation products would not be as prone to rearrangements such as *ac*-**3**-$X^- \rightarrow$ **6** (Scheme I). Methoxy substituents are known to enhance the C_β nucleophilicity of alkenes, and methoxycarbene complexes $[L_nM{=}C(OCH_3)R]^+$ are less electrophilic at C_α and thus less prone to 1,2 proton shifts.[30] Hence, we set out to synthesize and study the reactivity of α-methoxyvinyl complexes of the formula $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(OCH_3){=}CHR)$. These should have three important resonance contributors, X–XII, as shown in eq v. While this work was in progress, similar studies involving related iron complexes

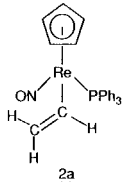
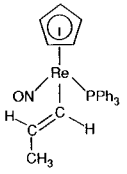
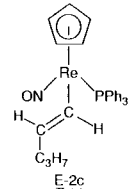
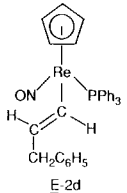
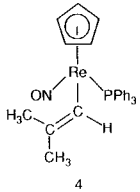
(27) Casey, C. P.; Anderson, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 1230.

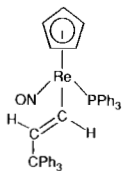
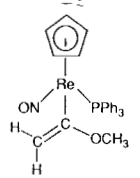
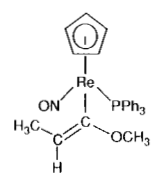
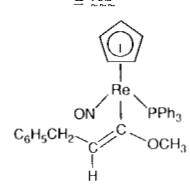
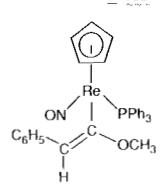
(28) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin: Menlo Park, CA, 1972; pp 546–586.

(29) Bodner, G. S.; Gladysz, J. A., to be submitted for publication.

(30) See, for example, iron alkylidene and α-alkoxycarbene complexes: Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258.

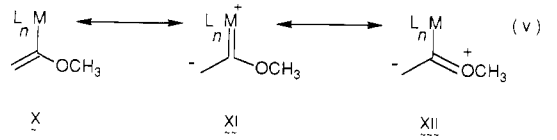
Table I. NMR Characterization of New Vinylrhenium Complexes

compound	^{1}H NMR,[a] ppm				^{13}C{^{1}H} NMR,[b] ppm							^{31}P{^{1}H} NMR,[c] ppm
	C_5H_5	Re—C—H_α	Re—C=C—H_β	other	C_5H_5	Re—C_α	Re—C_β	other	*i*-PPh_3	*o*/*m*-PPh_3	*p*-PPh_3	
 2a	5.08 (s)	8.41 (ddd, $^3J_{HH}$ = 18, $^3J_{HH}$ = 12, $^3H_{HP}$ = 2)	5.75 (dm, $^3J_{HH}$ = 12, $^2J_{HH}$ = 4, $^4J_{HP}$ = 3, $H_{\beta E}$);[d,e] 4.86 (ddd, $^3J_{HH}$ = 18, $^2J_{HH}$ = 4, $^4J_{HP}$ = 2, $H_{\beta Z}$)	7.39 (m, 3 C_6H_5)	91.7 (s)[f]	139.2 (d, J = 10)[g]	121.1 (s)[g]		135.2 (d, J = 56)	133.3 (d, J = 10); 128.2 (d, J = 10)	130.1 (s)	21.0 (s)
 E-2b	5.03 (s)	7.56 (dm, $^3J_{HH}$ = 16, $^4J_{HH}$ = 1, $^3J_{HP}$ = 3)[d,e]	5.00 (m, $^3J_{HH}$ = 16, $^3J_{HH}$ = 6, $^4J_{HP}$ = 3)[d,e]	7.39 (m, 3 C_6H_5); 1.71 (dt, $^3J_{HH}$ = 6, $^4J_{HH}$ = 1, $^5J_{HP}$ = 1, CH_3)[d,e]	91.0 (s)	122.8 (d, J = 13)	132.0 (d, J = 3)	25.1 (s, C_γ)	136.0 (d, J = 54)	133.7 (d, J = 11); 128.1 (d, J = 11)	130.0 (s)	21.4 (s)
Z-2b	5.04 (s)	*h*	6.17 (m, $^3J_{HH}$ = 6, $^3J_{HH}$ = 6)	1.86 (dm, $^3J_{HH}$ = 6, CH_3)	90.7 (s)	*h*	*h*	20.5 (s, C_γ)	*h*	*h*	*h*	*h*
 E-2c	5.02 (s)	7.58, (dm, $^3J_{HH}$ = 16, $^3J_{HP}$ = 3)[d,e]	5.08 (m, $^3J_{HH}$ = 16)[e]	7.39 (m, 3 C_6H_5); 1.98 (m, $CH_\gamma H_{\gamma'}$);[e] 0.97 (m, $CH_\delta H_{\delta'}$);[e] 0.65 (dd, $^3J_{HH}$ = 7, $^3J_{HH}$ = 7, CH_3)	91.2 (s)	122.1 (d, J = 12)	138.3 (d, J = 3)	42.2 (s, C_γ); 24.1 (s, C_δ); 13.8 (s, C_ϵ)	136.1 (d, J = 53)	133.6 (d, J = 10); 128.0 (d, J = 10)	129.9 (s)	21.2 (s)
Z-2c	*h*	*h*	*h*	*h*	90.5 (s)	123.6 (d, J = 11)	140.3 (d, J = 3)	37.3 (s, C_γ); 23.6 (s, C_δ); 14.3 (s, C_ϵ)	*h*	*h*	*h*	*h*
 E-2d	4.92 (s)	7.68 (dm, $^3J_{HH}$ = 16, $^3J_{HP}$ = 2)	6.67 (m, $^3J_{HH}$ = 16)	7.30 (m, 3 C_6H_5); 7.02 (m, C_6H_5); 3.36–3.16 (m, CH_2)	91.4 (s)	125.5 (d, J = 11)	136.0 (d, J = 5)	46.7 (s, CH_2); CC_6H_5 at: 143.6 (s, ipso), 128.5 (s), 128.0 (s), 124.8 (s, para)	136.1 (d, J = 54)	133.6 (d, J = 11); 128.1 (d, J = 11)	129.9 (s)	21.5 (s)
 4	5.01 (s)	7.14 (br d, $^3J_{HP}$ = 8)		7.39 (m, 3 C_6H_5); 1.87 (br s, CH_3); 1.82 (br s, $CH_{3'}$)	90.6 (s)	115.8 (d, J = 11)	139.7 (d, J = 3)	30.3 (s, C_γ); 24.9 (s, $C_{\gamma'}$)	136.3 (d, J = 52)	134.1 (d, J = 9); 128.4 (d, J = 9)	130.2 (s)	22.0 (s)

 E-8	4.99 (s)	7.60 (dd, $^3J_{HH}$ = 17, $^3J_{HP}$ = 3)	6.16 (dd, $^3J_{HH}$ = 17, $^4J_{HP}$ = 2)	7.50–6.50 (m, 6 C_6H_5)	91.7 (s)[f]	132.7 (d, J = 9)	143.5 (br s)	65.9 (s, C_γ); CC_6H_5 at: 149.5 (s, ipso), 131.3 (s), 127.8 (s), 125.9 (s, para)	137.0 (d, J = 53)	134.3 (d, J = 11); 128.9 (d, J = 11)	130.7 (s)	21.1 (s)
 10a	5.07 (s)		4.47 (s, $H_{\beta E}$); 3.93 (s, $H_{\beta Z}$)	7.48–7.36 (m, 3 C_6H_5); 2.99 (s, OCH_3)	91.0 (s)	168.6 (d, J = 12)	93.4 (s)	54.8 (s, OCH_3)	137.0 (d, J = 52)	134.4 (d, J = 10); 128.5 (d, J = 10)	130.4 (s)	22.2 (s)[j]
 Z-10b	5.07 (s)		4.76 (q, $^3J_{HH}$ = 6)	7.48–7.36 (m, 3 C_6H_5); 2.80 (s, OCH_3); 1.91 (d, $^3J_{HH}$ = 6, CH_3)	90.4 (s)	162.6 (d, J = 11)	102.9 (s)	54.8 (s, OCH_3); 17.3 (s, CH_3)	137.4 (d, J = 53)	134.4 (d, J = 11); 128.4 (d, J = 11)	130.3 (s)	23.0 (s)
 Z-10d	5.06 (s)		4.86 (dd, $^3J_{HH}$ = 7, $^3J_{HH}$ = 7)	7.55–7.13 (m, 4 C_6H_5); 3.74 (dd, $^2J_{HH}$ = 7, $^3J_{HH}$ = 7, CH_2); 2.82 (s, OCH_3)	90.5 (s)	162.6 (d, J = 11)	109.4 (s)	54.2 (s, OCH_3); 39.1 (s, CH_2); CC_6H_5 at: 146.2 (s, ipso), 129.1 (s), 128.5 (s), 125.5 (s, para)	137.1 (d, J = 53)	134.3 (d, J = 10); 128.5 (d, J = 10)	130.3 (s)	22.4 (s)
 Z-10e	5.14 (s)		5.89 (s)	7.55–7.37 (m, 3 C_6H_5); 7.27–7.00 (m, C_6H_5); 3.01 (s, OCH_3)	91.0 (s)	170.9 (d, J = 11)	112.4 (s)	55.3 (s, OCH_3); CC_6H_5 at: 143.5 (s, ipso), 129.9 (s), 127.9 (s), 123.4 (s, para)	136.4 (d, J = 54)	134.4 (d, J = 10); 128.5 (d, J = 9)	130.4 (d, J = 2)	23.3 (s)
F-10e	5.28 (s)		4.67 (s)	3.76 (s, OCH_3)	91.4 (s)	170.4 (d, J = 10)	92.9 (s)	59.5 (s, OCH_3); CC_6H_5 at: 140.3 (s, ipso), 128.0 (s), 127.2 (s), 123.2 (s, para)	136.2 (d, J = 53)	134.6 (d, J = 10); 128.9 (d, J = 10)	130.8 (d, J = 2)	20.2 (s)

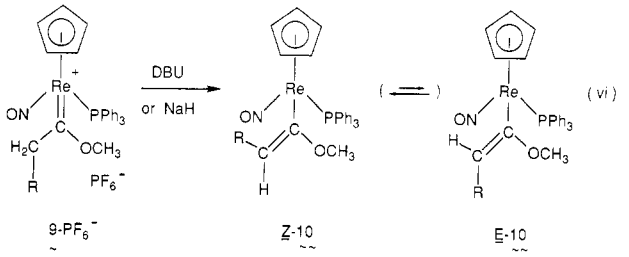
[a] ^1H NMR spectra were taken at 200–300 MHz in $CDCl_3$ (CH=CHR complexes) or CD_2Cl_2 ($C(OCH_3)$=CHR complexes) at ambient probe temperature and were referenced to internal $(CH_3)_4Si$ and $CHDCl_2$ (5.32 ppm), respectively, unless noted. All couplings (J) are in hertz. [b] ^{13}C NMR spectra were taken at 50–75 MHz in $CDCl_3$ (CH=CHR complexes) or CD_2Cl_2 ($C(OCH_3)$=CHR complexes) at ambient probe temperature and were referenced to internal $(CH_3)_4Si$ and CD_2Cl_2 (53.8 ppm), respectively, unless noted. All couplings (J) are to ^{31}P and are in hertz. [c] ^{31}P NMR spectra were taken at 32.2 MHz in CH_2Cl_2 at ambient probe temperature and were referenced to external 85% H_3PO_4. [d] Assigned by broad-band ^{31}P decoupling. [e] Assigned by single-frequency decoupling of neighboring proton resonances. [f] This spectrum recorded at −78 °C. [g] Assignment based upon the ambient-temperature ^1H-coupled spectrum obtained with the gated decoupler on during the pulse delay and off during acquisition: 138.5 (dd, $^1J_{^{13}C-^1H}$ = 138 Hz, $^2J_{^{13}C-^{31}P}$ = 11 Hz, C_α), 122.2 (t, $^1J_{^{13}C-^1H}$ = 153 Hz, C_β), 91.8 (d pent, $^1J_{^{13}C-^1H}$ = 180 Hz, $^2J_{^{13}C-^1H}$ = $^3J_{^{13}C-^1H}$ = 6 Hz, C_5H_5). [h] Not located. [i] This ^{13}C spectrum recorded in CD_2Cl_2. [j] This ^{31}P spectrum recorded in THF.

were reported by Malisch[4d,e] and Davies.[5]



X XI XII

By analogy to eq iii, deprotonations of α-methoxycarbene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=C(OCH_3)CH_2R)]^+PF_6^-$ (**9-PF$_6^-$**) were examined. The α-methoxycarbene complexes either had been previously reported[25] or were prepared by alkylation of the corresponding acyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_2R)$ with $(CH_3)_3O^+PF_6^-$. Reaction of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=C(OCH_3)CH_3)]^+PF_6^-$ (**9a-PF$_6^-$**) with NaH in THF gave, after workup, α-methoxyvinyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(OCH_3)=CH_2)$ (**10a**) in 75% yield (eq vi).



9-PF$_6^-$ Z-10 E-10

a, R = H, 75%

b, R = CH_3, 72%

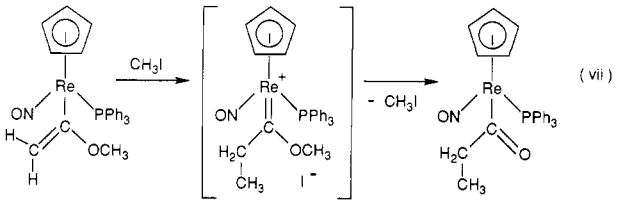
d, R = $CH_2C_6H_5$, 81%

e, R = C_6H_5, 83%

Reactions of α-methoxycarbene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=C(OCH_3)CH_2CH_3)]^+PF_6^-$ (**9b-PF$_6^-$**), $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=C(OCH_3)CH_2CH_2C_6H_5)]^+PF_6^-$ (**9d-PF$_6^-$**), and $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=C(OCH_3)CH_2C_6H_5)]^+PF_6^-$ (**9e-PF$_6^-$**) with DBU in CH_2Cl_2 or THF gave, after workup and recrystallization, α-methoxyvinyl complexes $(Z)\text{-}(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(OCH_3)=CHR)$ ((*Z*)-**10**: **b**, R = CH_3; **d**, R = $CH_2C_6H_5$; **e**, R = C_6H_5) in 72–83% overall yields from the corresponding acyl complexes. The assignment of these compounds as *Z* C=C geometric isomers was based upon several pieces of evidence. First, both (*Z*)-**10b** and (*Z*)-**10d** exhibited a 33 ± 5% ^{1}H NOE enhancement[31,32] of the vinyl hydrogen resonance upon irradiation of the α-methoxy resonance,[5a] as would be expected of *Z* geometric isomers. Second, the structure of (*Z*)-**10d** was verified by X-ray crystallography, as described below. As with the other vinyl complexes, α-methoxyvinyl complexes **10** were characterized by ^{1}H, ^{13}C, and ^{31}P NMR (Table I) and by IR, mass spectrometry, and microanalysis (Experimental Section).

Interestingly, when the reactions of **9b-PF$_6^-$**, **9d-PF$_6^-$**, and **9e-PF$_6^-$** with DBU were monitored by ^{31}P NMR at −78 °C, transients assigned as *E* geometric isomers were observed. Typical kinetic ratios were as follows. (*Z*/*E*)-**10d**: CH_2Cl_2, (44 ± 2):(56 ± 2); THF, (23 ± 2):(77 ± 2). (*Z*/*E*)-**10e**: CH_2Cl_2, (53 ± 2):(47 ± 2); THF, (32 ± 2):(68 ± 2). Both **10b** and **10d** equilibrated over the course of a few hours in CH_2Cl_2 at room temperature to (98 ± 1):(2 ± 1) *Z*/*E* mixtures. However, **10e** equilibrated only to a (62 ± 2):(38 ± 2) *Z*/*E* mixture, and some data on *E*-**10e** are included in Table I.

4. Reactions of α-Methoxyvinyl Complexes $(Z)\text{-}(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(OCH_3)=CHR)$. 1,3-Asymmetric Induction. The α-methoxyvinyl complex **10a** (0.8 M in CH_2Cl_2) and CH_3I (3 equiv) reacted over the course of 4 h at room temperature. Workup gave propionyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_2CH_3)$ (**11**; eq vii)[25] in 82% yield. However, when the



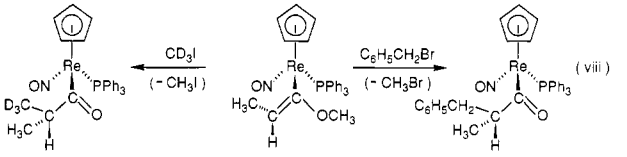
10a 9b-I$^-$ 11

reactants were more concentrated (or less rigorously purified) appreciable quantities of acetyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH_3)$[25] and the dimethylation product, isobutyroyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH(CH_3)_2)$ (**12**, a new compound; vide infra), were also produced. The structures of these products were confirmed by isolation and comparison to independently synthesized samples. The diastereotopic methyl groups in **12** were readily differentiated in ^{1}H and ^{13}C NMR spectra.

The conversion **10a** → **11** was observed to proceed via an intermediate with spectroscopic properties very similar to those of methoxycarbene complex **9b-PF$_6^-$**: ^{1}H NMR (δ, CD_2Cl_2, −35 °C, two Re=C isomers) 5.71, 6.01 (s, C_5H_5); 3.70, 4.15 (s, OCH_3); 0.79, 1.11 (t, CCH_3). The structure of this intermediate was therefore assigned as **9b-I$^-$**, $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=C(OCH_3)CH_2CH_3)]^+I^-$ (eq vii). Iodide ion then effects a well-precedented O-demethylation[33] to give the acyl complex product. Since chiral metal acyl complexes are in themselves useful compounds and their diastereomeric purities can be readily assayed,[17,34] we made no attempt to block or avoid this dealkylation process.

Side-by-side reactions of CH_3I (3 equiv, CH_2Cl_2) with α-methoxyvinyl complex **10a** and ethenyl complex **2a** were conducted at room temperature. Complex **10a** was 55% consumed after 0.5 h, but **2a** was <5% consumed. Complex **10a** was >98% consumed after 3 h, but **2a** was only 40% consumed after 24 h. Hence, the α-methoxy substituent significantly enhances the nucleophilicity of the vinyl ligand.

We next examined the effectiveness of substituted α-methoxyvinyl complexes in 1,3-asymmetric induction reactions. First, treatment of complex (*Z*)-**10b** with CH_3I (CH_2Cl_2, 24 h) gave isobutyroyl complex **12** in 88% yield. Analogous reaction of (*Z*)-**10b** with CD_3I gave (eq viii) labeled isobutyroyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH(CH_3)CD_3)$ (**12-γ-d_3**). Analysis by ^{1}H and ^{13}C NMR showed the label to be present chiefly on one methyl group. Integration indicated a (96 ± 2):(4 ± 2) ratio of diastereomers.



(SR,RS)-12-γ-d_3 Z-10b (SR,RS)-13

Complex (*Z*)-**10b** was likewise treated with $C_6H_5CH_2Br$. Acyl complex $(SR,RS)\text{-}(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH(CH_3)CH_2C_6H_5)$ ((*SR*,*RS*)-**13**) was subsequently isolated in 71% yield (eq viii). Product stereochemistry was assigned from a crystal structure of a solvate of (*SR*,*RS*)-**13**, as described elsewhere.[20b,35] By analogy, the predominant isomer of **12-γ-d_3** prepared above was assigned *SR*,*RS* stereochemistry. Complex (*Z*)-**10d** was similarly treated with CH_3I (eq ix). The opposite acyl complex diastereomer, (*SS*,*RR*)-**13**, was subsequently isolated in 88% yield. Diastereomers (*SR*,*RS*)-**13** and (*SS*,*RR*)-**13** showed no tendency

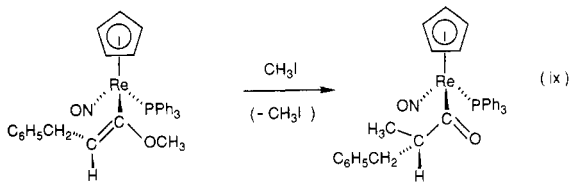
(31) Noggle, J. H.; Shirmer, R. E. *The Nuclear Overhauser Effect*; Academic: New York, 1971.

(32) (a) Hall, L. D.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1980**, *102*, 5703. (b) Sanders, J. K. M.; Mersh, J. D. *Prog. Nucl. Magn. Reson. Spectros.* **1983**, *15*, 353. (c) Hunter, B. K.; Baird, M. C. *Organometallics* **1985**, *4*, 1481.

(33) (a) Davison, A.; Reger, D. L. *J. Am. Chem. Soc.* **1972**, *94*, 9237. (b) Cutler, A. R. *Ibid.* **1979**, *101*, 604.

(34) See references in: (a) Liebeskind, L. S.; Welker, M. E.; Fengl, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 6328. (b) Davies, S. G.; Easton, R. J. C.; Walker, J. C.; Warner, P. *Tetrahedron* **1986**, *42*, 175.

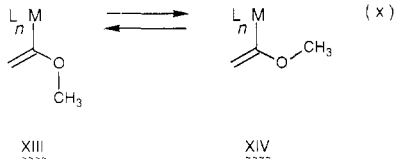
(35) Bodner, G. S.; Patton, A. T.; Smith, D. E.; Georgiou, S.; Tam, W.; Wong, W.-K.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1987**, *6*, 1954.



to interconvert under the workup conditions employed. HPLC analyses of both crude products before workup indicated diastereomer ratios of (99 ± 1):(1 ± 1).

Finally, complex (*Z*)-**10e** was treated with $(CH_3)_3O^+PF_6^-$ (CH_2Cl_2, 0.5 h) and then iodide source $Ph_3PCH_3^+I^-$. The more reactive alkylating agent was used to minimize *Z*/*E* equilibration of (*Z*)-**10e** on the time scale of the reaction. Acyl complex (*SS*,*RR*)-(η^5-C_5H_5)Re(NO)(PPh_3)(COCH(CH_3)C_6H_5) ((*SS*,*RR*)-**14**) was isolated in 61% yield (74% based upon recovered (*Z*)-**10e**). HPLC of the crude product indicated a (98 ± 1):(2 ± 1) ratio of diastereomers. The opposite diastereomer, (*SR*,*RS*)-**14**, was prepared earlier by an enolate methylation reaction.[17]

5. Structures of Vinyl and α-Methoxyvinyl Complexes. A knowledge of the orientations of the vinyl and α-methoxyvinyl ligands about the Re–C_α bond is critical for interpreting the stereochemistry of the above reactions. To facilitate analysis, θ will be used to represent the ON–Re–C_α–C_β torsion angle throughout this paper. This angle is easily viewed in Newman projection format. Note also that α-methoxyvinyl complexes can exhibit isomerism about the C_α–OCH_3 bond, as shown by XIII (s-cis) and XIV (s-trans) in eq x. The s-cis isomer is the more stable for most organic methyl vinyl ethers.[36]



We encountered considerable difficulty in obtaining suitable single crystals for X-ray analysis, so vinyl ligand orientations were first probed by extended Hückel molecular orbital (EHMO) calculations on the model complexes (η^5-C_5H_5)Re(NO)(PH_3)(CH=CH_2) and (η^5-C_5H_5)Re(NO)(PH_3)(C(OH)=CH_2). Figure 2 shows the variation in E_{total} as the Re–C_α bond was rotated in these complexes. The PH_3 ligand was held in the Re–P conformation earlier found to be optimum for ethyl complex (η^5-C_5H_5)Re(NO)(PH_3)(CH_2CH_3),[13d] and the hydroxyl group of (η^5-C_5H_5)Re(NO)(PH_3)(C(OH)=CH_2) was held in the s-cis conformation. Variation of the PH_3 and hydroxyl geometries did not significantly affect E_{total}. Local minima were found at θ = 30–35° and 180°, closely corresponding to isomers observed for alkylidene ligands in [(η^5-C_5H_5)Re(NO)(PPh_3)(=CHR)]$^+$ complexes (see IV and V above). With (η^5-C_5H_5)Re(NO)(PH_3)(CH=CH_2), the minimum at θ = 30° was particularly broad and shallow.

The θ dependence of the HOMO of model complex (η^5-C_5H_5)Re(NO)(PH_3)(CH=CH_2) was examined. At the E_{total} minima at θ = 30° and 180°, the HOMO was an antibonding combination of the (η^5-C_5H_5)Re(NO)(PH_3)$^+$ fragment d orbital HOMO (see III) and the H_2C=CH fragment π orbital, as is usual for donor-atom-substituted ethylenes.[37a,b] The H_2C=CH π and π* orbitals are both of appropriate symmetry to mix with the d orbital shown in III. However, the π orbital is 1.07 eV lower in energy than the d orbital, whereas the π* orbital is 4.10 eV higher in energy. Hence, mixing of the π and d orbitals dominates. This is shown schematically in Figure 3. At θ = 90° and 270°, where the fragment frontier orbitals[38] are orthogonal, the HOMO of

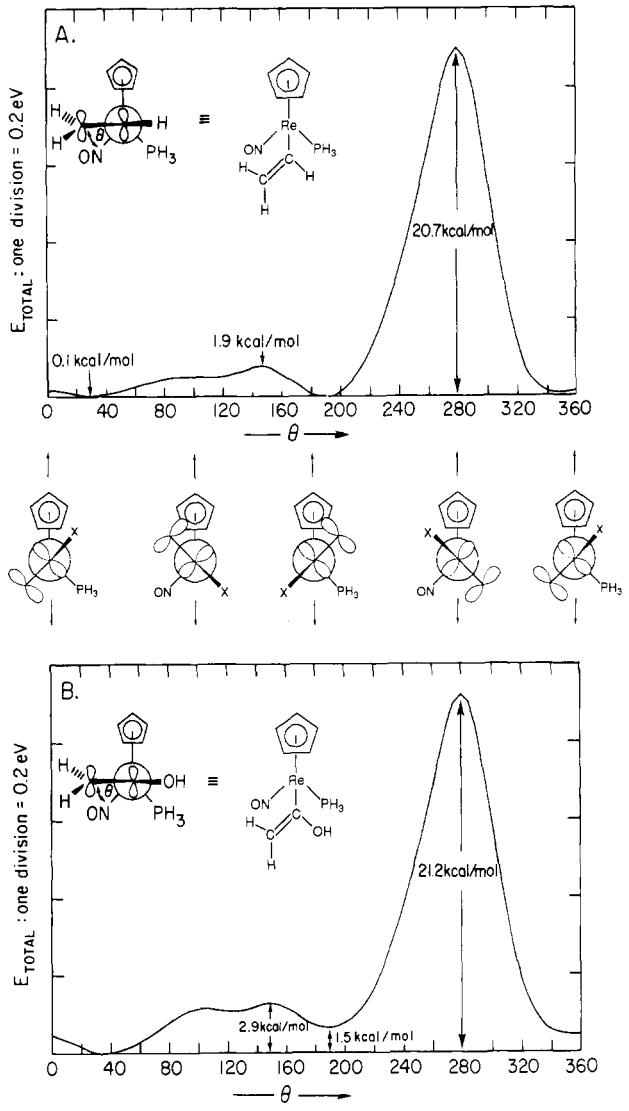


Figure 2. Variation in E_{total} as the vinyl ligands are rotated in (A) (η^5-C_5H_5)Re(NO)(PH_3)(CH=CH_2) and (B) (η^5-C_5H_5)Re(NO)(PPh_3)(C(OH)=CH_2) (calculated every 5° by the extended Hückel method with weighted H_{ij} formula).

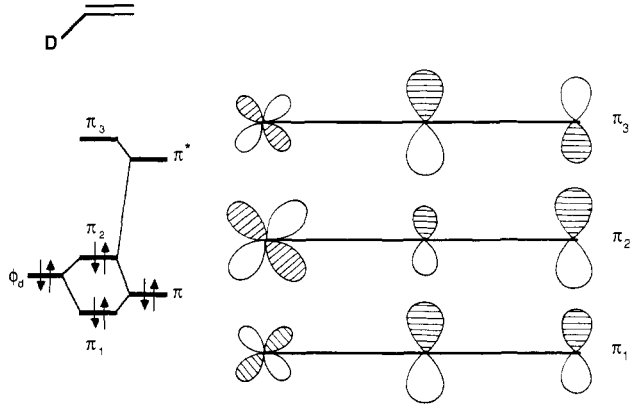


Figure 3. Qualitative MO diagram for Re–C_α–C_β π bonding in vinyl complexes (η^5-C_5H_5)Re(NO)(PR_3)(CH=CHR).

(36) (a) Owen, N. L.; Sheppard, N. *Trans. Faraday Soc.* **1964**, *60*, 634. (b) Owen, N. L.; Seip, H. M. *Chem. Phys. Lett.* **1970**, *5*, 162. (c) Samdal, S.; Seip, H. M. *J. Mol. Struct.* **1975**, *28*, 193. (d) Bernardi, F.; Epiotis, N. D.; Yates, R. L.; Schlegel, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 2385. (e) Durig, J. R.; Compton, D. A. C. *J. Chem. Phys.* **1978**, *69*, 2028.

(37) (a) Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361. (b) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; pp 163–165. (c) *Ibid.*, p 94.

(38) We use the definition of frontier orbitals and frontier MO theory summarized in: Kahn, S. D.; Pau, C. F.; Overman, L. E.; Hehre, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 7381.

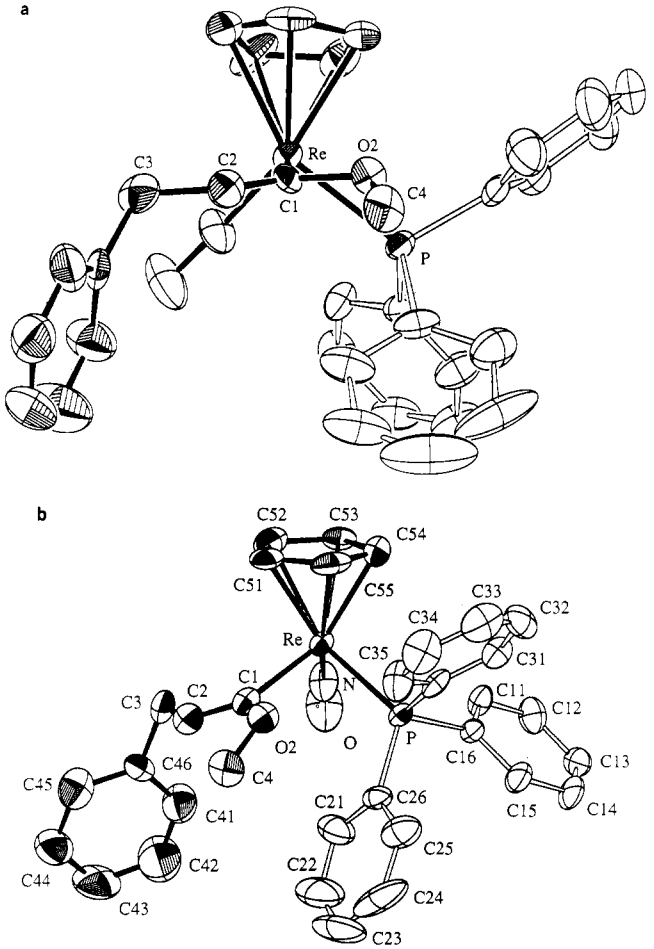


Figure 4. Molecular structure of α-methoxyvinyl complex (Z)-$(\eta^5$-$C_5H_5)Re(NO)(PPh_3)(C(OCH_3)=CHCH_2C_6H_5)$ ((Z)-**10d**): top, Newman-type projection down the C_α–Re bond; bottom, numbering scheme.

$(\eta^5$-$C_5H_5)Re(NO)(PH_3)(CH=CH_2)$ resembled the d orbital shown in III. The HOMO energy was at a minimum at $\theta = 80°$, contrary to expectations from Walsh's rule.[37c]

Further analysis of the EHMO data revealed important *non-frontier* MO interactions. Four additional occupied orbitals of the $(\eta^5$-$C_5H_5)Re(NO)(PH_3)^+$ fragment exhibited energies close to or above that of the $H_2C=CH$ fragment π orbital (0.515 and 0.308 eV above π; 0.045 and 0.082 eV below π). In conformations with $\theta = 90°$ and 270°, the latter two were of appropriate symmetry and ideal energy to strongly mix with the π orbital. The energies of the molecular orbitals resulting from this mixing showed the greatest variation with θ (0.22 and 0.14 eV vs 0.12 eV for the HOMO).

The LUMO of $(\eta^5$-$C_5H_5)Re(NO)(PH_3)(CH=CH_2)$ was mainly an antibonding combination of metal d and NO π^* orbitals, and its energy showed less θ dependence (0.08 eV). Orbitals essentially equivalent to those described above were found in model α-hydroxyvinyl complex $(\eta^5$-$C_5H_5)Re(NO)(PH_3)(C(OH)=CH_2)$. The θ dependences of the orbital energies were similar to those of $(\eta^5$-$C_5H_5)Re(NO)(PH_3)(CH=CH_2)$ in phase but differed somewhat in amplitude.

X-ray data were first obtained for α-methoxyvinyl complex (Z)-$(\eta^5$-$C_5H_5)Re(NO)(PPh_3)(C(OCH_3)=CHCH_2C_6H_5)$ ((Z)-**10d**) under the conditions summarized in Table II. Refinement, described in the Experimental Section, yielded the structure shown in Figure 4. Positional parameters, bond distances, and bond angles are summarized in Tables III–V. The torsion angle θ was found to be 47°, in reasonable agreement with one of the minima predicted in Figure 2B, and the methoxy group adopted the s-cis conformation.

X-ray data were next obtained on phenylpropenyl complex (E)-$(\eta^5$-$C_5H_5)Re(NO)(PPh_3)(CH=CHCH_2C_6H_5)\cdot CH_2Cl_2$ ((E)-**2d**·CH_2Cl_2) under conditions summarized in Table II. This compound differs from (Z)-**10d** by a C_α methoxy substituent and the stereochemistry of the C_β benzyl substituent. Refinement, described in the Experimental Section, yielded the structure shown in Figure 5. Positional parameters, bond distances, and bond angles are given in Tables III–V. The torsion angle θ was found to be 175.5°, in good agreement with one of the minima predicted in Figure 2A, but opposite to the one found for (Z)-**10d**. A crystal of (E)-**2d**·CH_2Cl_2 was dissolved in CD_2Cl_2 at −78 °C, and a ^1H NMR spectrum was immediately recorded at −90 °C. The spectrum was identical with one where the sample was kept at room temperature before cooling to −90 °C.

Difference NOE ^1H NMR experiments[32] were conducted on (E)-**2d** and selected model compounds in CD_2Cl_2. The η^5-C_5H_5 resonance of (E)-**2d** was irradiated. Enhancements of 4.1% in the H_α vinyl proton and 0.9% in the H_β vinyl proton were observed. Analogous experiments were done with the *ac* and *sc* Re=C isomers of benzylidene complex $[(\eta^5$-$C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]^+PF_6^-$ (refer to VIII and IX, Figure 1).[13a] Enhancements of 4.2% and 0.0%, respectively, were found in the H_α resonances (with the former being upfield of the latter). An identical experiment was conducted with methylidene complex $[(\eta^5$-$C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$ (−30 °C),[18] and enhancements of 1.9% and 0.0% were found in the upfield and downfield H_α resonances, respectively. These data suggest that, in solution, (E)-**2d** exists predominantly in a Re–C_α conformation

Table II. Summary of Crystallographic Data for Vinyl Complexes (E)-$(\eta^5$-$C_5H_5)Re(NO)(PPh_3)(CH=CHCH_2C_6H_5)\cdot CH_2Cl_2$ ((E)-**2d**·CH_2Cl_2) and (Z)-$(\eta^5$-$C_5H_5)Re(NO)(PPh_3)(C(OCH_3)=CHCH_2C_6H_5)$ ((Z)-**10d**)

compd	(E)-**2d**·CH_2Cl_2	(Z)-**10d**
molecular formula	$C_{32}H_{29}NOPRe\cdot CH_2Cl_2$	$C_{33}H_{31}NO_2PRe$
formula wt	745.63	690.80
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a, Å	11.908 (3)	13.883 (3)
b, Å	10.356 (2)	9.369 (5)
c, Å	25.054 (7)	11.205 (4)
α, deg		105.90 (3)
β, deg	90.60 (2)	89.18 (3)
γ, deg		99.94 (3)
V, Å^3	3090 (1)	1380 (1)
Z	4	2
d_{calcd}, g/cm^3	1.60	1.66
d_{obsd}, g/cm^3	1.60	1.65
cryst dimens, mm	0.27 × 0.31 × 0.32	0.17 × 0.26 × 0.34
diffractometer	Nicolet R3	Syntex P$\bar{1}$
temp of collection, °C	22	22
radiation, Å	λ(Mo Kα) 0.71069	λ(Mo Kα) 0.71069
data collection method	ω	θ–2θ
reflcns measd	$\pm h,+k,+l$	$+h,\pm k,\pm l$
scan speed, deg/min^{-1}	5–20 (variable)	3.0
2θ scan range, deg	$4 \le 2\theta \le 50$	$3 \le 2\theta \le 50$
scan range	$K\alpha_1$ − 0.8 to $K\alpha_2$ + 0.8	$K\alpha_1$ − 1.0 to $K\alpha_2$ + 1.0
total bkgd time/scan time	1.0	1.0
no. of reflcns between std	197	97
decay	≤2% variation	≤2% variation
total unique data	5442	4354
cutoff for obsd data	$4\sigma(F_o)$	$2.5\sigma(I)$
obsd data	4276	3432
abs coeff (μ), cm^{-1}	43.2	45.2
abs correction method	ψ scans	ψ scans
no. of reflcns	7	3
method of refinement	block matrix least squares	block matrix least squares
T_{max}/T_{min}	1.72	2.33
no. of variables	469	343
$R = \sum(\lvert F_o - F_c\rvert)/\sum F_o$	0.0316	0.0547
$R_w = \sum(\lvert F_o - F_c\rvert)w^{1/2}/\sum(F_o)w^{1/2}$	0.0345	0.0567
goodness of fit	0.967	1.50
weighting factor, ω	$1/(\sigma^2(F_o) + 0.001/(F_o)^2)$	$1/(\sigma^2(F_o) + 0.0045(F_o)^2)$
Δ/σ (max)	0.075	0.099
$\Delta\rho$ (max), e Å^{-3}	0.53, 1.4 Å from Re	2.55, 1.0 Å from Re

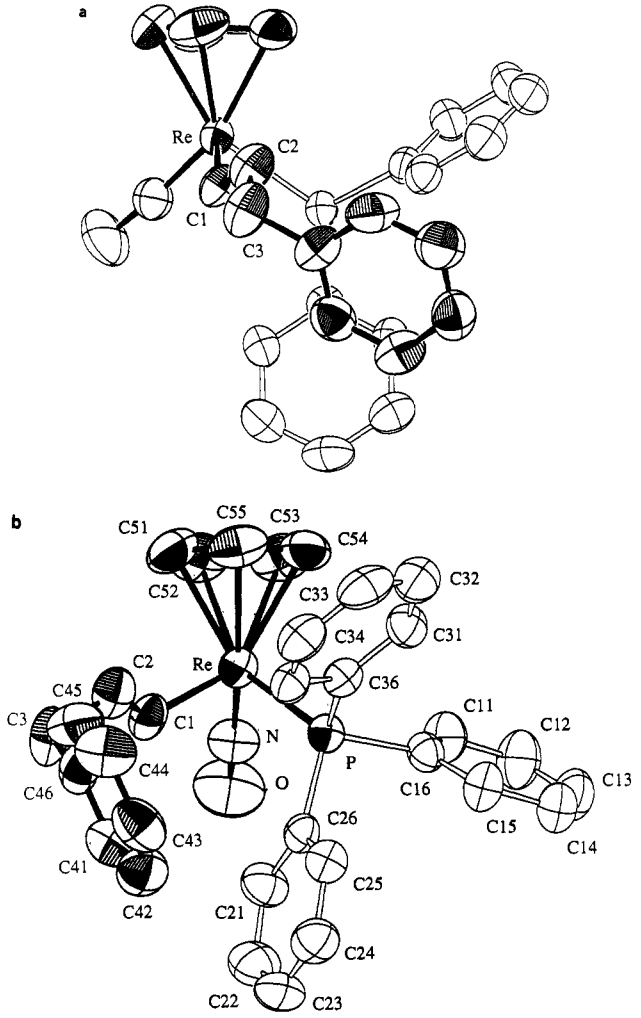


Figure 5. Molecular structure of vinyl complex (*E*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH=$CHCH_2C_6H_5$)·CH_2Cl_2 ((*E*)-**2d**·CH_2Cl_2): top, Newman-Type projection down the C_α–Re bond with one PPh_3 phenyl ring omitted; bottom, numbering scheme.

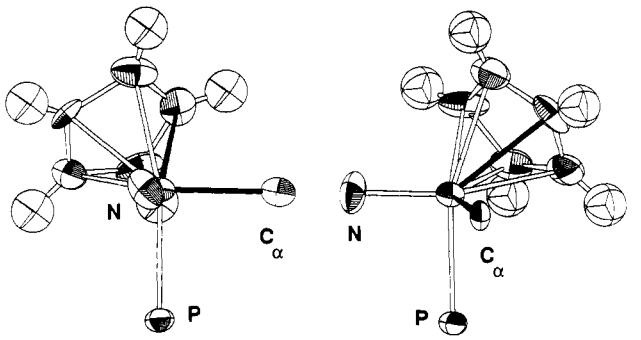


Figure 6. Views of (*Z*)-**10d** emphasizing the steric influence of the cyclopentadienyl ligand in the N–Re–P plane.

that has the H_α proton in a position similar to that in a *ac*-alkylidene complex (compare VI and VIII, Figure 1)—i.e., with θ near 0°. This contrasts with the crystal structure.

Discussion

1. Structure and Bonding about Rhenium. We analyze the structures of vinyl complexes (*E*)-**2d** and (*Z*)-**10d** first, since they have an important bearing upon the above reactions. Both compounds exhibit the ca. 90° P–Re–N, P–Re–C1, and N–Re–C1 bond angles expected for octahedral complexes (Table V). The acute C51–Re–C1 angles (88.0 (2)°, 82.6 (4)°) indicate that one of the cyclopentadienyl carbons extends into the C_α side of the N–Re–P plane. This feature is emphasized in the partial structures

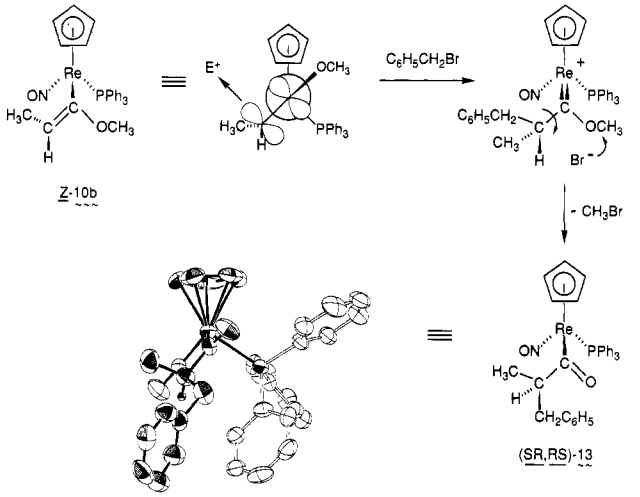


Figure 7. Analysis of the direction of electrophilic attack upon α-methoxyvinyl complex (*Z*)-**10b**.

given in Figure 6. The metal–ligand bond distances in (*E*)-**2d** and (*Z*)-**10d** (Table IV) are identical within experimental error, even though the orientations of the vinyl ligands differ significantly.

As noted above, vinyl complexes **2** are expected to have two important resonance contributors, I and II (eq i). Their C_β nucleophilicity and apparently low thermal barriers to C=C bond isomerization[39] are expected consequences of alkylidene-like resonance contributor II. The α-methoxyvinyl complexes **10** should have a third type of resonance contributor, XII (eq v). Their enhanced C_β nucleophilicity is an expected consequence of this third contributor.

As expected from the above valence-bond analysis, the Re–C_α bonds in (*E*)-**2d** and (*Z*)-**10d** (2.123 (6) and 2.129 (10) Å) are shorter than those in rhenium alkyl complexes (–)-(*R*)-(η^5-C_5H_5)Re(NO)(PPh_3)($CH_2C_6H_5$) (2.203 (8) Å)[19a] and (*SS*,*RR*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH($CH_2C_6H_5$)C_6H_5) (2.215 (4) Å).[13a] This 0.08–0.09-Å difference is likely too large to attribute solely to sp^2/sp^3 hybridization effects.[40] The Re—C_α bonds are distinctly longer than the Re=C_α double bond in benzylidene complex *ac*-[(η^5-C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]$^+PF_6^-$ (1.949 (6) Å).[13a] They are also very slightly longer than the Re–C_α bonds in formyl complex (η^5-C_5H_5)Re(NO)(PPh_3)(CHO) (2.055 (10) Å) and acyl complex (*SR*,*RS*)-**13** (2.081 (7) Å).[20b,35] These complexes have alkylidene-like Re=C_α resonance contributors similar to II but a much closer energy match between the d orbital shown in III and the ligand π* orbitals.[35]

2. Structure, Bonding, and Orientation of the Vinyl Ligands. The vinyl ligand C=C bond lengths in (*E*)-**2d** and (*Z*)-**10d** (1.320 (9), 1.319 (12) Å) are identical within experimental error and quite close to those in ethylene and methyl vinyl ether (1.339, 1.342 Å).[36b,c,40b] Otherwise, the vinyl ligands have very different structures. In this section, we examine the interwoven factors that contribute to the Re–C_α conformations and C=C geometric isomers observed.

A. Re–C_α Conformations: Electronic Effects. Given the alkylidene-like Re=C_α resonance contributors II and XI, it should to a first approximation be electronically optimal for vinyl and

(39) Since we have shown that C=C bond isomerization can be acid-catalyzed, the existence of a purely thermal isomerization is questionable. Reger has observed the *Z*/*E* isomerization of related iron–vinyl complexes (η^5-C_5H_5)Fe(CO)(L')(C(R)=CR'R'') under similar acid-catalyzed conditions, as well as in the presence of redox reagents.[3a,g,h] However, C=C isomerization barriers of only ca. 17 kcal/mol have been found in deprotonated imines Li^+H_2C=CHNR]$^-$ under rigorously acid-free conditions: Lee, J. Y.; Lynch, T. J.; Mao, D. T.; Bergbreiter, D. E.; Newcomb, M. *J. Am. Chem. Soc.* **1981**, *103*, 6215. For other vinyl complexes that undergo *Z* ⇄ *E* isomerization, see ref 7c, d, f, and i.

(40) (a) Compare, for example, H_3C–C bond lengths in ethane (1.534 Å) and propene (1.501 Å). (b) March, J. A. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 19. (c) Churchill, M. R. In *Perspectives in Structural Chemistry*; Dunitz, J. D., Ibers, J. A., Eds.; Wiley: New York, 1967; Vol. 3, pp 153–155.

Table III. Positional Parameters of Non-Hydrogen Atoms ($\times 10^4$) in (*E*)-**2d**·CH_2Cl_2 and (*Z*)-**10d** and Their Estimated Standard Deviations[a]

atom	(*E*)-**2d**·CH_2Cl_2			(*Z*)-**10d**		
	x	*y*	*z*	*x*	*y*	*z*
Re	6379.5 (2)	8695.2 (2)	5789.8 (2)	1257.2 (3)	2672.0 (4)	3186.8 (3)
P	7644 (1)	8873 (1)	6514 (1)	2213 (3)	2123 (3)	1417 (2)
N	5162 (4)	8820 (4)	6171 (2)	1090 (8)	4402 (10)	2986 (8)
O	4273 (4)	8849 (5)	6404 (3)	948 (9)	5603 (10)	2872 (9)
C(51)	6596 (8)	8545 (7)	4887 (3)	856 (10)	1210 (13)	4560 (11)
C(52)	5745 (6)	7705 (9)	5016 (3)	115 (11)	2017 (13)	4562 (11)
C(53)	6213 (7)	6738 (7)	5347 (3)	−308 (9)	1604 (16)	3322 (12)
C(54)	7347 (6)	7007 (7)	5412 (3)	174 (9)	491 (14)	2569 (11)
C(55)	7601 (6)	8131 (8)	5129 (3)	898 (10)	257 (13)	3358 (13)
C(1)	6594 (5)	10722 (6)	5715 (2)	2566 (8)	3445 (10)	4315 (9)
C(2)	7328 (6)	11427 (6)	5452 (3)	2788 (9)	4608 (12)	5302 (10)
C(3)	7349 (6)	12887 (6)	5441 (3)	2190 (10)	5773 (13)	5825 (10)
O(2)				3233 (6)	2431 (8)	3932 (7)
C(4)				4239 (9)	2929 (14)	4378 (12)
C(11)	6819 (5)	6609 (6)	6996 (3)	857 (8)	3007 (12)	23 (9)
C(12)	6753 (6)	5713 (7)	7408 (3)	526 (10)	3372 (13)	−992 (10)
C(13)	7518 (6)	5749 (7)	7823 (3)	1098 (9)	3250 (13)	−2027 (10)
C(14)	8360 (6)	6656 (6)	7838 (3)	1980 (10)	2745 (15)	−2053 (10)
C(15)	8410 (5)	7560 (6)	7434 (2)	2297 (1)	2390 (14)	−1020 (10)
C(16)	7631 (4)	7573 (5)	7010 (2)	1733 (8)	2508 (10)	33 (8)
C(21)	6493 (5)	10748 (6)	7094 (3)	3632 (11)	4674 (14)	2099 (13)
C(22)	6364 (6)	11678 (7)	7483 (3)	4533 (15)	5481 (20)	2122 (18)
C(23)	7281 (6)	12170 (6)	7745 (3)	5331 (16)	4930 (32)	1600 (24)
C(24)	8330 (6)	11733 (6)	7617 (3)	5162 (13)	3427 (35)	974 (19)
C(25)	8466 (4)	10777 (5)	7228 (2)	4236 (10)	2469 (18)	889 (13)
C(26)	7542 (4)	10274 (5)	6967 (2)	3464 (8)	3127 (13)	1480 (10)
C(31)	9724 (4)	7762 (6)	6251 (2)	1738 (10)	−837 (12)	−87 (10)
C(32)	10821 (5)	7788 (7)	6047 (3)	1738 (10)	−2384 (13)	−387 (12)
C(33)	11282 (5)	8931 (8)	5887 (2)	2329 (12)	−2911 (14)	313 (14)
C(34)	10668 (5)	10062 (7)	5914 (2)	2896 (12)	−1961 (16)	1292 (14)
C(35)	9578 (4)	10059 (5)	6110 (2)	2887 (12)	−451 (14)	1600 (12)
C(36)	9103 (4)	8911 (5)	6282 (2)	2323 (8)	141 (11)	900 (9)
C(41)	8304 (6)	13701 (6)	6280 (3)	2716 (13)	8096 (15)	5100 (13)
C(42)	9233 (7)	14127 (7)	6567 (3)	3234 (17)	9462 (21)	5225 (18)
C(43)	10240 (6)	14293 (7)	6309 (4)	3830 (14)	1015.7 (16)	6270 (18)
C(44)	10314 (7)	14036 (8)	5774 (4)	3857 (12)	9498 (16)	7207 (15)
C(45)	9371 (7)	13612 (7)	5498 (3)	3303 (12)	8056 (14)	7056 (13)
C(46)	8348 (6)	13423 (5)	5748 (3)	2740 (8)	7357 (11)	5991 (10)
C(S)	6523 (9)	−930 (12)	8593 (6)			
Cl(SA)	6566 (3)	330 (3)	9056 (1)			
Cl(SB)	5263 (4)	−1500 (4)	8469 (2)			

[a] Positional parameters for hydrogen atoms are in the supplementary material.

α-methoxyvinyl ligands to adopt Re–C_α conformations that maximize rhenium–carbon π bonding. In frontier MO theory terminology,[38] the C=C π^* acceptor lobe on C_α should maximally overlap with the d orbital shown in III.[41] This would occur with $\theta = 0°$ and 180°. X-ray crystal structures of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^{n+}$ complexes show that a variety of unsaturated ligands (L = =COR (see Figure 7),[35] =CHR (see V),[13a] η^2-RCH=X[18,42]) adopt conformations that maximize overlap of their acceptor orbitals with the d orbital shown in III. Any slight deviations are readily ascribable to steric effects. However, we have also noted the possibility of conformation-influencing *repulsive* interactions involving d orbitals when donor orbitals are present on ligating atoms.[43]

The EHMO calculations on model compounds $(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(CH{=}CH_2)$ and $(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(C(OH){=}CH_2)$ (Figure 2) show two Re–C_α conformational minima that are in good agreement with those expected from frontier MO theory.[44] However, vinyl ligands are not as good π acceptors as acyl and alkylidene ligands,[45] and a more thorough analysis of the data indicates additional significant Re–C_α conformation-determining factors. As previously and perceptively noted by Fenske, the vinyl ligand is somewhat unusual in that both acceptor and donor orbitals are present on C_α.[45] Hence, attractive *and* repulsive interactions can play important roles in bonding to metals. Accordingly, we find a close energy match between the π orbital of the $H_2C{=}CH$ fragment and the fourth and fifth occupied orbitals of the $(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)^+$ fragment. In conformations with $\theta = 90°$ and 270°, these are of appropriate symmetry to mix, and a strongly destabilizing interaction results. Less pronounced repulsive interactions, with different θ dependences, are evident in other molecular orbitals. In essence, the Re–C_α frontier MO interaction (Figure 3) and fragment orbital energetics render the repulsive interactions weaker at $\theta = 0°$ and 180° than at $\theta = 90°$ and 270°. Hence, several electronic effects contribute to M–C_α conformations of metal–vinyl complexes, and their relative importance will be a sensitive function of metal and

(41) The α-methoxy substituent has two major effects upon the C=C π^* orbital: (1) The orbital polarizes toward C_α, which increases Re—C_α overlap. (2) The energy is raised, which diminishes the Re—C_α frontier orbital interaction. Also, the α-methoxy substituent will polarize the C=C π orbital toward C_β (which should diminish π repulsive interactions) and raise its energy.[37a,b]

(42) (a) Buhro, W. E.; Georgiou, S.; Fernández, J. M.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1986**, *5*, 956. (b) Buhro, W. E.; Etter, M. C.; Georgiou, S.; Gladysz, J. A.; McCormick, F. B. *Ibid.* **1987**, *6*, 1150.

(43) (a) Buhro, W. E.; Georgiou, S.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 3346. (b) Buhro, W. E.; Zwick, B. D.; Georgiou, S.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.*, in press.

(44) (a) Seeman and Davies have advocated the use of $PPhH_2$ in place of PH_3 as a better EHMO model for the compounds described in this paper.[44b,c] Such a substitution is certainly likely to give more pronounced maxima in Figure 2 and may affect the relative energies and exact locations of the minima. However, our simpler calculations should still reveal key electronic interactions. The desirability of calculations on larger models with full geometry optimization is widely recognized.[44b,c] (b) Seeman, J. I.; Davies, S. G. *J. Am. Chem. Soc.* **1985**, *107*, 6522. (c) Davies, S. G.; Seeman, J. I.; Williams, I. H. *Tetrahedron Lett.* **1986**, *27*, 619.

(45) Kostić, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974.

Table IV. Bond Distances in (*E*)-**2d**·CH_2Cl_2 and (*Z*)-**10d**[a]

		distance, Å	
		(*E*)-**2d**·CH_2Cl_2	(*Z*)-**10d**
Re	P	2.353 (1)	2.358 (3)
Re	N	1.749 (5)	1.750 (11)
N	O	1.215 (7)	1.216 (15)
Re	C(1)	2.123 (6)	2.129 (10)
C(1)	C(2)	1.320 (9)	1.319 (12)
C(2)	C(3)	1.513 (9)	1.474 (18)
C(3)	C(46)	1.514 (9)	1.511 (15)
O(2)	C(4)		1.443 (14)
C(1)	O(2)		1.419 (14)
Re	C(51)	2.285 (7)	2.328 (14)
Re	C(52)	2.313 (8)	2.319 (14)
Re	C(53)	2.318 (8)	2.251 (12)
Re	C(54)	2.303 (8)	2.261 (11)
Re	C(55)	2.292 (7)	2.291 (13)
P	C(16)	1.834 (5)	1.843 (11)
P	C(26)	1.847 (5)	1.818 (11)
P	C(36)	1.838 (5)	1.820 (11)
C(51)	C(52)	1.377 (12)	1.378 (21)
C(52)	C(53)	1.410 (11)	1.440 (18)
C(53)	C(54)	1.386 (11)	1.410 (18)
C(54)	C(55)	1.398 (11)	1.432 (20)
C(55)	C(51)	1.404 (12)	1.404 (17)
C(11)	C(12)	1.391 (10)	1.380 (18)
C(12)	C(13)	1.375 (10)	1.387 (17)
C(13)	C(14)	1.375 (10)	1.384 (20)
C(14)	C(15)	1.381 (9)	1.386 (19)
C(15)	C(16)	1.402 (8)	1.397 (15)
C(16)	C(11)	1.390 (8)	1.378 (17)
C(21)	C(22)	1.380 (10)	1.342 (24)
C(22)	C(23)	1.366 (10)	1.360 (32)
C(23)	C(24)	1.369 (10)	1.371 (39)
C(24)	C(25)	1.400 (9)	1.424 (24)
C(25)	C(26)	1.376 (7)	1.397 (19)
C(26)	C(21)	1.382 (8)	1.405 (16)
C(31)	C(32)	1.408 (8)	1.396 (17)
C(32)	C(33)	1.367 (10)	1.379 (23)
C(33)	C(34)	1.382 (10)	1.365 (19)
C(34)	C(35)	1.393 (8)	1.396 (20)
C(35)	C(36)	1.387 (7)	1.373 (20)
C(36)	C(31)	1.404 (8)	1.392 (14)
C(41)	C(42)	1.383 (10)	1.328 (24)
C(42)	C(43)	1.379 (11)	1.379 (27)
C(43)	C(44)	1.372 (12)	1.359 (28)
C(44)	C(45)	1.383 (10)	1.402 (19)
C(45)	C(46)	1.389 (11)	1.373 (17)
C(46)	C(41)	1.367 (10)	1.365 (21)
Cl(SA)	C(S)	1.746 (14)	
Cl(SB)	C(S)	1.639 (12)	

[a] See Figure 3 for atomic numbering; C(S) is the solvate carbon. Distances of bonds to hydrogen atoms are given in the supplementary material.

vinyl ligand fragment orbital energies.[45]

B. Re–C_α Conformations: Steric Effects. The conformations of many molecules arise from combinations of steric and electronic effects that are difficult to partition. As noted above, we have principally employed frontier MO interactions, as opposed to steric effects of the PPh_3 ligand, to rationalize the Re–C_α–X_β planes of unsaturated ligands (L) in $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^{n+}$ complexes. This approach contrasts with a model that has been presented for related iron complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(L)]^{n+}$,[44b,c] but which has been mainly applied when L is a saturated alkyl ligand.[46] In view of the diminished π acidity

(46) As would be intuitively expected, the HOMO of the $(\eta^5\text{-}C_5H_5)Fe(CO)(PH_3)^+$ fragment calculates to be lower in energy (0.034 eV) than that of the $(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)^+$ fragment. Thus, M–C_α frontier MO interactions in $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(L)]^{n+}$ complexes should be diminished. This is evidenced by the lower Fe=C_α rotational barriers for alkylidene ligands in $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(=CHR)]^+$ complexes (ca. 8 kcal/mol, compared to 15–21 kcal/mol in analogous rhenium complexes[13a,b,15]): Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411 (ref 49). Studabaker, W. B. Ph.D. Thesis, University of North Carolina, Chapel Hill, 1986; p 97. Hence, PPh_3 ligand bulk should be a more important M–C_α conformation-determining factor in iron complexes of unsaturated ligands.

Table V. Bond Angles in (*E*)-**2d**·CH_2Cl_2 and (*Z*)-**10d**[a]

			angles, deg	
			(*E*)-**2d**·CH_2Cl_2	(*Z*)-**10d**
P	Re	N	95.8 (2)	93.3 (3)
P	Re	C(1)	85.1 (2)	89.2 (3)
N	Re	C(1)	94.4 (2)	98.3 (4)
Re	C(1)	C(2)	132.2 (5)	130.0 (9)
Re	C(1)	H(1)	120.5 (39)	
Re	C(1)	O(2)		110.4 (5)
C(1)	O(2)	C(4)		118.4 (8)
C(2)	C(1)	O(2)		119.4 (10)
C(1)	C(2)	C(3)	124.9 (6)	126.8 (12)
C(1)	C(2)	H(2)	124.2 (32)	116.6 (13)
C(2)	C(1)	H(1)	107.1 (39)	
C(2)	C(3)	C(46)	111.7 (5)	113.1 (11)
C(3)	C(2)	H(2)	110.5 (32)	116.6 (11)
Re	N	O	174.8 (5)	177.9 (10)
C(1)	Re	C(51)	88.0 (2)	82.6 (4)
C(1)	Re	C(52)	113.8 (3)	102.5 (4)
C(1)	Re	C(53)	146.3 (2)	138.9 (4)
C(1)	Re	C(54)	130.8 (2)	136.0 (5)
C(1)	Re	C(55)	96.3 (3)	99.3 (4)
P	Re	C(51)	133.7 (3)	127.0 (3)
P	Re	C(52)	151.9 (2)	153.3 (3)
P	Re	C(53)	119.2 (2)	125.6 (3)
P	Re	C(54)	93.3 (2)	94.5 (3)
P	Re	C(55)	99.9 (2)	96.3 (3)
N	Re	C(51)	130.4 (3)	139.7 (4)
N	Re	C(52)	103.0 (2)	108.3 (5)
N	Re	C(53)	105.0 (3)	100.3 (5)
N	Re	C(54)	134.6 (2)	125.2 (5)
N	Re	C(55)	161.7 (2)	160.0 (5)
C(52)	C(51)	C(55)	109.4 (7)	108.2 (12)
C(51)	C(52)	C(53)	107.4 (7)	108.4 (11)
C(52)	C(53)	C(54)	107.8 (7)	108.1 (12)
C(53)	C(54)	C(55)	108.9 (7)	106.0 (10)
C(51)	C(55)	C(54)	106.6 (7)	109.3 (12)
Re	P	C(16)	117.1 (2)	114.9 (4)
Re	P	C(26)	119.4 (2)	119.2 (3)
Re	P	C(36)	111.0 (2)	112.4 (4)
P	C(16)	C(15)	120.7 (4)	119.5 (9)
P	C(16)	C(11)	121.4 (4)	122.2 (8)
P	C(26)	C(21)	119.1 (4)	116.9 (10)
P	C(26)	C(25)	122.1 (4)	123.8 (9)
P	C(36)	C(31)	120.0 (4)	120.3 (10)
P	C(36)	C(35)	120.4 (4)	118.9 (7)
C(16)	P	C(26)	99.1 (2)	99.9 (5)
C(16)	P	C(36)	104.1 (2)	104.2 (4)
C(26)	P	C(36)	104.2 (2)	104.4 (5)
C(11)	C(12)	C(13)	120.0 (6)	118.9 (12)
C(12)	C(13)	C(14)	121.1 (6)	120.7 (12)
C(12)	C(11)	C(16)	120.3 (6)	122.0 (10)
C(11)	C(16)	C(15)	117.9 (5)	118.1 (11)
C(13)	C(14)	C(15)	118.7 (6)	119.2 (11)
C(14)	C(15)	C(16)	121.9 (5)	121.0 (13)
C(21)	C(22)	C(23)	120.3 (6)	125.6 (18)
C(21)	C(26)	C(25)	118.5 (5)	119.2 (11)
C(22)	C(23)	C(24)	119.4 (6)	115.2 (19)
C(22)	C(21)	C(26)	121.2 (5)	119.2 (14)
C(23)	C(24)	C(25)	120.6 (6)	123.8 (19)
C(24)	C(25)	C(26)	120.0 (5)	116.9 (15)
C(31)	C(32)	C(33)	120.0 (6)	118.6 (11)
C(31)	C(36)	C(35)	119.5 (5)	120.1 (11)
C(32)	C(31)	C(36)	119.7 (5)	120.2 (12)
C(32)	C(33)	C(34)	120.3 (5)	121.6 (13)
C(33)	C(34)	C(35)	120.8 (6)	119.8 (16)
C(34)	C(35)	C(36)	119.7 (5)	119.7 (12)
C(3)	C(46)	C(41)	122.3 (6)	122.0 (10)
C(3)	C(46)	C(45)	120.8 (6)	118.8 (12)
C(41)	C(42)	C(43)	119.4 (7)	119.7 (20)
C(41)	C(46)	C(45)	116.9 (6)	119.2 (11)
C(42)	C(41)	C(46)	122.4 (7)	121.8 (15)
C(42)	C(43)	C(44)	119.9 (7)	121.0 (15)
C(43)	C(44)	C(45)	119.3 (7)	118.3 (14)
C(44)	C(45)	C(46)	122.1 (7)	119.9 (14)
Cl(SA)	C(S)	Cl(SB)	114.5 (7)	

[a] See Figure 3 for atomic numbering; C(S) is the solvate carbon. Additional bond angles involving hydrogen atoms are in the supplementary material.

of vinyl ligands,[45] it is likely appropriate to view the PPh_3 ligand bulk as a significant Re–C_α conformation-determining factor for the complexes reported in this paper. This would reinforce the electronic preference for Re–C_α conformations with θ near 0° and 180°.

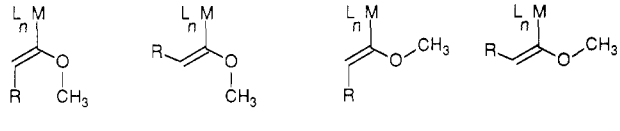
Additional steric effects upon Re–C_α conformations are possible. First, it would not be surprising if conformational minima deviated slightly from θ = 0° to lessen interaction between the NO ligand and the C_β substituent cis to rhenium (see VI, Figure 1). This is suggested by both EHMO calculations in Figure 2. Also, PPh_3 ligand bulk should favor Re–C_α rotation to positive θ. Second, both calculations show a slight energy maximum near θ = 145°, which is approximately coincident with rotation of C_β of the vinyl ligand over the cyclopentadienyl ligand (θ = 135°).

The EHMO calculations do not clearly predict whether Re–C_α conformations with θ near 0° or 180° should be preferred. However, since the NO ligand is smaller than the PPh_3 and cyclopentadienyl ligands, we have been biased that conformations with θ near 0° should be favored. This places the larger C_α substituent (=CHR) syn to the NO ligand. Furthermore, alkylidene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHR)]^+$ favor Re=C_α conformations with θ near 0° (see IV and V) by 1.4–>2.7 kcal/mol.[13] However, note that if the Re–PPh_3 rotamers are averaged, the PPh_3 ligand bulk should equally destabilize conformations with θ = 0° and 180°, leaving the relative sizes of the cyclopentadienyl and NO ligands as the remaining steric conformation-determining factor. Figure 6 emphasizes the substantial steric influence of the cyclopentadienyl ligand in the N–Re–P plane.[47]

Accordingly, the crystal structure of (*Z*)-**10d** exhibits a Re–C_α conformation with θ = 47° (Figure 4),[48] close to the broad minimum at θ = 30° found in the corresponding EHMO calculation (Figure 2B). Surprisingly, the crystal structure of (*E*)-**2d** shows a Re–C_α conformation with θ = 175.5°, contrary to expectations (Figure 5). However, the difference ^1H NOE data suggest that the Re–C_α conformation with θ near 0° is more stable in solution. Further, as analyzed below, the conformation with θ near 0° is more reactive toward protonation.[47]

C. C=C Geometric Isomerism. Any C_β alkyl substituent cis to rhenium will sterically interact with some rhenium ligand in nearly all Re–C_α conformations. Hence, *E* (trans) C=C isomers should be favored for monosubstituted vinyl complexes **2b–d**, regardless of θ.

The α-methoxyvinyl complexes **10b**, **10d**, and **10e** can in principle exist as four C=C/C_α—OCH_3 isomers: XV ("U"-shaped), XVI, XVII ("sickle"-shaped), and XVIII ("W"-shaped).



XV XVI XVII XVIII

The (*Z*)-**10** C=C isomers predominate in solution, and s-cis C_α—OCH_3 isomers are commonly favored in methyl vinyl ethers.[36] Note that in W *Z*/s-trans isomer XVIII, both the C_α methoxy and C_β alkyl substituents will have unfavorable steric interactions with rhenium ligands. Hence, we conclude that sickle *Z*/s-cis isomer XVI, which is found in the crystal structure of (*Z*)-**10d**, is the most stable in solution.

The question arises as to how the lower stability of (*E*)-**10b**, (*E*)-**10d**, and (*E*)-**10e** can be accounted for. The U *E*/s-cis isomer XV has an unfavorable steric interaction between the cis C_α methoxy and C_β alkyl substituents. This interaction is diminished in sickle *E*/s-trans isomer XVII but at the expense of the s-cis C_α–OCH_3 conformation. Note that sickle isomers XVI and XVII are comparable sterically but should prefer θ that differ by ca. 180°. Apparently, of all of these possibilities, it is thermodynamically optimum to place the C_β alkyl substituent cis to rhenium as in XVI. Concurrently, θ opens to 40–50° to minimize interaction of the C_β alkyl substituent with the NO ligand.[49]

The initial formation of appreciable amounts of (*E*)-**10b**, (*E*)-**10d**, and (*E*)-**10e** upon deprotonation of α-methoxycarbene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=C(OCH_3)CH_2R)]^+PF_6^-$ (**9**-PF_6^-) can be rationalized. Compounds **9**-PF_6^-, like other methoxycarbene complexes, exist as mixtures of C_α–OCH_3 isomers.[25] Since they have no conformation-enforcing C_α=C_β double bond, steric interactions between the C_α methoxy and C_β alkyl substituents should be less than in (*E*)-**10b**, (*E*)-**10d**, and (*E*)-**10e**. Hence, transition states for the formation of (*E*)-**10** and (*Z*)-**10** should not differ in energy as much as (*E*)-**10** and (*Z*)-**10**. Finally, we note that in the enolate anion corresponding to complex **10d**, which lacks an *O*-methyl group, the *E* C=C isomer is favored.[17,50]

D. Structures of Related Complexes. Several previous structural studies are particularly relevant to the above discussion. First, Reger has reported the X-ray crystal structures of three iron–vinyl complexes of the formula $(\eta^5\text{-}C_5H_5)Fe(CO)(L')(C(R)=CR'R'')$ (L' = PPh_3, $P(OPh)_3$).[3c-e] He has analyzed their Fe–C_α conformations[3e] and finds OC–Fe–C_α–C_β torsion angles near θ = 45° and 225°. These complexes differ from ours in several ways. First, the M–C_α frontier MO interactions should be diminished.[46] Second, the nature of the π repulsive interactions will be altered. Third, all compounds studies contained either trisubstituted or tetrasubstituted C=C double bonds, so additional steric M–C_α conformation-determining factors are present.

Davies has reported that deprotonation of iron α-methoxycarbene complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(=C(OCH_3)\text{-}CH_2R)]^+$ gives vinyl complexes $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(C\text{-}(OCH_3)=CHR)$ that are exclusively *Z* C=C isomers.[5a] The vinyl complex with R = CH_3 was structurally characterized and adopts M–C_α and C_α–OCH_3 conformations very similar to those of (*Z*)-**10d**. Bruce has similarly prepared ruthenium α-alkoxyvinyl complexes $(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)(C(OR)=CHR)$[6] and finds the compound analogous to **10e** to exist as a 1:1 mixture of *Z*/*E* C=C isomers, similar to our observation. However, the corresponding α-isopropoxyvinyl complex $(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)\text{-}(C(OCH(CH_3)_2)=CHC_6H_5)$ is one C=C isomer in solution. Its crystal structure shows *E* C=C and s-trans C_α-oxygen isomers, similar to XVII. Hence, conformational generalizations about one class of vinyl complexes must be extrapolated to other classes with caution.

3. Mechanism of 1,3-Asymmetric Induction. The preceding conformational analysis leads to the following key generalizations: (1) The vinyl complexes reported in this paper preferentially adopt Re–C_α conformations with θ near 0° and 180°; this is due to a complex mixture of electronic and steric factors. (2) Interaction of the C_β substituent cis to rhenium with the NO ligand can distort θ in the former conformer up to ca. 45°. This conformational model will undoubtedly be more fully developed and refined as additional structural, dynamic, and theoretical data become available. However, the present stage of sophistication suffices for an analysis of 1,3-asymmetric induction in the alkylation reactions described above. Deviations as much as 60° from θ =

(47) The question of which Re–C_α conformation of (*E*)-**2d** (θ near 0° or 180°) is more stable can be approached by analyzing whether there should be a greater energy difference between vinyl complex Re–C_α conformers VI and VII (Figure 1) or alkylidene complex Re=C_α conformers VIII and IX (where ΔG are known and favor VIII).[13] Considerations: (1) There is a R/NO interaction in VI that is not present in VIII; however, this interaction is diminished by the longer Re–C_α bond in VI and any deviation from θ = 0°. (2) While IX has three C_β substituents that can interact with the $\eta^5\text{-}C_5H_5$ and PPh_3 ligands, VII has two; C_β should be about the same distance from the rhenium in each.

(48) Twist angles of 44° still allow appreciable C=C π overlap in strained alkenes such as *trans*-cyclooctene: Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312. Hence, significant Re–C_α frontier orbital overlap should be maintained in (*Z*)-**10d**.

(49) For a related analysis of the stabilities of silyl ketene acetal C=C and C=O isomers, see: Wilcox, C. S.; Babston, R. E. *J. Org. Chem.* **1984**, *49*, 1451.

(50) This assumes that (a) the slow deprotonation conditions (hours, 0 °C)[17] give the thermodynamically favored enolate C=C isomer and (b) the stereochemistry of enolate alkylation is analogous to that of (*Z*)-**10b**, (*Z*)-**10d**, and (*Z*)-**10e**.

0° and 180° do not affect the mechanism presented below. Furthermore, since the product alkylidene complexes show strong conformational preferences for θ = 0° and 180°,[13] the model improves as the reaction coordinate progresses.

The alkylation reactions shown in eq viii (right) and ix are easiest to analyze. The former connects a reactant ((*Z*)-**10b**) that is a lower homologue of structurally characterized (*Z*)-**10d** with an acyl complex product ((*SR,RS*)-**13**) whose stereochemistry has been determined by an X-ray crystal structure.[20b,35] The latter connects a structurally characterized reactant ((*Z*)-**10d**) with an acyl complex product ((*SS,RR*)-**13**) whose stereochemistry has been established by a crystal structure of its diastereomer. The former is shown in expanded form in Figure 7.

We consider four limiting transitions states for these reactions, two of which are shown in Figure 1. First, a Re–C_α conformer with θ near 0° (VI) could undergo electrophilic attack upon the C_β face anti to the bulky PPh_3 ligand to give alkylidene product VIII. This is consistent with the observed stereochemistry, as shown in Figure 7. Second, a Re–C_α conformer with θ near 180° (VII) could be attacked upon the C_β face anti to the PPh_3 ligand to give alkylidene product IX. This gives the opposite configuration at carbon and is inconsistent with the predominant stereochemistry. From Figures 1 and 6, it seems likely that the cyclopentadienyl ligand sterically hinders this mode of electrophilic attack. Finally, there are two corresponding transition states in which the electrophile attacks the C_β face syn to the bulky PPh_3 ligand. However, in numerous reactions involving C_α[13] and C_β[14,17] attack upon unsaturated ligands (L) in $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^{n+}$ complexes, we have never noted significant amounts of products that could arise via reactant approach syn to the PPh_3 ligand.

The low-temperature reactions of **2a–d** and CF_3SO_3H provide further evidence that Re–C_α conformer VI is more reactive than conformer VII. Note that electrophilic attack upon the former gives, regardless of direction, an *ac* (*t*) Re=C_α isomer (Figure 1),[22] whereas attack upon the latter gives an *sc* (*k*) Re=C_α isomer. A control experiment above shows that the slow thermal interconversion of these Re=C_α isomers is not accelerated by CF_3SO_3H. Protonation of the smallest vinyl ligand, that in ethenyl complex **2a**, gives a (71 ± 2):(29 ± 2) ratio to *ac*/*sc* ethylidene isomers. A similar kinetic ratio is observed in the reaction of **2a** with $Ph_3C^+PF_6^-$ to give **7**-PF_6^- (eq iv). Protonation of the C_β-substituted vinyl complexes (*E*)-**2b–d** gives ca. 90:10 ratios of *ac*/*sc* alkylidene products. Thus, we conclude that Re–C_α conformers with θ near 0° (VI) are more reactive than conformers with θ near 180° (VII) and that the difference is greater for C_β-substituted vinyl complexes. Hence, the only other transition state consistent with the stereochemistry of eq viii—attack upon VII from the C_β face syn to PPh_3—is rejected as unlikely by two criteria.

We assume an identical stereochemistry of electrophilic attack upon all of the vinyl complexes and make product diastereomer assignments accordingly. Thus, deuteriation of propenyl complex (*E*)-**2b** with CF_3SO_3D must yield predominantly the propylidene complex diastereomer (*SR,RS*)-*ac*-**1b**-*β*-*d*-$CF_3SO_3^-$, and deuteriomethylation of (*E*)-**2b** with CD_3SO_3F must yield predominantly the isobutylidene complex diastereomer (*SS,RR*)-*ac*-**3**-FSO_3^--*γ*-d_3 (Scheme I). The minor diastereomers formed in the above reactions can arise from electrophilic attack upon the C_β face anti to the PPh_3 in VII (Figure 1) or from small amounts of the opposite C=C geometric isomers.

4. Conclusion. From the preceding mechanistic analysis, we generalize the key factors responsible for efficient asymmetric induction in reactions of rhenium complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^{n+}$, where L is an η^1 unsaturated ligand, as follows: (1) The ligand L adopts a Re–C_α conformation that maximizes or has a high degree of frontier orbital overlap and minimizes any Re–C_α π repulsive interactions. (2) With weaker π accepting ligands such as vinyl, the influence of PPh_3 ligand bulk upon the Re–C_α conformation increases, but any effect reinforces 1. (3) The attacking reagent approaches the ligand face opposite to the bulky PPh_3 ligand. (4) For the specific case of C_β electrophilic attack upon vinyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CX{=}CHR)$ (X = H, OCH_3), conformations with θ near 0° are more reactive than those with θ near 180°.

We have previously shown that factors 1 and 3 account for the high 1,2-asymmetric induction observed in C_α nucleophilic attack upon alkylidene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHR)]^+$ (see IV and V).[13] We have also used 3 to explain the high 1,3-asymmetric induction found for C_β electrophilic attack upon acetylide complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C{\equiv}CR)$.[14] Factors 1–4 also account for the 1,3-asymmetric induction observed in C_β electrophilic attack upon enolates derived from the deprotonation of acyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COR)$.[17] However, there are reactions of other types of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^{n+}$ complexes in which the mechanisms of 1,*n*-asymmetric induction are different[18] or remain unexplained.[16] The latter provide challenges for future conformational and transition-state analyses.

In an elegant series of papers, Davies and Liebeskind have reported related examples of 1,3-asymmetric induction in reactions of iron complexes $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(L)$.[5,34] Although we caution that the energies of key metal fragment orbitals will differ in these complexes,[46] the above analysis can be adapted to account for many of their stereochemical results. Indeed, Davies and Liebeskind have reported similar interpretations but with greater emphasis upon steric M–C_α conformation-determining effects.[5,34,44b,c,51]

This study further demonstrates the versatility and effectiveness of the $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$ moiety as a stereogenic transmitter. It should now be possible, by adding nucleophiles to the alkylidene complexes that are initial products of C_β electrophilic attack upon vinyl complexes, to construct contiguous chiral centers α and β to the rhenium. Furthermore, the $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$ moiety can be readily detached from most ligands—often with retention of configuration at rhenium.[13e,18] Hence, as recycle capabilities are developed and refined, we expect the $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$ moiety to become a useful chiral auxiliary for organic synthesis. Finally, this study has shown the $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$ moiety to be both a useful and a sterically and electronically unique C=C double-bond donor substituent.

Experimental Section

General Procedures. All reactions were carried out under a dry N_2 atmosphere. All chromatography was conducted in air unless noted. IR spectra were recorded on Perkin-Elmer Model 521 and 1500 (FT) spectrometers. NMR spectra were recorded on Bruker WP-200 and Varian SC-300, XL-300 (^1H, ^{13}C), and FT-80A (^{31}P) spectrometers as outlined in Table I. Mass spectra were obtained on AEI-MS9 and VG Micromass 7070E spectrometers. Microanalyses were conducted by Galbraith and Schwarzkopf Laboratories. Melting points were determined in evacuated capillaries and were not corrected.

Solvents were purified as follows: acetone and ethyl acetate, distilled from CaH_2; benzene, ether, and THF, distilled from Na/benzophenone; hexanes and pentane, distilled from Na; CH_2Cl_2, $CHCl_3$, CD_2Cl_2, and $CDCl_3$, distilled from P_2O_5; C_6D_6, CD_3CN, and acetone-d_6, distilled from CaH_2.

Starting materials were purified as follows: $Ph_3C^+PF_6^-$ (Aldrich or Columbia), precipitated from CH_2Cl_2/ethyl acetate; CF_3SO_3H (Aldrich), distilled under vacuum; $HBF_4{\cdot}Et_2O$ (Aldrich), used as received; $(CF_3SO_2)_2O$ (Alfa), refluxed over and distilled from P_2O_5; CF_3SO_3D, prepared by mixing the anhydride with 1.0 equiv of D_2O in an ampule (4–5 days, until homogeneous), followed by distillation;[52] $C_6H_5CH_2Br$ (Aldrich), washed with concentrated H_2SO_4, H_2O, and $NaHCO_3$ (saturated), dried over anhydrous Na_2CO_3, vacuum distilled [30–32 °C (0.06 mm)], and stored over Cu turnings (dark, −20°C); CH_3I (Aldrich) and CD_3I (KOR), distilled from P_2O_5 and stored over Cu ribbon at −20 °C; CH_3OSO_2F (Aldrich) and CD_3OSO_2F (Aldrich), refluxed over and distilled from CaH_2; $(CH_3)_3O^+BF_4^-$ (Alfa) and $(CH_3)_3O^+PF_6^-$ (Aldrich), washed with CH_2Cl_2; $Ph_3PCH_3^+I^-$ (Aldrich), used as received; DBU (Aldrich),[23c] vacuum distilled from LAH [62–64 °C (0.06 mm)]; NaH and KH (Alfa, Aldrich; both oil dispersions), washed with hexanes and

(51) Davies, S. G.; Seeman, J. I. *Tetrahedron Lett.* **1984**, *25*, 1845.

(52) Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753. Pasto, D. J.; Gadberry, J. F. *Ibid.* **1978**, *100*, 1469.

dried in vacuo; $N(C_2H_5)_3$ (Fischer), used as received.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH_2CH_2C_6H_5)]^+PF_6^-$ (1d-PF_6^-). A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_2CH_2C_6H_5)$ (0.400 g, 0.604 mmol),[25] CH_2Cl_2 (40 mL), and a stir bar. The solution was cooled to −78 °C, and $Ph_3C^+PF_6^-$ (0.258 g, 0.664 mmol, 1.1 equiv) was added with stirring. After 0.5 h, the reaction was warmed to room temperature and stirred for an additional 2 h. Then hexanes (20 mL) were added, and solvent was removed via oil pump vacuum. The resulting yellow powder was triturated with hexanes, washed with cold acetone, and dried in vacuo to give 0.438 g (0.543 mmol, 90%) of 1d-PF_6^-, mp 148–150 °C dec. IR (cm^{-1}, KBr): $\nu_{N\equiv O}$ 1706 s. ^1H NMR (δ, CD_3CN): 15.59 (ddd, $J_{H_\alpha H_\beta}$ = 8 Hz, $J_{H_\alpha H_{\beta'}}$ = 8 Hz, $J_{H_\alpha P}$ = 4 Hz, Re=CH_α), 7.90–7.40 (m, 4 C_6H_5), 5.93 (s, C_5H_5), 3.72–3.51 (m, $CH_2C_6H_5$), 2.69 (m, =$CHCH_2$). ^{13}C NMR (ppm, CD_3CN): 312.7 (d, J_{CP} = 6 Hz, C_α), PPh_3 at 133.7 (d, J_{CP} = 10 Hz), 133.0 (s, p), 130.1 (d, J_{CP} = 11 Hz); CC_6H_5 at 149.0 (s, ipso), 127.2 (s), 127.1 (s), 125.1 (s, p); 100.1 (s, C_5H_5), 58.4 (s, C_β), 34.6 (s, C_γ). $^{31}P\{^1H\}$ NMR (ppm, C_6H_5Cl): 17.5 (s). Anal. Calcd for $C_{32}H_{30}F_6NOP_2Re$: C, 47.63; H, 3.72. Found: C, 47.98; H, 3.85.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH=CH_2)$ (2a). A Schlenk flask was charged with $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH_3)]^+PF_6^-$ (1a-PF_6^-; 0.150 g, 0.209 mmol),[13b] CH_2Cl_2 (15 mL), and a stir bar. The solution was cooled to −15 °C (ethylene glycol/CO_2), and DBU (0.063 mL, 0.418 mmol, 2.0 equiv)[23c] was added with stirring. After 0.5 h, the resulting orange solution was warmed to room temperature and stirred for an additional 1 h. Solvent was removed under oil pump vacuum, and the residue was extracted with benzene. The extract was filtered, and an equal volume of hexanes was added. Solvents were removed by rotary evaporation, and the resulting orange oil was dissolved in benzene. This was passed through a plug of silica gel that had been previously treated with $N(C_2H_5)_3$ with 50:50:10 (v/v/v) ethyl acetate/hexanes/$N(C_2H_5)_3$ as eluent. The orange band was collected, and solvents were removed under oil pump vacuum to give an orange bubble-up solid. The solid was dissolved in ether, and hexanes were added. Solvents were removed under oil pump vacuum to give 2a as an orange powder (0.093 g, 0.163 mmol, 78%), mp 163–165 °C dec. IR (cm^{-1}, $CHCl_3$): $\nu_{N\equiv O}$ 1641 s. MS (16 eV, m/e, ^{187}Re): 571 (M^+, 100%), 467 ($M^+ - C_2H_3 - C_6H_5$, 32%), 262 (Ph_3P^+, 7%). Anal. Calcd for $C_{25}H_{23}NOPRe$: C, 52.62; H, 4.07. Found: C, 52.46; H, 4.18.

Preparation of (E)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH=CHCH_3)$ ((E)-2b). A Schlenk flask was charged with $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH_2CH_3)]^+PF_6^-$ (1b-PF_6^-; 0.300 g, 0.411 mmol),[13b] CH_2Cl_2 (30 mL), and a stir bar. Then DBU (0.115 mL, 0.770 mmol, 1.5 equiv) was added with stirring. After 1 h, the reaction was worked up as described for the preparation of 2a. The orange bubble-up solid was dissolved in CH_2Cl_2, layered with three volumes of hexanes, and kept at −20 °C for 4 days. Red crystals formed, which were collected by filtration and dried in vacuo. A second crop was similarly obtained from the filtrate for a total of 0.190 g (0.325 mmol, 79%) of (E)-2b, mp 184–186 °C dec. IR (cm^{-1}, $CHCl_3$): $\nu_{N\equiv O}$ 1641 s. MS (16 eV, m/e, ^{187}Re): 585 (M^+, 100%), 544 ($M^+ - C_3H_5$, 7%), 467 ($M^+ - C_3H_5 - C_6H_5$, 17%), 323 ($M^+ - PPh_3$, 5%), 262 (Ph_3P^+, 39%). Anal. Calcd for $C_{26}H_{25}NOPRe$: C, 53.46; H, 4.28. Found: C, 53.86; H, 4.44.

Preparation of (E)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH=CHCH_2CH_2CH_3)$ ((E)-2c). Complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH_2CH_2CH_2CH_3)]^+PF_6^-$ (1c-PF_6^-; 0.250 g, 0.330 mmol)[13b] and DBU (0.074 mL, 0.495 mmol, 1.5 equiv) were reacted in CH_2Cl_2 (25 mL), analogous to the procedure used to prepare (E)-2b. An identical workup gave red crystals of (E)-2c (0.172 g, 0.280 mmol, 85%), mp 163–164 °C dec. IR (cm^{-1}, $CHCl_3$): 1641 s. MS (16 eV, m/e, ^{187}Re): 613 (M^+, 100%), 584 ($M^+ - C_2H_5$, 23%), 467 ($M^+ - C_5H_9 - C_6H_5$, 12%), 262 (Ph_3P^+, 26%). Anal. Calcd for $C_{28}H_{29}NOPRe$: C, 54.88, H, 4.77. Found: C, 54.80; H, 4.77.

Preparation of (E)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH=CHCH_2C_6H_5)\cdot CH_2Cl_2$ ((E)-2d·CH_2Cl_2). Complex 1d-PF_6^- (0.300 g, 0.372 mmol) and DBU (0.083 mL, 0.558 mmol, 1.5 equiv) were reacted in CH_2Cl_2 (30 mL), analogous to the procedure used to prepare (E)-2b. An identical workup gave a corresponding orange bubble-up solid, which was dissolved in CH_2Cl_2. Addition of hexanes precipitated an orange powder, which was collected by filtration, washed with cold ether, and dried in vacuo to give 0.226 g (0.342 mmol, 92%) of a (92 ± 2):(8 ± 2) (E)-2d/(Z)-2d mixture, mp 172–175 °C dec. Anal. Calcd for $C_{32}H_{29}NOPRe$: C, 58.16; H, 4.39. Found: C, 58.25; H, 4.44. MS (17 eV, m/e, ^{187}Re): 661 (M^+, 45%), 544 ($M^+ - C_9H_9$, 17%), 399 ($M^+ - PPh_3$, 9%), 262 (Ph_3P^+, 100%). A sample (0.063 g, 0.094 mmol) was dissolved in CH_2Cl_2 (1 mL), layered with hexanes (7 mL), and kept at −20 °C for 3 days. Orange prisms formed, which were collected by filtration, washed with cold ether (2 × 5 mL), and dried in vacuo to give (E)-2d·CH_2Cl_2 (0.065 g, 0.087 mmol, 93%; 86% from 1d-PF_6^-), mp 191–194 °C dec. IR (cm^{-1}, KBr): $\nu_{N\equiv O}$ 1644 s. Anal. Calcd for $C_{33}H_{31}Cl_2NOPRe$: C, 53.15; H, 4.20; Cl, 9.51. Found: C, 53.02; H, 4.32; Cl, 9.42. The presence of the solvate was confirmed by ^1H NMR in $CDCl_3$.

Reactions of Vinyl Complexes 2a–d with Acids. The following procedures are representative.

A. ^1H NMR Monitored Experiments. A 5-mm NMR tube was charged with ethenyl complex 2a (0.0047 g, 0.008 mmol) and $CD_2Cl_2/(CH_3)_4Si$ (0.300 mL) and was capped with a septum and frozen in liquid N_2. Then CF_3SO_3H (0.0008 mL, 0.009 mmol, 1.1 equiv) was added. The tube was thawed, shaken once, and transferred to a −78 °C NMR probe. A ^1H NMR spectrum was recorded immediately. Ethylidene complexes ac-1a-$CF_3SO_3^-$ and sc-1a-$CF_3SO_3^-$ were the only products. Integrations of the Re=CH_α resonances indicated a (71 ± 2):(29 ± 2) ratio of isomers.

B. Isolation of 1b-$CF_3SO_3^-$ from the Reaction of 2b with CF_3SO_3H. A Schlenk flask was charged with 2b (0.100 g, 0.171 mmol) and CH_2Cl_2 (10 mL). Then CF_3SO_3H (0.018 mL, 0.20 mmol) was added with stirring. The volatiles were removed under oil pump vacuum, and the residual oil was triturated with ether and then hexane. The oil was dissolved in CH_2Cl_2 (5 mL), and ether (40 mL) and hexanes (40 mL) were then added. The solvents were slowly removed under oil pump vacuum. The resulting powder was dried overnight under oil pump vacuum to give 1b-$CF_3SO_3^-$ (0.115 g, 0.157 mmol, 91%) that was pure by ^1H NMR (δ, $CDCl_3$, 200 MHz): 15.8 (t, J_{HH} = 8 Hz, H_α), 7.8–7.3 (m, phenyl), 6.0 (s, C_5H_5), 3.4–2.9 (m, H_β), 2.8–2.4 (m, $H_{\beta'}$), 0.8 (distorted t, J_{HH} = 6 Hz, H_γ).

C. Reaction of 2b with $CHCl_2CO_2H$. A 5-mm NMR tube was charged with propenyl complex (E)-2b (7.5 mg, 0.013 mmol) and $CD_2Cl_2/(CH_3)_4Si$ (0.300 mL) and was capped with a septum and transferred to a −68 °C NMR probe. A t_0 ^1H NMR spectrum was recorded. The tube was then frozen in liquid N_2, and $CHCl_2CO_2H$ (0.0011 mL, 0.013 mmol) was added. The tube was returned to the −68 °C NMR probe, and the ^1H NMR methyl resonances indicated a (66 ± 2):(34 ± 2) ratio of 1b-$CHCl_2CO_2^-$ ((90 ± 2):(10 ± 2) ac/sc) to 2b ((82 ± 2):(18 ± 2) E/Z).

D. Reaction of (E)-2b with CF_3SO_3D. A 5-mm NMR tube was charged with (E)-2b (0.012 g, 0.021 mmol) and CD_2Cl_2 (0.300 mL) and was capped with a septum. The tube was shaken to dissolve the (E)-2b, cooled in liquid N_2, and transferred to a −75 °C NMR probe. A t_0 ^1H NMR spectrum was recorded. The tube was removed from the probe and frozen in liquid N_2. Then CF_3SO_3D (0.002 mL, 0.022 mmol) was added by syringe. The tube was thawed, shaken once, and returned to the −75 °C NMR probe. Analysis by ^1H NMR indicated that 78% of the resulting 1b-$CF_3SO_3^-$ contained a single deuterium and that the ac-1b-β-d_x-$CF_3SO_3^-$/sc-1b-β-d_x-$CF_3SO_3^-$ ratio was (87 ± 2):(13 ± 2). The relative areas of the ac-1b H_β proton resonances (highfield > lowfield) indicated a (76 ± 2):(24 ± 2) ratio of ac-1b-β-d_1 diastereomers.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH(CH_3)_2)]^+FSO_3^-$ (3-FSO_3^-). In a typical experiment, a Schlenk flask was charged with 2b (0.096 g, 0.164 mmol), CH_2Cl_2 (1.0 mL), and a stir bar. This mixture was cooled to −25 °C (CO_2/CCl_4), and CH_3OSO_2F (0.150 mL, 1.85 mmol, 11.3 equiv) was added with stirring. After 17 min, volatiles were removed under oil pump vacuum while a reaction temperature of −25 °C was maintained. Complete removal of CH_3OSO_2F usually required 5–7 h. The residue was taken up in CD_2Cl_2, rapidly transferred to a 5-mm NMR tube, and frozen in liquid N_2. The tube was transferred to a cooled NMR probe and ^1H NMR spectra were recorded from −25 to −10 °C. Complex 3-FSO_3^- was present in ≥95% spectroscopic yield. Complexes 1b-FSO_3^- (2–3%) and 5 (2–3%) were also present; under careful conditions, no isobutylene complex was observed. IR (cm^{-1}, thin film): $\nu_{N\equiv O}$ 1712 s. ^1H NMR (δ, CD_2Cl_2, −3 °C): 15.16 (d, $J_{H_\alpha H_\beta}$ = 11 Hz, Re=CH_α), 7.80–6.90 (m, PPh_3), 5.96 (s, C_5H_5), 3.96 (m, $J_{H_\alpha H_\beta}$ = 11 Hz, $J_{H_\beta H_\gamma}$ = 7 Hz, $J_{H_\beta H_{\gamma'}}$ = 7 Hz, CH_β), 0.98 (d, $J_{H_\gamma H_\beta}$ = 7 Hz, CH_3), 0.22 (d, $J_{H_{\gamma'} H_\beta}$ = 7 Hz, CH'_3). ^{13}C NMR (ppm, CD_2Cl_2, −3 °C): 319.5 (d, J_{CP} = 9 Hz, C_α), PPh_3 at 134.0 (d, J_{CP} = 11 Hz), 133.2 (s, p), 131.6 (d, J_{CP} = 61 Hz, ipso), 130.6 (d, J_{CP} = 12 Hz); 100.0 (s, C_5H_5), 56.5 (s, C_β), 21.4 (s, C_γ), 18.7 (s, $C_{\gamma'}$).

Preparation of (SS,RR)-ac-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH(CH_3)(CD_3))]^+FSO_3^-$ ((SS,RR)-ac-3-FSO_3^--γ-d_3). A 5-mm NMR tube was charged with (E)-2b (0.0060 g, 0.010 mmol) and $CD_2Cl_2/(CH_3)_4Si$ (0.300 mL) and was capped with a septum. The tube was shaken vigorously to effect dissolution and was transferred to a −25 °C NMR probe, where a t_0 ^1H NMR spectrum was recorded. The tube was removed from the probe, and CD_3SO_3F (0.009 mL, 0.10 mmol) was added. The tube was returned to the probe, and a ^1H NMR spectrum showed an (E)-2b/(Z)-2b equilibrium mixture to be present. Over the course of 20 min, >90% conversion to (SS,RR)-ac-3-FSO_3^--γ-d_3 occurred, as assayed by ^1H NMR integration of the methyl resonances. A small amount of 1b-FSO_3^- formed, but no 6-d_3-FSO_3^- was detected.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH=C(CH_3)_2)$ (4). Complex (E)-2b (0.076 g, 0.130 mmol) and CH_3OSO_2F (0.115 mL, 1.30

mmol, 10 equiv) were reacted in CH_2Cl_2 (1 mL), analogous to the procedure used to prepare **3**-FSO_3^-. The residue was taken up in cold CH_2Cl_2 (3 mL), and 2.0 mL of a 1.17 M *t*-BuOH solution of *t*-BuO^-K^+ was added. The reaction was warmed to room temperature and filtered. The filtrate was washed with degassed H_2O (3 × 30 mL) and saturated aqueous NaCl (30 mL) and dried over Na_2SO_4. The drying agent was removed by filtration, and the filtrate was concentrated by rotary evaporation. Hexanes were added, giving an undesired brown precipitate that was removed by filtration. The filtrate was concentrated by rotary evaporation until a cloud point was reached. The sample was stored at −20 °C overnight. Red crystals formed, which were collected by filtration and dried in vacuo to give 0.047 g (0.079 mmol, 60%) of **4**, mp 204–205 °C dec. IR (cm^{-1}, KBr): $\nu_{N\equiv O}$ 1622 s. MS (15 eV, *m/e*, ^{187}Re): 599 (M^+, 100%), 544 ($M^+ - C_4H_7$, 8%), 467 ($M^+ - C_4H_7 - C_6H_5$, 6%), 337 ($M^+ - PPh_3$, 17%), 262 (Ph_3P^+, 91%). Anal. Calcd for $C_{27}H_{27}NOPRe$: C, 54.17; H, 4.55. Found: C, 54.06; H, 4.64.

Preparation of 3-BF_4^- from 4 and HBF_4·Et_2O. A 5-mm NMR tube was charged with **4** (0.0132 g, 0.022 mmol) and CD_2Cl_2 (0.300 mL) and was capped with a septum. The tube was frozen in liquid N_2, and HBF_4·Et_2O (0.004 mL, 1.60 g/mL,[53] 1.8 equiv) was added. The tube was thawed and shaken, and a ^1H NMR spectrum was recorded at 7 °C. The only resonances present were due to isobutylidene complex **3**-BF_4^-, Et_2O, and excess HBF_4·Et_2O.

Preparation of *ac*-[(η^5-C_5H_5)Re(NO)(PPh_3)(=CHC(CH_3)$_3$)]$^+$$FSO_3^-$ (*ac*-5-FSO_3^-). A Schlenk tube was charged with **4** (0.100 g, 0.167 mmol), CH_2Cl_2 (10 mL), and a stir bar. Then CH_3OSO_2F (0.054 mL, 0.669 mmol, 4.0 equiv) was added with stirring. After 10 h, volatiles were removed under oil pump vacuum (5–7 h). The resulting yellow foam was extracted with CH_2Cl_2. The extract was filtered through a medium-porosity glass frit, and an equal volume of hexanes was added to the filtrate. Solvents were removed by rotary evaporation, and the resulting yellow powder was dissolved in $CHCl_3$, layered with three volumes of hexanes, and kept at −20 °C for 3 days. This gave yellow crystals, which were collected by filtration, washed with cold $CHCl_3$, and dried in vacuo to give 0.107 g (0.150 mmol, 90%) of *ac*-5-FSO_3^-, mp 212–215 °C dec. IR (cm^{-1}, KBr): $\nu_{N\equiv O}$ 1702 s. ^1H NMR (δ, CD_2Cl_2): 15.18 (s, Re=CH_α), 8.00–7.30 (m, PPh_3), 5.94 (s, C_5H_5), 0.91 (s, CH_3). ^{13}C NMR (ppm, CD_2Cl_2): 320.8 (d, J_{CP} = 8 Hz, C_α), PPh_3 at 134.0 (d, J_{CP} = 11 Hz), 133.2 (s, p), 131.6 (d, J_{CP} = 61 Hz, ipso), 130.6 (d, J_{CP} = 11 Hz); 100.1 (s, C_5H_5), 61.2 (s, C_β), 27.9 (s, C_γ). $^{31}P\{^1H\}$ NMR (ppm, CH_2Cl_2): 16.6 (s). Anal. Calcd for $C_{28}H_{30}FNO_4PReS$: C, 47.18; H, 4.21. Found: C, 47.26; H, 4.23.

Preparation of *ac*-[(η^5-C_5H_5)Re(NO)(PPh_3)(=CHCH_2CPh_3)]$^+$-PF_6^-·CH_2Cl_2 (*ac*-7-PF_6^-·CH_2Cl_2). **A.** A Schlenk tube was charged with **2a** (0.150 g, 0.263 mmol), CH_2Cl_2 (15 mL), and a stir bar. The solution was cooled to −78 °C, and $Ph_3C^+PF_6^-$ (0.102 g, 0.263 mmol, 1.0 equiv) was added with stirring. After 0.5 h, the reaction was warmed to room temperature and stirred for an additional 2 h. Then hexanes (20 mL) were added, and solvents were removed by rotary evaporation. The resulting yellow solid was triturated with ether and hexanes to give 0.244 g (0.234 mmol, 89%) of crude 7-PF_6^-·$(CH_2Cl_2)_x$; analysis by ^1H NMR showed the presence of *ac* (δ 15.15) and *sc* (δ 16.10) Re=C geometric isomers. The solid was dissolved in CH_2Cl_2, layered with four volumes of hexanes, and kept at room temperature for 2 days. Yellow prisms formed, which were collected by filtration and dried in vacuo to give 0.222 g (0.213 mmol, 81%) of *ac*-7-PF_6^-·CH_2Cl_2, mp 200–202 °C dec. IR (cm^{-1}, KBr): $\nu_{N\equiv O}$ 1715 s. ^1H NMR (δ, CD_2Cl_2): 15.15 (dd, $J_{H_\alpha H_\beta}$ = 10 Hz, $J_{H_\alpha H_{\beta'}}$ = 3 Hz, Re=CH_α), 7.80–6.90 (m, 6 C_6H_5), 5.56 (s, C_5H_5), 4.72 (dd, $J_{H_\beta H_\alpha}$ = 10 Hz, $J_{H_\beta H_{\beta'}}$ = 19 Hz, CH_β), 2.55 (dd, $J_{H_{\beta'} H_\alpha}$ = 3 Hz, $J_{H_{\beta'} H_\beta}$ = 19 Hz, $CH_{\beta'}$). ^{13}C NMR (ppm, CD_2Cl_2): 305.4 (d, J_{CP} = 8 Hz, C_α), CPh_3 at 146.1 (s, ipso); other CPh_3 and PPh_3 not resolved; 99.5 (s, C_5H_5), 65.5 (s, C_β), 58.5 (s, C_γ). $^{31}P\{^1H\}$ NMR (ppm, C_6H_5Cl): 18.3 (s). Anal. Calcd for $C_{44}H_{38}F_6NOP_2Re$·CH_2Cl_2: C, 51.76; H, 3.83. Found: C, 51.70; H, 3.85.

B. A septum-capped NMR tube was charged with **2a** (0.0058 g, 0.010 mmol) and $CD_2Cl_2/(CH_3)_4Si$ (0.350 mL) was inserted into a −71 °C NMR probe to record a t_0 spectrum. The tube was moved to a −78 °C bath, and $Ph_3C^+PF_6^-$ (0.0046 g, 0.012 mmol, 1.2 equiv) in CD_2Cl_2 (0.050 mL) was added. The tube was shaken and returned to the −71 °C probe. Complex 7-PF_6^- had formed as a (76 ± 2):(24 ± 2) ratio of *ac*/*sc* Re=C isomers, as determined by integration of the Re=CHR resonances at δ 15.2 and 16.1, respectively. ^1H NMR of *sc*-7-PF_6^- (δ, CD_2Cl_2): 16.10 (dd, $J_{H_\alpha H_\beta}$ = 12 Hz, $J_{H_\alpha H_{\beta'}}$ = 3 Hz, Re=CH_α), 5.55 (s, C_5H_5), 4.00 (dd, $J_{H_\beta H_\alpha}$ = 12 Hz, $J_{H_\beta H_{\beta'}}$ = 18 Hz, CH_β), 2.72 (dd, $J_{H_{\beta'} H_\alpha}$ = 3 Hz, $J_{H_{\beta'} H_\beta}$ = 18 Hz, $CH_{\beta'}$).

Preparation of (*E*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH=CHCPh_3) ((*E*)-8). Complex 7-PF_6^-·CH_2Cl_2 (0.120 g, 0.115 mmol) and DBU (0.026 mL, 0.173 mmol, 1.5 equiv) were reacted in CH_2Cl_2 (12 mL), analogous to the procedure used to prepare (*E*)-**2b**. An identical workup gave red crystals of (*E*)-**8** (0.082 g, 0.101 mmol, 88%), dec pt ≥240 °C. IR (cm^{-1}, KBr): $\nu_{N\equiv O}$ 1642 s. MS (16 eV, *m/e*, ^{187}Re): 813 (M^+, 88%), 544 ($M^+ - C_{21}H_{17}$, 100%), 262 (Ph_3P^+, 22%). Anal. Calcd for $C_{44}H_{37}NOPRe$: C, 65.01; H, 4.56. Found: C, 65.20; H, 4.64.

Preparation of [(η^5-C_5H_5)Re(NO)(PPh_3)(=C(OCH_3)CH_2CH_3)$^+$$PF_6^-$ (9b-PF_6^-). A Schlenk flask was charged with (η^5-C_5H_5)Re(NO)-(PPh_3)($COCH_2CH_3$) (0.904 g, 1.54 mmol),[25] CH_2Cl_2 (100 mL), and a stir bar. Then $(CH_3)_3O^+PF_6^-$ (0.621 g, 3.01 mmol, 2.0 equiv) was added, and the mixture was stirred for 2 h. The reaction was then filtered, and solvent was removed from the filtrate by rotary evaporation. The residue was taken up in CH_2Cl_2, and ether was added by slow vapor diffusion. The resulting yellow crystals were collected by filtration and dried in vacuo to give 1.04 g (1.37 mmol, 90%) of 9b-PF_6^-, mp 192–195 °C dec. IR (cm^{-1}, CH_2Cl_2): $\nu_{N\equiv O}$ 1703 s. ^1H NMR (δ, CD_2Cl_2, −28 °C): 7.56–7.27 (m, PPh_3); major isomer at 5.64 (s, C_5H_5), 4.08 (s, OCH_3), 2.26 (m, CH_2), 1.09 (t, J_{HH} = 8 Hz, CCH_3); minor isomer at 5.89 (s, C_5H_5), 3.76 (s, OCH_3), 2.73 (m, CH_2), 0.80 (t, J_{HH} = 7 Hz, CCH_3). ^{13}C NMR (ppm, CD_2Cl_2, −30 °C): major isomer at 304.9 (d, J_{CP} = 9 Hz, C_α), PPh_3 at 133.1 (d, J_{CP} = 9 Hz), 132.4 (s, p), 131.8 (d, J_{CP} = 60 Hz, ipso), 129.6 (d, J_{CP} = 12 Hz); 96.0 (s, C_5H_5), 61.9 (s, OCH_3), 53.0 (s, C_β), 12.1 (s, C_γ); minor isomer at 302.4 (d, J_{CP} = 6 Hz, C_α), PPh_3 at 132.6 (s, p), 130.7 (d, J_{CP} = 62 Hz, ipso), 129.8 (d, J_{CP} = 14 Hz); 96.6 (s, C_5H_5), 66.8 (s, OCH_3), 44.2 (s, C_β), 10.4 (s, C_γ). $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2, −20 °C): 13.8 (s, minor isomer), 10.6 (s, major isomer). Anal. Calcd for $C_{27}H_{28}F_6NO_2P_2Re$: C, 42.63; H, 3.71. Found: C, 42.45; H, 3.70.

Preparation of [(η^5-C_5H_5)Re(NO)(PPh_3)(=C(OCH_3)-$CH_2CH_2C_6H_5$)]$^+$$PF_6^-$ (9d-PF_6^-). Complex (η^5-C_5H_5)Re(NO)(PPh_3)-($COCH_2CH_2C_6H_5$) (0.300 g, 0.446 mmol)[25] and $(CH_3)_3O^+PF_6^-$ (0.184 g, 0.893 mmol, 2.0 equiv) were reacted in CH_2Cl_2 (30 mL), analogous to the procedure used to prepare 9b-PF_6^-. An identical workup gave yellow crystals of 9d-PF_6^- (0.289 g, 0.352 mmol, 79%), mp 210–214 °C dec. IR (cm^{-1}, CH_2Cl_2): $\nu_{N\equiv O}$ 1706 s. ^1H NMR (δ, CD_2Cl_2, −21 °C): 7.50 (m, PPh_3), 7.20 (m, CC_6H_5), 2.90–2.40 (m, 2 CH_2); major isomer at 5.70 (s, C_5H_5), 3.70 (s, OCH_3); minor isomer at 5.60 (s, C_5H_5), 4.10 (s, OCH_3). ^{13}C NMR (ppm, CD_2Cl_2, −24 °C): major isomer, 299.2 (d, J_{CP} = 5 Hz, C_α), PPh_3 at 133.0 (d, J_{CP} = 11 Hz), 132.6 (s, p), 131.8 (d, J_{CP} = 60 Hz, ipso), 129.9 (d, J_{CP} = 11 Hz); CC_6H_5 at 140.5 (s, ipso), 129.0 (s), 128.9 (s), 126.7 (s, p); 96.5 (s, C_5H_5), 66.8 (s, OCH_3), 61.0 (s, C_β), 21.9 (s, C_γ); minor isomer, 302.0 (s, C_α), PPh_3 at 133.0 (d, J_{CP} = 11 Hz), 132.4 (s, p), 130.3 (d, J_{CP} = 55 Hz), 129.7 (d, J_{CP} = 12 Hz); CC_6H_5 at 139.2 (s, ipso), 128.9 (s), 128.5 (s), 127.2 (s, p); 96.2 (s, C_5H_5), 62.4 (s, OCH_3), 52.5 (s, C_β), 33.8 (s, C_γ). $^{31}P\{^1H\}$ NMR (ppm, CH_2Cl_2, −78 °C): 14.0 (s, major isomer), 9.8 (s, minor isomer). Anal. Calcd for $C_{33}H_{32}F_6NO_2P_2Re$: C, 47.37; H, 3.85. Found: C, 47.21; H, 4.03.

Preparation of (η^5-C_5H_5)Re(NO)(PPh_3)(C(OCH_3)=CH_2) (10a). A Schlenk flask was charged with [(η^5-C_5H_5)Re(NO)(PPh_3)(=C-(OCH_3)CH_3)]$^+$$PF_6^-$ (9a-PF_6^-; 0.815 g, 1.09 mmol),[25] THF (80 mL), and a stir bar. Then NaH (0.105 g, 4.36 mmol, 4.0 equiv) was added, and the mixture was stirred overnight. The resulting orange suspension was filtered, and solvent was removed from the filtrate by rotary evaporation. The resulting orange solid was extracted several times with cold CH_2Cl_2. The extract was filtered, hexanes were added to the filtrate, and solvents were removed by rotary evaporation to give **10a** (0.494 g, 0.83 mmol, 75%) as an orange powder, mp 202–204 °C dec. IR (cm^{-1}, CH_2Cl_2): $\nu_{N\equiv O}$ 1651 s. MS (70 eV, *m/e*, ^{187}Re): 601 (M^+, 5%), 572 ($M^+ - C_2H_5$, 48%), 569 ($M^+ - CH_3OH$, 9%), 544 ($M^+ - C_3H_5O$, 33%), 262 (Ph_3P^+, 100%). Anal. Calcd for $C_{26}H_{25}NO_2PRe$: C, 51.99; H, 4.20. Found: C, 51.66; H, 4.06.

Preparation of (*Z*)-(η^5-C_5H_5)Re(NO)(PPh_3)(C(OCH_3)=$CHCH_3$) ((*Z*)-10b). A Schlenk flask was charged with 9b-PF_6^- (1.00 g, 1.31 mmol), CH_2Cl_2 (100 mL), and a stir bar. Then DBU (2.9 mL, 1.97 mmol, 1.5 equiv)[23c] was added with stirring. After 1 h, solvent was removed from the deep orange solution by rotary evaporation. The orange residue was dissolved in benzene and passed through a plug of silica gel that had previously been treated with $N(C_2H_5)_3$ with 70:30:10 (v/v/v) ethyl acetate/hexanes/$N(C_2H_5)_3$ as eluent. The orange band was collected, and solvents were removed by rotary evaporation. The orange residue was dissolved in CH_2Cl_2 and layered with hexanes. Orange crystals formed, which were collected by filtration and dried in vacuo to give 0.560 g (0.91 mmol, 72%) of (*Z*)-**10b**, mp 191–193 °C dec. IR (cm^{-1}, CH_2Cl_2): $\nu_{N\equiv O}$ 1646 s. MS (70 eV, *m/e*, ^{187}Re): 615 (M^+, 11%), 583 ($M^+ - CH_3OH$, 66%), 572 ($M^+ - C_3H_7$, 13%), 467 ($M^+ - C_4H_7O - C_6H_5$, 36%), 262 (Ph_3P^+, 100%). Anal. Calcd for $C_{27}H_{27}NO_2PRe$: C, 52.76; H, 4.43. Found: C, 52.59; H, 4.49.

Preparation of (*Z*)-(η^5-C_5H_5)Re(NO)(PPh_3)(C(OCH_3)=$CHCH_2C_6H_5$) ((*Z*)-10d). Complex 9d-PF_6^- (0.049 g, 0.059 mmol) and DBU (0.020 mL, 0.134 mmol, 2.3 equiv) were reacted in CH_2Cl_2 (5 mL),

(53) Density taken from: Bruno, J. M.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 1663, 1668.

analogous to the procedure used to prepare (*Z*)-**10b**. An identical workup gave orange crystals of (*Z*)-**10d** (0.033 g, 0.048 mmol, 81%), mp 209.5–215 °C dec. IR (cm^{-1}, CH_2Cl_2): $\nu_{N\equiv O}$ 1645 s. MS (70 eV, *m/e*, ^{187}Re): 691 (M^+, 9%), 659 ($M^+ - CH_3OH$, 100%), 572 ($M^+ - C_9H_{11}$, 12%), 544 ($M^+ - C_{10}H_{11}O$, 25%), 467 ($M^+ - C_{10}H_{11}O - C_6H_5$, 16%). Anal. Calcd for $C_{33}H_{31}NO_2PRe$: C, 57.38; H, 4.52. Found: C, 57.23; H, 4.77.

Preparation of (*Z*)-(η^5-C_5H_5)Re(NO)(PPh$_3$)(C(OCH$_3$)=CHC$_6$H$_5$) ((*Z*)-10e). A Schlenk flask was charged with (η^5-C_5H_5)Re(NO)(PPh$_3$)($COCH_2C_6H_5$) (0.398 g, 0.602 mmol),[25] CH_2Cl_2 (10 mL), and a stir bar. Then $(CH_3)_3O^+BF_4^-$ (0.134 g, 0.905 mmol, 1.5 equiv) was added with stirring. After 1.5 h, the reaction was filtered into a Schlenk tube, and DBU (0.135 mL, 0.903 mmol, 1.5 equiv) was added; the yellow solution immediately turned deep red. After 0.75 h, solvent was removed by rotary evaporation. The resulting dark oil was dissolved in benzene and purified and recrystallized as described for (*Z*)-**10b** above. This gave orange prisms of (*Z*)-**10e** (0.336 g, 0.497 mmol, 83%), mp 172.5–178 °C dec. IR (cm^{-1}, thin film): $\nu_{N\equiv O}$ 1650 s. MS (70 eV, *m/e*, ^{187}Re): 677 (M^+, 11%), 645 ($M^+ - CH_3OH$, 100%), 467 ($M^+ - C_{15}H_{14}O$, 16%), 262 (Ph_3P^+, 91%). Anal. Calcd for $C_{32}H_{29}NO_2PRe$: C, 56.80; H, 4.29. Found: C, 56.49; H, 4.52.

Reaction of 10a with CH_3I. A 5-mm NMR tube was charged with **10a** (0.023 g, 0.038 mmol), CD_2Cl_2 (0.500 mL), and CH_3I (0.007 mL, 0.133 mmol, 3.0 equiv) and was capped with a septum. After 4 h (during which time ^{31}P and ^1H NMR showed the intermediacy of **9b**-I^-), solvent was removed by rotary evaporation. The residue was extracted in benzene and passed through a silica gel column with 70:30 (v/v) hexanes/ethyl acetate as eluent. Solvent was removed from the yellow product fraction to give a yellow oil. This was dissolved in CH_2Cl_2 (5 mL), and four volumes of hexanes were added. Solvent was removed by rotary evaporation to give (η^5-C_5H_5)Re(NO)(PPh$_3$)($COCH_2CH_3$) (**11**)[25] as a yellow powder (0.019 g, 0.031 mmol, 82%), which was pure by ^1H NMR.

Preparation of (η^5-C_5H_5)Re(NO)(PPh$_3$)(COCH(CH$_3$)$_2$) (12). A Schlenk flask was charged with (*Z*)-**10b** (0.400 g, 0.651 mmol), CH_2Cl_2 (40 mL), and a stir bar. Then CH_3I (0.081 mL, 1.30 mmol, 2.0 equiv) was added with stirring. After 24 h, solvent was removed via oil pump vacuum, and the residue was extracted with benzene. An equal volume of hexanes was added to the extract, and solvent was removed by rotary evaporation. The resulting yellow solid was triturated with hexanes, washed with cold ether, and dried in vacuo to give 0.352 g (0.573 mmol, 88%) of **12**, mp >210 °C. IR (cm^{-1}, thin film): $\nu_{N\equiv O}$ 1654 s, $\nu_{C=O}$ 1558 m. ^1H NMR (δ, CD_2Cl_2): 7.47–7.41 (m, PPh_3), 5.21 (s, C_5H_5), 2.89 (m, J_{HH} = 7 Hz, CH), 0.97 (d, J_{HH} = 7 Hz, CH_3), 0.13 (d, J_{HH} = 7 Hz, CH_3'). ^{13}C NMR (ppm, $CDCl_3$): 260.7 (br s, C=O), PPh_3 at 136.2 (d, J_{CP} = 56 Hz, ipso), 133.8 (d, J_{CP} = 11 Hz), 130.5 (s, p), 128.6 (d, J_{CP} = 11 Hz); 92.6 (s, C_5H_5), 58.6 (s, CH), 20.7 (s, CH_3), 19.2 (s, CH_3'). $^{31}P\{^1H\}$ NMR (ppm, CH_2Cl_2): 16.3 (s). MS (CI, *m/e*, ^{187}Re): 616 (MH^+, 69%), 572 ($M^+ - C_3H_7$, 97%), 544 ($M^+ - C_4H_7O$, 19%), 262 (Ph_3P^+, 33%), 185 (Ph_2P^+, 100%). Anal. Calcd for $C_{27}H_{27}NO_2PRe$: C, 52.76; H, 4.43. Found: C, 52.84; H, 4.54.

Preparation of (*SR,RS*)-(η^5-C_5H_5)Re(NO)(PPh$_3$)(COCH(CH$_3$)(CD$_3$)) ((*SR,RS*)-12-*d*$_3$). Complex (*Z*)-**10b** (0.300 g, 0.489 mmol) and CD_3I (0.093 mL, 1.47 mmol, 3.0 equiv) were reacted in CH_2Cl_2 (20 mL), analogous to the procedure used to prepare **12**. An identical workup afforded 0.260 g (0.420 mmol, 86%) of (*SR,RS*)-**12**-d_3. IR (cm^{-1}, CH_2Cl_2): $\nu_{N\equiv O}$ 1649 s, $\nu_{C=O}$ 1556 m. ^1H NMR (δ, CD_2Cl_2): CH_3 at 0.96 (d, J_{HH} = 7 Hz). ^{13}C NMR (ppm, CD_2Cl_2): 259.0 (d, J_{CP} = 9 Hz, C=O), PPh_3 at 136.9 (d, J_{CP} = 55 Hz, ipso), 134.2 (d, J_{CP} = 11 Hz), 131.0 (s, p), 129.0 (d, J_{CP} = 11 Hz); 93.0 (s, C_5H_5), 58.7 (s, CH), 20.7 (s, CH_3); MS (CI, *m/e*, ^{187}Re): 619 (MH^+, 59%), 572 ($M^+ - C_3H_4D_3$, 97%), 544 ($M^+ - C_4H_4D_3O$, 19%), 262 (Ph_3P^+, 39%), 185 (Ph_2P^+, 100%).

Preparation of (*SR,SR*)-(η^5-C_5H_5)Re(NO)(PPh$_3$)(COCH(CH$_3$)(CH$_2$C$_6$H$_5$)) ((*SR,RS*)-13). A Schlenk flask was charged with (*Z*)-**10b** (0.120 g, 0.195 mmol), CH_2Cl_2 (12 mL), and a stir bar. Then $C_6H_5CH_2Br$ (0.035 mL, 0.293 mmol, 1.5 equiv) was added with stirring. After 2 days, the reaction mixture was heated at 50 °C for an additional 6 h. Solvent was removed via oil pump vacuum, and the residue was dissolved in acetone and chromatographed on a silica gel column with 40:60 ethyl acetate/hexanes as the eluent. The yellow product band was collected, and solvents were removed by rotary evaporation. The residue was dissolved in CH_2Cl_2 and layered with hexanes. Yellow prisms formed, which were collected by filtration and dried in vacuo to give 0.095 g (0.137 mmol, 70%) of (*SR,RS*)-**13**, mp 201–204 °C dec. IR (cm^{-1}, CH_2Cl_2): $\nu_{N\equiv O}$ 1651 s, $\nu_{C=O}$ 1557 m. ^1H NMR (δ, CD_2Cl_2): 7.61–7.16 (m, 4 C_6H_5), 5.23 (s, C_5H_5), 2.99 (m, CH_α), 2.08 (dd, $J_{H_\beta H_{\beta'}}$ = 14 Hz, $J_{H_\beta H_\alpha}$ = 3 Hz, CH_β), 1.65 (dd, $J_{H_{\beta'} H_\beta}$ = 14 Hz, $J_{H_{\beta'} H_\alpha}$ = 12 Hz, $CH_{\beta'}$), 0.88 (d, $J_{H_{\beta''} H_\alpha}$ = 7 Hz, CH_3). ^{13}C NMR (ppm, $CDCl_3$): 258.8 (d, J_{CP} = 10 Hz, C=O), PPh_3 at 136.0 (d, J_{CP} = 55 Hz, ipso), 133.3 (d, J_{CP} = 11 Hz), 130.2 (s, p), 128.3 (d, J_{CP} = 11 Hz); CC_6H_5 at 142.0 (s, ipso), 129.2 (s), 127.5 (s), 124.9 (s, p); 92.5 (s, C_5H_5), 65.0 (s, CH), 37.3 (s, CH_2), 17.5 (s, CH_3). $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$): 15.9 (s). MS spectrum (CI, *m/e*, ^{187}Re): 692 (MH^+, 50%), 572 ($M^+ - C_9H_{11}$, 93%), 544 ($M^+ - C_{10}H_{11}O$, 21%), 262 (Ph_3P^+, 57%), 185 (Ph_2P^+, 100%). Anal. Calcd for $C_{33}H_{31}NO_2PRe$: C, 57.38; H, 4.52. Found: C, 57.11; H, 4.40.

Preparation of (*SS,RR*)-(η^5-C_5H_5)Re(NO)(PPh$_3$)(COCH(CH$_3$)(CH$_2$C$_6$H$_5$)) ((*SS,RR*)-13). Complex (*Z*)-**10d** (0.100 g, 0.145 mmol) and CH_3I (0.018 mL, 0.290 mmol, 2.0 equiv) were reacted in CH_2Cl_2 (10 mL), analogous to the procedure used to prepare (*SR,RS*)-**13**. After 2 days, solvent was removed under oil pump vacuum, and an identical workup afforded yellow prisms of (*SS,RR*)-**13** (0.088 g, 0.127 mmol, 88%), mp > 210 °C. IR (cm^{-1}, CH_2Cl_2): $\nu_{N\equiv O}$ 1648 s, $\nu_{C=O}$ 1558 m. ^1H NMR (δ, CD_2Cl_2): 7.49–7.14 (m, 4 C_6H_5), 5.17 (s, C_5H_5), 3.28 (dd, $J_{H_\beta H_{\beta'}}$ = 13 Hz, $J_{H_\beta H_\alpha}$ = 4 Hz, CH_β), 3.17 (m, CH), 2.09 (dd, $J_{H_{\beta'} H_\beta}$ = 13 Hz, $J_{H_{\beta'} H_\alpha}$ = 11 Hz, $CH_{\beta'}$), –0.03 (d, $J_{H_{\beta''} H_\alpha}$ = 6 Hz, CH_3). ^{13}C NMR (ppm, $CDCl_3$): 259.0 (d, J_{CP} = 9 Hz, C=O), PPh_3 at 135.9 (d, J_{CP} = 53 Hz, ipso), 133.3 (d, J_{CP} = 13 Hz), 130.2 (s, p), 128.2 (d, J_{CP} = 11 Hz); CC_6H_5 at 141.7 (s, ipso), 129.3 (s), 127.8 (s), 125.2 (s, p); 92.8 (s, C_5H_5), 66.1 (s, CH), 41.7 (s, CH_2), 14.0 (s, CH_3). $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$): 15.9 (s). MS (CI, *m/e*, ^{187}Re): 692 (MH^+, 48%), 572 $M^+ - C_9H_{11}$, 100%), 544 ($M^+ - C_{10}H_{11}O$, 24%), 262 (Ph_3P^+, 38%), 185 (Ph_2P^+, 81%). Anal. Calcd for $C_{33}H_{31}NO_2PRe$: C, 57.38; H, 4.52. Found: C, 57.34; H, 4.41.

Preparation of (*SS,RR*)-(η^5-C_5H_5)Re(NO)(PPh$_3$)(COCH(CH$_3$)(C$_6$H$_5$)) ((*SS,RR*)-14). A Schlenk flask was charged with (*Z*)-**10e** (0.050 g, 0.074 mmol), CH_2Cl_2 (4 mL), and a stir bar. Then $(CH_3)_3O^+PF_6^-$ (0.018 g, 0.087 mmol, 1.2 equiv) was added with stirring. After 0.5 h, the reaction mixture was filtered into a Schlenk tube, and $Ph_3PCH_3^+I^-$ (0.035 g, 0.087 mmol, 1.2 equiv) was added. The reaction was stirred for 8 h, and solvent was then removed by rotary evaporation. The residue was chromatographed on a silica gel column with CH_2Cl_2 as eluent. Some (*Z*)-**10e** (0.009 g, 0.013 mmol, 18%) eluted first. The product band was then collected, and solvents were removed by rotary evaporation. The residue was dissolved in CH_2Cl_2 and layered with pentane. Yellow prisms formed, which were collected by filtration and dried in vacuo to give 0.037 g (0.055 mmol, 74% based upon (*Z*)-**10e** consumed) of product, mp 225–229 °C dec. HPLC analyais indicated a (98 ± 1):(2 ± 1) ratio of (*SS,RR*)-**14**/(*SR,RS*)-**14**.[17] IR (cm^{-1}, thin film): $\nu_{N\equiv O}$ 1650 s, $\nu_{C=O}$ 1564 m. ^1H NMR (δ, $CDCl_3$): 7.50–7.42 (m, PPh_3), 7.30–7.18 (m, CC_6H_5), 4.79 (s, C_5H_5), 4.29 (q, J_{HH} = 7 Hz, CH), 0.61 (d, J_{HH} = 7 Hz, CH_3). ^{13}C NMR (ppm, $CDCl_3$): 253.7 (d, J_{CP} = 9 Hz, C=O), PPh_3 at 136.0 (d, J_{CP} = 55 Hz, ipso), 133.3 (d, J_{CP} = 11 Hz), 130.1 (d, J_{CP} = 2 Hz, p), 128.2 (d, J_{CP} = 10 Hz); CC_6H_5 at 143.7 (s, ipso), 128.3 (s), 127.7 (s), 125.3 (s, p); 91.7 (s, C_5H_5), 70.6 (s, CH), 16.2 (s, CH_3). $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$): 16.4 (s). MS (CI, *m/e*, ^{187}Re): 678 (MH^+, 29%), 572 ($M^+ - C_8H_{10}$, 100%), 544 ($M^+ - C_9H_{10}O$, 18%), 262 (Ph_3P^+, 26%), 185 (Ph_2P^+, 97%). Anal. Calcd for $C_{32}H_{29}NO_2PRe$: C, 56.80; H, 4.29. Found: C, 56.40; H, 4.56.

^1H NOED Experiments.[32] The following experiment is representative. A 5-mm NMR tube was charged with CD_2Cl_2 and (*E*)-**2d** (0.14 M), sealed under vacuum, and inserted into a broad-band probe of a Varian XL-300 spectrometer. The NOED experiment was performed as an array consisting of two spectra in which the first was obtained with 75% irradiation of the η^5-C_5H_5 resonance (100% irradiation was avoided to minimize complications of decoupler spill-over) and the second (off-resonance) with the decoupler frequency set >2 ppm from all resonances. Spectra were obtained at 21 °C in interleaved blocks of 32 transients with 8 steady states per block for a total of at least 1216 transients. The acquisition time was 3.0 s, and the pulse delay was 15 s (selected to be at least 3 times the T_1 of interest). Difference NOEs were calculated by subtraction of the off-resonance spectrum from the η^5-C_5H_5-irradiated spectrum. In a separate experiment, the H_α T_1 in (*E*)-**2d** was found to be 3.0 s.

X-ray Crystal Structure of (*E*)-2d·CH_2Cl_2. Crystals were grown as described above and mounted on fine glass fibers with epoxy cement. X-ray data were collected as summarized in Table II. Crystal symmetry and the unit cell parameters were obtained from photographic characterization and the best fit of the angular settings of 25 reflections ($22° \le 2\theta \le 27°$). The space group was uniquely determined by systematic absences in the intensity data. The data were corrected for *Lp* effects and for absorption (empirical Ψ-scan, seven reflections fitted to a six-parameter pseudoellipsoidal form).

The structure was solved by direct methods and subsequent difference Fourier syntheses. A solvate molecule, CH_2Cl_2, was found in the lattice for each molecule of (*E*)-**2d**. In the final refinement, all non-hydrogen atoms were refined with anisotropic temperature factors. All hydrogen atoms, except those of CH_2Cl_2, were found and were well-behaved on isotropic refinement. The CH_2Cl_2 hydrogen atoms were incorporated as idealized isotropic contributions (d(C–H) = 0.96 Å). Software (Nicolet

Corp., Madison, WI): P3 (data collection), SHEXTL (version 5.1; structure solution and refinement).

X-ray Crystal Structure of (*Z*)-10d. Suitable crystals were obtained by slow vapor diffusion of ether into a THF solution of (*Z*)-**10d**. The resulting orange prisms were mounted on fine glass fibers with epoxy cement, and X-ray data were collected as summarized in Table II. Crystal symmetry and unit cell parameters were determined as above from 15 centered reflections ($20° \leq 2\theta \leq 25°$). Data were corrected for *Lp* effects and for absorption based upon a series of Ψ scans. The general techniques employed have been previously described.[54]

The position of the rhenium was obtained from a three-dimensional Patterson map. Several least-squares refinements, followed by a difference Fourier synthesis, yielded all non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic temperature factors. All hydrogens were assigned and held in their calculated positions (d(C–H) = 0.95 Å).[55] Software: P$\bar{1}$ (data collection), modified SHELX-76 (data reduction and refinement).

MO Calculations. Extended Hückel calculations[56] were conducted with weighted H_{ij} formula. The rhenium and phosphorus atoms of the model compounds were assigned idealized octahedral and tetrahedral geometries, respectively. The C=C carbons were assigned idealized trigonal-planar geometries. The Re—C_α, C=C, C—H, C—O, and O—H bonds were assigned lengths of 2.10, 1.32, 1.09, 1.43, and 0.98 Å, respectively. The remaining bond lengths and H_{ij} and ζ parameters used were the same as reported previously.[13a,d,42a]

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Supplementary Material Available: Additional NOE data and tables of bond distances and angles, hydrogen atom coordinates, and anisotropic and isotropic thermal parameters for (*E*)-**2d** and (*Z*)-**10d** (10 pages); listing of observed and calculated structure factors (41 pages). Ordering information is given on any current masthead page.

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Synthesis, Photochemistry, and Electrochemistry of (P)Ge(R)$_2$ and (P)Ge(R)X (P = TPP or OEP, R = CH_3, $CH_2C_6H_5$, or C_6H_5, and X = Cl^-, OH^-, or ClO_4^-)

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Abstract: The synthesis and characterization of (P)Ge(R)$_2$ and (P)Ge(R)X, where P is the dianion of octaethylporphyrin (OEP) or the dianion of tetraphenylporphyrin (TPP), R is CH_3, $CH_2C_6H_5$, or C_6H_5, and X is ClO_4^-, Cl^-, or OH^-, is described. Each complex was characterized by ^1H NMR, IR, and UV–visible spectroscopy and electrochemistry. The investigated (P)Ge(R)$_2$ complexes can be reduced and oxidized by up to two electrons. The reductions are reversible but a rapid cleavage of the germanium–carbon bond follows the initial electrooxidation. The final oxidation product after the abstraction of one electron from (P)Ge(R)$_2$ was identified as (P)Ge(R)X, where X = ClO_4^-, Cl^-, or OH^- depending on the solvent/supporting electrolyte system. (P)Ge(R)Cl could also be generated from (P)Ge(R)$_2$ in solutions of degassed $CHCl_3$ by illumination with visible light. Electrochemical oxidation of (OEP)Ge(C_6H_5)$_2$, (OEP)Ge(C_6H_5)OH, and (OEP)Ge(C_6H_5)Cl gives the same final species which was spectroscopically and electrochemically identified as (OEP)Ge(C_6H_5)ClO_4. Interestingly, (OEP)Ge(C_6H_5)ClO_4 could be converted to (OEP)Ge(C_6H_5)OH by a one-electron electroreduction which was followed by reaction of the generated anion radical with trace H_2O in solution. Finally, an overall scheme for the oxidation and reduction of (P)Ge(R)$_2$ and (P)Ge(R)X porphyrins is presented.

The remarkable antitumor activity of *cis*-dichlorodiammineplatinum(II) (cisplatin)[2] has led to the search for new inorganic anticancer agents. One class of such candidates may include porphyrins and metalloporphyrins. Some porphyrins and metalloporphyrins are powerful photodynamic agents that can render cancer cells vulnerable to light at frequencies that correspond to wavelengths of the porphyrin absorption maxima.[3,4] For example, malignant tumors take up and retain hematoporphyrin to a much greater extent than do normal tissues.[5] The hematoporphyrin then sensitizes these cells so that they are killed by exposure to visible light.

Germanium porphyrins that contain σ-bonded alkyl or aryl ligands are also potential antitumor agents. In this regard, three properties of the alkyl or aryl Ge(IV) complexes are of importance. These are the following: the tendency of tetraphenylporphyrin derivatives to accumulate in malignant tissues,[6] the potential utility of metal alkyls to act as alkylating agents, and the nature of

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