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Registry No. 4, 86497-25-8; 5-CHCl₂CH₃, 86497-28-1; 6, 12130-88-0; 7, 86497-29-2; 8, 86507-83-7; 9a, 86497-31-6; 9b, 86497-33-8; 10a, 86497-34-9; 10b, 86497-35-0; Re2(CO)10, 14285-68-8; NO+BF4-, 14635-75-7; Li(C₂H₅)₃BH, 22560-16-3; NaBH₄, 16940-66-2; Ph₃C⁺PF₆⁻,

437-17-2; C₆H₅I⁺-O⁻, 536-80-1.

Supplementary Material Available: Tables of bond distances and angles, atomic coordinates, thermal parameters, and structure factors for 4 and 5-CHCl₂CH₃, and figures showing atom numbering and crystal packing (47 pages). Ordering information is given on any current masthead page.

Mechanism of Coupling of $=CH_2$ to $H_2C=CH_2$ at a Homogeneous $(\eta$ -C₅H₅)Re(NO)(PPh₃)⁺ Center. Remarkable Enantiomer Self-Recognition

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Abstract: The methylidene complex $[(\eta - C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-(1)$ couples to the ethylene complex $[(\eta - C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-(1)$ $C_{5}H_{5}Re(NO)(PPh_{3})(H_{2}C=CH_{2})]^{+}PF_{6}^{-}(2; ca. 50\%) at 273-308 K in CH_{2}Cl_{2}$. The byproduct $[(\eta-C_{5}H_{5})Re(NO)(PPh_{3})_{2}]^{+}PF_{6}^{-}(3; ca. 25\%) or, in the presence of CH_{3}CN, <math>[(\eta-C_{5}H_{5})Re(NO)(PPh_{3})(NCCH_{3})]^{+}PF_{6}^{-}(5; ca. 50\%) also forms.$ The rate of coupling is second order in 1 and not affected by the presence of 5-10 equiv of RCN. Data collected from 273 to 308 K give $\Delta H^* = 9.8 \pm 0.6 \text{ kcal/mol and } \Delta S^* = -33.8 \pm 1.0 \text{ eu}.$ At 298 K, $k_{-CH_2}/k_{-CD_2} = 0.39 \pm 0.03$. Surprisingly, optically pure 1 couples 2.3 times faster than racemic 1. Crossover experiments show that no PPh₃ dissociation or intermolecular =CH₂ scrambling occurs prior to the rate-determining coupling step, and that the RR and SS transition states are greatly preferred over the RS transition state (enantiomer self-recognition). Experiments with optically pure 1 show that 2 is formed with >98% retention at rhenium. An X-ray crystal structure of (+)-(SS)- $[(\eta$ -C₃H₃)Re(NO)(PPh₃)(NCCH(C₆H₅)CH₂CH₃)]⁺PF₆⁻ ((+)-(SS)-6) shows that RCN adducts also form with retention. These data are interpreted as evidence for the rate-determining

formation of initial ReCH₂ReCH₂ (7a) or ReCH₂CH₂Re (7b) intermediates. Subsequent rapid conversion to primary monomeric products 2 and $[(\eta - C_5H_5)Re(NO)(PPh_3)(S)]^+PF_6^-$ (8; S = CH₂Cl₂ or vacant coordination site) is proposed. Comparisons are made to other homogeneous and heterogeneous =CH₂ coupling reactions.

Metal-bound methylidenes (=CH₂) play key roles in homogeneous catalytic reactions such as olefin metathesis,³ olefin cyclopropanation,⁴ and the heterogeneous Fischer-Tropsch process.⁵ Hence their chemistry-and in particular carbon-carbon bondforming reactions—has been of intense interest.⁵⁻¹¹

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In a recent study, Pettit demonstrated that surface-bound =CH₂ rapidly dimerizes to H_2C =CH₂ in the absence of hydrogen.^{Se,f} Curiously, attempts to generate homogeneous $L_n M = CH_2$ complexes have often given $L_n M(H_2 C = CH_2)$ complexes in ca. 50% yields.^{7b,10,11} Schrock's isolable *nucleophilic* methylidene complex $(\eta$ -C₅H₅)₂Ta(CH₃)(=CH₂)^{6a,b} decomposes to the ethylene complex $(\eta$ -C₅H₅)₂Ta(CH₃)(H₂C=CH₂).^{6b} We have sought to explore the generality and better understand the mechanisms of such ethylene-forming reactions.

In the preceding paper,8d we described the synthesis and structural characterization of electrophilic C₅Me₅ methylidene complexes, $[(\eta - C_5 Me_5)Re(NO)(L)(=CH_2)]^+PF_6^-$ (L = PPh₃, $P(OPh)_3$), which are stable as solids to >100 °C. In this paper, we examine the decomposition chemistry of the much more reactive C_5H_5 methylidene $[(\eta-C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$ (1),^{8a,b} which is readily available in optically pure form.^{8c} We report herein that 1 undergoes smooth ambient temperature coupling to the ethylene complex $[(\eta - C_5H_5)Re(NO) (PPh_3)(H_2C=CH_2)]^+PF_6^-(2)$ and present stereochemical and

kinetic data that we interpret as evidence for ReCH₂ReCH₂ and/or ReCH₂CH₂Re intermediates. Furthermore, this transformation exhibits a remarkable degree of enantiomer self-rec-

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ognition:¹² (+)-(S)-1 couples virtually exclusively with (+)-(S)-1, and (-)-(R)-1 couples virtually exclusively with (-)-(R)-1.

Results

A sample of $[(\eta - C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-(1)$ was allowed to decompose in CD₂Cl₂ at room temperature. Proton NMR monitoring showed that two principal products, the ethylene complex $[(\eta - C_5H_5)Re(NO)(PPh_3)(H_2C=CH_2)]^+PF_6^-(2)$ and $[(\eta - C_5H_5)Re(NO)(PPh_3)_2]^+PF_6^-(3)$, formed (see Scheme I). In multiple runs, the 2:3 ratio at 25-35% decomposition ranged from 1.8:1.0 to 2.2:1.0, as measured by the relative areas of the C_5H_5 resonances (δ 5.74 and 5.22). After 95% decomposition, minor amounts of other C_5H_5 -containing products were detectable (δ 5.99, 5.84, 5.25), and the 2:3 ratio increased to 2.5-2.9:1.0. Ethylene complex 2 was subsequently isolated in 46-48% yields (92–96% of theory) as beige crystals from CH_2Cl_2 /hexane or as corn-yellow crystals from acetone/ether (2-acetone monosolvate). Yields of 2 and 2:3 ratios appeared very slightly higher when 1 was decomposed under $H_2C = CH_2$. The identity of 3 was confirmed by NMR comparison to an independently prepared authentic sample $(BF_4^- \text{ salt}).^{8b}$

The possibility of secondary reactions during the =CH₂ coupling was probed by decomposing $[(\eta - C_5H_5)Re(NO)(PPh_3) (=CD_2)$]⁺PF₆⁻ (1-d₂) under H₂C=CH₂. The ratio of C₅H₅ to ethylenic protons in the resulting 2 was shown by ${}^{1}H$ NMR to be (97 ± 1) : (3 ± 1) . Reaction of this 2 with Li(C₂H₅)₃BH gave the known¹³ ethyl complex $(\eta - C_5H_5)Re(NO)(PPh_3)(C_2H_{5-x}D_x)$ $(4-d_r)$ in 15-40% yields. Mass spectral analysis (Experimental Section) indicated a (96 ± 1) : (3 ± 1) : <2 ratio of $(\eta$ -C₅H₅)Re- $(NO)(PPh_3)(CD_2CD_2H):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3):(\eta-C_5H_5)Re(NO)(PPh_3)(PPh_3)(PPh_3):(\eta-C_5H_5)Re(NO)(PPh_3)(PPh_3)(PPh_3):(\eta-C_5H_5)Re(NO)(PPh_3)(PPh_3):(\eta-C_5H_5)Re(NO)(PPh_3)(PPh_3)(PPh_3):(\eta-C_5H_5)Re(NO)(PPh_3)(PPh_3):(\eta-C_5H_5)Re(NO)(PPh_3)(PPh_3)(PPh_3):(\eta-C_5H_5)Re(NO)(PPh_3)(PPh_3)(PPh_3)(PPh_3):(\eta-C_5H_5)Re(NO)(PPh_3)(PPh_3):(\eta-C_5H_5)Re(NO)(PPh_3)(PPh_3)(PPh_3):(\eta-C_5H_5)Re(NO)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3)(PPh_3$ C_5H_5)Re(NO)(PPh₃)($C_2D_2H_3$). Thus, under 1 atm of H_2C = CH_2 , 1 undergoes = CH_2 coupling much more readily than olefin metathesis, and 2 is essentially inert toward $H_2C=CH_2$ exchange.

A stream of H₂C=CH₂ was passed first through a -78 °C CH_2Cl_2 solution of 1 and then through a -78 °C trap. The solution of 1 was warmed to 0 °C and then to room temperature while maintaining the H₂C=CH₂ stream. An internal standard was added to the trap and the contents were analyzed by ¹H NMR. No cyclopropane was detected. Authentic cyclopropane (3%) was added; a 1.5% yield would have been easily detected.

A 48:52 mixture of 1 and $[(\eta - C_5H_5)Re(NO)(PPh_3 - d_{15}) - d_{15})$ $(=CD_2)$]⁺PF₆⁻ (1- d_{17}) was dissolved in CH₂Cl₂ at 25 °C. After 0.5 h (ca. 70% decomposition), $Li(C_2H_5)_3BH$ was added and the resulting $(\eta - C_5H_5)Re(NO)(PPh_3)(CH_3) - d_x$ recovered (25%). Mass spectral analysis showed that this material was almost entirely $(\eta$ -C₅H₅)Re(NO)(PPh₃)(CH₃) and $(\eta$ -C₅H₅)Re(NO)- $(PPh_3-d_{15})(CD_2H)$ (3:2 ratio). Intermediate label distributions $(\eta$ -C₅H₅)Re(NO)(PPh₃)(CHD₂) and $(\eta$ -C_kH₅)Re(NO)(PPh₃ d_{15} (CH₃) constituted only 4% and 5% of the PPh₃- d_0 and PPh₃- d_{15} products, respectively. This experiment shows that no equilibria that would allow intermolecular PPh₃ or ==CH₂ exchange occur prior to the rate-determining step in the coupling. The decomposition of 1 cannot be studied in the presence of PPh₃ because rapid reaction occurs at -78 °C to give $[(\eta - C_5H_5)Re(NO) (PPh_3)(CH_2PPh_3)]^+PF_6^{-.8b}$

The decomposition rate of 1 was measured by ¹H NMR in CD_2Cl_2 and found to follow the second-order expression d[1]/dt = $-k_{obsd}$ [1]². Data were obtained from 273 to 308 K and over a range of $[1]_0$ as summarized in the first four entries of Table Following the convention for *n*th order reactions $n[a] \rightarrow n[a]$ I. products,¹⁴ the k_{obsd} were divided by 2 to obtain rate constants k. These rate constants were then used to obtain the provisional activation parameters $\Delta H^* = 9.8 \pm 0.6$ kcal/mol and $\Delta S^* = -32.2$ \pm 1.0 eu.

The rate of decomposition of 1 showed a marked inverse secondary deuterium isotope effect, $k_{\text{--CH}}/k_{\text{--CD}} = 0.39 \pm 0.03$, at Scheme I. Proposed Mechanism of =CH₂ Coupling



298 K (Table I). The customary normalization for the anticipated number of deuteriums in the transition state¹⁵ gives $k_{\rm H}/k_{\rm D} = 0.79$ ((0.39)^{1/4}). Secondary kinetic α -deuterium isotope effects in the 0.80-0.95 range are commonly associated with transition states involving $sp^2 \rightarrow sp^3$ carbon hybridization changes.^{15,16}

The decomposition rate of 1 was not affected by the presence of 3-10 equiv of CH₃CN or CH₃CH₂CH(C₆H₅)CN (Table I). However, these additives changed the decomposition stoichiometry dramatically. Now, equimolar quantities of 2 and nitrile complexes $[(\eta - C_5 H_5) Re(NO)(PPh_3)(NCR)]^+ PF_6^-$ (5, R = CH₃; 6, R = $CH(C_6H_5)CH_2CH_3$) were the exclusive products. These data will be interpreted (Discussion) as evidence for the sequence of intermediates shown in Scheme I. Adducts 5 and 6 (BF_4^- salts) were independently synthesized by treating $[(\eta - C_5H_5)Re$ - $(NO)(PPh_3)(CO)]^+BF_4^-$ with anhydrous $(CH_3)_3N^+-O^-$ in CH₃CN or CH₃CH₂CH(C₆H₅)CN/CH₂Cl₂. Importantly, 6 was obtained as a ca. 1:1 mixture of diastereomers that gave distinct 200-MHz C₅H₅ ¹H NMR resonances (δ 5.54 and 5.55).

The decomposition rate of 1 was not affected by the presence of $(\eta$ -C₅H₅)Re(NO)(PPh₃)(CH₃) (entries 10 and 11, Table I). A sample of 1 was allowed to couple in the presence of 0.89 equiv of $(\eta$ -C₅H₅)Re(NO)(PPh₃)(CD₃). The $(\eta - C_5 H_5) \text{Re}(\text{NO})$ - $(PPh_3)(CD_xH_{3-x})$ was recovered (43%) and analyzed by mass spectrometry. A 23:39:29:9 ratio of CD₃:CD₂H:CDH₂:CH₃ was found. Complete randomization of the label would have given a 19:42:31:8 ratio. Hence = CH₂/CH₃ hydride transfer is much faster than $=CH_2$ coupling. No $(\eta - C_5 H_5) Re(NO)$ - $(PPh_3)(C_2H_5)-d_x$ was detected in this reaction.

The stereochemical course of the methylidene coupling was investigated next. First, the rates of decomposition of (+)-(S)-1 and (-)-(R)-1 (>99% ee)^{8c,17} were measured under conditions

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Scheme II. Enantiomer Self-Recognition in the $=CH_2$ Coupling^a



labeled product

labeled product

^a Since $2 \cdot d_{15}$ cannot be separated from $2 \cdot d_4$, the additional prediction that they should have opposite configurations (Scheme III) cannot be tested.



identical with that of (\pm) -1 (entry 12, Table I). Surprisingly, the rate increased by a factor of 2.32 ± 0.20 ! Importantly, racemic and optically active 1 gave identical ¹H NMR spectra over a range of temperatures and concentrations. Hence a selective, stabilizing complexation or association of (+)-(S)-1 with (-)-(R)-1 is unlikely.

A 50:50 mixture of (+)-(S)-1- d_2 and (-)-(R)-1- d_{15} ¹⁷ was dissolved in CH₂Cl₂ at 25 °C and allowed to couple to 2 (Scheme II). After isolation, this 2 was treated with Li(C₂H₅)₃BH and the resulting $(\eta$ -C₅H₅)Re(NO)(PPh₃)(CH₂CH₃)- d_x (4- d_x) analyzed by mass spectrometry. The $(\eta$ -C₅H₅)Re(NO)(PPh₃- d_{15})(CH₂CH₃): $(\eta$ -C₅H₅)Re(NO)(PPh₃- d_{15})(C₂D₂H₃) and $(\eta$ -C₅H₅)Re(NO)(PPh₃)(CD₂CD₂H₃) (η -C₅H₅)Re(NO)-(PPh₃)(C₂D₂H₃) ratios were (98 ± 1):(2 ± 1) and (96 ± 1):(4 ± 1), respectively. Hence H₂C=CD₂-containing products, which



Figure 1. ORD spectra of $(+)-(R)-[(\eta-C_5H_5)Re(NO)(PPh_3)(H_2C=CH_2)]^+PF_6^- ((+)-(R)-2) (--), (+)-(S)-[(\eta-C_5H_5)Re(NO)(PPh_3)-(NCCH_3)]^+PF_6^- ((+)-(S)-5) (---); (+)-(SS)-[(\eta-C_5H_5)Re(NO)-(PPh_3)(NCCH(C_6H_5)CH_2CH_3)]^+PF_6^- ((+)-(SS)-6) (----), and (-)-(RS)-[(\eta-C_5H_5)Re(NO)(PPh_3)(NCCH(C_6H_5)CH_2CH_3)]^+PF_6^- ((-)-(RS)-6) (-----).$

can only arise from the reaction of (+)-(S)-1- d_2 with (-)-(R)-1- d_{15} , are virtually absent in Scheme II. This proves that the R,R and S,S transition states for methylidene coupling are distinctly preferred over the R,S and S,R transition states.

Decomposition of (+)-(S)-1 (>99% ee)¹⁷ gave (+)-2 of high optical rotation (Scheme III), suggestive of appreciable stereoselectivity. This (+)-2 was treated with Li(C₂H₅)₃BH as described above for the racemate to give (+)- $(\eta$ -C₅H₅)Re(NO)(PPh₃)-(CH₂CH₃) ((+)-4), $[\alpha]^{25}_{589}$ +114°. Since dextrorotatory 4 has been previously shown to have an S configuration (Scheme II, step c) with $[\alpha]^{25}_{589}$ +116°,^{8c} it is formed with overall retention and >98% stereoselectivity. Since nucleophilic attack upon coordinated olefins (Scheme III, step b) proceeds with retention at the metal,¹⁸ coupling of (+)-(S)-1 must likewise occur with *retention* at rhenium to give (+)-(R)-2.^{17a}

The decomposition of (+)-(S)-1 in the presence of 10 equiv of CH₃CN gave $[(\eta$ -C₅H₅)Re(NO)(PPh₃)(NCCH₃)]⁺PF₆⁻ (5) with a substantial optical rotation (0 °C run: $[\alpha]^{25}_{589} + 330^{\circ}$; 25 °C run: +248°). Nitrile complex 5 showed no optical activity loss over the course of 1.5 days at 25 °C in CH₂Cl₂. In order to assay the trapping stereoselectivity, (+)-(S)-1 was decomposed at 0 °C in the presence of (-)-(S)-CH₃CH₂CH(C₆H₅)CN.¹⁹ The adduct obtained, $[(\eta$ -C₅H₅)Re(NO)(PPh₃)(NCCH(C₆H₅)CH₂CH₃)]⁺-PF₆⁻ ((+)-6, Scheme III, step d) gave $[\alpha]^{25}_{589} + 170^{\circ}$ and consisted of a single diastereomer by 200-MHz ¹H NMR. Similarly, a sample of (-)-6 (diastereomer of (+)-6), $[\alpha]^{25}_{589} -207^{\circ}$, was

^{(17) (}a) The priority sequences for assigning R/S absolute configurations to the complexes in this paper are as follows:^{17b} η^5 -C₅H₅ > PPh₃ > NO > alkyl, alkylidene, nitrile, but η^5 -C₅H₅ > PPh₃ > η^2 -H₂C=CH₂ > NO. In complexes with more than one chiral center, the rhenium configuration is specified first. (b) Stanley, K.; Baird, M. C. J. Am. Chem. Soc. 1975, 97, 6598. Sloan, T. E. Top. Stereochem. 1981, 12, 1. (c) Unless otherwise specified, (+) and (-) refer to rotations at 589 nm.

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Table I. Decomposition of $[(\eta - C_s H_s)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-(1)$: Summary of Rate Measurements in CD_2Cl_2

entry	substrate (additive)	temp, K	concn, M	$k_{obsd}, M^{-1} s^{-1}$
1	(±)-1	273	0.059	$\begin{array}{c} 0.013 \pm 0.001 \\ 0.014 \pm 0.001 \end{array}$
				av 0.014 ± 0.001
2	(±)-1	283	0.0 69	0.026 ± 0.001 0.026 ± 0.001
				av 0.026 ± 0.001
3	(±)- 1	298	$\begin{array}{c} 0.058 \\ 0.062 \\ 0.082 \\ 0.170 \\ 0.180 \\ 0.255 \end{array}$	$\begin{array}{c} 0.062 \pm 0.007 \\ 0.061 \pm 0.004 \\ 0.060 \pm 0.006 \\ 0.057 \pm 0.006 \\ 0.064 \pm 0.007 \\ 0.057 \pm 0.019 \\ av 0.060 \pm 0.003 \end{array}$
4	(±)-1	308	0.053 0.054 0.054	0.115 ± 0.006 0.137 ± 0.006 0.123 ± 0.005 av 0.125 ± 0.012
5	(±)-1-d ₂	298	$\begin{array}{c} 0.050 \\ 0.052 \\ 0.053 \\ 0.055 \end{array}$	$\begin{array}{c} 0.151 \pm 0.004 \\ 0.157 \pm 0.003 \\ 0.143 \pm 0.006 \\ 0.164 \pm 0.006 \end{array}$
				av 0.154 ± 0.010
6	(\pm) -1 (5 equiv CH ₃ CN)	298	0.166	0.061 ± 0.012
7	(\pm) -1 (10 equiv CH ₃ CN)	298	0.051 0.193	0.058 ± 0.010 0.063 ± 0.024
8	(±)-1 (6 equiv $CH_3CH_2CH(C_6H_5)CN)$	298	0.070	0.059 ± 0.009
9	(\pm) -1 (CH ₃ CN solvent)	283	0.069 0.065	$\begin{array}{c} 0.038 \pm 0.001 \\ 0.036 \pm 0.002 \end{array}$
10	(±)-1 (0.76 equiv $(\eta$ -C ₅ H ₅)Re(NO)(PPh ₃)(CH ₃))	283	0.075	0.027 ± 0.002
11	(±)-1 (1.09 equiv $(\eta - C_{s}H_{s})Re(NO)(PPh_{3})(CH_{3}))$	283	0.054	0.026 ± 0.001
12a	(+)-(<i>S</i>)-1	298	0.054	0.135 ± 0.007
12Ъ	(-)-(R)-1	298	0.061 0.053 0.058	$\begin{array}{c} 0.144 \pm 0.004 \\ 0.135 \pm 0.004 \\ 0.143 \pm 0.006 \end{array}$
				av 0.139 ± 0.005

synthesized from (-)-(R)-1 and (-)-(S)-CH₃CH₂CH(C₆H₅)CN. No (+)-6 could be detected in the crude reaction mixture by ¹H NMR. A CDCl₃ solution containing (-)-6 and (+)-6 in a 1:99 ratio was prepared, and a 200-MHz ¹H NMR spectrum was recorded. The η -C₅H₅ resonances integrated as (99.0 ± 0.5):(1.0 ± 0.5). It was estimated that as little as 0.5% of (-)-6 could be detected in the presence of (+)-6. Thus, (+)-6 is formed with >99% stereoselectivity.

To aid in the assignment of rhenium configuration, ORD and CD spectra of (+)-(R)-2, (+)-5, (+)-6, and (-)-6 were recorded (Figures 1 and 2). For optically active complexes $(\eta$ -C₅H₅)-Re(NO)(PPh₃)(X), there is a good empirical correlation between absolute configuration and the sign of the ORD or CD spectrum at >500 nm (or the sign between the two x-axis crossings generally observed).^{8c} This suggests that (+)-6 is (+)-(SS)-6, (-)-6 is (-)-(RS)-6,¹⁷ and (+)-5 is (+)-(S)-5. In order to unambiguously establish these configurations, we determined the X-ray crystal structure of (+)-6.

Slow diffusion of hexane into a CH₂Cl₂ solution of (+)-6 gave suitable crystals for X-ray analysis. X-ray data were collected at -158 °C by using monochromated Mo K α (0.71069 Å) radiation on a Syntex PI automatic diffractometer. Three standard reflections were taken every 100 reflections. These varied by less than 3%. The unit cell was monoclinic with lattice parameters a = 10.909 (5) Å, b = 11.841 (5) Å, c = 12.878 (4) Å, and β = 106.7 (7)°. Systematic absences were consistent with the space group P2₁. Of 5939 reflections collected with $2\theta < 50^\circ$, 5682 reflections with $I \ge 3\sigma$ were used in the final refinement.

The position of the rhenium was obtained from a three-dimensional Patterson map. Fourier synthesis combined with



Figure 2. CD spectra of $(+)-(R)-[(\eta-C_5H_5)Re(NO)(PPh_3)(H_2C = CH_2)]^+PF_6^- ((+)-(R)-2) (-----), (+)-(S)-[(\eta-C_5H_5)Re(NO)(PPh_3)-(NCCH_3)]^+PF_6^- ((+)-(S)-5) (----), (+)-(SS)-[(\eta-C_5H_5)Re(NO)-(PPh_3)(NCCH(C_6H_5)CH_2CH_3)]^+PF_6^- ((+)-(SS)-6) (-----), and (-)-(RS)-[(\eta-C_5H_5)Re(NO)(PPh_3)(NCCH(C_6H_5)CH_2CH_3)]^+PF_6^- ((-)-(RS)-6) (--).$

least-squares refinement yielded all non-hydrogen atoms. Absorption corrections were applied and all non-hydrogen atoms were (with the exception of the PPh₃ phenyl rings) refined anisotropically. All hydrogens were located from a difference Fourier map and were not refined.²⁰ The final *R* index was 0.028 with R_w

⁽²⁰⁾ In-house programs were used for data refinement. One of these incorporated modifications of the programs CARESS by R. W. Broach (University of Wisconsin) and PROFILE by P. Coppens, P. Becker, and R. H. Blessing (SUNY, Buffalo).



Figure 3. Stereoview of the molecular structure of (+)-(SS)- $[(\eta$ -C₅H₅)Re(NO)(PPh₃)(NCCH(C₆H₅)CH₂CH₃)]+PF₆⁻ ((+)-(SS)-6).

Table II. Se	elected Bond	Lengths and	Angles in	$(+)-(SS)-6^{a}$
--------------	--------------	-------------	-----------	------------------

 		e (,
 atoms	distance, A	atoms	angle, deg
 Re-N2 Re-P1 Re-N1 Re-C ₅ H ₅ ^b N2-C1 C1-C2	2.089 (8) 2.377 (2) 1.767 (6) 2.282 1.131 (10) 1.454 (10)	Re-N2-C1 N2-C1-C2 N2-Re-N1 N1-Re-P1 P1-Re-N2 Re-N1-O16	168.5 (6) 177.9 (8) 102.9 (3) 92.5 (3) 87.0 (3) 174.3 (6)
 N1-016	1.194 (8)		

^a See Figure 3 for numbering of atoms. ^b Average distance from Re to C₅H₅ carbons; the tilt of the C₅H₅ least-squares plane with respect to the vector between Re and C_sH_s centroid (1.937 Å) is 87.0°.

$= 0.047.^{21}$

Up to this point, structure analysis was carried out with the SS configuration of (+)-6. The configuration was inverted through a mirror plane by changing the sign of the y coordinates. An identical series of refinements on the resulting RR diastereomer yielded a final R factor (0.058, $R_w = 0.082$) significantly greater than that of the SS diastereomer. This difference, according to Hamilton's R-factor significance test,²² indicates that the probability of (+)-6 having the SS configuration is >99.5%. Inspection of the ratios of observed and calculated values of F_{hkl} and $F_{h-k,l}$ further substantiates the assignment of the SS configuration to (+)-6.23

A stereoview of the molecular structure of (+)-(SS)-6 is given in Figure 3. An exhaustive list of bond distances and angles and two crystal-packing diagrams are provided in the supplementary material. Important bond distances and angles are summarized in Table II. The R-C=N-Re moiety is significantly distorted from linearity. Also, this crystal structure provides an independent confirmation of the absolute configuration of the nitrile (-)-(S)- $CH_3CH_2CH(C_6H_5)CN$ and the carboxylic acid (+)-(S)- $CH_3CH_2CH(C_6H_5)COOH$ from which the nitrile is commonly derived.^{19,24}

In summary, (+)-(SS)-6 is formed from (+)-(R)-1 with overall retention at rhenium. By analogy, the S configuration is assigned to (+)-5.

Discussion

Mechanism of $= CH_2$ Coupling. The foregoing data exclude many possible mechanisms for the coupling of 1. We shall first consider the constraints imposed by the coupling stoichiometry.

Since the nitrile additives CH₃CN and CH₃CH₂CH(C₆H₅)CN alter the coupling stoichiometry (Scheme I) but not the rate (Table I, entries 6-8), they must scavenge an intermediate formed after the rate-determining step. Hence we propose that concurrent with the formation of ethylene complex 2 (Scheme I, step b), the weakly solvated species $[(\eta - C_5H_5)Re(NO)(PPh_3)(S)]^+PF_6^-(8)$ is produced. By itself, 8 disproportionates as shown in step c of Scheme I. This accounts for the approximate 2:1 ratios of 2:3 observed. However, in the presence of a nitrile, 8 is trapped as $[(\eta C_5H_5$ Re(NO)(PPh₃)(NCR)]⁺PF₆⁻ (Scheme I, step e).

We now consider the =CH₂ coupling stereochemistry at rhenium. As noted, 2 is formed with retention. The nitrile adduct (+)-(SS)-6 is formed, via 8, with overall retention from 1. Brunner has shown that substitutions in closely related compounds such as $(\eta - C_5H_5)Mn(NO)(L)(CO_2CH_3) \rightarrow (\eta - C_5H_5)Mn(NO)(L')$ - (CO_2CH_3) occur dissociatively and with retention or (partial) racemization.²⁵ The pyramidal fragment $(\eta - C_5H_5)Mn(NO)$ -(CO₂CH₃) and isoelectronic homologues²⁶ have appreciable configurational stability. We therefore conclude that the solvent displacement $8 \rightarrow 6$ must proceed with retention. Hence 8 must form from 1 with retention. The moderate dependence of the optical purity of acetonitrile adduct (+)-(S)-5 (configurationally stable at 25 °C) upon the temperature of the (+)-(S)-1 coupling requires a slightly configurationally labile intermediate and thus provides further support for this mechanistic interpretation.

We now turn to the initial steps of the $=CH_2$ coupling. The lack of exchange between 1 and $[(\eta - C_5H_5)Re(NO)(PPh_3 - d_{15}) - d_{15}]$ $(=CD_2)$]⁺PF₆⁻ (1- d_{17}) excludes both preequilibrium PPh₃ dissociation and any preequilibrium process that would scramble the =CH₂ ligands. In view of the second-order kinetics and the fact that both primary monomeric products 2 and 8 are formed with retention at rhenium, we propose that the initial and rate-determining step is the mutually front-side attack of two Re=CH₂ moieties. As working models, we suggest the initial formation of dimeric intermediates 7a ("closed") and/or 7b ("open"), as shown in Scheme I. The transition state for $1 + 1 \rightarrow 7$ would nicely account for the inverse secondary kinetic isotope effect, $k_{\rm H}/k_{\rm D} = 0.79$. Transannular steric interactions that would attend the formation of 7 would explain the much greater kinetic stability of the bulkier pentamethyl homologue of 1, $[(\eta - C_5Me_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^{-.8d}$

None of our data rigorously distinguish between 7a and 7b as the initial intermediate. We favor 7a because direct formation of 7b would require the joining of the *positive* ends of two $\leftarrow +$ Re=CH₂ dipoles. The highly negative ΔS^* seems more appropriate for 7a than 7b. However, activation entropies have not proven to be reliable criteria for distinguishing concerted vs. stepwise 2 + 2 (and other) olefin cycloadditions. The latter have ΔS^* as low as -30 eu and occur via transition states that closely resemble the one which would lead to 7b.27

Stable homologues of both 7a and 7b are known. A (η - C_5H_5)-substituted TiCH₂TiCH₂ metallocycle was isolated by Grubbs and Ott from a reaction that generated $(\eta$ -C₅H₅)₂Ti-

⁽²¹⁾ All least-squares refinements computed the agreement factors R and (21) An least squares reinference computed the agreement actors R and R_w according to $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w_i||F_o| - |F_c||^2 / \sum w_i|F_o|^2]^{1/2}$, where F_o and F_c are the observed and calculated structure factors, respectively, and $w_i^{1/2} = 1/\sigma(F_o)$. The function minimized in all least-squares refinements was $\sum w_i ||F_o| - |F_c||^2$. (22) Hamilton, W. C. Acta Crystallogr. 1965, 18, 502. (23) Kartha, G.; Ahmed, F. R.; Barnes, W. H. Acta Crystallogr. 1962, 15, 226

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(=CH₂).²⁸ Several MCH₂CH₂M' species have been synthesized.^{29,30} The bis(rhenium) complex (CO)₅ReCH₂CH₂Re(CO)₅ has been characterized by an X-ray crystal structure. The X-ray crystal structure of (n-C5H5)2((C2H5)3AlCl)ZrCH2CH2Zr- $(ClAl(C_2H_5)_3)(\eta$ -C₅H₅)₂ showed the novel arrangement of core atoms 9.30 A full carbon-carbon bond is present, but some



bonding of each zirconium to the β CH₂ remains. Hence 9 is a model for the potential CH_2 coupling step $7a \rightarrow 7b$. However, no MCH₂CH₂M' complex has been isolated from a reaction thought to involve a $L_n M = CH_2$ intermediate.

The 2.3-fold increase observed in the decomposition rate of optically pure 1 (Table I, entry 12) is close to the idealized value¹² of 2.0 which would be expected if the (+)-(S)-1/(+)-(S)-1 and (-)-(R)-1/(-)-(R)-1 coupling transition states were distinctly lower in energy (>2.5 kcal/mol) than the (+)-(S)-1/(-)-(R)-1 coupling transition state. The terms homochiral and heterochiral³¹ can be used to differentiate transition states of these types. The essentially exclusive operation of homochiral coupling is dramatically verified by the $(+)-(S)-1-d_2/(-)-(R)-1-d_{15}$ crossover experiment (Scheme II). Hence $k_{obsd} = 2k_{RR} + 2k_{SS}$,¹⁴ and the ΔS^* calculated previously (from $k_{obsd}/2$), -32.2 ± 1.0 eu, must be corrected to -33.8 ± 1.0 eu. This gives $\Delta G^*_{298} = 19.9 \pm 0.9$ kcal/mol.

We had expected that the rate of decomposition of racemic 1 would be greater than that of optically active 1. Several (η -C₅H₅)Re(NO)(PPh₃)(X) systems undergo stereospecific reactions in which an attacking agent approaches -X from a direction opposite (antiperiplanar) to the Re-PPh₃ bond.^{13,32,33} If this constraint is placed upon both rheniums in a $_{\pi}2_{s} + _{\pi}2_{s}$ cycloaddition geometry³⁴ leading to 7a, then only two transition states, 10 (RS,SR) and 11 (RR,SS), are possible. An unfavorable steric



interaction clearly exists in 11. This transition-state model thus predicts that heterochiral coupling is favored. Since this is contrary to experimental fact, the model must be incorrect.

In considering other transition-state models, we are reluctant to challenge the assumption that attack must occur anti to the Re-PPh₃ bond of each rhenium. This feature dominates the

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Improvised space-filling models have been used to assess the various $\pi^{2}_{s} + \pi^{2}_{a}$ modes of Re=CH₂ approach. In no case was a homochiral transition state judged to be distinctly more favorable than heterochiral transition state. The homochiral transition state did seem to be preferred in a twisted $\pi^{2}_{s} + \pi^{2}_{s}$ approach. However, we do not believe that this accounts for the coupling stereospecificity in a convincing fashion.

Another relevant consideration is the HOMO of 1. As described in the preceding paper, it is likely to be a d orbital that is orthogonal to the $Re-PPh_3$ bond and bisected by the Re-NO bond. It may be more important than the bulky PPh₃ in controlling the direction of Re=CH₂ approach. Finally, several possible 7a structures have unfavorable steric interactions when comprised of R and S enantiomers ("product development control"). However, in summary we feel that more sophisticated experiments and/or theoretical studies are needed to rigorously interpret the preference for homochiral coupling.

Enantiomer self-recognition can occur either in a kinetic or thermodynamic sense. The homochiral coupling of 1 is an example of the former type. Documented cases of this phenomenon are scarce and have been elegantly summarized by Wynberg and Feringa.^{12,35} For instance, the reductive coupling of racemic camphor (LiAlH₄/TiCl₃) gave a 65:35 ratio of homochiral:heterochiral olefinic products.^{12,35a} The only nonpolymeric product from the reaction of Fe(CO)₅ with olefin norborn-5-en-2-one was a cyclopentanone (15%) derived from two olefins of identical chirality.^{35b} Similar observations have been made in the reductive coupling of substituted phenols^{35c} and in electron transfer between hexahelicene and hexahelicene radical anion.^{35d} These examples differ from ours in that a reagent is needed to effect reaction.

Ideally, rate studies with racemic and resolved substrates and an exhaustive product analysis should be conducted to clearly demonstrate enantiomer self-recognition in a dimerization process. Warner has proposed that an alkoxide-substituted bridgehead olefin intermediate dimerizes via a trans-1,4-biradical to give only homochiral products (19%).³⁶ This selectivity was attributed to a Li⁺ template effect. Woodward and Hoffmann predicted that the *heterochiral* $_{\star}2_{s} + _{\star}2_{a}$ dimerization of strained cyclic trans olefins would be preferred.³⁷ To our knowledge, this has not been tested experimentally.38

Ancillary Chemistry and Structural Data. While 1 did not convert ethylene to cyclopropane, we have observed 15-25% yields of cyclopropylbenzene when 1 is decomposed in the presence of excess styrene.³⁹ Ethylene is not a very reactive olefin toward coordinatively saturated $L_n M = CH_2$ species, and 1 simply reacts with itself at a faster rate. Less stable, more electrophilic $L_n M = CHR$ species such as $[(\eta - C_5 H_5)Fe(L)(L')(=CHR)]^+X^$ convert olefins to cyclopropanes at a substantially faster rate.7,40

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Methylidene 1 has been previously shown to rapidly abstract α -hydrides from the alkyl (η -C₅H₅)Re(NO)(PPh₃)(CH₂OCH₃) and formyl (η-C₅H₅)Re(NO)(PPh₃)(CHO) at -70 °C.^{8b} Hence the facile exchange of hydride and deuteride between 1 and $(\eta$ - C_5H_5 Re(NO)(PPh₃)(CD₃) is precedented.

We are aware of an X-ray crystal structure of one other rhenium-nitrile complex, $[(CO)_3Re(NCCH_3)_3]^+BF_4^{-41}$ The average distances of the Re-N (2.13 Å), N=C (1.14 Å), and C-CH₃ (1.46 Å) bonds were similar to those found in (+)-(SS)-6 (Table II). A slight deviation of $\angle N$ -C-CH₃ from linearity, 174.7°, was also noted.

Generality of $=CH_2 \rightarrow H_2C ==CH_2$ Coupling. Several recent studies bear an important relationship to this work. Schrock has studied the decomposition of the nucleophilic methylidene (η - $C_5H_5)_2Ta(=CH_2)$ and found a second-order coupling to (η - $C_5H_5)_2Ta(CH_3)(H_2C=CH_2)$ and " $(\eta - C_5H_5)_2Ta(CH_3)$ " analogous to that in Scheme I.66 The latter species was not directly observed but could be trapped by the addition of CO, $H_2C=CH_2$, or phosphines. Brookhart and Husk^{7b} have reported that the labile electrophilic methylidenes $[(\eta - C_5H_5)Mo(CO)_2(PPh_3)(=$ $(H_2)^+CF_3SO_3^-$ and $[(\eta - C_5H_5)W(CO)_2(PPh_3)(=CH_2)^+$ $CF_3SO_3^-$ couple at $\gtrsim -70$ and $\gtrsim -20$ °C, respectively, to give $[(\eta - C_5H_5)M(CO)_2(PPh_3)(H_2C=CH_2)]^+CF_3SO_3^-$ and detectable $[(\eta - C_5H_5)M(CO)_2(PPh_3)(S)]^+CF_3SO_3^-$ or $(\eta - C_5H_5)M(CO)_2^-$ (PPh₃)(OSO₂CF₃) species.

Casey found that reaction of $(\eta$ -C₅H₅)Re(NO)(CO)(CH₃) with $Ph_{3}C^{+}BF_{4}^{-}$ gave $[(\eta - C_{5}H_{5})Re(NO)(CO)(H_{2}C=CH_{2})]^{+}BF_{4}^{-.10d}$ It was proposed^{10d} that initial formation of $[(\eta - C_5H_5)Re(NO) (CO)(=CH_2)]^+BF_4^-$ was followed by methyl transfer from starting material to give $(\eta - C_5 H_5) Re(NO)(CO)(CH_2 CH_3);$ subsequent β -hydride abstraction by Ph₃C⁺BF₄⁻ would give the ethylene complex product. We have shown that except for degenerate hydride transfer, 1 is unreactive toward $(\eta \cdot C_5 H_5)$ Re- $(NO)(PPh_3)(CH_3)$. Furthermore, ethyl complex $(\eta - C_5H_5)Re$ -(NO)(PPh₃)(CH₂CH₃) undergoes α -hydride abstraction when treated with Ph₃C⁺PF₆^{-,13} Hence a corresponding mechanism cannot operate in our PPh3-substituted compounds.

Masters has reported that the stoichiometric reduction of $Cr(CO)_6$ by AlH₃ gives ethylene as the exclusive (>95%) organic product.⁴² The initial formation of (CO)₅Cr=CH₂, and a subsequent four-centered coupling, were suggested.

In view of the forementioned data of Pettit, ^{5e,f} it is clear that there is a striking tendency for M=CH₂ species, be they homogeneous, heterogeneous, nucleophilic, or electrophilic, to couple to (coordinated) $H_2C=CH_2$. We believe that these couplings should share many of the features found for the coupling of 1. We also predict that if a means of generating homogeneous $L_n M = C\dot{H}_2$ species $(L_n \neq alkyl)^{11}$ from CO/H_2 can be found, the selective catalytic reaction $CO/H_2 \rightarrow H_2C=CH_2$ will be possible.

Experimental Section

General. General procedures employed for this study were identical with those given in a previous paper.8c

Starting Materials. Methyl complexes (\pm) -, (-)-(R)-, and (+)-(S)- $(\eta$ -C₅H₅)Re(NO)(PPh₃)(CH₃) were synthesized by NaBH₄ reduction of $[(\eta - C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ as described previously.^{8b,c} Analogous NaBD₄ reductions gave $(\eta - C_5H_5)Re(NO)(PPh_3)(CD_3)$ and $(\eta$ -C₅H₅)Re(NO)(PPh₃-d₁₅)(CD₃). These were treated with Ph₃C⁺PF₆ to give the corresponding methylidene complexes $(1, 1-d_2, 1-d_{17})$, which were (unless noted) isolated prior to use as previously described.8b,c $Li(C_2H_5)_3BH$ (1.0 M in THF) and C_6D_5Br were obtained from Aldrich and used without purification. The latter was converted to C₆D₅MgBr and treated with PCl₃ (Mallinckrodt) to give PPh₃- d_{15} .⁴³ Racemic $CH_3CH_2CH(C_6H_5)COOH$ was obtained from Aldrich, resolved by the method of Petterson,⁴⁴ and converted to (-)-(S)-CH₃CH₂CH(C₆H₃)CN as described by Cram and Haberfield.¹⁹ Ethylene was purchased from Matheson and used without purification. Silane Ph₃SiCH₃ was prepared

from Ph₃SiCl and CH₃MgBr analogously to a literature procedure.⁴⁵

Isolation of $[(\eta-C_5H_5)Re(NO)(PPh_3)(H_2C=CH_2)]^+PF_6^-(2)$ from the Decomposition of $[(\eta-C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-(1)$. To 20 mL of CH₂Cl₂ at -78 °C was added 0.233 g (0.332 mmol) of 1. The resulting solution was allowed to warm to room temperature with stirring. After 4 h, solvent was removed under vacuum to give a red-purple solid. The solid was taken up in CHCl₃ and then filtered through glass wool, whereupon yellow crystals spontaneously precipitated. These were collected, washed with small amounts of cold CHCl₃ and hexane, and then diffusion recrystallized from acetone/ether. Corn-yellow crystals (0.122 g, 0.158 mmol, 48%; 96% of theory) of 2-acetone were obtained. An identical experiment conducted under 1 atm of H₂C=CH₂ gave 0.131 g (0.170 mmol, 51%) of 2-acetone. An experiment in which the first crop of crystals were recrystallized from CH2Cl2/hexane gave beige unsolvated 2 in 46% yield (92% of theory).

Data for 2: mp 205-222 °C dec; 2-acetone 202-212 °C dec; IR (cm⁻¹, CH_2Cl_2) ν_{NO} 1726 (s); ¹H NMR, 2-acetone (δ , CD_2Cl_2) 7.59–7.31 (m, 15 H), 5.74 (s, 5 H), 3.62 (m, 2 H), 2.68 (m, 2 H), 2.12 (s, 6 H, acetone); $(\delta, \text{ acetone-}d_6)$ 7.68–7.48 (m, 15 H), 6.12 (s, 5 H), 3.80 (m, 2 H), 2.75 (m, 2 H); ¹³C NMR (ppm, acetone-d₆) 98.3, 35.5, 27.0, phenyl carbons; UV, 2 (nm, CHCl₃) 259 (pk, ϵ = 3500), 268 (sh, ϵ = 2500), 274 (sh, ϵ = 1700), 300 (sh, ϵ = 500). Anal. Calcd for C₂₅H₂₄F₆NOP₂Re + C₃H₆O: C, 43.41; H, 3.90; N, 1.81; P, 8.00; Found: C, 43.24; H, 3.97; N, 1.83; P, 8.09.

Conversion of 2 to $(\eta$ -C₅H₅)Re(NO)(PPh₃)(CH₂CH₃) (4). A 20-ml CH₂Cl₂ solution of 2 (0.214 g, 0.276 mmol) was cooled to -78 °C, and 1.0 M $Li(C_2H_5)_3BH$ in THF (0.340 mL, 0.340 mmol) was added. The solution was stirred for 15 min at ~78 °C and then 4 h at 25 °C. The solvent was removed under vacuum, and the residue was extracted with benzene. The extract was filtered through silica, concentrated to a residue, and then chromatographed in 90:10 hexane-ethyl acetate on silica gel. The orange band was collected and the solvent removed under vacuum to give 4 (0.062 g, 0.108 mmol, 39%), which was spectroscopically identical with an authentic sample.13

Decomposition of $1-d_2$ in the Presence of $H_2C=CH_2$. To 20 mL of CH_2Cl_2 at -78 °C was added 0.258 g (0.366 mmol) of 1- d_2 . A stream of $H_2C=CH_2$ was bubbled through the resulting solution, which was maintained at -78 °C for 1 h, -23 °C for 1 h, and 25 °C for 4 h. Yellow crystals of 2- d_x -acetone were isolated as described above (0.114 g, 0.146 mmol, 40%); ¹H NMR η -C₅H₅:H₂C=CH₂ ratio (97 ± 1):(3 ± 1). This material was converted to $4 - d_x$ as described in the previous experimental and subjected to mass spectral analysis. The ¹⁸⁷Re molecular ions for 4- d_4 , 4- d_2 , and 4 were at m/e 577, 575, and 573, respectively. The observed 70 eV 577:575:573 ratio for the $4-d_x$ mixture was 1620:1084:76. That for authentic $4 - d_4$ (prepared by reaction of Li(C₂H₅)₃BH with $2 - d_4$) was 1620:1053:16.2. The m/e 575:573 ratios in authentic $4 - d_2^{13b}$ and 4- d_0 were 1706:912 and 28:1547, respectively, These data gave 4- d_4 :4 $d_0:4-d_2$ as $(96 \pm 1):(3 \pm 1):<2$.

Decomposition of 1 in the Presence of $H_2C=CH_2$. Cyclopropane Assay. To 20 mL of CH₂Cl₂ at -78 °C was added 0.190 g (0.271 mmol) of 1. A gentle stream of $H_2C=CH_2$ was then passed through the solution. The exhaust gas was continuously passed through a trap maintained at -78 °C. The reaction was stirred for 1 h at -78 °C after which time CD_2Cl_2 (0.400 mL) was added to the trap. The CD_2Cl_2 solution was collected in a 5-mm NMR tube and maintained at -78 °C until a ¹H NMR spectrum was recorded. The reaction was warmed to 0 °C while the $H_2C = CH_2$ stream was continued. The reaction was kept for 1 h at 0 °C, and the trap contents were collected in CD_2Cl_2 as described above. Finally, the reaction was allowed to warm to 25 °C and stirred for an additional 2 h. The trap contents were again collected as described above. Internal standard Ph₃SiCH₃ (0.007 g, 0.027 mmol) was added each of the three NMR tubes. ¹H NMR analysis (-78 °C) showed no cyclopropane. Authentic gaseous cyclopropane (0.182 mL, 0.008 mmol, 3%) was added to each tube via syringe and proved to be easily detectable by ¹H NMR.

Decomposition of 1 in the Presence of $(\eta - C_5H_5)Re(NO)(PPh_3)(CD_3)$. To 20 mL of CH_2Cl_2 was added 0.080 g (0.142 mmol) of $(\eta - C_5H_5)Re$ - $(NO)(PPh_3)(CD_3)$ and 0.112 g (0.159 mmol) of 1. The reaction was stirred at room temperature for 4 h, and the solvent was removed under oil-pump vacuum. The resulting dark residue was taken up in benzene and filtered through silica. The orange filtrate was collected and the solvent removed under vacuum to give 0.034 g (0.061 mmol, 43%) of $(\eta - C_5H_5)Re(NO)(PPh_3)(CD_xH_3 - x)$. Mass spectral analysis (70 eV) indicated the absence of $(\eta - C_5H_3)Re(NO)(PPh_3)(CH_2CH_3)$ and a m/e563:562:561:560:559 ratio of 1933:12000:20430:22093:17080. The ¹⁸⁷Re molecular ions for the CD₃, CD₂H, CDH₂, and CH₃ labels were at m/e 562, 561, 560, and 559, respectively. The m/e

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563:562:561:560:559 ratio for authentic $(\eta$ -C₅H₅)Re(NO)(PPh₃)(CD₃) was found to be 2688:12090:4185:6980:1648. It was assumed that all label distributions would give identical M + 1, M⁺, M - 1, M - 2, and M - 3 ion ratios. The best linear combination of CD₃:CD₂H:CDH₂:CH₃ was found to be 23:39:29:9.

Codecomposition of 1 and 1- d_{17} . Assay of Recovered Starting Material. To 5 mL of CH₂Cl₂ at room temperature was added a mixture of 1 (0.100 g, 0.142 mmol) and $1-d_{17}$ (0.110 g, 0.153 mmol). The reaction was stirred for 0.5 h and then quenched with 1.0 M $Li(C_2H_5)_3BH$ in THF (0.14 mL, 0.14 mmol). After 10 min, solvent was removed under vacuum. The remaining orange residue was extracted with benzene. The extract was filtered through silica gel, concentrated, and chromatographed on a silica-gel column. The orange band was collected, and the benzene was removed under vacuum. This gave $(\eta$ -C₅H₃)Re(NO)-(PPh₃)(CH₃)-d_x as an orange solid (0.042 g, ca. 0.074 mmol, ca. 25%), which was subjected to mass spectral analysis. The ¹⁸⁷Re molecular ions for $(\eta - C_5H_5)Re(NO)(PPh_3)(CH_3) - d_{17}$, $-d_{15}$, $-d_2$, and d_0 were at m/e 576, 574, 561, and 559, respectively. The observed relative intensities were 633:398:62:942. Authentic $(\eta - C_5H_5)Re(NO)(PPh_3 - d_{15})(CD_2H)$ (prepared from 1- d_{17} and Li(C₂H₅)₃BH) gave a m/e 578:576:574 ratio of 410:633:373. Authentic $(\eta - C_5H_5)$ Re(NO)(PPh₃)(CH₃)- d_0 gave a m/e 561:559:557 ratio of 16:931:544. These data indicate $(\eta - C_5H_5)$ Re(NO)(PPh₃- d_{15})(CD₂H): $(\eta - C_5H_5)$ Re(NO)(PPh₃- d_{15})(CH₃) and $(\eta - C_5H_5)$ Re(NO)(PPh₃- d_{15})(CH₃) C₅H₅)Re(NO)(PPh₃)(CD₂H):(η-C₅H₅)Re(NO)(PPh₃)(CH₃) ratios of $(96 \pm 1):(4 \pm 1)$ and $(5 \pm 1):(95 \pm 1)$, respectively.

Rate of Decomposition of 1. In a typical experiment, a 5-mm NMR tube was charged with 0.019 g (0.027 mmol) of 1 and 0.0015 g (0.0055 mmol) of Ph₃Si(CH₃), capped with a septum, and cooled to -78 °C. Then 0.375 mL of CD₂Cl₂ was slowly added. The NMR tube was then quickly transferred to a NMR probe that had been preequilibrated to the desired decomposition temperature. The disappearance of 1 was monitored by integration of the δ 15.67 and 15.42 ¹H NMR resonances relative to the standard. Plots of 1/c vs. t gave the k_{obsd} in Table I. In the case of 1-d₂, disappearance of the η -C₅H₅ ¹H NMR resonance was monitored.

Reaction of 1 with PPh₃. ¹H NMR monitoring. A 5-mm septumcapped NMR tube was charged with 0.024 g (0.034 mmol) of 1 and 0.400 mL of CD₂Cl₂ and was cooled to -78 °C. Then a solution of 0.010 g (0.037 mmol) of PPh₃ in 0.200 mL of CD₂Cl₂ was injected, and the sample was immediately transferred to a preequilibrated -78 °C NMR probe. A spectrum was immediately recorded (ca. 2-3 min lag time after addition) and showed the formation of $[(\eta$ -C₅H₅)Re(NO)(PPh₃)-(CH₂PPh₃)]⁺PF₆⁻ to be complete.^{8b}

Synthesis of $[(\eta-C_5H_5)\text{Re}(NO)(\text{PPh}_3)(\text{NCCH}_3)]^+\text{BF}_4^-$ (5; BF₄⁻ salt) from $[(\eta-C_5H_5)\text{Re}(NO)(\text{PPh}_3)(\text{CO})]^+\text{BF}_4^-$. A 100-mL Schlenk flask was charged with 0.270 g (0.409 mmol) of $[(\eta-C_5H_5)\text{Re}(NO)(\text{PPh}_3)-(\text{CO})]^+\text{BF}_4^-$ and 20 mL of CH₃CN. Anhydrous (CH₃)₃N⁺-O⁻ (0.035 g, 0.471 mmol) was then added, and the solution immediately turned orange. The solution was stirred for 5 min after which the solvent was removed by rotary evaporation. The residue was taken up in CHCl₃ and ether was slowly admitted by diffusion. Orange-gold crystals of 5 (BF₄⁻ salt) formed, which were collected by filtration and dried (0.254 g, 0.378 mmol, 92%).

Data: mp 208 °C dec; IR (cm⁻¹, CH₂Cl₂) ν_{NO} 1704 (s); ¹H NMR (δ , CDCl₃) 7.57 (br s, 15 H), 5.57 (s, 5 H), 2.54 (s, 3 H); ¹³C NMR (ppm, CDCl₃) 140.4 (CN), phenyl carbons at 133.5 (d, $J_{^{13}C^{-31}P} = 54.1$ Hz), 133.2 (d, J = 10.9 Hz), 131.6, 129.4 (d, J = 10.7 Hz); 92.2 (C₅H₅), 4.1 (CH₃); UV (nm, CHCl₃) 259 (pk, $\epsilon = 3800$), 275 (sh, $\epsilon = 2500$), 308 (sh, $\epsilon = 700$). Anal. Calcd for C₂₃H₂₃BF₄N₂OPRe: C, 44.72; H, 3.45; N, 4.17; P, 4.61. Found: C, 44.57; H, 3.50; N, 4.10; P, 4.63.

Synthesis of a Mixture of $[(\eta-C_5H_5)Re(NO)(PPh_3)(NCCH(C_6H_5)-CH_2CH_3)]^+BF_4^-$ Diastereomers. A 100-mL Schlenk flask was charged with 0.135 g (0.205 mmol) of $[(\eta-C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$, 10 mL of CH₂Cl₂, and 0.297 g (2.050 mmol) of (\pm) -CH₃CH₂CH(C₆H₅)-CN. Anhydrous (CH₃)₃N⁺-O⁻ was then added, and the solution immediately turned orange. After 5 min, the solvent was removed under vacuum. The oily orange residue was washed with hexane until excess nitrile could no longer be detected by TLC. Proton NMR analysis indicated a ca. 1:1 mixture of diastereomers (CDCl₃, δ 5.58 and 5.59 for C₅H₅). The oily residue was dissolved in CH₂Cl₂. Rapid solvent removal under vacuum gave an orange solid (0.135 g, 0.161 mmol, 79%). Characterization: see (+)-(SS)-6 and (-)-(RS)-6.

Decomposition of 1 in the Presence of CH₃CN. A 5-mm NMR tube was charged with 0.019 g (0.026 mmol) of 1, capped with a septum, and cooled to -78 °C. Then 0.400 mL of CD₂Cl₂ and 0.007 mL (0.005 g, 0.132 mmol) of CH₃CN were added by syringe. The tube was transferred to -70 °C NMR probe. A ¹H NMR spectrum showed that no reaction had occurred. The solution was allowed to warm to 25 °C and the appearance of 2 (δ 5.74) and 5 (δ 5.51) was monitored. At all times, the 2:5 ratio was (50 \pm 2):(50 \pm 2).

A 100-mL Schlenk flask was charged with 0.110 g (0.156 mmol) of 1 and cooled to -78 °C. Then 10 mL of CH₂Cl₂ followed by 0.042 mL (0.033 g, 0.794 mmol) of CH₃CN was added. The solution was stirred for 15 min at -78 °C, slowly warmed to 25 °C, and then stirred for 30 min more. The solvent was removed under vacuum and the residue was dissolved in a small amount of cold CHCl₃ and filtered through a glass-wool plug. Yellow crystals of 2 formed, which were isolated and recrystallized from acetone/ether as described above (0.055 g, 0.071 mmol, 91% of theory). Solvent was removed from the supernate and the residue recrystallized from CHCl₃/ether to give orange-gold crystals of 5 (0.053 g, 0.073 mmol, 93% of theory): ¹H NMR (δ , CDCl₃) 7.52 (m, 15 H), 5.53 (s, 5 H), 2.4, (s, 3 H).

Experiments with Optically Active Substrates. These were done analogously to the previous experiments with racemic substrates. The (+)-(R)-2 isolated from the decomposition of (+)-(S)-1 gave $[\alpha]^{25}_{589}$ 88.6° (c 0.59, CHCl₃). The (+)-(S)-5 isolated from the decomposition of (+)-(S)-1 in the presence of 10 equiv of CH₃CN at 0 °C gave $[\alpha]^{25}_{589}$ 330.6° (c 0.56, CHCl₃). The (+)-(R)-2 was converted to (+)-(S)-4 $(\text{Li}(C_2H_5)_3\text{BH}, 16\%)$, which gave $[\alpha]^{25}_{589}$ 114° (c 0.23, CHCl₃).

Codecomposition of (+)-(S)-1 d_2 and (-)-(R)-1- d_{15} . To 5 mL of CH₂Cl₂ at room temperature was added a mixture of (+)-(S)-1- d_2 (0.119 g, 0.169 mmol) and (-)-(R)-1- d_{15} (0.128 g, 0.176 mmol). The reaction was stirred for 5 h and the solvent was removed under vacuum. Ethylene complex 2- d_x was isolated as yellow crystals (0.110 g, 0.153 mmol, ca. 89% of theory) from CH₂Cl₂/hexane as described above. The 2- d_x was converted to $4-d_x$ as described above and subjected to mass spectral analysis. The ¹⁸⁷Re molecular ions for $4-d_{17}$, $4-d_{15}$, $4-d_4$, and $4-d_2$ were at m/e 590, 588, 577, and 575, respectively. The observed 16-eV relative intensities for $4-d_x$ were 18:498:723:457. Authentic $4-d_{15}$ (prepared from $1-d_{15}$ and CH₃Li)¹³ gave a m/e 590:588:586 ratio of 7:498:287. Authentic $4-d_4$ gave a m/e 579:577:575 ratio of 12:723:428. These data indicate $4-d_{17}:4-d_{15}$ and $4-d_4:4-d_2$ ratios of $(2 \pm 1):(98 \pm 1)$ and $(96 \pm 1):(4 \pm 1)$, respectively.

Synthesis of (+)-(SS)- $[(\eta-C_5H_5)Re(NO)(PPh_3)(NCCH(C_6H_5)-CH_2CH_3)]^+PF_6^-((+)-(SS)-6)$. A solution of 0.200 g (0.358 mmol) of (+)-(S)- $(\eta-C_5H_5)Re(NO)(PPh_3)(CH_3)$ in 10 mL of CH₂Cl₂ was cooled to -78 °C and 0.139 g (0.358 mmol) of Ph₃C⁺PF₆⁻ was then added. The reaction was stirred for 1 h at -78 °C and then 0.520 g (3.60 mmol) of (-)-(S)-CH₃CH₂CH(C₆H₅)CN was added. The reaction was warmed to 0 °C and stirred for 5 h. The solvent was then removed under vacuum and the resulting orange oil was washed with hexane to remove excess nitrile. The remaining orange oil was then extracted with benzene until the extracts were colorless. A yellowish solid remained, which was recrystallized from CH₂Cl₂/hexane to give (+)-(R)-2 (0.091 g, 0.127 mmol, 71% of theory). The benzene extracts were combined and the solvent was removed. The resulting orange solid was recrystallized from CH₂Cl₂/hexane to give orange needles of (+)-(SS)-6 (0.122 g, 0.147 mmol, 82% of theory).

Data for (+)-(*SS*)-6: mp 177-178 °C; $[\alpha]^{25}_{389}$ 169.7° (*c* 0.35, CHCl₃); IR (cm⁻¹, CHCl₃) ν_{NO} 1703 (s); ¹H NMR (δ , CDCl₃) 7.54-7.12 (m) and 6.84 (m, 2 H) (C₆H₅, 20 H total); 5.54 (s, 5 H), 4.50 (t, *J* = 7.5 Hz, CH), 1.90 (m, *J* \simeq 7 Hz, CH₂), 0.92 (*t*, *J* = 7.3 Hz, CH₃); ¹³C NMR (ppm, CDCl₃) 145.0 (CN), phenyl carbons at 133.6 (d, J¹³C-³¹P = 53.5 Hz), 133.2 (d, *J* = 10.9 Hz), 132.4, 131.6, 129.3 (d, *J* = 10.6 Hz) 129.2, 128.3, 127.6; 92.4 (C₅H₅), 40.1 (CH), 28.2 (CH₂), 11.3 (CH₃); UV (nm, CHCl₃) 261 (pk, ϵ = 3900), 276 (sh, ϵ = 1800).

Synthesis of (-)- $(\hat{R}S)$ - $[(\eta-C_5H_5)Re(NO)(PPh_3)(NCCH(C_6H_5)-CH_2CH_3)]^+PF_6^-$ ((-)-(RS)-6). A 100-mL Schlenk flask was charged with 15 mL of CH₂Cl₂ and cooled to -78 °C, whereupon 0.200 g (0.285 mmol) of (-)-(R)-1 was added. Neat (-)-(S)-CH₃CH₂CH₂CH(C₆H₃)CN (0.062 g, 0.427 mmol) was then syringed in and the solution was warmed to 0 °C and stirred for 5 h. The solvent was then removed under vacuum and the resulting orange oil was washed with hexane to remove excess nitrile. The remaining orange oil was then extracted with benzene until the extracts were colorless. A yellowish solid remained, which was recrystallized from CH₂Cl₂/hexane to give (-)-(S)-2 (0.090 g, 0.125 mmol, 88% of theory). The benzene extracts were combined and solvent was removed under vacuum. The resulting orange foam-up solid, (-)-(RS)-6 (0.095 g, 0.114 mmol, 80%), gave only oils when recrystallizations were attempted from a variety of solvent systems.

Data on (-)-(*RS*)-6: mp 87–93 °C; $[\alpha]^{25}_{589}$ -207° (*c* 0.68, CHCl₃); IR (cm⁻¹, CHCl₃) ν_{NO} 1701 (s); ¹H NMR (δ , CDCl₃) 7.55–7.24 (m) and 7.04 (m, 2 H) (C₆H₅, 20 H total); 5.55 (s, 5 H), 4.47 (br t, *J* = 6.7 Hz, CH), 1.60 and 1.42 (two br m, *J* \simeq 7 Hz, -CH₂), 0.65 (t, *J* = 7.3 Hz, -CH₃); ¹³C NMR (ppm, CDCl₃) 145.0 (CN), phenyl carbons at 133.8 (d, *J*_{13C,21p} = 52.1 Hz), 133.4 (d, *J* = 10.5 Hz), 131.7, 131.4, 129.4 (d, *J* = 10.7 Hz), 129.3, 128.6, 127.7; 92.4 (C₅H₅), 40.4 (CH), 28.4 (CH₂), 11.2 (CH₃); UV (nm, CHCl₃) 260 (pk, ϵ = 3900), 276 (sh, ϵ = 1900).

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Supplementary Material Available: Tables of crystallographic data, bond lengths, and angles, atomic coordinates, and structure factors for (+)-(SS)-6, and figures showing atom numbering and crystal packing (36 pages). Ordering information is given on any current masthead page.

Iodocyclization of Allylic Alcohol Derivatives Containing Internal Nucleophiles. Control of Stereoselectivity by Substituents in the Acyclic Precursors

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Abstract: The effect of various substituents on the diastereoselectivity of a number of kinetically controlled iodocyclizations has been studied. The reaction of 3-hydroxy-4-alkenoic acids (1a-n) with iodine in a neutral two-phase medium gives stereoselective ring closure, usually to the cis-3-hydroxy-4-iodoalkyl lactone. The stereoselectivity is unaffected by protection of alcohol moiety (1b,c), but replacement of the hydroxyl group with a methyl substituent (1e) lowers the stereoselectivity significantly. A 2-methyl substituent (1j-m) can have a dramatic effect on the diastereoselectivity of the reaction. Esters and ketones (10a-c) undergo a related jodocvclization with similar stereoselectivity. In the absence of an internal nucleophile (13, 16) iodohydrin formation results in reversed diastereoselectivity of iodine attack.

Halolactonization of unsaturated carboxylic acids or their salts has been widely utilized since Bougault's initial systematic study early in this century.¹ The reaction has been invaluable both in synthesis and in structure elucidation, but for many years its potential to produce highly functionalized products with stereochemical control at two adjacent centers in the lactone ring itself remained unexplored.² Recent activity in the field of acyclic stereoselection has, however, included several studies³ which demonstrate that synthetically useful levels of asymmetric induction, directed by substituents in acyclic precursors, can be achieved in the iodolactonization of substituted alkenoic acids. We describe in this paper our investigation of iodolactonization and related reactions directed by an oxygen substituent in the 3-position of 4-alkenoic acids,⁴ esters, and other allylic alcohol derivatives. We have found that even though the product distributions often show high stereoselectivity in a predictable way, there are some striking anomalies which underscore the mechanistic subleties of the reaction.

Results and Discussion

Iodolactonization of 3-Hydroxy-4-alkenoic Acids. When the 3-hydroxy-4-alkenoic acid 1a is treated at 0 °C with iodine in a two-phase reaction mixture of ether-tetrahydrofuran-aqueous bicarbonate, the major product is the iodo lactone 3a with the iodoethyl and hydroxyl groups cis. The ratio of diastereomers (cis (3a):trans (4a)) is high (96:4), and it can be quantified easily in this case and those described later by high-pressure liquid chromatographic analysis of the crude reaction mixture. The stereochemical assignments are made by methanolysis of the iodo lactone mixture, producing the epoxides 5a and 6a, which can be compared by capillary gas chromatography to an authentic mixture prepared by Sharpless epoxidation⁵ of the corresponding allylic alcohol ester 2. Since the stereoselectivity of the Sharpless



reaction is quite predictable, this is a reliable method for assigning stereochemistries to the iodo lactone products, and it also serves as an indirect check of the lactone product ratios. It is noteworthy that the iodolactonization-methanolysis sequence complements the Sharpless procedure by producing mainly the threo-hydroxy epoxide where the major Sharpless diastereomer is erythro.

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