FT NMR measurements made use of equipment obtained by NSF Departmental instrumentation grants.

Registry No. 4, 86497-25-8; **5**-$CHCl_2CH_3$, 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; $Re_2(CO)_{10}$, 14285-68-8; $NO^+BF_4^-$, 14635-75-7; $Li(C_2H_5)_3BH$, 22560-16-3; $NaBH_4$, 16940-66-2; $Ph_3C^+PF_6^-$, 437-17-2; $C_6H_5I^+-O^-$, 536-80-1.

Supplementary Material Available: Tables of bond distances and angles, atomic coordinates, thermal parameters, and structure factors for **4** and **5**·$CHCl_2CH_3$, 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 $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)^+$ Center. Remarkable Enantiomer Self-Recognition

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Abstract: The methylidene complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$ (**1**) couples to the ethylene complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C=CH_2)]^+PF_6^-$ (**2**; ca. 50%) at 273–308 K in CH_2Cl_2. The byproduct $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)_2]^+PF_6^-$ (**3**; ca. 25%) or, in the presence of CH_3CN, $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH_3)]^+PF_6^-$ (**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 $\Delta H^\ddagger = 9.8 \pm 0.6$ kcal/mol and $\Delta S^\ddagger = -33.8 \pm 1.0$ 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 PPh_3 dissociation or intermolecular $=CH_2$ 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*)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH(C_6H_5)CH_2CH_3)]^+PF_6^-$ ((+)-(*SS*)-**6**) shows that RCN adducts also form with retention. These data are interpreted as evidence for the rate-determining formation of initial $\overline{ReCH_2ReCH_2}$ (**7a**) or $ReCH_2CH_2Re$ (**7b**) intermediates. Subsequent rapid conversion to primary monomeric products **2** and $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(S)]^+PF_6^-$ (**8**; S = CH_2Cl_2 or vacant coordination site) is proposed. Comparisons are made to other homogeneous and heterogeneous $=CH_2$ coupling reactions.

Metal-bound methylidenes ($=CH_2$) 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 bond-forming reactions—has been of intense interest.[5-11]

In a recent study, Pettit demonstrated that surface-bound $=CH_2$ rapidly dimerizes to $H_2C=CH_2$ in the absence of hydrogen.[5e,f] Curiously, attempts to generate *homogeneous* $L_nM=CH_2$ complexes have often given $L_nM(H_2C=CH_2)$ complexes in ca. 50% yields.[7b,10,11] Schrock's isolable *nucleophilic* methylidene complex $(\eta\text{-}C_5H_5)_2Ta(CH_3)(=CH_2)$[6a,b] decomposes to the ethylene complex $(\eta\text{-}C_5H_5)_2Ta(CH_3)(H_2C=CH_2)$.[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 C_5Me_5 methylidene complexes, $[(\eta\text{-}C_5Me_5)Re(NO)(L)(=CH_2)]^+PF_6^-$ (L = PPh_3, $P(OPh)_3$), 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 $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$ (**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 $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C=CH_2)]^+PF_6^-$ (**2**) and present stereochemical and kinetic data that we interpret as evidence for $\overline{ReCH_2ReCH_2}$ and/or $ReCH_2CH_2Re$ 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 $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$ (**1**) was allowed to decompose in CD_2Cl_2 at room temperature. Proton NMR monitoring showed that two principal products, the ethylene complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C=CH_2)]^+PF_6^-$ (**2**) and $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)_2]^+PF_6^-$ (**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^- salt).[8b]

The possibility of secondary reactions during the $=CH_2$ coupling was probed by decomposing $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CD_2)]^+PF_6^-$ (**1**-d_2) under $H_2C=CH_2$. The ratio of C_5H_5 to ethylenic protons in the resulting **2** was shown by ^1H NMR to be (97 ± 1):(3 ± 1). Reaction of this **2** with $Li(C_2H_5)_3BH$ gave the known[13] ethyl complex $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(C_2H_{5-x}D_x)$ (**4**-d_x) in 15–40% yields. Mass spectral analysis (Experimental Section) indicated a (96 ± 1):(3 ± 1): <2 ratio of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CD_2CD_2H)$:$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_3)$:$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(C_2D_2H_3)$. 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.

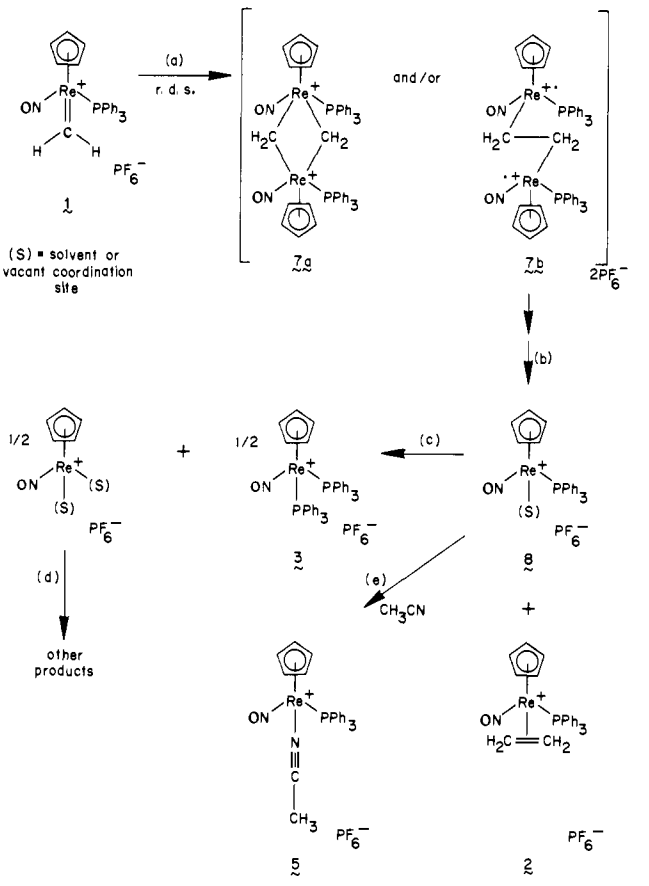
A stream of $H_2C=CH_2$ was passed first through a −78 °C CH_2Cl_2 solution of **1** and then through a −78 °C trap. The solution of **1** was warmed to 0 °C and then to room temperature while maintaining the $H_2C=CH_2$ stream. An internal standard was added to the trap and the contents were analyzed 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 $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3\text{-}d_{15})(=CD_2)]^+PF_6^-$ (**1**-d_{17}) was dissolved in CH_2Cl_2 at 25 °C. After 0.5 h (ca. 70% decomposition), $Li(C_2H_5)_3BH$ was added and the resulting $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$-$d_x$ recovered (25%). Mass spectral analysis showed that this material was almost entirely $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ and $(\eta\text{-}C_5H_5)Re(NO)(PPh_3\text{-}d_{15})(CD_2H)$ (3:2 ratio). Intermediate label distributions $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHD_2)$ and $(\eta\text{-}C_kH_5)Re(NO)(PPh_3\text{-}d_{15})(CH_3)$ constituted only 4% and 5% of the PPh_3-d_0 and PPh_3-d_{15} products, respectively. This experiment shows that no equilibria that would allow intermolecular PPh_3 or $=CH_2$ exchange occur prior to the rate-determining step in the coupling. The decomposition of **1** cannot be studied in the presence of PPh_3 because rapid reaction occurs at −78 °C to give $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2PPh_3)]^+PF_6^-$.[8b]

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

The rate of decomposition of **1** showed a marked *inverse* secondary deuterium isotope effect, $k_{=CH_2}/k_{=CD_2} = 0.39 \pm 0.03$, at 298 K (Table I). The customary normalization for the anticipated number of deuteriums in the transition state[15] gives $k_H/k_D = 0.79$ ($(0.39)^{1/4}$). 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]

Scheme I. Proposed Mechanism of $=CH_2$ Coupling



The decomposition rate of **1** was not affected by the presence of 3–10 equiv of CH_3CN or $CH_3CH_2CH(C_6H_5)CN$ (Table I). However, these additives changed the decomposition stoichiometry dramatically. Now, equimolar quantities of **2** and nitrile complexes $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(NCR)]^+PF_6^-$ (**5**, R = CH_3; **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 $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ with anhydrous $(CH_3)_3N^+\text{–}O^-$ in CH_3CN or $CH_3CH_2CH(C_6H_5)CN/CH_2Cl_2$. Importantly, **6** was obtained as a ca. 1:1 mixture of diastereomers that gave distinct 200-MHz C_5H_5 ^1H NMR resonances (δ 5.54 and 5.55).

The decomposition rate of **1** was not affected by the presence of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (entries 10 and 11, Table I). A sample of **1** was allowed to couple in the presence of 0.89 equiv of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CD_3)$. The $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CD_xH_{3-x})$ was recovered (43%) and analyzed by mass spectrometry. A 23:39:29:9 ratio of CD_3:CD_2H:CDH_2:CH_3 was found. Complete randomization of the label would have given a 19:42:31:8 ratio. Hence $=CH_2/CH_3$ hydride transfer is much faster than $=CH_2$ coupling. No $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(C_2H_5)$-$d_x$ 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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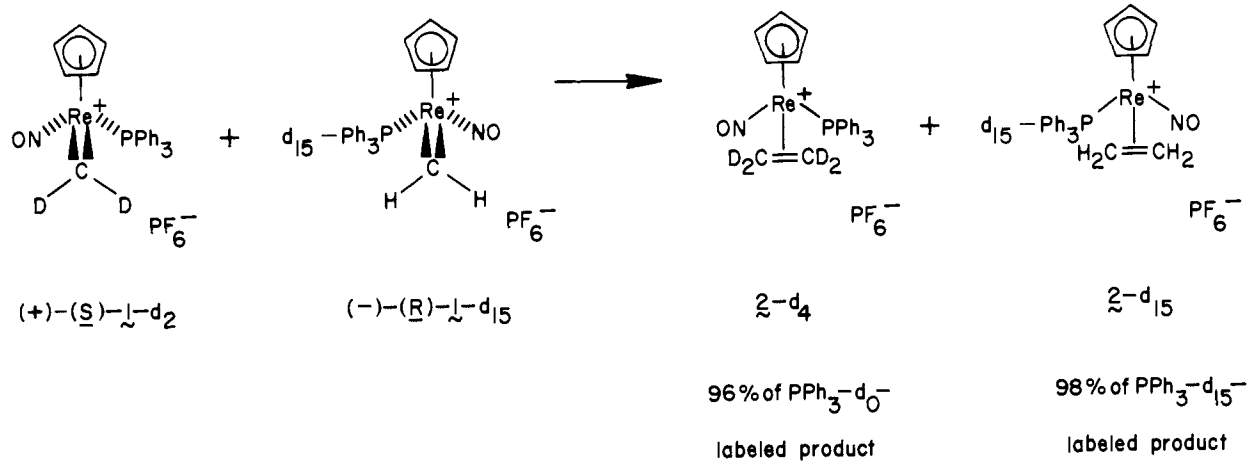
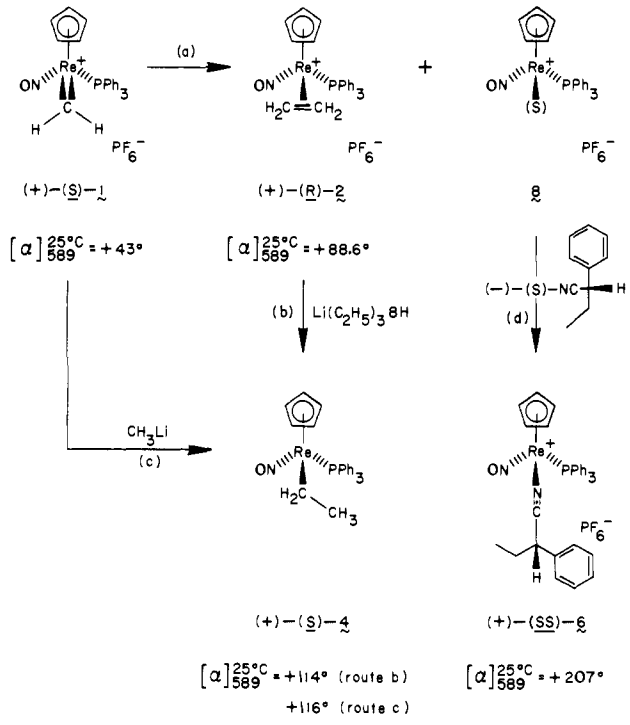
Scheme II. Enantiomer Self-Recognition in the $=CH_2$ Coupling[a]



[a] Since **2**-d_{15} cannot be separated from **2**-d_4, the additional prediction that they should have opposite configurations (Scheme III) cannot be tested.

Scheme III. Stereochemistry of $=CH_2$ Coupling



identical with that of (±)-**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 CH_2Cl_2 at 25 °C and allowed to couple to **2** (Scheme II). After isolation, this **2** was treated with $Li(C_2H_5)_3BH$ and the resulting $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_3)$-$d_x$ (**4**-d_x) analyzed by mass spectrometry. The $(\eta\text{-}C_5H_5)Re(NO)(PPh_3\text{-}d_{15})(CH_2CH_3)$:$(\eta\text{-}C_5H_5)Re(NO)(PPh_3\text{-}d_{15})(C_2D_2H_3)$ and $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CD_2CD_2H)$:$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(C_2D_2H_3)$ ratios were (98 ± 1):(2 ± 1) and (96 ± 1):(4 ± 1), respectively. Hence $H_2C=CD_2$-containing products, which 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.*

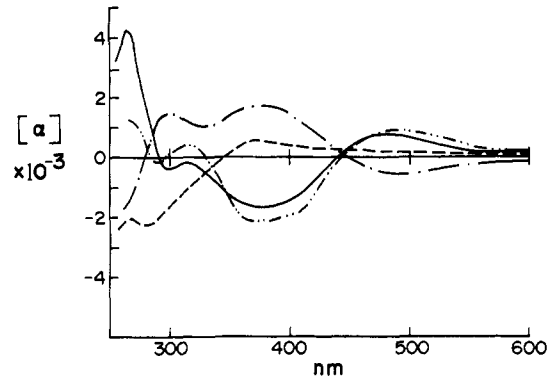


Figure 1. ORD spectra of (+)-(*R*)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C=CH_2)]^+PF_6^-$ ((+)-(*R*)-**2**) (—), (+)-(*S*)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH_3)]^+PF_6^-$ ((+)-(*S*)-**5**) (- - -); (+)-(*SS*)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH(C_6H_5)CH_2CH_3)]^+PF_6^-$ ((+)-(*SS*)-**6**)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

Decomposition of (+)-(*S*)-**1** (>99% ee)[17] gave (+)-**2** of high optical rotation (Scheme III), suggestive of appreciable stereoselectivity. This (+)-**2** was treated with $Li(C_2H_5)_3BH$ as described above for the racemate to give $(+)\text{-}(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_3)$ ((+)-**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 CH_3CN gave $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH_3)]^+PF_6^-$ (**5**) with a substantial optical rotation (0 °C run: $[\alpha]^{25}_{589}$ +330°; 25 °C run: +248°). Nitrile complex **5** showed no optical activity loss over the course of 1.5 days at 25 °C in CH_2Cl_2. In order to assay the trapping stereoselectivity, (+)-(*S*)-**1** was decomposed at 0 °C in the presence of (−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$.[19] The adduct obtained, $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH(C_6H_5)CH_2CH_3)]^+PF_6^-$ ((+)-**6**, Scheme III, step d) gave $[\alpha]^{25}_{589}$ +170° and consisted of a single diastereomer by 200-MHz ^1H NMR. Similarly, a sample of (−)-**6** (diastereomer of (+)-**6**), $[\alpha]^{25}_{589}$ −207°, was

(17) (a) The priority sequences for assigning *R*/*S* absolute configurations to the complexes in this paper are as follows:[17b] $\eta^5\text{-}C_5H_5$ > PPh_3 > NO > alkyl, alkylidene, nitrile, *but* $\eta^5\text{-}C_5H_5$ > PPh_3 > $\eta^2\text{-}H_2C=CH_2$ > 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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(19) Cram, D. J.; Haberfield, P. *J. Am. Chem. Soc.* **1961**, *83*, 2354.

Table I. Decomposition of $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$ (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	0.013 ± 0.001
				0.014 ± 0.001
				av 0.014 ± 0.001
2	(±)-1	283	0.069	0.026 ± 0.001
				0.026 ± 0.001
				av 0.026 ± 0.001
3	(±)-**1**	298	0.058	0.062 ± 0.007
			0.062	0.061 ± 0.004
			0.082	0.060 ± 0.006
			0.170	0.057 ± 0.006
			0.180	0.064 ± 0.007
			0.255	0.057 ± 0.019
				av 0.060 ± 0.003
4	(±)-**1**	308	0.053	0.115 ± 0.006
			0.054	0.137 ± 0.006
			0.054	0.123 ± 0.005
				av 0.125 ± 0.012
5	(±)-1-d_2	298	0.050	0.151 ± 0.004
			0.052	0.157 ± 0.003
			0.053	0.143 ± 0.006
			0.055	0.164 ± 0.006
				av 0.154 ± 0.010
6	(±)-1 (5 equiv CH_3CN)	298	0.166	0.061 ± 0.012
7	(±)-1 (10 equiv CH_3CN)	298	0.051	0.058 ± 0.010
			0.193	0.063 ± 0.024
8	(±)-1 (6 equiv $CH_3CH_2CH(C_6H_5)CN$)	298	0.070	0.059 ± 0.009
9	(±)-1 (CH_3CN solvent)	283	0.069	0.038 ± 0.001
			0.065	0.036 ± 0.002
10	(±)-**1** (0.76 equiv $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$)	283	0.075	0.027 ± 0.002
11	(±)-1 (1.09 equiv $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$)	283	0.054	0.026 ± 0.001
12a	(+)-(*S*)-1	298	0.054	0.135 ± 0.007
			0.061	0.144 ± 0.004
12b	(−)-(*R*)-1	298	0.053	0.135 ± 0.004
			0.058	0.143 ± 0.006
				av 0.139 ± 0.005

synthesized from (−)-(*R*)-**1** and (−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$. No (+)-**6** could be detected in the crude reaction mixture by ^1H NMR. A $CDCl_3$ solution containing (−)-**6** and (+)-**6** in a 1:99 ratio was prepared, and a 200-MHz ^1H NMR spectrum was recorded. The η-C_5H_5 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 $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(X)$, 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 CH_2Cl_2 solution of (+)-**6** gave suitable crystals for X-ray analysis. X-ray data were collected at −158 °C by using monochromated Mo Kα (0.710 69 Å) radiation on a Syntex P$\bar{1}$ 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 $P2_1$. Of 5939 reflections collected with $2\theta < 50°$, 5682 reflections with $I \geq 3\sigma$ were used in the final refinement.

The position of the rhenium was obtained from a three-dimensional Patterson map. Fourier synthesis combined with least-squares refinement yielded all non-hydrogen atoms. Absorption corrections were applied and all non-hydrogen atoms were (with the exception of the PPh_3 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

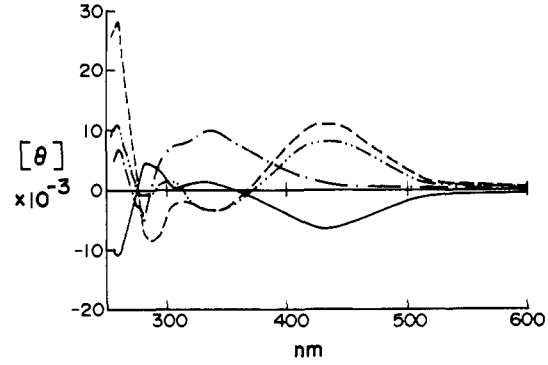

Figure 2. CD spectra of (+)-(*R*)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH_2)]^+PF_6^-$ ((+)-(*R*)-**2**) (·····), (+)-(*S*)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH_3)]^+PF_6^-$ ((+)-(*S*)-**5**) (- - -), (+)-(*SS*)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH(C_6H_5)CH_2CH_3)]^+PF_6^-$ ((+)-(*SS*)-**6**)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

(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).

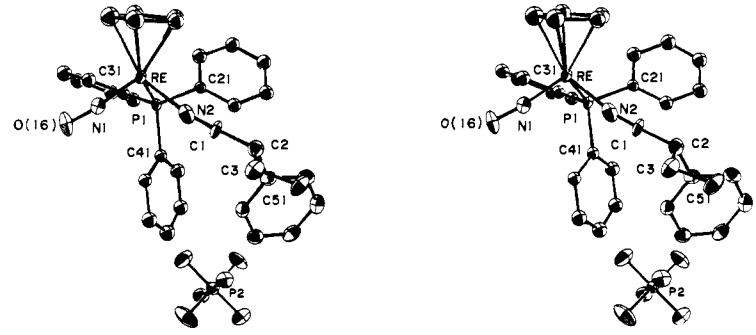

Figure 3. Stereoview of the molecular structure of (+)-(*SS*)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH(C_6H_5)CH_2CH_3)]^+PF_6^-$ ((+)-(*SS*)-**6**).

Table II. Selected Bond Lengths and Angles in (+)-(*SS*)-**6**[a]

atoms	distance, Å	atoms	angle, deg
Re-N2	2.089 (8)	Re-N2-C1	168.5 (6)
Re-P1	2.377 (2)	N2-C1-C2	177.9 (8)
Re-N1	1.767 (6)	N2-Re-N1	102.9 (3)
Re-C_5H_5[b]	2.282	N1-Re-P1	92.5 (3)
N2-C1	1.131 (10)	P1-Re-N2	87.0 (3)
C1-C2	1.454 (10)	Re-N1-O16	174.3 (6)
N1-O16	1.194 (8)		

[a] See Figure 3 for numbering of atoms. [b] Average distance from Re to C_5H_5 carbons; the tilt of the C_5H_5 least-squares plane with respect to the vector between Re and C_5H_5 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 CH_3CN and $CH_3CH_2CH(C_6H_5)CN$ 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 $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(S)]^+PF_6^-$ (**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 $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(NCR)]^+PF_6^-$ (Scheme I, step e).

We now consider the $=CH_2$ 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 $(\eta\text{-}C_5H_5)Mn(NO)(L)(CO_2CH_3) \rightarrow (\eta\text{-}C_5H_5)Mn(NO)(L')(CO_2CH_3)$ occur dissociatively and with retention or (partial) racemization.[25] The pyramidal fragment $(\eta\text{-}C_5H_5)Mn(NO)(CO_2CH_3)$ and isoelectronic homologues[26] have appreciable configurational stability. We therefore conclude that the solvent displacement **8** → **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 $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3\text{-}d_{15})(=CD_2)]^+PF_6^-$ (**1**-d_{17}) excludes both preequilibrium PPh_3 dissociation and any preequilibrium process that would scramble the $=CH_2$ 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 $Re{=}CH_2$ 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** → **7** would nicely account for the inverse secondary kinetic isotope effect, k_H/k_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**, $[(\eta\text{-}C_5Me_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$.[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 ←+ $Re{=}CH_2$ dipoles. The highly negative $\Delta S^\ddagger$ 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 $\Delta S^\ddagger$ 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 $(\eta\text{-}C_5H_5)$-substituted $TiCH_2TiCH_2$ metallocycle was isolated by Grubbs and Ott from a reaction that generated $(\eta\text{-}C_5H_5)_2Ti$-

(21) All least-squares refinements computed the agreement factors *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 $\sum w_i||F_o| - |F_c||^2$.

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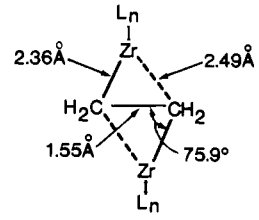
($=CH_2$).[28] Several MCH_2CH_2M' species have been synthesized.[29,30] The bis(rhenium) complex $(CO)_5ReCH_2CH_2Re(CO)_5$ has been characterized by an X-ray crystal structure. The X-ray crystal structure of $(\eta\text{-}C_5H_5)_2((C_2H_5)_3AlCl)ZrCH_2CH_2Zr(ClAl(C_2H_5)_3)(\eta\text{-}C_5H_5)_2$ showed the novel arrangement of core atoms **9**.[30] A full carbon–carbon bond is present, but some

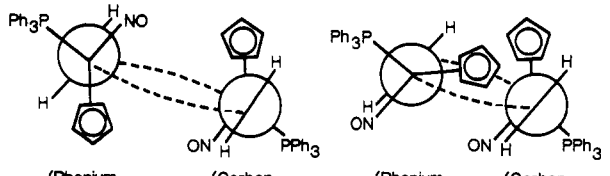


9

bonding of each zirconium to the β CH_2 remains. Hence **9** is a model for the potential CH_2 coupling step **7a** → **7b**. However, no MCH_2CH_2M' complex has been isolated from a reaction thought to involve a $L_nM{=}CH_2$ intermediate.

The 2.3-fold increase observed in the decomposition rate of optically pure **1** (Table I, entry 12) is close to the idealized value[12] 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 *heterochiral*[31] 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 $\Delta S^{\ddagger}$ calculated previously (from $k_{obsd}/2$), −32.2 ± 1.0 eu, must be corrected to −33.8 ± 1.0 eu. This gives $\Delta G^{\ddagger}_{298} = 19.9 \pm 0.9$ kcal/mol.

We had expected that the rate of decomposition of racemic **1** would be greater than that of optically active **1**. Several (η-C_5H_5)Re(NO)(PPh_3)(X) systems undergo stereospecific reactions in which an attacking agent approaches −X from a direction opposite (antiperiplanar) to the Re–PPh_3 bond.[13,32,33] If this constraint is placed upon both rheniums in a $_\pi2_s + _\pi2_s$ cycloaddition geometry[34] leading to **7a**, then only two transition states, **10** (*RS*,*SR*) and **11** (*RR*,*SS*), are possible. An unfavorable steric



10 (heterochiral) **11** (homochiral)

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–PPh_3 bond of each rhenium. This feature dominates the chemistry of all (η-C_5H_5)Re(NO)(PPh_3)(X) systems studied to date. Within this constraint, there are a number of possible coupling geometries. For instance, if the left-most rheniums in **10** and **11** are raised slightly from the plane of the paper, transition states that would be reasonable precursors to **7b** are obtained. While this attenuates some of the steric interactions in **11**, **10** would still seem to be the lower energy transition state.

Improvised space-filling models have been used to assess the various $_\pi2_s + _\pi2_a$ modes of $Re{=}CH_2$ 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 $_\pi2_s + _\pi2_s$ 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 PPh_3 in controlling the direction of $Re{=}CH_2$ 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 ($LiAlH_4/TiCl_3$) 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* $_\pi2_s + _\pi2_a$ 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 $L_nM{=}CH_2$ species, and **1** simply reacts with itself at a faster rate. Less stable, more electrophilic $L_nM{=}CHR$ species such as $[(\eta\text{-}C_5H_5)Fe(L)(L')(=CHR)]^+X^-$ 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 $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2OCH_3)$ and formyl $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$ at −70 °C.[8b] Hence the facile exchange of hydride and deuteride between **1** and $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CD_3)$ 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–CH_3 (1.46 Å) bonds were similar to those found in (+)-(*SS*)-**6** (Table II). A slight deviation of ∠N–C–CH_3 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 $(\eta\text{-}C_5H_5)_2Ta(=CH_2)$ and found a second-order coupling to $(\eta\text{-}C_5H_5)_2Ta(CH_3)(H_2C=CH_2)$ and "$(\eta\text{-}C_5H_5)_2Ta(CH_3)$" analogous to that in Scheme I.[6b] 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 $[(\eta\text{-}C_5H_5)Mo(CO)_2(PPh_3)(=CH_2)]^+CF_3SO_3^-$ and $[(\eta\text{-}C_5H_5)W(CO)_2(PPh_3)(=CH_2)]^+CF_3SO_3^-$ couple at ≳−70 and ≳−20 °C, respectively, to give $[(\eta\text{-}C_5H_5)M(CO)_2(PPh_3)(H_2C=CH_2)]^+CF_3SO_3^-$ and detectable $[(\eta\text{-}C_5H_5)M(CO)_2(PPh_3)(S)]^+CF_3SO_3^-$ or $(\eta\text{-}C_5H_5)M(CO)_2(PPh_3)(OSO_2CF_3)$ species.

Casey found that reaction of $(\eta\text{-}C_5H_5)Re(NO)(CO)(CH_3)$ with $Ph_3C^+BF_4^-$ gave $[(\eta\text{-}C_5H_5)Re(NO)(CO)(H_2C=CH_2)]^+BF_4^-$.[10d] It was proposed[10d] that initial formation of $[(\eta\text{-}C_5H_5)Re(NO)(CO)(=CH_2)]^+BF_4^-$ was followed by methyl transfer from starting material to give $(\eta\text{-}C_5H_5)Re(NO)(CO)(CH_2CH_3)$; subsequent β-hydride abstraction by $Ph_3C^+BF_4^-$ would give the ethylene complex product. We have shown that except for degenerate hydride transfer, **1** is unreactive toward $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$. Furthermore, ethyl complex $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_3)$ undergoes α-hydride abstraction when treated with $Ph_3C^+PF_6^-$.[13] Hence a corresponding mechanism cannot operate in our PPh_3-substituted compounds.

Masters has reported that the stoichiometric reduction of $Cr(CO)_6$ by AlH_3 gives ethylene as the exclusive (>95%) organic product.[42] The initial formation of $(CO)_5Cr=CH_2$, 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 $M=CH_2$ 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 $L_nM=CH_2$ 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 (±)-, (−)-(*R*)-, and (+)-(*S*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ were synthesized by $NaBH_4$ reduction of $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ as described previously.[8b,c] Analogous $NaBD_4$ reductions gave $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CD_3)$ and $(\eta\text{-}C_5H_5)Re(NO)(PPh_3\text{-}d_{15})(CD_3)$. These were treated with $Ph_3C^+PF_6^-$ 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 C_6D_5MgBr and treated with PCl_3 (Mallinckrodt) to give $PPh_3\text{-}d_{15}$.[43] Racemic $CH_3CH_2CH(C_6H_5)COOH$ was obtained from Aldrich, resolved by the method of Petterson,[44] and converted to (−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$ as described by Cram and Haberfield.[19] Ethylene was purchased from Matheson and used without purification. Silane Ph_3SiCH_3 was prepared from Ph_3SiCl and CH_3MgBr analogously to a literature procedure.[45]

Isolation of $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C=CH_2)]^+PF_6^-$ (2) from the Decomposition of $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$ (1). To 20 mL of CH_2Cl_2 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 $CHCl_3$ and then filtered through glass wool, whereupon yellow crystals spontaneously precipitated. These were collected, washed with small amounts of cold $CHCl_3$ 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 $H_2C=CH_2$ gave 0.131 g (0.170 mmol, 51%) of **2**·acetone. An experiment in which the first crop of crystals were recrystallized from CH_2Cl_2/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); (δ, 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); ^{13}C NMR (ppm, acetone-d_6) 98.3, 35.5, 27.0, phenyl carbons; UV, **2** (nm, $CHCl_3$) 259 (pk, ε = 3500), 268 (sh, ε = 2500), 274 (sh, ε = 1700), 300 (sh, ε = 500). Anal. Calcd for $C_{25}H_{24}F_6NOP_2Re + C_3H_6O$: 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 $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_3)$ (4). A 20-ml CH_2Cl_2 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 $\eta\text{-}C_5H_5$:$H_2C=CH_2$ 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 ^{187}Re 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 $Li(C_2H_5)_3BH$ 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 ± 1):(3 ± 1):<2.

Decomposition of 1 in the Presence of $H_2C=CH_2$. Cyclopropane Assay. To 20 mL of CH_2Cl_2 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 Ph_3SiCH_3 (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 $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CD_3)$. To 20 mL of CH_2Cl_2 was added 0.080 g (0.142 mmol) of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CD_3)$ 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 $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CD_xH_{3-x})$. Mass spectral analysis (70 eV) indicated the absence of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_3)$ and a *m/e* 563:562:561:560:559 ratio of 1933:12 000:20 430:22 093:17 080. The ^{187}Re molecular ions for the CD_3, CD_2H, CDH_2, and CH_3 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 (η-C_5H_5)Re(NO)(PPh_3)(CD_3) was found to be 2688:12 090:4185:6980:1648. 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 CD_3:CD_2H:CDH_2:CH_3 was found to be 23:39:29:9.

Codecomposition of 1 and 1-d_{17}. Assay of Recovered Starting Material. To 5 mL of CH_2Cl_2 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 (η-C_5H_5)Re(NO)(PPh_3)(CH_3)-d_x as an orange solid (0.042 g, ca. 0.074 mmol, ca. 25%), which was subjected to mass spectral analysis. The ^{187}Re molecular ions for (η-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 (η-C_5H_5)Re(NO)(PPh_3-d_{15})(CD_2H) (prepared from **1**-d_{17} and $Li(C_2H_5)_3BH$) gave a *m/e* 578:576:574 ratio of <10:633:373. Authentic (η-C_5H_5)Re(NO)(PPh_3)(CH_3)-d_0 gave a *m/e* 561:559:557 ratio of 16:931:544. These data indicate (η-C_5H_5)Re(NO)(PPh_3-d_{15})(CD_2H):(η-C_5H_5)Re(NO)(PPh_3-d_{15})(CH_3) and (η-C_5H_5)Re(NO)(PPh_3)(CD_2H):(η-C_5H_5)Re(NO)(PPh_3)(CH_3) ratios of (96 ± 1):(4 ± 1) and (5 ± 1):(95 ± 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 $Ph_3Si(CH_3)$, capped with a septum, and cooled to −78 °C. Then 0.375 mL of CD_2Cl_2 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 ^{1}H NMR resonances relative to the standard. Plots of $1/c$ vs. t gave the k_{obsd} in Table I. In the case of **1**-d_2, disappearance of the η-C_5H_5 ^{1}H NMR resonance was monitored.

Reaction of 1 with PPh_3. ^{1}H NMR monitoring. A 5-mm septum-capped NMR tube was charged with 0.024 g (0.034 mmol) of **1** and 0.400 mL of CD_2Cl_2 and was cooled to −78 °C. Then a solution of 0.010 g (0.037 mmol) of PPh_3 in 0.200 mL of CD_2Cl_2 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 [(η-C_5H_5)Re(NO)(PPh_3)(CH_2PPh_3)]$^+PF_6^-$ to be complete.[8b]

Synthesis of [(η-C_5H_5)Re(NO)(PPh_3)($NCCH_3$)]$^+BF_4^-$ (5; BF_4^- salt) from [(η-C_5H_5)Re(NO)(PPh_3)(CO)]$^+BF_4^-$. A 100-mL Schlenk flask was charged with 0.270 g (0.409 mmol) of [(η-C_5H_5)Re(NO)(PPh_3)(CO)]$^+BF_4^-$ and 20 mL of CH_3CN. Anhydrous $(CH_3)_3N^+$-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 $CHCl_3$ and ether was slowly admitted by diffusion. Orange-gold crystals of **5** (BF_4^- salt) formed, which were collected by filtration and dried (0.254 g, 0.378 mmol, 92%).

Data: mp 208 °C dec; IR (cm^{-1}, CH_2Cl_2) ν_{NO} 1704 (s); ^{1}H NMR (δ, $CDCl_3$) 7.57 (br s, 15 H), 5.57 (s, 5 H), 2.54 (s, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 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 (C_5H_5), 4.1 (CH_3); UV (nm, $CHCl_3$) 259 (pk, ε = 3800), 275 (sh, ε = 2500), 308 (sh, ε = 700). Anal. Calcd for $C_{25}H_{23}BF_4N_2OPRe$: 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 [(η-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 [(η-C_5H_5)Re(NO)(PPh_3)(CO)]$^+BF_4^-$, 10 mL of CH_2Cl_2, and 0.297 g (2.050 mmol) of (±)-$CH_3CH_2CH(C_6H_5)$-CN. Anhydrous $(CH_3)_3N^+$-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 ($CDCl_3$, δ 5.58 and 5.59 for C_5H_5). The oily residue was dissolved in CH_2Cl_2. 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 CH_3CN. 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 CD_2Cl_2 and 0.007 mL (0.005 g, 0.132 mmol) of CH_3CN were added by syringe. The tube was transferred to −70 °C NMR probe. A ^{1}H 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 ± 2):(50 ± 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 CH_2Cl_2 followed by 0.042 mL (0.033 g, 0.794 mmol) of CH_3CN 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 $CHCl_3$ 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 $CHCl_3$/ether to give orange-gold crystals of **5** (0.053 g, 0.073 mmol, 93% of theory): ^{1}H NMR (δ, $CDCl_3$) 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, $CHCl_3$). The (+)-(*S*)-**5** isolated from the decomposition of (+)-(*S*)-**1** in the presence of 10 equiv of CH_3CN at 0 °C gave $[\alpha]^{25}_{589}$ 330.6° (*c* 0.56, $CHCl_3$). The (+)-(*R*)-**2** was converted to (+)-(*S*)-**4** ($Li(C_2H_5)_3BH$, 16%), which gave $[\alpha]^{25}_{589}$ 114° (*c* 0.23, $CHCl_3$).

Codecomposition of (+)-(*S*)-1-d_2 and (−)-(*R*)-1-d_{15}. To 5 mL of CH_2Cl_2 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 CH_2Cl_2/hexane as described above. The **2**-d_x was converted to **4**-d_x as described above and subjected to mass spectral analysis. The ^{187}Re 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 CH_3Li)[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 ± 1):(98 ± 1) and (96 ± 1):(4 ± 1), respectively.

Synthesis of (+)-(*SS*)-[(η-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*)-(η-C_5H_5)Re(NO)(PPh_3)(CH_3) in 10 mL of CH_2Cl_2 was cooled to −78 °C and 0.139 g (0.358 mmol) of $Ph_3C^+PF_6^-$ was then added. The reaction was stirred for 1 h at −78 °C and then 0.520 g (3.60 mmol) of (−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$ 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 CH_2Cl_2/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 CH_2Cl_2/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; $[\alpha]^{25}_{589}$ 169.7° (*c* 0.35, $CHCl_3$); IR (cm^{-1}, $CHCl_3$) ν_{NO} 1703 (s); ^{1}H NMR (δ, $CDCl_3$) 7.54–7.12 (m) and 6.84 (m, 2 H) (C_6H_5, 20 H total); 5.54 (s, 5 H), 4.50 (t, J = 7.5 Hz, CH), 1.90 (m, $J \simeq 7$ Hz, CH_2), 0.92 (*t*, J = 7.3 Hz, CH_3); ^{13}C NMR (ppm, $CDCl_3$) 145.0 (CN), phenyl carbons at 133.6 (d, $J_{^{13}C-^{31}P}$ = 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 (C_5H_5), 40.1 (CH), 28.2 (CH_2), 11.3 (CH_3); UV (nm, $CHCl_3$) 261 (pk, ε = 3900), 276 (sh, ε = 1800).

Synthesis of (−)-(*RS*)-[(η-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 CH_2Cl_2 and cooled to −78 °C, whereupon 0.200 g (0.285 mmol) of (−)-(*R*)-**1** was added. Neat (−)-(*S*)-$CH_3CH_2CH(C_6H_5)CN$ (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 CH_2Cl_2/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, $CHCl_3$); IR (cm^{-1}, $CHCl_3$) ν_{NO} 1701 (s); ^{1}H NMR (δ, $CDCl_3$) 7.55–7.24 (m) and 7.04 (m, 2 H) (C_6H_5, 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, $-CH_2$), 0.65 (t, J = 7.3 Hz, $-CH_3$); ^{13}C NMR (ppm, $CDCl_3$) 145.0 (CN), phenyl carbons at 133.8 (d, $J_{^{13}C-^{31}P}$ = 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 (C_5H_5), 40.4 (CH), 28.4 (CH_2), 11.2 (CH_3); UV (nm, $CHCl_3$) 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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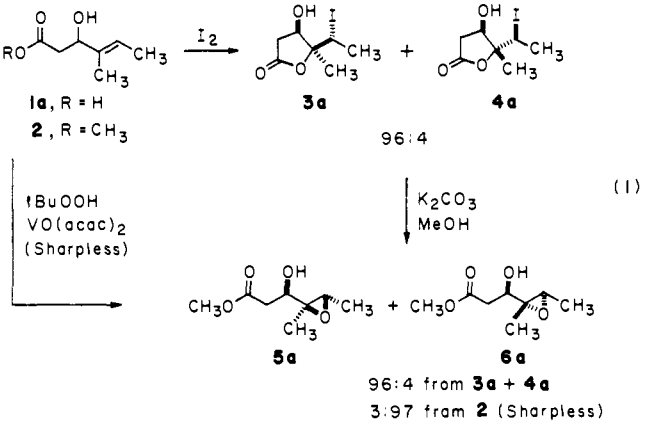
Abstract: The effect of various substituents on the diastereoselectivity of a number of kinetically controlled iodocyclizations has been studied. The reaction of 3-hydroxy-4-alkenoic acids (**1a–n**) with iodine in a neutral two-phase medium gives stereoselective ring closure, usually to the *cis*-3-hydroxy-4-iodoalkyl 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 iodocyclization 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 studies[3] 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 epoxidation[5] of the corresponding allylic alcohol ester **2**. Since the stereoselectivity of the Sharpless



(1)

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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