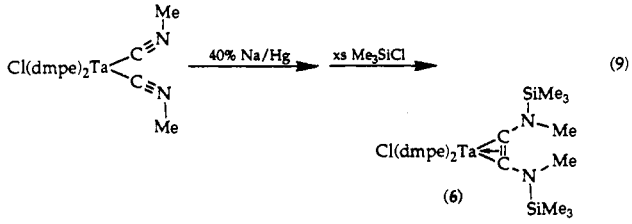
to dark brown. Addition of an excess of Me_3SiCl caused a very slow color change to dark green over a 12-h period. The isolated green product was very soluble in hydrocarbon solvents. It displayed no C≡NR stretches in the IR spectrum but did have a band at 1539 cm^{-1}, characteristic of the C–C acetylene stretch observed for the dicarbonyl and mixed CO/CNR coupled products. The $^{31}P\{^1H\}$ NMR spectrum exhibited a single, broad resonance indicating a symmetric arrangement of the dmpe ligands. Finally, the ^1H NMR showed single N–Me and $SiMe_3$ resonances and two PCH_3 and PCH_2 signals consistent with the coupled species, $[Ta\{(Me_3Si)(Me)NC{\equiv}CN(Me)(SiMe_3)\}(dmpe)_2Cl]$ (**6**) (eq 9).

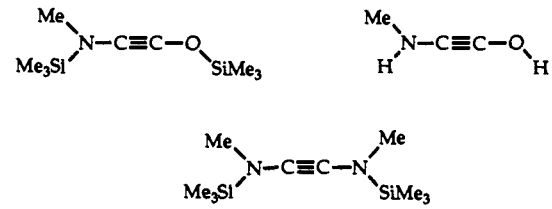


(9)

No attempt has been made to isolate or identify intermediates in this reaction, but sufficient precedent now exists that we can presume with some confidence that it proceeds by sequence of steps shown in Scheme I. Reduction of $[Ta(CNMe)_2(dmpe)_2Cl]$ should generate the tantalum(–I) anion, $[Ta(CNMe)_2(dmpe)_2]^-$, which, when allowed to react with Me_3SiCl, should afford the aminocarbyne complex, $[Ta\{CN(Me)(SiMe_3)\}(CNMe)(dmpe)_2]$. The slow rate of the coupling step may be the result of unfavorable steric interactions between the two methyl groups of the substituted acetylene ligand in **6**. This ligand would most likely be strongly distorted from planarity. X-ray quality crystals of this species could not be obtained, however, so this suggesion has not been evaluated.

Conclusions

Reductive coupling of CO and CNR ligands by low-valent group V transition metals has now been achieved in all combinations. In addition to the previously reported ($Me_3SiOC{\equiv}COSiMe_3$) and (HOC≡COH) moieties, three new highly functionalized acetylene ligands have been formed by reductive coupling reactions, as shown below. The cross coupling of CO and



CNMe ligands proceeds by a mechanism analogous to that previously reported for the symmetric carbon monoxide and isocyanide reductive coupling reactions. Aminocarbyne intermediates were isolated, one of which has been crystallographically characterized. Addition of Me_3SiCl to $[Nb\{CN(Me)(SiMe_2Bu^t)\}(CO)(dmpe)_2]$ generated the asymmetric coupled product $[Nb\{(^tBuMe_2Si)(Me)(NC{\equiv}CO(SiMe_3)\}(dmpe)_2Cl]$, demonstrating that these aminocarbyne complexes are on the reductive coupling reaction pathway. Addition of aqueous acid to $[Ta\{(Me_3Si)OC{\equiv}CN(Me)(SiMe_3)\}(dmpe)_2Cl]$ provided the first stabilized hydroxy(alkylamino)acetylene complex, $[TaH(HOC{\equiv}CNHMe)(dmpe)_2Cl]Cl$. Finally, reductive coupling of two isocyanide ligands in $[Ta(CNMe)_2(dmpe)_2Cl]$ has been accomplished, demonstrating that all three combinations of CO and CNR ligands can be linked by reductive coupling reactions using the same metal framework.

Acknowledgment. This work was supported by a grant from the National Science Foundation.

Supplementary Material Available: Atomic positions and thermal parameters for all crystallographically characterized compounds (17 pages); tables of observed and calculated structure factors for all crystallographically characterized compounds (140 pages). Ordering information is given on any current masthead page.

Mechanism of Equilibration of Diastereomeric Chiral Rhenium Alkene Complexes of the Formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHR)]^+BF_4^-$. The Metal Traverses between Alkene Enantiofaces without Dissociation!

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Received December 5, 1991

Abstract: The (*RS,SR*)/(*RR,SS*) diastereomers of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHR)]^+BF_4^-$ (**1**: R = (**a**) CH_3, (**b**) $CH_2CH_2CH_3$, (**c**) $CH_2C_6H_5$, (**d**) C_6H_5, (**e**) $CH(CH_3)_2$, (**g**) $Si(CH_3)_3$) differ in the alkene enantioface bound to rhenium, and interconvert in chlorocarbons at 95–100 °C. Isomerization is nondissociative (no incorporation of deuterated alkenes or PPh_3) and occurs with retention of configuration at rhenium and without scrambling of *E*/*Z* deuterium labels. The latter excludes mechanisms that involve intermediate carbocations $ReCH_2CHR^+$ and alkylidene complexes, and nucleophilic addition to the alkene. The isomerization of (*RR,SS*)-**1d** to (*RS,SR*)-**1d** proceeds (96.5 °C) with $k(H)/k(=CHD_E)$ = 1.64, $k(H)/k(=CHD_Z)$ = 1.07, and $k(H)/k(=CDC_6H_5)$ = 1.15. Triethylamine promotes the isomerization of substrates that bear allylic protons via σ-allyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH{=}CHR')$. However, rate data suggest that "conducted tour" mechanisms involving transient binding to *R*C=C substituents are unlikely. These results are best accommodated by a mechanism in which the rhenium moves through the π nodal plane of the alkene via a carbon–hydrogen "σ bond complex" involving H_E and/or a vinyl hydride oxidative addition product.

Chiral transition-metal reagents and catalysts are now extensively utilized for the elaboration of achiral alkenes to optically active organic molecules.[1] When the substrate alkenes coordinate to chiral metal fragments, two π diastereomers are possible. These

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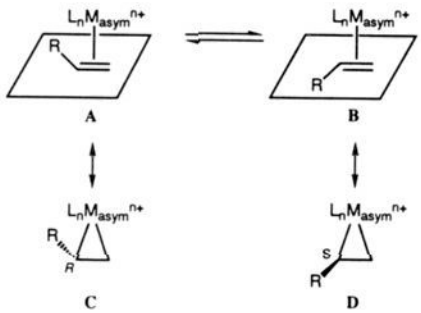
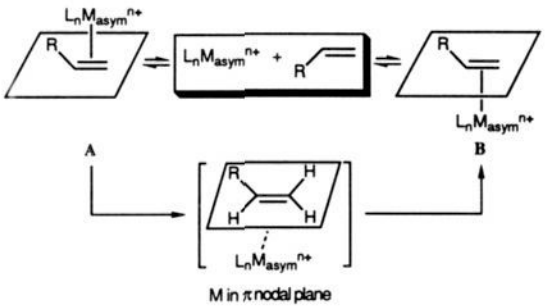
Scheme I. Configurational Diastereomerism in Alkene Complexes of Chiral Metal Fragments



Scheme II. Interconversion of Diastereomeric π Alkene Complexes; Possible Dissociative and Nondissociative Pathways



differ in the alkene enantioface bound to the metal, as illustrated by **A** and **B** in Scheme I for monosubstituted alkenes. Alkene complexes are often viewed as metallacyclopropanes (**C**, **D**), in which case the absolute configuration of the ligand-based stereocenter can be specified by conventional *R*/*S* descriptors.[2]

The interconversion of such π diastereomers plays a key role in a variety of asymmetric transformations. In principle, several distinct mechanisms can be formulated.[3] The most precedented would be for the alkene to dissociate and the metal fragment to reattach to the opposite face, as sketched in Scheme II. This is equivalently viewed as either a net "rotation" of the alkene moiety or a "migration" of the metal fragment. Alternatively, intramolecular mechanisms can be considered. These would require the metal fragment to pass through the π nodal plane without dissociation—a process that might be mediated by a carbon–hydrogen "σ bond complex" or a formal oxidative addition. Also, an alkene substituent could serve as a transient binding site. This variant would constitute a "conducted tour"[4] isomerization mechanism. To our knowledge, such nondissociative pathways have not previously received serious consideration in the literature.

We have conducted an extensive study of alkene complexes of the chiral rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**).[5-9]

Scheme III. Thermodynamic Enantioface Binding Selectivities for the Monosubstituted Alkene Complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHR)]^+BF_4^-$ (**1**)

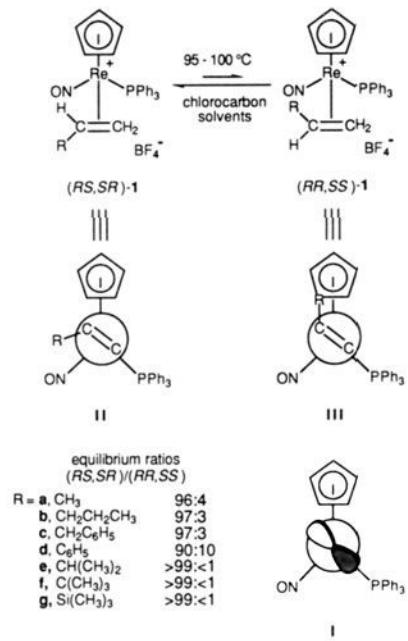


Table I. Equilibration of Diastereomeric Alkene Complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHR)]^+BF_4^-$ (**1**) in C_6D_5Cl at 100 °C; (*RS*,*SR*)/(*RR*,*SS*) Ratios as a Function of Time[a]

	time, h			
complex, R =	0	6	12	24
a, CH_3	67:33	91:9	96:4	96:4
b, $CH_2CH_2CH_3$	50:50	86:14	94:6	97:3
c, $CH_2C_6H_5$	64:36	90:10	96:4	97:3
d, C_6H_5	63:37	82:18	88:12	90:10
e, $CH(CH_3)_2$	73:27	>99:<1	>99:<1	
g, $Si(CH_3)$	73:27	>99:<1	>99:<1	

[a] Abstracted from ref 6.

The monosubstituted alkene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHR)]^+BF_4^-$ (**1**) are commonly accessed as ca. 2:1 mixtures of (*RS*,*SR*)/(*RR*,*SS*) diastereomers, the structures of which are illustrated in Scheme III. Importantly, both diastereomers can usually be isolated in pure form.

We have previously shown that (*RS*,*SR*)-**1** and (*RR*,*SS*)-**1** equilibrate in hydrochlorocarbon solvents at 95–100 °C.[6] Generally, ≥96:4 mixtures are obtained. Thus, **I** exhibits very high thermodynamic selectivity for binding one monosubstituted alkene enantioface. The origin of this selectivity follows readily from stereoelectronic considerations that have previously been discussed at length. In brief, (*RS*,*SR*)-**1** and (*RR*,*SS*)-**1** adopt the idealized structures **II** and **III** (Scheme III). Both of these maximize overlap of the d orbital HOMO of **I** with the alkene π^* acceptor orbitals. However, the latter is destabilized by steric interactions between the alkene substituent and the cyclopentadienyl ligand.

In this paper, we present a detailed account of the unusual mechanism by which equilibrium is reached in Scheme III. A portion of this study has been communicated.[9]

Results

1. Isomerization Rate Trends. During the course of acquiring the equilibrium data on alkene complexes **1** in Scheme III,

(1) Lead references to an extensive literature: (a) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345. (b) Waymouth, R.; Pino, P. *J. Am. Chem. Soc.* **1990**, *112*, 4911. (c) Landis, C. R.; Halpern, J. *Ibid.* **1987**, *109*, 1746. (d) Erker, G.; Nolte, R.; Aul, R.; Wilker, S.; Krüger, C.; Noe, R. *Ibid.* **1991**, *113*, 7594. (e) Woodard, S. S.; Finn, M. G.; Sharpless, K. B. *Ibid.* **1991**, *113*, 106, and following paper in that issue. (f) Burk, M. J. *Ibid.* **1991**, *113*, 8518. (g) Sharpless, K. B.; Amberg, W.; Beller, M.; Chen, H.; Hartung, J.; Kawanami, Y.; Lübben, D.; Manoury, E.; Ogino, Y.; Shibata, T.; Ukita, T. *J. Org. Chem.* **1991**, *56*, 4585.

(2) (a) Paiaro, G.; Panunzi, A. *J. Am. Chem. Soc.* **1964**, *86*, 5148. (b) We specify the configuration of the carbon stereocenter *after* that of the metal stereocenter.

(3) Diastereomers can also interconvert by pathways involving inversion of configuration of the chiral metal fragment (see Scheme V). However, configurationally labile metal complexes are not commonly employed in asymmetric synthesis.

(4) (a) Ford, W. T.; Cram, D. J. *J. Am. Chem. Soc.* **1968**, *90*, 2606, 2612. (b) Chu, K. C.; Cram, D. J. *Ibid.* **1972**, *94*, 3521. (c) Reissig, H.-U.; Huisgen, R. *Ibid.* **1979**, *101*, 3648.

(5) (a) Bodner, G. S.; Fernández, J. M.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 4082. (b) Bodner, G. S.; Peng, T.-S.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1191.

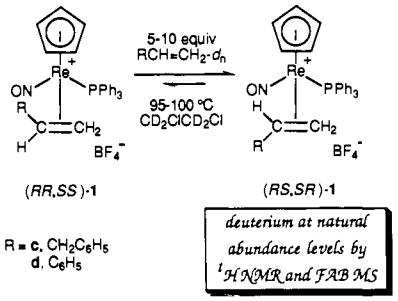
(6) Peng, T.-S.; Arif, A. M.; Gladysz, J. A. *Helv. Chim. Acta* **1992**, *75*, 442.

(7) Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4958.

(8) Kowalczyk, J. J.; Arif, A. M.; Gladysz, J. A. *Chem. Ber.* **1991**, *124*, 729.

(9) Peng, T.-S.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1990**, 902.

Scheme IV. Equilibration of (*RR,SS*)/(*RS,SR*)-**1** in the Presence of Deuterated Alkenes



isomerizations were monitored by NMR spectroscopy. Importantly, each diastereomer generally exhibits distinct cyclopentadienyl, vinyl, and allylic proton ^{1}H NMR resonances.[5b] The resulting crude rate data are summarized in Table I. If, for example, a phenyl C=C substituent were to provide a unique equilibration pathway (see below), this might be suggested by a rate acceleration relative to aliphatic alkene complexes. However, the styrene complex **1d** does not isomerize at a faster rate than propene, 1-pentene, and allylbenzene complexes **1a–c**.

Similarly, alkene complexes that bear allylic protons isomerize at rates comparable to those that lack allylic protons (**1a–c** vs **1d**; **1e** vs **1g**). Only for isopropylethylene and (trimethylsilyl)ethylene complexes **1e,g**, which have the bulkiest substituents and exhibit the greatest K_{eq}, are enhanced rates observed. These data are consistent with, but by no means require, a unified, substituent-independent, equilibration mechanism.

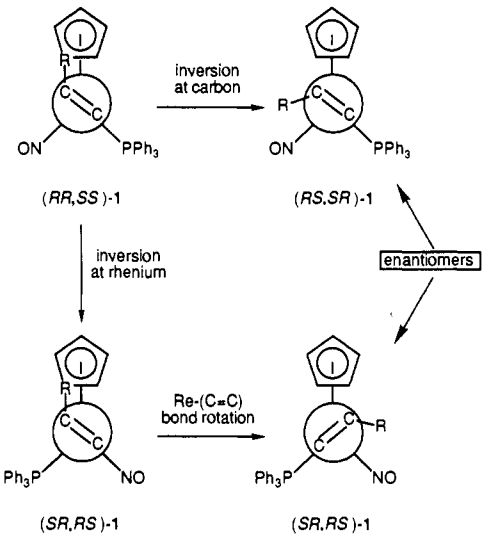
2. Isomerization Occurs without Alkene Dissociation. Next, complexes **1** were equilibrated in the presence of deuterated alkenes, as shown in Scheme IV. First, a (68 ± 2):(32 ± 2) mixture of allylbenzene complexes (*RS,SR*)/(*RR,SS*)-**1c** (ca. 0.1 M, CD_2ClCD_2Cl) was treated with 5 equiv of allylbenzene-d_2, $C_6H_5CD_2CH{=}CH_2$. The sample was kept at 95 °C for 20 h, and a (95 ± 2):(5 ± 2) (*RS,SR*)/(*RR,SS*)-**1c** mixture formed. No deuterium was incorporated, as assayed by careful ^{1}H NMR analysis of the well-resolved allylic protons. The sample was kept at 95 °C for another 68 h, and analogous experiments were conducted in C_6D_5Cl (95 °C, 72 h) and acetone-d_6 (80 °C, 135 h). In no case was evidence for an allylbenzene-d_2 ligand found.

We sought to conduct similar experiments that would have enhanced detection limits. Thus, the diastereomerically pure styrene complex (*RR,SS*)-**1d** (ca. 0.02 M, CD_2ClCD_2Cl) was treated with 10 equiv of styrene-d_8, $C_6D_5CD{=}CD_2$ (Scheme IV). The sample was kept at 100 °C for 11 h, and a (79 ± 2):(21 ± 2) (*RS,SR*)/(*RR,SS*)-**1d** mixture formed. No deuterium was incorporated, as assayed by ^{1}H NMR analysis of the well-resolved vinylic protons. The sample was kept at 100 °C for another 37 h. A (89 ± 2):(11 ± 2) (*RS,SR*)/(*RR,SS*)-**1d** mixture formed, which was subsequently isolated in >99% yield. A FAB mass spectrum showed deuterium to be present at the natural abundance level.

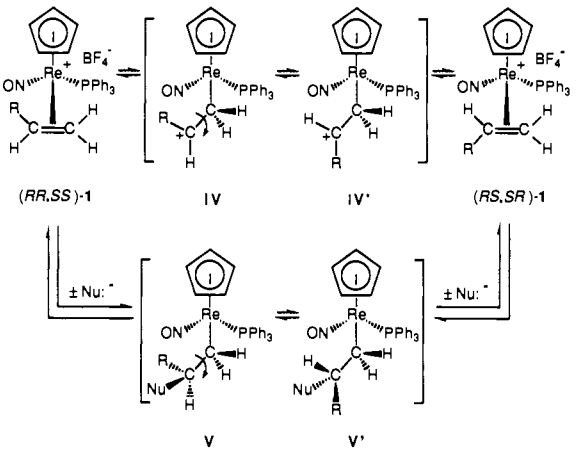
A comparable experiment was conducted at 100 °C in the more polar solvent, CD_3CN. After 48 h, a (90 ± 2):(10 ± 2) (*RS,SR*)/(*RR,SS*)-**1d** mixture had formed. Also, ca. 2% of the previously characterized substitution product $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCCD_3)]^+BF_4^-$ was present.[10] No deuterium was incorporated into **1d**, as assayed by ^{1}H NMR and mass spectrometry. Thus, based upon the preceding experiments, we conclude that the equilibration of the diastereomeric alkene complexes (*RS,SR*)/(*RR,SS*)-**1** occurs without alkene ligand dissociation.

Finally, a $CDCl_2CDCl_2$ solution of (*RS,SR*)-**1d** and 10 equiv of styrene-d_8 was kept at 130 °C for 12 h and then 150 °C for 6 h. No substitution occurred, as assayed by ^{1}H NMR and mass spectrometry. Although the lowest energy substitution pathway could be either associative or dissociative, this experiment establishes a strikingly high lower bound on the temperature regime for styrene ligand dissociation.

Scheme V. Interconversion of Diastereomers of **1**; Possible Configurational Processes at Carbon and Rhenium



Scheme VI. Interconversion of Diastereomers of **1**; Possible Carbocation and Nucleophilic Addition Mechanisms



3. Isomerization Occurs with Retention at Rhenium and without Phosphine Dissociation. From the data presented above, diastereomers of **1** could in principle interconvert by inversion at either carbon *or* rhenium. The distinction between these two pathways is diagrammed in Scheme V. We have previously described the synthesis of alkene complexes **1** in optically active form and by a route that allows the assignment of absolute configuration.[5b] Also, the enantiomers of each diastereomer can generally be differentiated by the chiral NMR shift reagent (+)-Eu(hfc)$_3$.[5b]

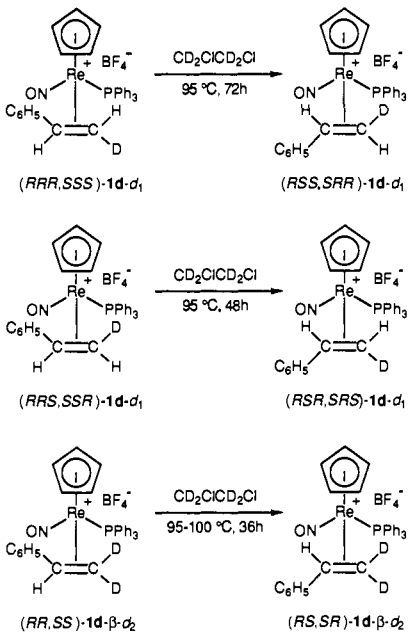
Accordingly, the optically active styrene complex[2b,5b] (−)-(*SS*)-**1d** (>98% ee) was kept in C_6D_5Cl at 95 °C for 72 h. Isomerization to a (84 ± 2):(16 ± 2) mixture of diastereomers occurred. Addition of (+)-Eu(hfc)$_3$ and ^{1}H NMR analysis showed these to be the previously characterized complex (−)-(*SR*)-**1d**[5b] and the reactant (−)-(*SS*)-**1d**, respectively. Each was of >98% ee. Thus, isomerization occurs with retention at rhenium and inversion at carbon.

It has been shown earlier that the equilibration of diastereomeric amido complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NHCHRR')$ and alkoxide complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OCHRR')$ involves initial PPh_3 ligand dissociation.[11] Thus, the isomerization of styrene complex (*RR,SS*)-**1d** was repeated in the presence of PPh_3-d_{15} (2 equiv). After 10 h at 95 °C in CD_2ClCD_2Cl, a (55 ± 2):(45 ± 2) (*RS,SR*)/(*RR,SS*)-**1d** mixture had formed.

(10) Fernández, J. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207.

(11) (a) Dewey, M. A.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1351. (b) Saura-Llamas, I.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 2136.

Scheme VII. Interconversion of Deuterated Styrene Complexes **1d**-d_n



Analysis by mass spectrometry showed the absence of any PPh_3-d_{15} incorporation.

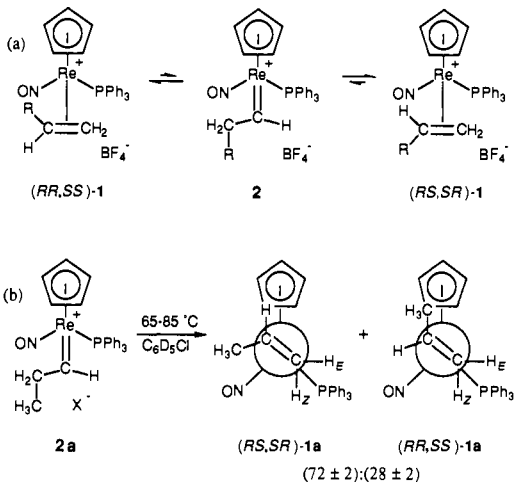
4. Isomerization Occurs by Exchange of the Alkene Enantioface. Might the isomerization of **1** occur by a simple rotation of the =CHR terminus? This interesting possibility is consistent with all data above, and several variants can be envisioned. For example, the alkene ligand could "slip"[12] to give an alkyl complex with a C_β carbocation, as illustrated by **IV** in Scheme VI. Subsequent rotation about the C_α–C_β bond and recoordination of C_β would consummate diastereomer interconversion. Alternatively, coordinated alkenes are activated toward nucleophilic attack,[12] and alkyl cuprates readily add to **1**.[13] Thus, diastereomers might interconvert by the two-step addition/elimination process shown in Scheme VI. The BF_4^- counteranion and solvent constitute potential nucleophiles.

Importantly, any cis or trans C=C substituents would be scrambled by these pathways. Thus, the labeled styrene ligands (*E*)-$C_6H_5CH{=}CHD$ and (*Z*)-$C_6H_5CH{=}CHD$ were prepared and converted to the corresponding complexes **1d**-d_1. Diastereomers were separated chromatographically as previously described.[5b] The deuterated carbon constitutes a third stereocenter. Thus, the (*E*)-diastereomers can be designated as (*RSS*,*SRR*)-**1d**-d_1 or (*E*)-(*RS*,*SR*)-**1d**-d_1 (more stable) and (*RRR*,*SSS*)-**1d**-d_1 *or* (*E*)-(*RR*,*SS*)-**1d**-d_1 (less stable).

The *E* diastereomer (*RRR*,*SSS*)-**1d**-d_1 was kept in CD_2ClCD_2Cl at 95 °C for 72 h (Scheme VII). A (89 ± 2):(11 ± 2) mixture of diastereomers formed. The major diastereomer was isolated, and a ^1H NMR spectrum showed that the deuterium remained trans to the phenyl group, indicative of (*RSS*,*SRR*)-**1d**-d_1. An analogous result was obtained with the *Z* diastereomer (*RRS*,*SSR*)-**1d**-d_1 (Scheme VII). Thus, isomerization involves exchange of the entire alkene enantioface bound to rhenium, and not just the =CHR terminus.

5. Isomerization Does Not Involve Alkylidene Intermediates. Alkylidene complexes of the formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH_2R)]^+X^-$ (**2**) are easily prepared and undergo 1,2-hydrogen shifts at 65–85 °C to give alkene complexes **1**.[14] Thus, the microscopic reverse provides another pathway for the isomerization of **1**, as sketched in Scheme VIIIa. Importantly, rearrangements of deuterated propylidene complexes **2a**-d_n have been studied. The data, which are summarized in Scheme VIIIb, show that the hydrogen shift is not stereoselective at the migration terminus.

Scheme VIII. Interconversion of Diastereomers of **1**; Data on Potential Alkylidene Intermediates: (a) Possible Mechanism; (b) Deuterium Labeling Experiments



deuterium in reactant[a]	deuterium in H_Z, H_E of product	
D_α (Re=CDCH$_2$CH$_3$)	40 ± 3 % H_Z 60 ± 3 % H_E	44 ± 3 % H_Z 56 ± 3 % H_E
2 D_β (Re=CHCD$_2$CH$_3$)	53 ± 3 % H_Z 47 ± 3 % H_E	40 ± 3 % H_Z 60 ± 3 % H_E

[a] data from reference 14

Table II. Rates of Isomerization of Styrene Complexes (*RR*,*SS*)-**1d**-d_n to (*RS*,*SR*)-**1d**-d_n (ca. 0.003 M, CD_2ClCD_2Cl)

compd	temp, °C	10^5k_1,[a] s^{-1}
(*RR*,*SS*)-**1d**	106.4	7.66 ± 0.18
	101.3	4.70 ± 0.03
	96.5	2.77 ± 0.01
	96.5	2.46 ± 0.03[b]
	91.5	1.50 ± 0.01
	86.6	0.94 ± 0.01
$\Delta H^\ddagger$ = 28.6 ± 0.7 kcal/mol; $\Delta S^\ddagger$ = 2.1 ± 2.0 eu		
(*RRR*,*SSS*)-**1d**-d_1	96.5	1.69 ± 0.02
(*RRS*,*SSR*)-**1d**-d_1	96.5	2.58 ± 0.01
(*RR*,*SS*)-**1d**-α-d_1	96.5	2.40 ± 0.02
$k(H)/k(=CHD_E)$ = 1.64; $k(H)/k(=CHD_Z)$ = 1.07; $k(H)/k(=CDC_6H_5)$ = 1.15		

[a] See footnote 15 for data on error limits; these do not reflect the temperature uncertainty. [b] This experiment was conducted in the presence of 0.5 equiv of Et_3N.

If Scheme VIIIa were operative, one or both of the (*E*)- and (*Z*)-styrene-d_1 complexes, (*RRR*,*SSS*)-**1d**-d_1 and (*RRS*,*SSR*)-**1d**-d_1 (Scheme VII), would give an alkylidene complex, $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CDCH_2C_6H_5)]^+BF_4^-$, which is deuterated at C_α. However, Scheme VIIIb shows that a C_α deuterium label is scrambled into *both* $=CH_2$ positions of *both* diastereomers of **1**. Hence, an alkylidene mechanism is inconsistent with the fidelity of the *E*/*Z* deuterium labels maintained in Scheme VII.

As a further probe, the dideuterated styrene ligand $C_6H_5CH{=}CD_2$ was prepared and converted to the corresponding complex **1d**-β-d_2. A CH_2ClCH_2Cl solution of (*RR*,*SS*)-**1d**-β-d_2 was kept at 95–100 °C for 36 h (Scheme VII). A (88 ± 2):(12 ± 2) mixture of (*RS*,*SR*)/(*RR*,*SS*)-**1d**-β-d_2 formed. Subsequent ^1H and ^2H NMR analysis showed that both $=CD_2$ positions retained their original deuterium level, with no leakage into the =CHR terminus.

6. Activation Parameters and Kinetic Isotope Effects. The rate of isomerization of (*RR*,*SS*)-**1d** to (*RS*,*SR*)-**1d** was monitored

(12) (a) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308. (b) Cameron, A. D.; Smith, V. H., Jr.; Baird, M. C. *J. Chem. Soc., Dalton Trans.* **1988**, 1037.

(13) Peng, T.-S.; Gladysz, J. A. *Tetrahedron Lett.* **1990**, *31*, 4417.

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

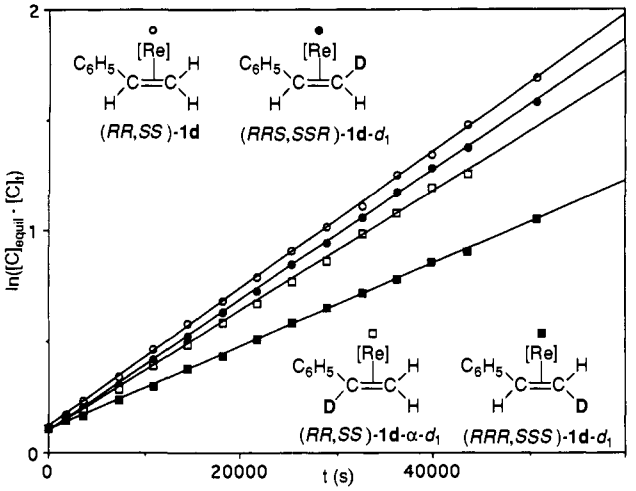
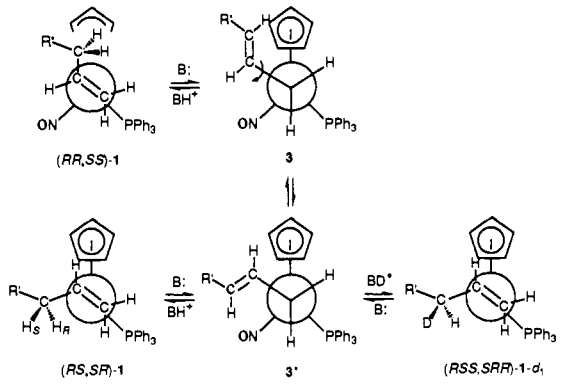


Figure 1. Representative rate data for the isomerization of (*RR*,*SS*)-**1d**-d_n to (*RS*,*SR*)-**1d**-d_n (CD_2ClCD_2Cl, 96.5 °C).

Scheme IX. Interconversion of Diastereomers of **1**; Possible Base-Catalyzed Isomerization Pathway



by ^1H NMR spectroscopy through 80% conversion at 86.6 to 106.4 °C. The approach to equilibrium was first order, as indicated by linear plots of ln ($[C]_{equil} - [C]_t$) vs time.[15] These data gave the forward rate constants (k_1) summarized in Table II. An Eyring plot gave $\Delta H^{\ddagger} = 29 \pm 1$ kcal/mol and $\Delta S^{\ddagger} = 2 \pm 2$ eu.[16]

Next, the rates of isomerization of the (*E*)-styrene-d_1 complex (*RRR*,*SSS*)-**1d**-d_1, the (*Z*)-styrene-d_1 complex (*RRS*,*SSR*)-**1d**-d_1, and the α-styrene-d_1 complex (*RR*,*SS*)-[(η^5-C_5H_5)Re(NO)(PPh$_3$)(H_2C=CDC_6H_5)]$^+BF_4^-$ ((*RR*,*SS*)-**1d**-α-d_1) were similarly monitored at 96.5 °C. These data gave a $k(H)/k(=CHD_E)$ of 1.64, a $k(H)/k(=CHD_Z)$ of 1.07, and a $k(H)/k(=CDC_6H_5)$ of 1.15. Representative plots are given in Figure 1. Also, added triethylamine had no effect upon the rate of isomerization of (*RR*,*SS*)-**1d** (96.5 °C; see below).

7. Base-Promoted Isomerization. Alkene complexes **1** that bear allylic protons react, under appropriate conditions, with K^+ *t*-BuO^- to give neutral σ allyl complexes (η^5-C_5H_5)Re(NO)(PPh$_3$)(CH_2CH=CHR) (**3**).[17] This suggests that the isomerization of **1** might be promoted by base, as sketched in Scheme IX. The initially formed σ allyl complex must undergo rotation about the C_α–C_β bond (**3** ⇄ **3'**)—a process documented to be exceedingly facile.[17] Reprotonation would give isomerized **1**. Since this amounts to a net rotation of the =CHR terminus, any *Z*/*E* deuterium labels would be scrambled.

Table III. Rates of Isomerization of Allylbenzene Complex (*RR*,*SS*)-**1c** to (*RS*,*SR*)-**1c** in CD_2ClCD_2Cl (0.02 M)

entry	temp, °C	base (equiv)	half-life	10^5k_1, s^{-1}
1	94.5		5.6 h	3.46 ± 0.02
2	94.5	Et_3N (1.00)	<10 min	138 ± 2
3	70.2		>100 h	
4	70.2	Et_3N (0.50)	4.0 h	4.85 ± 0.05
5	70.2	Et_3N (0.75)	35 min	32.2 ± 0.3
6	70.2	Et_3N (1.0)	25 min	47.5 ± 0.2
7	70.2	pyridine (1.0)	≃50 h	

Of the compounds in Scheme III, allylbenzene complex (*RR*,*SS*)-**1c** should have the most acidic allylic protons. Thus, (*RR*,*SS*)-**1c** was treated with 1.0 equiv of triethylamine in CD_2ClCD_2Cl. The sample was kept at 70 °C and monitored by ^1H NMR spectroscopy. Isomerization occurred over the course of 3 h to give a (98 ± 1):(2 ± 1) (*RS*,*SR*)/(*RR*,*SS*) mixture. The forward rate constant, k_1 (entry 6, Table III), was calculated as described above. A small cyclopentadienyl resonance at δ 4.95 was attributed to the previously characterized[17] cinnamyl complex (η^5-C_5H_5)Re(NO)(PPh$_3$)(CH_2CH=CHC_6H_5) (**3c**, 4%). A side-by-side reaction was conducted without triethylamine. After 15 h, only a (7 ± 2):(93 ± 2) (*RS*,*SR*)/(*RR*,*SS*) mixture had formed.

Parallel experiments were conducted at 95 °C, as summarized in entries 1 and 2 of Table III. Isomerization proceeded 40 times faster in the presence of triethylamine. Also, rates were measured at 70 °C with 0.75 and 0.50 equiv of triethylamine (entries 4 and 5). Although k_1 values decreased, these substoichiometric reactions established the operation of catalysis. When pyridine (pK_{BH^+} 5.2) was substituted for triethylamine (pK_{BH^+} 10.7), rates were barely faster than in the absence of added base.

One consequence of the mechanism in Scheme IX would be the potential for deuterium incorporation. Thus, (*RR*,*SS*)-**1c** and 1.0 equiv of triethylamine were reacted in acetone-d_6, a solvent prone to hydrogen/deuterium exchange. The sample was kept at 70 °C, and the integrals of the allylic protons in the product (*RS*,*SR*)-**1c** were monitored relative to that of the =CHR proton. Data are summarized in Table IV. Importantly, deuterium was incorporated into both diastereotopic allylic positions. One proton exchanged more rapidly than the other.[18]

Similar results were obtained in experiments starting with the more stable diastereomer (*RS*,*SR*)-**1c**. However, no deuterium was incorporated when the isomerization of (*RR*,*SS*)-**1c** was conducted at 90 °C in the *absence* of triethylamine. Thus, it is unlikely that the isomerization of (*RR*,*SS*)-**1c** in the absence of base proceeds via the spontaneous loss of an allylic proton to give HBF_4 and the cinnamyl complex **3c**.

Discussion

1. Dissociative vs Nondissociative Isomerization. Many complexes of monosubstituted alkenes and chiral transition-metal fragments have been reported in the literature.[19,20] In several

(15) (a) Capellos, C.; Bielski, B. H. J. *Kinetic Systems*; Wiley: New York, 1972; Chapter 8. (b) The linearity of ln ($[C]_{equil} - [C]_t$) vs time plots is sensitive to the value of $[C]_{equil}$ (or K_{eq}) and provides a check of these data. The program CONINFIN gave the best fit with a 89.3:10.7 (*RS*,*SR*)/(*RR*,*SS*) equilibrium ratio (101.3 °C), in good agreement with earlier data.[6] This value was used to calculate forward rate constants (k_1) from the slopes ($k_1 + k_{-1}$). (c) Error limits on rate constants represent standard deviations on the slopes of ln ($[C]_{equil} - [C]_t$) vs time plots.

(16) Standard deviations for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values were estimated according to: Wiberg, K. B. *Physical Organic Chemistry*; Wiley: New York, 1964; pp 378–379.

(17) Bodner, G. S.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *Organometallics* **1989**, *8*, 2399.

(18) On the basis of ^1H NMR assignments made earlier,[5b] deuterium is more rapidly incorporated into the H_S allylic position, as sketched in Scheme IX. Preferential electrophilic attack upon the C_β=C_γ face that is anti to the metal has been established with related iron allyl complexes: Rosenblum, M. *J. Organomet. Chem.* **1986**, *300*, 191.

(19) These compounds, and K_{eq} data, are surveyed in ref 6. Lead references: (a) (η^5-C_5H_5)Mo(NO)(CO)(H_2C=CHR): Faller, J. W.; Lambert, C.; Mazzieri, M. R. *J. Organomet. Chem.* **1990**, *383*, 161. (b) (η^5-C_5H_5)Ru(L)(L')(H_2C=CHR): Consiglio, G.; Pregosin, P.; Morandini, F. *J. Organomet. Chem.* **1986**, *308*, 345. (c) [(η^5-C_5H_5)Fe(CO)(PPh$_3$)(H_2C=CHR)]$^+X^-$: Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258. (d) Pt(II) complexes: Erickson, L. E.; Jones, G. S.; Blanchard, J. L.; Ahmed, K. J. *Inorg. Chem.* **1991**, *30*, 3147.

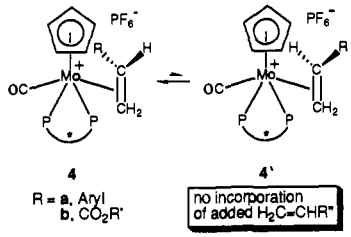
(20) (a) Kegley, S. E.; Bergstrom, D. T.; Crocker, L. S.; Weiss, E. P.; Berndt, W. G.; Rheingold, A. L. *Organometallics* **1991**, *10*, 567. (b) Kegley, S. E.; Walter, K. A.; Bergstrom, D. T.; Putnam, P. J.; MacFarland, D. K.; Young, B. Y.; Rheingold, A. L., manuscript in preparation.

Table IV. Isomerization of Allylbenzene Complex **1c** in Acetone-d_6 (0.02 M); Deuterium Incorporation Data

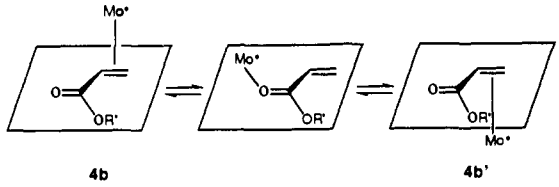
substrate	temp, °C	Et_3N	t, h	(*RS,SR*)/(*RR,SS*)	% protium[a] =CHR	=CHCHH′	=CHCHH′
(*RR,SS*)-**1c**	70	1 equiv	11	92:8	100	85	65
			48	97:3	100	73	19
			120	97:3	100	60	8
(*RS,SR*)-**1c**	70	1 equiv	11	97:3	100	93	94
			48	95:5	100	65	17
			120	95:5	100	60	5
(*RR,SS*)-**1c**	90		48	85:15	100	105	105
			120	95:5	100	104	104

[a] Integrals of ^1H NMR resonances of (*RS,SR*)-**1c**; chemical shifts: δ 4.74 (=CHR), 3.55 (=CHCHH′), 3.04 (=CHCHH′).[5b]

Scheme X. Intramolecular Isomerization of Diastereomeric Molybdenum Alkene Complexes



proposed via following pathway (R = CO_2R'):

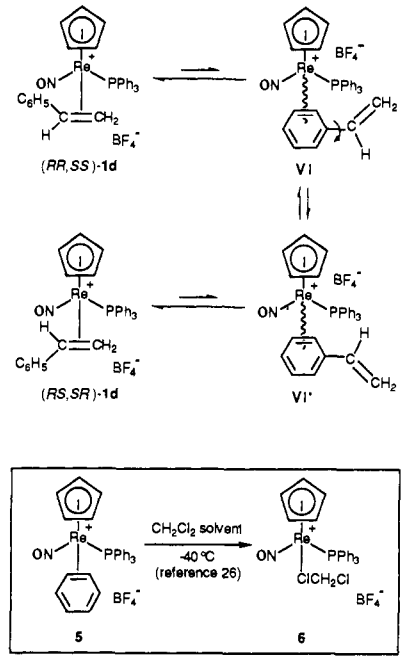


cases, diastereomers of the types **A** and **B** (Scheme I) have been observed to interconvert. However, few tests of whether such processes are dissociative or nondissociative have been conducted.[20,21] In important recent work, Kegley has shown that styrenes and acrylate esters can bind to molybdenum fragments to the formulae $[(\eta^5\text{-}C_5H_5)Mo(CO)(PR_2CH_2)_2]^+$ (**4**) with high thermodynamic selectivities (Scheme X) and that diastereomers equilibrate by a nondissociative mechanism.[20]

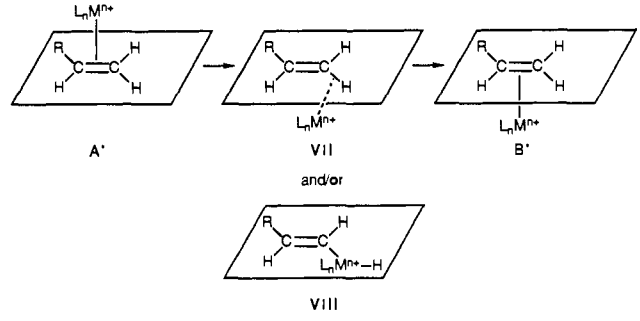
However, the exact mechanism followed should be highly dependent upon the transition metal fragment. For example, coordinatively unsaturated reaction intermediates appear to be much more accessible with first-row metals than third-row metals. Norton has established that reductive eliminations from osmium complexes $(CO)_4Os(X)(Y)$ follow binuclear pathways that have no counterpart in iron chemistry, thus avoiding the 16-valence-electron species $(CO)_4Os$.[22] We find, in all cases examined to date, that substitution reactions of cationic rhenium complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(L)]^+X^-$ are associative.[23,24] Also, Casey has documented some novel multistep rearrangements of cyclopentadienyl rhenium complexes, the intricacy of which circumvents intermediates with vacant coordination sites.[25]

2. "Conducted Tour" Isomerization. Although the above data exclude a variety of nondissociative isomerization mechanisms for **I** (Schemes VI and VIII), one possibility merits further analysis. Specifically, a C=C substituent such as a phenyl ring or heteroatom might mediate isomerization by providing a "relay"

Scheme XI. Interconversion of Diastereomers of Styrene Complex **1d**; A Possible "Conducted Tour" Mechanism



Scheme XII. Interconversion of Diastereomers of Alkene Complexes; Possible "σ Bond Complex" and Oxidative Addition Mechanism



binding site—a motif frequently referred to as a "conducted tour" process.[4] For example, the styrene complex (*RR,SS*)-**1d** could initially isomerize to the η^2-arene complex **VI** shown in Scheme XI. Subsequent rotation about the aryl–vinyl carbon–carbon bond, and a return of rhenium to the alkene moiety, would afford (*RS,SR*)-**1d**.

However, several observations argue against phenyl ring participation in the isomerization of (*RR,SS*)-**1d**. First, isomerization occurs at about the same rate as the other alkene complexes (Table I). Second, the sizable $k(H)/k(=CHD_E)$ of 1.64 (Table II) would not be accounted for. Third, the η^2-benzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}C_6H_6)]^+BF_4^-$ (**5**) has been independently generated[26] and undergoes rapid substitution at −40 °C by the

(21) However, some elegant mechanistic studies have established nondissociative exo/endo isomerization in cases where the metal fragment is achiral: (a) McNally, J. P.; Cooper, N. J. *Organometallics* **1988**, *7*, 1704. (b) Bercaw, J. E.; Burger, B. J.; Green, M. L. H.; Santarsiero, B. D.; Sella, A.; Trimmer, M. S.; Wong, L.-L. *J. Chem. Soc., Chem. Commun.* **1989**, 734.

(22) Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139.

(23) Liu, Y.; Garner, C. M., unpublished data, University of Utah.

(24) Substitution reactions of $M(CO)_5(THF)$ become progressively more associative in the series Cr, Mo, W: Wieland, S.; van Eldik, R. *Organometallics* **1991**, *10*, 3110.

(25) Casey, C. P.; Vosejpka, P. C.; Gavney, J. A., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 4083.

(26) Agbossou, S. K.; Bodner, G. S.; Patton, A. T.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1184.

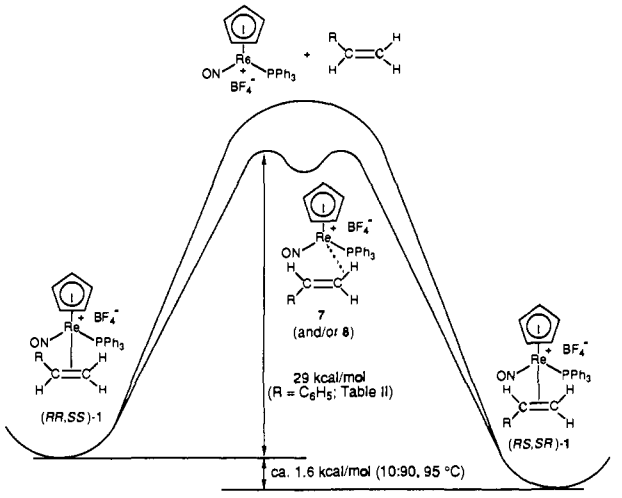


Figure 2. Energy/reaction coordinate diagram for the dissociative and nondissociative isomerization of **1**.

weak donor ligand dichloromethane to give $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**6**) as shown in Scheme XI. Thus, considerable styrene ligand displacement would occur under the isomerization conditions, especially in the strong donor solvent acetonitrile (observed: ca. 2%).

Nonetheless, we believe there is an excellent chance that conducted tour mechanisms may operate with other classes of alkene ligands, or in other complexes. For example, Kegley has proposed that the molybdenum acrylate complexes **4b** shown in Scheme X equilibrate via migration of the molybdenum to the carbonyl oxygen.[20] Alkene complexes with halide, alkoxy, and amide substituents could logically isomerize by similar pathways.

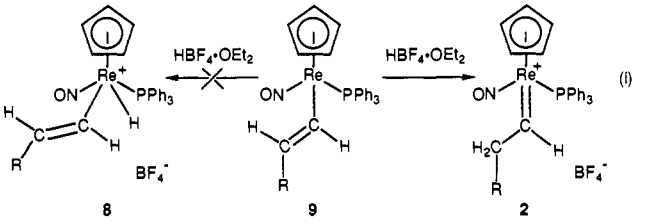
3. Carbon–Hydrogen "σ Bond Complex" vs Oxidative Addition. We are able to identify two isomerization mechanisms that remain viable after the preceding analysis. As sketched in Scheme XII, one involves moving the rhenium through the alkene π nodal plane via a carbon–hydrogen "σ bond complex" (**VII**). The other entails a formal oxidative addition to give a vinyl hydride complex (**VIII**). In either case, we presume that the alkene hydrogen that gives the largest kinetic deuterium isotope effect, H_E (Table II), is involved. Each mechanism will be considered in turn.

Many carbon–hydrogen σ bond complexes have now been characterized.[27-29] Those that are isolable are generally part of a chelate with a stronger donor group ("agostic" complexes). However, monodentate species have been detected by a variety of techniques, and several distinct bonding geometries have been suggested.[28,29] Hence, **VII** should be viewed as a "generic" structure. Also, bond strengths have been estimated as ca. 10 kcal/mol. Thus, a σ bond complex can appreciably stabilize the transition state for nondissociative isomerization relative to that of dissociative isomerization, as sketched in Figure 2.

Alternatively, a vinyl hydride complex could serve as the energy minimum in Figure 2. Another possibility is that a σ bond complex subsequently rearranges to a vinyl hydride complex, placing additional minima on the reaction coordinate. Kafafi and Margrave have observed the photochemical conversion of matrix-generated iron/ethylene σ bond complexes to vinyl hydride complexes.[29] Norton and Bercaw have shown that the thermal reductive elimination of methane from tungsten methyl hydride complexes involves initial formation of tungsten/methane σ bond complexes.[30,31] Thus, oxidative additions to carbon–hydrogen bonds are likely to frequently involve σ bond complexes.

However, the formation of vinyl hydride complex **VIII** from σ bond complex **VII** would not necessarily be productive for isomerization. For example, if **VII** has the metal in the π nodal plane as depicted, oxidative addition would not be required to transport the metal between alkene enantiofaces. Alternatively, σ bond complexes with the metal slightly removed from the π nodal plane could be considered.

In principle, vinyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH{=}CHR)$ (**9**) and $HBF_4{\cdot}OEt_2$ might react to give vinyl hydride complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H)(CH{=}CHR)]^+BF_4^-$ (**8**). An authentic sample of **8** would allow several tests of its intermediacy in Figure 2. However, as shown in eq i, carbon pro-



(i)

tonation occurs instead to give alkylidene complexes **2**.[32] We had expected that **8** would be rapidly deprotonated to **9** by triethylamine and susceptible to rearrangement and other trapping reactions. Significantly, the isomerization of styrene complex (*RR,SS*)-**1d** is unaffected by added triethylamine (Table II).

4. Precedents from Related Chemistry. The involvement of σ bond complexes in metal alkene chemistry has been considered in several additional contexts. For example, reactions of coordinatively unsaturated metal fragments with alkenes can give either π complexes or vinyl hydride oxidative addition products.[33] Bergman has studied the reaction of the thermally generated iridium species $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)$ and ethylene in detail.[33] He has obtained good evidence that σ bond complexes are precursors to the vinyl hydride complex $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(H)(CH{=}CH_2)$, and likely the ethylene complex $(\eta^5\text{-}C_5Me_5)Ir(PMe_3)(H_2C{=}CH_2)$ as well. His data bound k_H/k_D (145 °C) for the formation of a σ bond complex from *free* ethylene as between 1.16 and 1.49.

Photochemical and thermal rearrangements of alkene complexes to vinyl hydride complexes have also been observed.[34] Matrix and NMR studies by Perutz have similarly provided evidence for intermediate σ bond complexes, or solvent-caged alternatives. A mechanism involving a simple rotation of a nondissociable solvent-caged alkene might be considered for the isomerization of **1**. However, this would not account for the magnitude of $k(H)/k(=CHD_E)$ (1.64). Other arguments have been made against solvent-caged species as alternatives to σ bond complexes for related reactions.[31]

Ideally, our kinetic deuterium isotope effects should be compared to those for (1) the formation of σ bond complexes from *coordinated* alkenes and (2) oxidative additions of carbon–hydrogen bonds of coordinated alkenes. In all cases, transition states would be markedly bent. Data for the first type of isotope effect do not appear to be available. However, appreciable *equilibrium* deuterium isotope effects have been observed in agostic σ bond complexes.[27] From vibrational zero-point energy considerations, and the product-like nature of the transition state leading to **7**

(27) (a) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1. (b) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299. (c) Zhang, K.; Gonzalez, A. A.; Mukerjee, S. L.; Chou, S.-J.; Hoff, C. D.; Kubat-Martin, K. A.; Barnhart, D.; Kubas, G. J. *J. Am. Chem. Soc.* **1991**, *113*, 9170.

(28) (a) O'Driscoll, E.; Simon, J. D. *J. Am. Chem. Soc.* **1990**, *112*, 6580 and references therein. (b) Brown, C. E.; Ishikawa, Y.-I.; Hackett, P. A.; Rayner, D. M. *Ibid.* **1990**, *112*, 2530. (c) Morse, J. M., Jr.; Parker, G. H.; Burkey, T. J. *Organometallics* **1989**, *8*, 2471. (d) Sprague, J. R.; Arrivo, S. M.; Spears, K. G. *J. Phys. Chem.* **1991**, *95*, 10528. (e) Dobson, G. R.; Asali, K. J.; Cate, C. D.; Cate, C. W. *Inorg. Chem.* **1991**, *30*, 4471. (f) Wasserman, E. P.; Moore, C. B.; Bergman, R. G. *Science* **1992**, *255*, 315.

(29) Kafafi, Z. H.; Hauge, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 7550.

(30) (a) Bullock, R. M.; Headford, C. E. L.; Hennessy, K. M.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 3897. (b) Parkin, G.; Bercaw, J. E. *Organometallics* **1989**, *8*, 1172.

(31) For related processes that involve σ bond complexes, see: Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332.

(32) Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P. C.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7688.

(33) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732.

(34) Bell, T. W.; Haddleton, D. M.; McCamley, A.; Partridge, M. G.; Perutz, R. N.; Willner, H. *J. Am. Chem. Soc.* **1990**, *112*, 9212 and references therein.

in Figure 2, our $k(H)/k(=CHD_E)$ of 1.64 appears fully consistent with a σ bond complex mechanism.

To our knowledge, the best model for the second type of kinetic isotope effect has been reported by Jones and Feher.[35] They measured a k_H/k_D (−40 °C) of 1.4 for the conversion of a rhodium η^2-arene complex (1,3,5-trideuteriobenzene) to an aryl hydride complex.[35] Thus, our $k(H)/k(=CHD_E)$ value, which would be even greater at −40 °C, is also consistent with an oxidative addition transition state. However, the possibility appears to remain that the rhodium-based isotope effect might reflect the rate-determining formation of a σ bond complex. This ambiguity would also arise with analogous kinetic isotope effects derived from alkene complexes.

Obviously, the mechanism of isomerization of alkene complexes **1** can be further probed by experiments with related substrates. In work to date,[36] we find that diastereomers of the corresponding trans alkene complexes equilibrate with comparable facility. Thus, a hydrogen atom *E* to the alkene substituent is not required. We have also shown that analogous diastereomeric π aldehyde complexes interconvert via intermediate σ complexes.[37] A strong conceptual relationship between this process and the σ bond complex mechanism sketched in Scheme XII and Figure 2 is evident.

5. Summary. A heretofore unanticipated reaction of alkene complexes—nondissociative exchange of the C=C enantioface bound to the metal—has been discovered. The detection and study of this process was facilitated by the chirality of the rhenium fragment **I**. Other alkene complexes are likely to exhibit similar thermal behavior. However, in many cases this will be invisible to conventional spectroscopic probes. For example, when the metal fragment is achiral, enantioface exchange interconverts enantiomers as opposed to diastereomers.

We suggest that the metal traverses through the alkene π nodal plane via a carbon–hydrogen σ bond complex. However, an alternative oxidation addition pathway has not been rigorously excluded. Regardless, this process constitutes an important conceptual link to alkene complexation and carbon–hydrogen bond activation reactions described by others.[33-35] Another unusual reaction involving the vinylic carbon–hydrogen bonds of alkene complexes **1** will be described in a subsequent paper.[38]

Experimental Section

General Data. General procedures were identical with those described in the previous paper,[6] and additional data are provided in the supplementary material. $CDCl_2CDCl_2$ (Cambridge Isotopes), styrene-d_8, (+)-Eu(hfc)$_3$, and PPh_3-d_{15} (Aldrich) were used as received.

Isomerization of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH_2C_6H_5)]^+BF_4^-$ (1c) in the Presence of $C_6H_5CD_2CH{=}CH_2$. The following experiment is representative. A 5-mm NMR tube was charged with a (68 ± 2):(32 ± 2) (*RS,SR*)/(*RR,SS*)-**1c** mixture (18.7 mg, 0.025 mmol),[5,6] CD_2ClCD_2Cl (0.25 mL), and $C_6H_5CD_2CH{=}CH_2$ (0.017 mL, 0.125 mmol) and capped with a septum. The sample was freeze–pump–thaw degassed and transferred to a 95 °C bath. After 20 h, a ^{1}H NMR spectrum showed a (95 ± 2):(5 ± 2) (*RS,SR*)/(*RR,SS*)-**1c** mixture, as assayed by integration of the cyclopentadienyl resonances. The integrals of the allylic and vinylic protons were within 5% of theory. The sample was kept at 95 °C for another 88 h. Subsequent ^{1}H NMR spectra were unchanged.

Isomerization of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHC_6H_5)]^+BF_4^-$ (1d) in the Presence of Styrene-d_8. A. Complex (*RR,SS*)-**1d** (0.007 g, 0.010 mmol),[5b] CD_2ClCD_2Cl (0.50 mL), and styrene-d_8 (13 μL, 0.100 mmol) were combined in a 5-mm NMR tube as above. The sample was transferred to a 100 °C probe and monitored by ^{1}H NMR spectroscopy. After 48 h, a (89 ± 2):(11 ± 2) (*RS,SR*)/(*RR,SS*)-**1d** mixture had formed, as assayed by integration of the cyclopentadienyl resonances. The integrals of the vinylic protons were within 5% of theory. The solution was added to hexane (10 mL). The resulting tan powder was collected by filtration to give **1d** (0.007 g, 0.010 mmol, >99%; (89 ± 2):(11 ± 2) (*RS,SR*)/(*RR,SS*)). MS[39] 648 (M^+, 59%), 544 ($M^+ - C_8H_8$, 100%). No **1d**-d_8 (*m/z* 656) was detected. **B.** Complex (*RS,SR*)-**1d** (0.007 g, 0.010 mmol),[5b] $CDCl_2CDCl_2$ (0.80 mL), and styrene-d_8 (13 μL, 0.100 mmol) were combined in a 5-mm NMR tube as above and kept at 130 °C (12 h) and 160 °C (6 h; some decomposition). An identical workup gave **1d** (0.006 g, 0.008 mmol, 82%; (88 ± 2):(12 ± 2) (*RS,SR*)/(*RR,SS*)). MS[39] 648 (M^+, 59%), 544 ($M^+ - C_8H_8$, 100%). No **1d**-d_8 was detected.

Isomerization of (*RR,SS*)-1d in the Presence of PPh_3-d_{15}. A Schlenk flask was charged with (*RR,SS*)-**1d** (0.011 g, 0.015 mmol), CH_2ClCH_2Cl (1.5 mL), PPh_3-d_{15} (8.3 mg, 0.030 mmol), and a stir bar and capped with a septum. The solution was stirred at 95 °C for 10 h. Workup as in the preceding experiment gave **1d** (0.011 g, 0.011 mmol, >99%; (55 ± 2):(45 ± 2) (*RS,SR*)/(*RR,SS*)). MS[39] 648 (M^+, 90%), 544 ($M^+ - C_8H_8$, 100%). No **1d**-d_{15} (*m/z* 663) was detected.

Isomerization of (−)-(*SS*)-1d. In an experiment analogous to the preceding one, (−)-(*SS*)-**1d** (0.008 g, 0.011 mmol)[5b] and C_6H_5Cl (2 mL) were stirred at 95 °C for 72 h. Workup gave **1d** as a light yellow powder (0.007 g, 0.010 mmol, 88%), which was dissolved in CD_2Cl_2 (3.7 mg/0.5 mL). A ^{1}H NMR spectrum showed two cyclopentadienyl resonances (δ 5.81, 5.26; (84 ± 2):(16 ± 2)). Next (+)-Eu(hfc)$_3$ (0.018 g, 0.015 mmol) was added. After 2 h, a ^{1}H NMR spectrum showed only two cyclopentadienyl resonances (δ 6.10 (*SR*), 5.41 (*SS*)).[5b]

Isomerization of 1d-d_n. A. In an experiment analogous to the preceding one, (*RRR,SSS*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(HDC{=}CHC_6H_5)]^+BF_4^-$ ((*RRR,SSS*)-**1d**-d_1, 0.025 g, 0.035 mmol) and CH_2ClCH_2Cl (3 mL) were stirred at 95 °C for 72 h. Workup gave **1d**-d_1 (0.023 g, 0.031 mmol, 91%; (89 ± 2):(11 ± 2) (*RSS,SRR*)/(*RRR,SSS*)). The sample was washed with CH_2Cl_2 to give (*RSS,SRR*)-**1d**-d_1 (0.013 g, 0.017 mmol, 50%) as a yellow powder, mp 248–251 °C dec.[40] **B.** In an experiment analogous to the preceding one, (*RRS,SSR*)-**1d**-d_1 (0.015 g, 0.020 mmol) and CH_2ClCH_2Cl (1.5 mL) were stirred at 95 °C for 48 h. Workup gave **1d**-d_1 (0.013 g, 0.018 mmol, 91%; (88 ± 2):(12 ± 2) (*RSR,SRS*)/(*RRS,SSR*)). The sample was washed with CH_2Cl_2 to give (*RSR,SRS*)-**1d**-d_1 as a yellow powder (0.009 g, 0.012 mmol, 60%), mp 247–250 °C dec.[40] **C.** In an experiment analogous to the preceding one, (*RR,SS*)-**1d**-β-d_2 (0.011 g, 0.015 mmol) and CH_2ClCH_2Cl (2 mL) were stirred at 95–100 °C for 36 h. Workup gave **1d**-β-d_2 (0.011 g, 0.015 mmol, >99%; (88 ± 2):(12 ± 2) (*RS,SR*)/(*RR,SS*)). The sample was washed with CH_2Cl_2 to give (*RS,SR*)-**1d**-β-d_2 (0.005 g, 0.006 mmol, 43%).[40] ^{2}H NMR (46 MHz; $CH_2Cl_2/CDCl_3$) 3.00 (br s, =CD), 2.80 ppm (br s, =CD′).

Rate Measurements. All experiments were conducted in CD_2ClCD_2Cl (ca. 0.01 M for **1d**, 0.02 M for **1c**) in septum-sealed 5-mm NMR tubes. Temperatures were calibrated before and after each run with ethylene glycol. Concentrations were assayed by integration of the cyclopentadienyl ^{1}H NMR resonances (3600- and 600-s intervals for thermal and base promoted reactions, respectively). Standard procedures gave the data in Tables II and III.[15,16]

H/D Exchange Experiments. The following is representative. A 5-mm NMR tube was charged with (*RR,SS*)-**1c** (0.008 g, 0.010 mmol), acetone-d_6 (0.5 mL), and Et_3N (1.4 μL) and capped with a septum. The tube was kept at 70 °C for 120 h. ^{1}H NMR spectra were periodically acquired. Data: Tables III and IV.

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Supplementary Material Available: Details of the preparation of deuterated ligands and complexes **1**-d_n (6 pages). Ordering information is given on any current masthead page.

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(39) Conditions: (+)-FAB, 5 kV, Ar, 3-nitrobenzyl alcohol/$CHCl_3$ matrix, *m/z* (relative intensity), ^{187}Re.
(40) NMR data resemble those reported for undeuterated analogues[5b] and are given in the supplementary material.