Organometallics 1984, *3*, 879-886

analogous η^2-alkyne complexes.[1b]

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Registry No. 1, 89637-02-5; 2, 89637-03-6; 3, 89637-04-7; 4, 89655-90-3; 5, 89637-06-9; 6, 87585-21-5; 7, 74718-70-0; $[CpFeCO(PPh_3)(C{=}CMe_2)]BF_4$, 80642-54-2; $Ph_2Cu(CN)Li_2$, 80473-66-1; $(CH_2{=}CH)_2Cu(CN)Li_2$, 80473-65-0; $CpFeCO(PPh_3)I$, 12099-18-2; $CpFeCO(PPh_3)(\eta^1\text{-}C{\equiv}CPh)$, 12313-22-3.

Reactions of Benzylrhenium Complexes $(\eta^5\text{-}C_5H_5)Re(NO)(L)(CH_2Ar)$ with $Ph_3C^+PF_6^-$. Analysis of the Re–C_α Rotamers Involved in α-Hydride Abstraction

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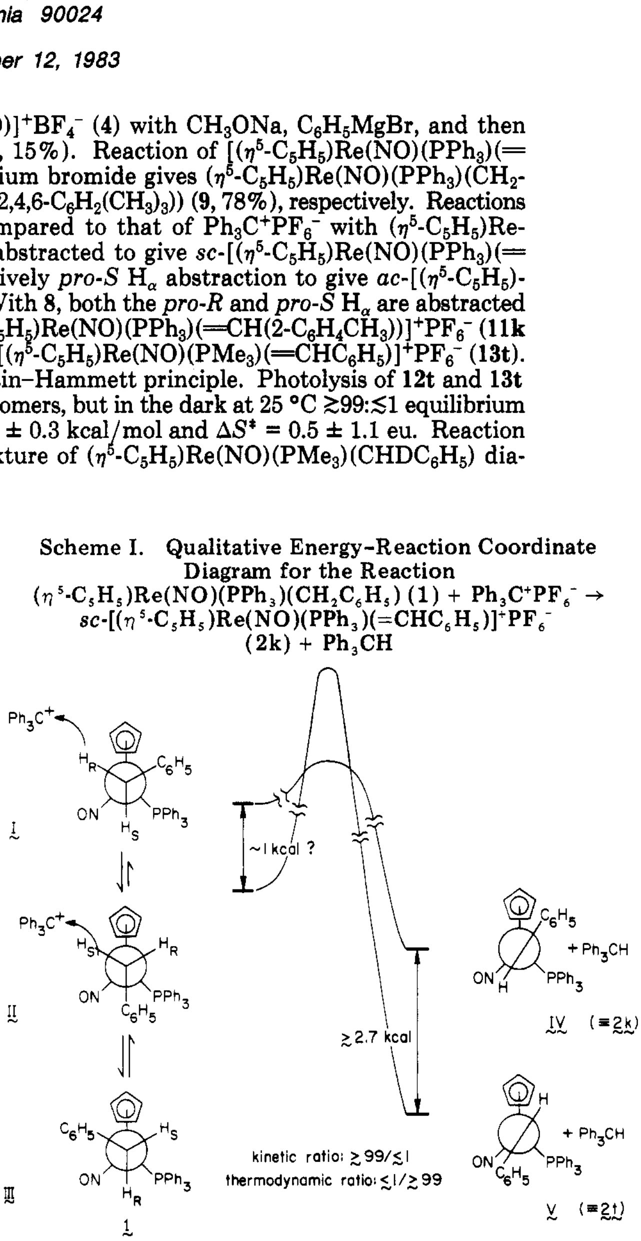
Sequential reaction of $[(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(CO)]^+BF_4^-$ (4) with CH_3ONa, C_6H_5MgBr, and then $BH_3{\cdot}THF$ gives $(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(CH_2C_6H_5)$ (7, 15%). Reaction of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH_2)]^+PF_6^-$ with $o\text{-}CH_3C_6H_4MgBr$ and mesitylmagnesium bromide gives $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2\text{-}(2\text{-}C_6H_4CH_3))$ (8, 52%) and $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2(2,4,6\text{-}C_6H_2(CH_3)_3))$ (9, 78%), respectively. Reactions of $Ph_3C^+PF_6^-$ with 7, 8, and 9 are examined and compared to that of $Ph_3C^+PF_6^-$ with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)$ (1). With 1, the *pro-R* H_α is abstracted to give *sc*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHC_6H_5)]^+PF_6^-$ (**2k**). In contrast, 9 undergoes exclusively *pro-S* H_α abstraction to give *ac*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH(2,4,6\text{-}C_6H_2(CH_3)_3))]^+PF_6^-$ (**12t**). With 8, both the *pro-R* and *pro-S* H_α are abstracted to give approximately equal amounts of *sc*- and *ac*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH(2\text{-}C_6H_4CH_3))]^+PF_6^-$ (**11k** and **11t**). With 7, the *pro-S* H_α is abstracted to give *ac*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)({=}CHC_6H_5)]^+PF_6^-$ (**13t**). These data are discussed within the context of the Curtin–Hammett principle. Photolysis of **12t** and **13t** at −78 °C gives ca. 50:50 mixtures of **t**/**k** (*ac*/*sc*) Re═C isomers, but in the dark at 25 °C $\gtrsim$99:$\lesssim$1 equilibrium mixtures are reestablished. For **12k** → **12t**, $\Delta H^* = 18.8 \pm 0.3$ kcal/mol and $\Delta S^* = 0.5 \pm 1.1$ eu. Reaction of **13t** with $Li(C_2H_5)_3BD$ gives a $(77 \pm 1){:}(23 \pm 1)$ mixture of $(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(CHDC_6H_5)$ diastereomers.

Introduction

We recently reported a detailed study of the reaction of benzyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)$ (1) with $Ph_3C^+PF_6^-$.[3] Hydride abstraction occurred at −78 °C to give benzylidene *sc*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHC_6H_5)]^+PF_6^-$ (**2k**).[4] Subsequently, **2k** isomerized to a new Re═C geometric isomer, *ac*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHC_6H_5)]^+PF_6^-$ (**2t**), with $t_{1/2}$ of 443 min at 4 °C and 17 min at 29.5 °C. The structures of **2k** and **2t** are represented in Scheme I in Newman projection form (IV, V).

Nucleophiles (Nu) were found to attack C_α of the benzylidene ligand of **2k** and **2t** either stereospecifically or with high stereoselectivity to give adducts $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH(Nu)C_6H_5)$. X-ray crystallography established that attack occurred preferentially from a direction anti to the bulky PPh_3 ligand. Studies with deuterium-labeled substrates (*SS*,*RR*)- and (*SR*,*RS*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CHDC_6H_5)$[4b] then demonstrated that $Ph_3C^+PF_6^-$ abstracts essentially only the *pro-R* α-hydride of 1 and that abstraction occurs from a direction anti to the PPh_3. This direction allows overlap of the rhenium d orbital HOMO, the plane of which contains the Re–PPh_3 bond and is perpendicular to the Re–NO bond,[3] with the developing

Scheme I. Qualitative Energy–Reaction Coordinate Diagram for the Reaction $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)$ (1) + $Ph_3C^+PF_6^-$ → *sc*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHC_6H_5)]^+PF_6^-$ (2k) + Ph_3CH



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[2] To whom correspondence should be addressed at the Department of Chemistry, University of Utah, Salt Lake City, UT 84112. Fellow of the Alfred P. Sloan Foundation (1980–1984) and Camille and Henry Dreyfus Teacher-Scholar Grant Recipient (1980–1985).

[3] Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* 1982, *104*, 4865.

[4] (a) The designations **k** ("kinetic") and **t** ("thermodynamic") will be used to indicate synclinal (*sc*) and anticlinal (*ac*) isomers, respectively (see Scheme I). The latter nomenclature is defined in *Pure Appl. Chem.* 1976, *45*, 11. See section E-5.6, p 24. (b) In complexes with more than one chiral center, the rhenium configuration is specified first.

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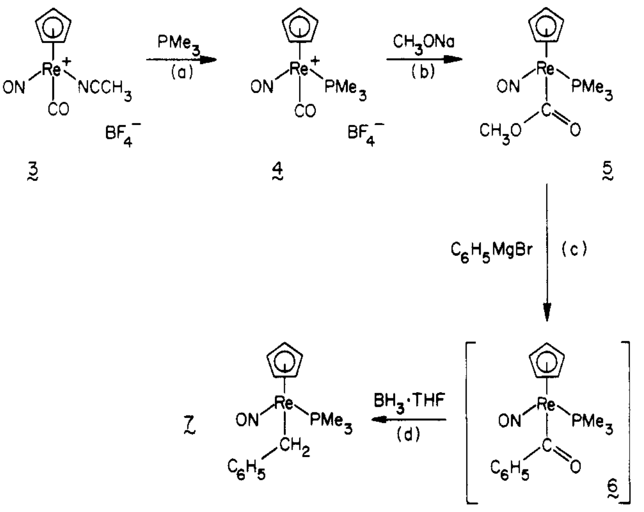
Scheme II. Synthesis of $(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(CH_2C_6H_5)$ (7)



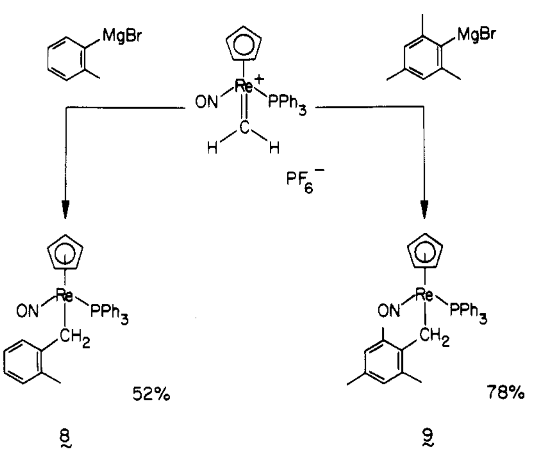
C_α p orbital in the transition state.

A priori, there are three staggered Re–C_α rotamers of 1—I, II, and III in Scheme I—that could react with $Ph_3C^+PF_6^-$. However, the constraints imposed by the deuterium-labeling studies summarized above are best rationalized by invoking I as the most reactive rotamer. It is easily seen that if hydride were abstracted anti to the PPh_3 in rotamer II, it would be the *pro-S* hydride *and* the wrong product Re=C isomer **2t** would be obtained. It is important to note that I is likely the least stable Re–C_α rotamer, since its C_6H_5 substituent must reside between the bulky PPh_3 and medium-sized C_5H_5 ligands. Rotamer III is likely the most stable and is found in the crystal structure of (−)-(*R*)-1.[5] However, since the H_α in III are nearly orthogonal to the rhenium d orbital HOMO, hydride abstraction should require a prohibitively high activation energy.

It is not unusual for a less stable isomer to be the more reactive one. In many such cases, the more stable of two possible products is obtained, and the transition state is considered product-like. However, of the two possible product Re=C isomers in Scheme I, the *least* stable **2k** (IV), is formed exclusively. The more stable starting material rotamer II would give the more stable product Re=C isomer **2t** (V) directly. In the context of the Curtin–Hammet principle,[6] this result is provocative. If the rotamers I, II, and III are rapidly equilibrating on the time scale of the reaction of 1 with $Ph_3C^+PF_6^-$, then the *hypothetical* transition state connecting II and V (Scheme I) must be of *higher* energy than the transition state connecting I and IV. In other words, despite the fact that I and IV are the least stable rotamers, there is some *special stability* associated with the transition state that interconverts them.

In a companion paper,[7] we show that a Scheme I type situation also prevails in the reaction of $Ph_3C^+PF_6^-$ with linear alkyls $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2R)$ (R = CH_3, CH_2CH_3, $CH_2CH_2CH_2CH_3$). In this paper, we further probe the generality of Scheme I by conducting similar experiments with $Ph_3C^+PF_6^-$ and $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2Ar)$ (Ar = substituted aryl) and $(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(CH_2C_6H_5)$ complexes. We find that with a sufficient increase in aryl bulk, or a dimunation of phosphine bulk, rotamers analogous to II appear to become the most reactive toward hydride abstraction.[8]

Scheme III. Syntheses of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2Ar)$ Complexes



Results

1. Syntheses of Substrates. The previously reported[9] nitrile complex $[(\eta^5\text{-}C_5H_5)Re(NO)(NCCH_3)(CO)]^+BF_4^-$ (3, Scheme II) was generated in situ and treated with PMe_3. Phosphine complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(CO)]^+BF_4^-$ (4) was subsequently isolated in 65% yield. The CH_3CN in 3 did not exchange with CD_3CN on the time scale of this reaction.[10] Hence the substitution must be associative.

The synthesis of $(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(CH_2C_6H_5)$ (7) was attempted by a route similar to that used to prepare 1.[3] Reduction of 4 with $NaBH_4$ gave $(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(CH_3)$ as an air-sensitive orange solid in 74% yield. The reaction of $(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(CH_3)$ with $Ph_3C^+PF_6^-$ was ^1H NMR monitored. Methylidene $[(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(=CH_2)]^+PF_6^-$ and an unidentified byproduct (δ 5.62) formed. Solutions of this methylidene, like its PPh_3 analogue,[9,11] decomposed upon warming to room temperature. Unfortunately, reaction of $[(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(=CH_2)]^+PF_6^-$ and C_6H_5Li at −78 °C always gave, in addition to 7, significant quantities of $(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(CH_3)$. We were unable to conveniently separate these alkyls, so this route to 7 was abandoned in favor of the one shown in steps b–d of Scheme II.

Reaction of 4 with CH_3OH/CH_3ONa gave "ester" $(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(CO_2CH_3)$ (5) as a yellow oil (Scheme II). Sequential treatment of 5 with C_6H_5MgBr and, following solvent removal, $BH_3{\cdot}THF$ gave 7 as a red oil in 15% overall yield from 4. The transformation 5 → 7 proceeds via the oily acyl $(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(COC_6H_5)$ (6).[12]

Substituted benzyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2Ar)$ were prepared as shown in Scheme III. Methylidene $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$ was generated in situ at −78 °C as previously described.[9,11] Subsequent reaction with $o\text{-}CH_3C_6H_4MgBr$ gave $(\eta^5\text{-}$

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[5] Merrifield, J. H.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1204.

[6] Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83.

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

[8] This full paper, together with the previous two,[3,7] completes the publication of all experimental data compiled in: Kiel, W. A. Ph.D. Thesis, UCLA, 1982.

[9] Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

[10] We thank Mr. Savas Georgiou, University of Utah, for these data.

[11] Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5811.

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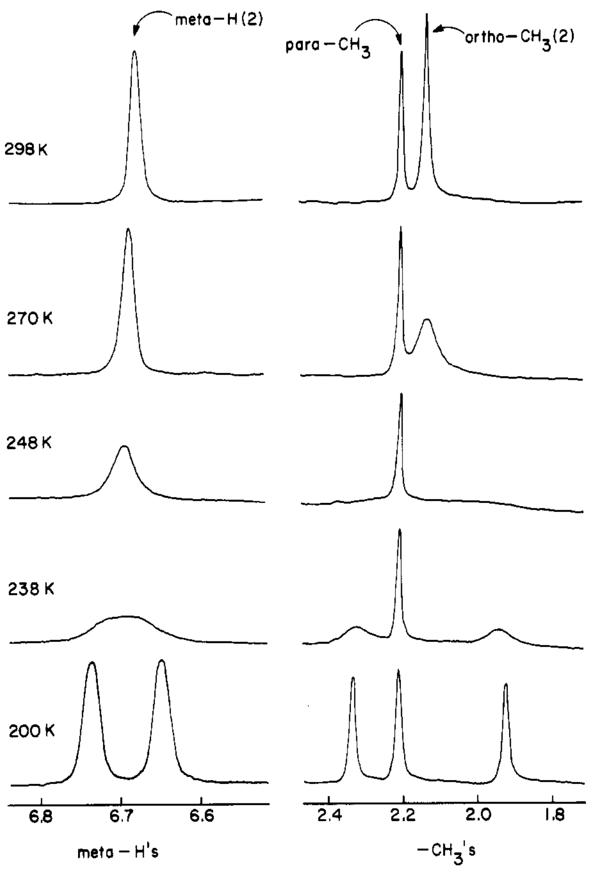


Figure 1. Variable-temperature 200-MHz ^1H NMR spectra of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2(2,4,6\text{-}C_6H_2(CH_3)_3))$ (**9**) in CD_2Cl_2.

$C_5H_5)Re(NO)(PPh_3)(CH_2(2\text{-}C_6H_4CH_3))$ (**8**) in 52% yield. A similar reaction with mesitylmagnesium bromide gave $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2(2,4,6\text{-}C_6H_2(CH_3)_3))$ (**9**) in 78% yield.

The 200 K ^1H NMR spectrum of **9** exhibited two meta H and ortho CH_3 resonances, suggesting a congested steric environment for the aryl group. As illustrated in Figure 1, the meta and ortho CH_3 resonances coalesced upon warming. Coalescence temperatures of 236 and 248 K were assigned, respectively. Calculation of the first-order rate constants using the slow exchange approximation ($k = 44.4$ s^{-1}, 236 K), the coalescence formula, and the fast exchange approximation ($k = 83.2$ s^{-1}, 270 K) gave a $\Delta G^{\ddagger}_{rot}$ for C_α–C_{ipso} of 12.0 ± 0.4 kcal/mol (Experimental Section).[13] The chemical shifts of these resonances were also temperature dependent, as is evident in Figure 1.

The two H_α in **9** (δ 3.20, 2.64) appeared as doublets of doublets in 200–300-MHz ^1H NMR spectra. The $J_{^{31}P-^1H_\alpha}$ and $J_{^1H_{\alpha R}-^1H_{\alpha S}}$ were measured over the temperature range −18 to 40 °C in CD_2Cl_2 (Figure 2). Below −18 °C, the ca. 1.2-Hz coupling of the δ 2.64 resonance was no longer resolvable. As will be described in the Discussion, $J_{^{31}P-^1H_\alpha}$ values have been previously correlated to Fe–C_α rotamer populations in $(\eta^5\text{-}C_5H_5)Fe(CO)(PX_3)(CH_2R)$ systems.[14]

2. Generation and Reactions of Re=CHAr Complexes. The reaction of $Ph_3C^+PF_6^-$ and **8** in CD_2Cl_2 was ^1H NMR monitored at −70 °C. Approximately equimolar quantities of two *o*-xylylidene complexes, *sc*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH(2\text{-}C_6H_4CH_3))]^+PF_6^-$ (**11k**)[4] and *ac*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH(2\text{-}C_6H_4CH_3))]^+PF_6^-$ (**11t**), formed cleanly. Upon warming to room temperature, **11k** isomerized to **11t**. These data will be interpreted (Discussion) as outlined in Scheme IV. In a preparative experiment, **11t** was obtained as yellow leafs in 50% yield.

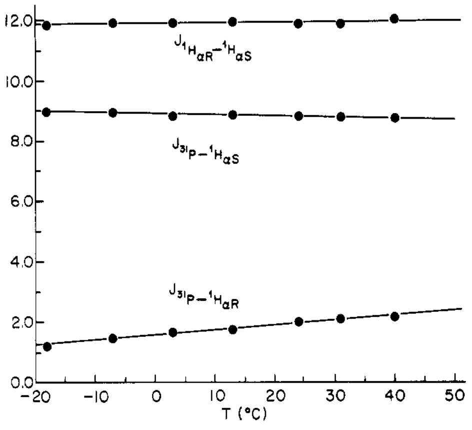
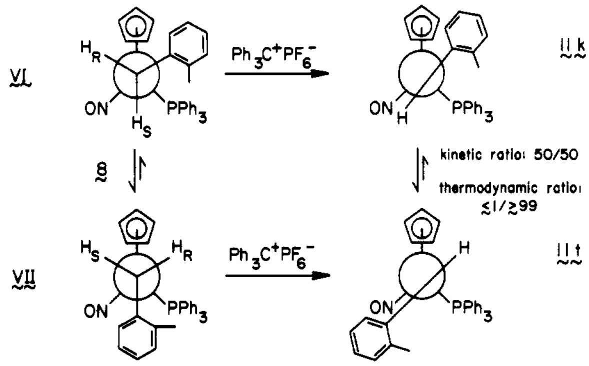


Figure 2. Variation of H_α coupling constants in $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2(2,4,6\text{-}C_6H_2(CH_3)_3))$ (**9**) with temperature.

Scheme IV. Reaction of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2(2\text{-}C_6H_4CH_3)$ (**8**) with $Ph_3C^+PF_6^-$



A similar reaction of $Ph_3C^+PF_6^-$ with **9** was ^1H NMR monitored. Spectra were broadened at −70 °C, but upon warming resonances sharpened. At all times, only one isodurylidene complex, *ac*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH(2,4,6\text{-}C_6H_2(CH_3)_3))]^+PF_6^-$ (**12t**), was present. Product **12t** was isolated in 20% yield. No isomerization was observed upon heating **12t** to 100 °C in $CDCl_2CDCl_2$. However, photolysis of a −78 °C CD_2Cl_2 solution of **12t** for 4 h cleanly gave a (45 ± 2):(55 ± 2) mixture of Re=C isomers; the new isomer **12k** predominated. Similar conditions had been shown to convert **2t** to a (55 ± 3):(45 ± 3) **2t**/**2k** photostationary state.[3] When the photolysate was warmed to room temperature, **12k** disappeared as **12t** returned to its initial concentration. These data will be interpreted (Discussion) as supporting the structural assignments and interconversions shown in Scheme V.

The more stable isodurylidene complex **12t** was treated with $Li(C_2H_5)_3BD$ at −78 °C. The isoduryl complex **9**-α-d_1, which has two chiral centers, was isolated in 78% yield. Analysis by ^1H NMR showed the δ 3.20 (H_α) resonance of **9** to be absent (detection limit 2%). Thus deuteride attack upon **12t** was essentially stereospecific and, by analogy to **2t**, was presumed to occur anti to the PPh_3 to give (*SS*,*RR*)-**9**-α-d_1 (Scheme V).[4b] When (*SS*,*RR*)-**9**-d_1 was treated with $Ph_3C^+PF_6^-$, the resulting isodurylidene complex was essentially unlabeled (≳98% **12t**-d_0). Thus, in contrast to **1**, $Ph_3C^+PF_6^-$ preferentially abstracts the *pro-S* H_α of **9** (Scheme V).

Samples of **12t** in CD_2Cl_2 were photolyzed, and the rates of isomerization of the resulting **12t**/**12k** mixtures to **12t** were measured by ^1H NMR. Data were obtained at −30.0

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[14] Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 4292.

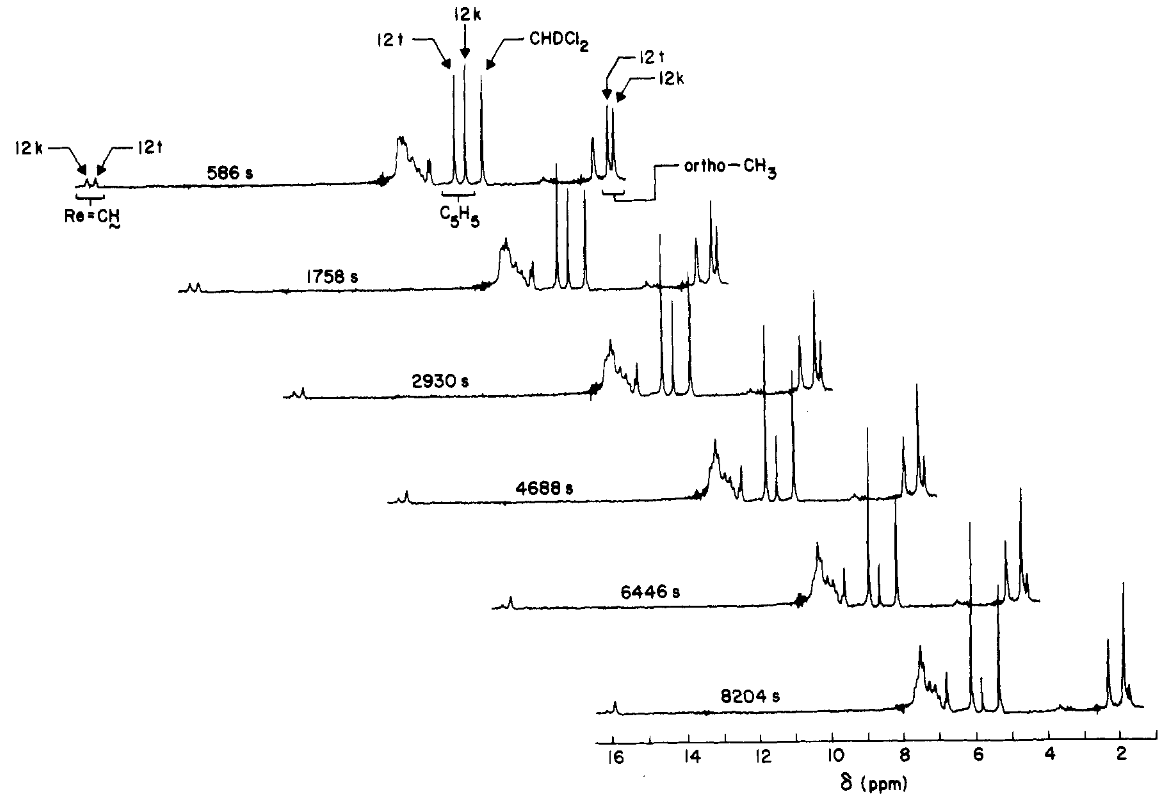
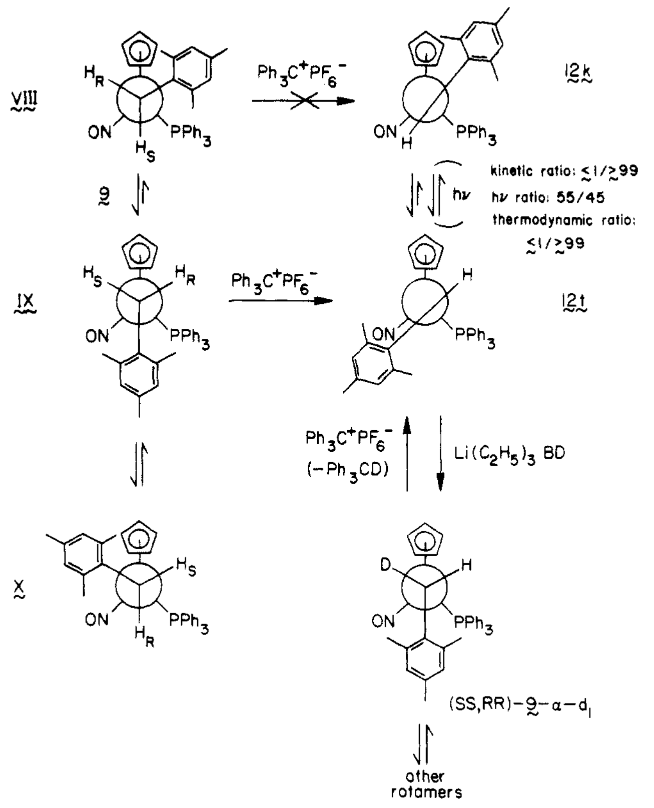
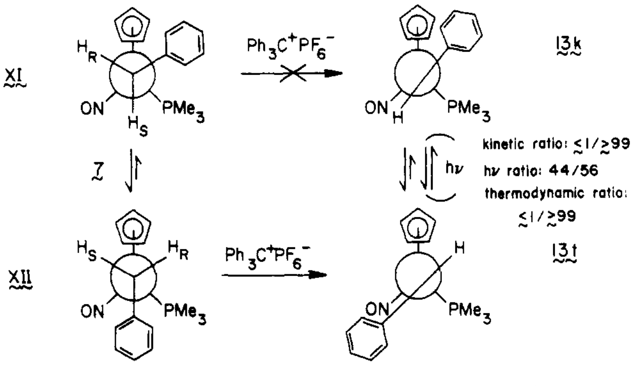


Figure 3. Isomerization of *sc*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH(2,4,6\text{-}C_6H_2)(CH_3)_3))]^+PF_6^-$ (**12k**) to *ac*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH(2,4,6\text{-}C_6H_2(CH_3)_3))]^+PF_6^-$ (**12t**) at -24.5 °C in CD_2Cl_2. The **12k**/**12t** mixture was generated by photolysis of **12t**. Chemical shifts are compiled in the Experimental Section. Minor spectrometer noise (δ 8.0, 2.7) and solvent impurities are evident.

Scheme V. Reaction of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2(2,4,6\text{-}C_6H_2(CH_3)_3))$ (9) with $Ph_3C^+PF_6^-$



Scheme VI. Reaction of $(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(CH_2C_6H_5)$ (7) with $Ph_3C^+PF_6^-$



± 0.2 °C ((0.80 ± 0.04) × 10^{-4} s^{-1}; (0.76 ± 0.02) × 10^{-4} s^{-1}), -24.5 ± 0.4 °C ((1.77 ± 0.03) × 10^{-4} s^{-1}), -20.1 ± 0.1 °C ((3.69 ± 0.06) × 10^{-4} s^{-1}), -20.0 ± 0.2 °C ((3.67 ± 0.12) × 10^{-4} s^{-1}), and -15.0 ± 0.1 °C ((7.25 ± 0.12) × 10^{-4} s^{-1}). These gave $\Delta H^{\ddagger} = 18.8 \pm 0.3$ kcal/mol and $\Delta S^{\ddagger} = 0.5 \pm 1.1$ eu. Some spectra from a typical rate experiment are given in Figure 3.

The reaction of $Ph_3C^+PF_6^-$ and **7** in CD_2Cl_2 was ^1H NMR monitored at -70 °C. A single Re=C isomer of benzylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)({=}CHC_6H_5)]^+PF_6^-$ (**13t**) formed. The reaction was warmed to room temperature, and **13t** was isolated in 69% yield. No isomerization was observed upon heating **13t** to 60 °C in $CDCl_3$. Photolysis of a CD_2Cl_2 solution of **13t** for 4 h at -78 °C gave a (56 ± 1):(44 ± 1) mixture of Re=C isomers. The original isomer predominated. When the photolysate was warmed to room temperature, the new benzylidene isomer **13k** disappeared as **13t** returned to its initial concentration. These data will be interpreted (Discussion) as supporting the structural assignments and interconversions shown in Scheme VI.

A sample of **13t** was treated with $Li(C_2H_5)_3BD$ at -78 °C. The deuterated benzyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(CHDC_6H_5)$ (**7**-α-d_1) was isolated and was analyzed by ^1H NMR. The relative areas of the two H_α resonances indicated that a (77 ± 1):(23 ± 1) mixture of 7-α-d_1 diastereomers had formed.

Discussion

Alkyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2R)$ where R = C_6H_5, CH_3, CH_2CH_3, and $CH_2CH_2CH_2CH_3$ react with $Ph_3C^+PF_6^-$ as outlined in Scheme I. The less stable product Re=C isomer is formed initially. However, isoduryl complex **9** reacts differently. The photochemical experiment in Scheme V establishes that the more stable product Re=C isomer is formed initially.

Two reasonable assumptions are made in Scheme V: (1) that the more stable isodurylidene Re=C isomer **12t** has, like **2t**, an *ac* conformation and (2) that deuteride adds anti to the bulky PPh_3 ligand of **12t** to give (*SS,RR*)-**9**-α-d_1. It then follows that deuteride is abstracted from (*SS,RR*)-**9**-α-d_1 from a direction anti to the PPh_3 ligand. Otherwise, **12k** would form initially. Furthermore, the deuterium labeling shows that the *pro-S* H_α of **9** is abstracted by $Ph_3C^+PF_6^-$. Hence, *we propose that rotamer IX of* **9** *is the most reactive toward* $Ph_3C^+PF_6^-$.

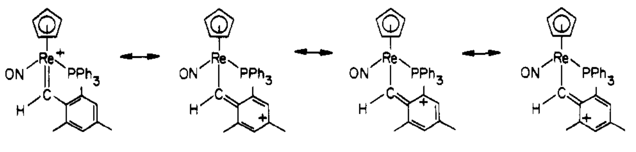
A similar analysis of the reaction of xylyl complex **8** with $Ph_3C^+PF_6^-$ is given in Scheme IV. Now approximately equimolar quantities of two *o*-xylylidene Re=C isomers are formed initially. In view of the conclusions from Schemes I and V, this suggests that *two* Re–C_α rotamers of **8** are reactive toward $Ph_3C^+PF_6^-$. The *pro-R* H_α would be abstracted from rotamer VI, whereas the *pro-S* H_α would be abstracted from rotamer VII.

In order to further interpret Schemes IV and V, it is necessary to ascertain whether rotation about the Re–C_α bonds of **8** and **9** is rapid relative to reaction with $Ph_3C^+PF_6^-$. If this is so, then the Curtin–Hammett principle[6] may be applied. As background, it should be noted that rotational barriers about transition metal–carbon σ bonds are generally in the 3–6 kcal/mol range.[14,15] In more congested alkyls such as $(\eta^5\text{-}C_5H_5)Fe(CO)_2[C(SCH_3)_3]$ ($\Delta G^\ddagger \simeq 8.7$ kcal/mol)[15b] barriers approach 10 kcal/mol.

We have probed the Re–C_α rotational barrier in **9** in two ways. First, Figure 2 shows that while the geminal coupling $J_{^1H_{\alpha R}-^1H_{\alpha S}}$ in **9** is essentially constant (11.9 Hz) between −18 and 40 °C, $J_{^{31}P-^1H_{\alpha R}}$ varies by ca. 1 Hz and $J_{^{31}P-^1H_{\alpha S}}$ varies by ca. 0.2 Hz. A similar experiment has been conducted by Baird with $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(CH_2C_6H_5)$.[14] He noted that if the $J_{^{31}P-^1H_\alpha}$ values exhibit a Karplus-like geometry dependence, then a change in temperature will, in the case of equilibrating rotamers, alter the relative rotamer populations and hence the observed $J_{^{31}P-^1H_\alpha}$. It is therefore evident that **9** is not locked in a single rotamer or a static mixture of rotamers.

Extrapolation of the data in Figure 2 to 0 K gives $J_{^{31}P-^1H_{\alpha S}}$ of 9.81 Hz and $J_{^{31}P-^1H_{\alpha R}}$ of −2.98 Hz. In his analysis of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(CH_2C_6H_5)$ and related compounds,[14] Baird suggested that $J_{^{31}P-^1H_\alpha} = 17 \pm 1$ Hz when phosphorus is antiperiplanar to H_α and $J_{^{31}P-^1H_\alpha} = 0 \pm 1$ Hz when phosphorus is gauche to H_α. If a similar relationship holds for **9**,[16] the extrapolated coupling constants suggest that rotamers IX and X are of approximately equal energy. A similar conclusion was reached in our earlier study regarding rotamers II and III of **1**.[3]

Second, the rotational barrier found for **12k** → **12t**, $\Delta H^\ddagger = 18.8 \pm 0.3$ kcal/mol ($\Delta G^\ddagger_{298K} = 18.6 \pm 0.6$ kcal/mol), is *lower* than that observed for **2k** → **2t**, $\Delta H^\ddagger = 20.9 \pm 0.4$ kcal/mol ($\Delta G^\ddagger_{298K} = 22.0 \pm 0.5$ kcal/mol).[3] Hence, there is no evidence for an extraordinary steric barrier to rotation about the Re=C bond of **12**, and we therefore suggest that a large (>10 kcal/mol) barrier to rotation about the Re–C_α bond of **9** is unlikely. The attenuated Re=C rotational barrier for **12k** → **12t** may be due to ground-state strain, or increased contributions from resonance forms XIII–XV. The latter would weaken the π bond.



12k XIII XIV XV

In summary, we assume, in the absence of any evidence to the contrary, that the Re–C_α rotamers of **8** and **9** interconvert rapidly on the time scale of the reaction with $Ph_3C^+PF_6^-$. One could still rationalize Scheme V by arguing that rotamer VIII of **9** is thermally inaccessible. However, since the analogous rotamer of **8**, VI (Scheme IV), does react with $Ph_3C^+PF_6^-$, we believe that VIII is an attainable rotamer and that the Curtin–Hammett principle may be applied to Schemes IV and V.

Thus, as the size of the R group in $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2R)$ is increased, the relative energies of the two types of transition states shown in Scheme I, *pro-R* H_α abstraction and *pro-S* H_α abstraction, gradually change. In Scheme IV, the transition-state free energies for *pro-R* and *pro-S* H_α abstraction from **8** are approximately equal. In Scheme V, the transition-state free energy for *pro-S* H_α abstraction from **9** is lower than that for *pro-R* H_α abstraction. Hence the stabilizing interaction that must be present in transition state for *pro-R* H_α abstraction from **1** (Scheme I), as well as aliphatic homologs such as $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_3)$, is diminished as the bulk of the aryl substituent is increased.

It should be emphasized that other products (but not **12k**) form in the reaction of **9** with $Ph_3C^+PF_6^-$. Reaction of the bulky neopentyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C(CH_3)_3)$[7] with $Ph_3C^+PF_6^-$ failed to give neopentylidene $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHC(CH_3)_3]^+PF_6^-$—a compound which we were able to prepare by another route.[17] Perhaps electron-transfer-initiated side reactions have a greater opportunity to compete in reactions of $Ph_3C^+PF_6^-$ with congested rhenium alkyls. We have also discussed the possibility that all hydride abstractions from rhenium alkyls by $Ph_3C^+PF_6^-$ may proceed via initial electron transfer.[7]

What is the nature of the attractive forces that stabilize the transition state for *pro-R* H_α abstraction from **1** and the corresponding ethyl, *n*-propyl, and *n*-pentyl complexes? Alternatively, can any destablizing interactions be identified in *pro-S* H_α abstraction? It is difficult to rationalize what would be a 1–2-kcal effect at 203 K in the context of such large, bulky molecules. However, the reaction of **7** with $Ph_3C^+PF_6^-$ (Scheme VI) indicates that the PPh_3 ligand is in some manner responsible. Diastereomerically pure 7-α-d_1 is not available, so we cannot be entirely certain which H_α is abstracted by $Ph_3C^+PF_6^-$. However, by analogy to Schemes IV and V, we interpret

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(15) (a) Jordan, R. F.; Tsang, E.; Norton, J. R. *J. Organomet. Chem.* **1978**, *149*, C53 and references therein. (b) McCormick, F. B.; Angelici, R. J.; Pickering, R. A.; Wagner, R. E.; Jacobson, R. A. *Inorg. Chem.* **1981**, *20*, 4108.

(16) (a) A reviewer has questioned the validity of quantitatively comparing $J_{^{31}P-^1H_\alpha}$ for homologous rhenium and iron complexes. We agree that any extrapolations must be provisional and cautiously stated. However, both types of complexes should exhibit $J_{^{31}P-^1H_\alpha} \approx 0$ at similar $^{31}P-M/C-^1H_\alpha$ dihedral angles, and $J_{^{31}P-^1H_\alpha}$ for $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (5 Hz)[9] is close to that of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(CH_3)$ (6.5 Hz).[16b] We know of no examples of widely differing $J_{^{31}P-^1H_\alpha}$. (b) Flood, T. C.; DiSanti, F. J.; Miles, D. *Inorg. Chem.* **1976**, *15*, 1910.

(17) Hatton, W. G., unpublished results in this laboratory.

the initial formation of the more stable benzylidene **13t** as indicating greater reactivity for rotamer XII and the *pro-S* H_α. Hence the PPh_3 ligand in **1** supplies some stabilizing interaction in the transition state for *pro-R* H_α abstraction or some destabilizing interaction in the transition state for *pro-S* H_α abstraction. We have executed numerous X-ray crystal structures of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ compounds[3,5,11,18] but have not seen evidence for attractive interactions involving the PPh_3 rings. In single-run experiments,[19] two other rhenium benzyl complexes have been synthesized, characterized by ^1H NMR, and treated with $Ph_3C^+PF_6^-$ in CD_2Cl_2 at −78 °C. Tolylphosphine complex $(\eta^5\text{-}C_5H_5)Re(NO)(P(4\text{-}C_6H_4CH_3)_3)(CH_2C_6H_5)$ behaved like **1**; the less stable benzylidene complex was the exclusive initial product. Phosphite complex $(\eta^5\text{-}C_5H_5)Re(NO)(P(OMe)_3)(CH_2C_6H_5)$ behaved like **7**; a ca. 90:10 mixture of benzylidene complexes, with the more stable one predominating, formed initially. On the basis of these limited data, it appears that phosphine size plays an important role in determining whether *pro-R* or *pro-S* H_α abstraction is preferred.

The restricted C_α–C_{ipso} rotation in *alkyl* **9** (Figure 1) is reminiscent of the C_α–C_{ipso} $\Delta G^\ddagger_{rot}$ of 9.1 ± 0.3 (−80 °C) and 10.4 ± 0.3 (−56 °C) kcal/mol found by Brookhart and Husk for *alkylidenes* $[(\eta^5\text{-}C_5H_5)Fe(CO)_2({=}CHC_6H_5)]^+CF_3SO_3^-$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2({=}CH(4\text{-}C_6H_4CH_3))]^+CF_3SO_3^-$.[20] The greater portion of the 12.0 ± 0.4 kcal/mol barrier in **9** is undoubtedly steric. However, it is worth noting that in the two X-ray crystal structures of benzyl $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$ systems completed to date,[3,5] the Re–C_α–C_{ipso} plane is perpendicular to the plane of the phenyl ring. Such an orientation is consistent with a hyperconjugative interaction between the Re–C_α bond and the phenyl ring.

In conclusion, this study has provided important limits on the generality of the relative energies of the transition states for *pro-R* and *pro-S* H_α abstraction in Scheme I. Other systems have been found in which the less stable of two equilibrating species reacts more rapidly to give the less stable of two other equilibrating species. For instance, the direct oxidative addition of H_2 to $RhCl(PPh_3)_3$ can occur, but addition of H_2 to $RhCl(PPh_3)_2$, generated by PPh_3 dissociation, is 10^4 times faster.[21] However, we know of no examples other than Scheme I where this has been so strongly suggested for nondissociative equilibria.[22] The substitution-induced changes in the relative energies of the transition states for *pro-R* and *pro-S* H_α abstraction (Schemes IV–VI) undoubtedly contain valuable information regarding transition-state structure and, in time, should help provide a more detailed understanding of these transformations.

Experimental Section

General Data. Instrumentation and general procedures employed for this study were identical with those given in previous papers,[3,7] except that the data in Figures 2 and 3 were obtained on Varian SC-300 and FT-80A NMR spectrometers, respectively.

Starting Materials. Rhenium complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(CO)_2]^+BF_4^-$ and $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ were prepared as described previously.[9] $Ph_3C^+PF_6^-$ was purchased from Aldrich and Columbia Organic and was purified and stored as previously described.[17c] Iodosobenzene diacetate was purchased from Aldrich or Eastman and converted to $C_6H_5I^+\text{–}O^-$ by the literature procedure.[23] PMe_3 was obtained from Strem Chemicals and used without purification. Grignard reagents C_6H_5MgBr, $o\text{-}CH_3C_6H_4MgBr$, and mesitylmagnesium bromide were prepared by standard methods[24] and used without standardization. Reagents $BH_3\cdot THF$, $Li(C_2H_5)_3BD$, and C_6H_5Li were obtained from Aldrich and used without standardization.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(CO)]^+BF_4^-$ (4). To $[(\eta^5\text{-}C_5H_5)Re(NO)(CO)_2]^+BF_4^-$ (4.39 g, 10.35 mmol)[9] in CH_3CN (150 mL) was added $C_6H_5I^+\text{–}O^-$ (3.03 g, 13.77 mmol). After 1 h, an aliquot was analyzed by ^1H NMR. No starting material C_5H_5 resonance was present. The CH_3CN was removed by rotary evaporation, and the residue was taken up in acetone and filtered through silica gel. The acetone was removed by rotary evaporation to give a dark oil that was washed with 3 × 100 mL of ether (to remove C_6H_5I). The residue was dissolved in acetone (50 mL) in a Schlenk flask, and PMe_3 (3.0 mL, 29.53 mmol) was added via gas-tight syringe. After 2 h, solvent was removed under aspirator vacuum. The resulting dark black oily solid was washed with THF to give a yellow powder that was in turn washed with ether. The powder was diffusion recrystallized from acetone/ether to give 3.18 g (6.73 mmol, 65%) of **4** as long yellow needles: mp >300 °C; IR (cm^{-1}, CH_2Cl_2) $\nu_{C\equiv O}$ 2004 (m), $\nu_{N\equiv O}$ 1761 (s); ^1H NMR (δ, CD_3CN) 6.00 (d, $J_{^1H\text{-}^{31}P} = 0.8$ Hz, C_5H_5), 1.93 (d, $J_{^1H\text{-}^{31}P} = 11.6$ Hz, PMe_3); ^{13}C NMR (ppm, CD_3CN) 197.16 (CO), 94.47 (C_5H_5), 20.18 (d, $J_{^{13}C\text{-}^{31}P} = 42.2$ Hz, PMe_3). Anal. Calcd for $C_9H_{14}BF_4NO_2PRe$: C, 22.89; H, 2.99. Found: C, 23.00; H, 3.01.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(CH_3)$. To a suspension of **4** (0.196 g, 0.415 mmol) in THF (20 mL) was added $NaBH_4$ (0.049 g, 1.29 mmol). The reaction was stirred for 3 h. Solvent was removed by rotary evaporation from the resulting bright orange solution. The residue was taken up in benzene and filtered through silica gel. The benzene was removed to give an orange oil, which was recrystallized from cold hexane to give 0.114 g (0.306 mmol, 74%) of $(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(CH_3)$ as orange flakes, mp 76–78 °C dec. This complex *must* be stored cold under N_2: IR (cm^{-1}, CH_2Cl_2) $\nu_{N\equiv O}$ 1632 (s); ^1H NMR (δ, $CDCl_3$) 5.01 (s, C_5H_5), 1.54 (d, $J_{^1H\text{-}^{31}P} = 9.8$ Hz, PMe_3), 0.72 (d, $J_{^1H\text{-}^{31}P} = 6.6$ Hz, $ReCH_3$); (δ, CD_2Cl_2) 4.99, 1.49, 0.64. Anal. Calcd for $C_9H_{17}NOPRe$: C, 29.03; H, 4.60. Found: C, 29.16; H, 4.70.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(CH_2C_6H_5)$ (7). A CH_3OH solution of CH_3ONa was prepared from Na (0.636 g, 27.6 mmol) and CH_3OH (20 mL). This was added to a −78 °C solution of **4** (0.603 g, 1.29 mmol) in CH_2Cl_2 (60 mL). The solution was allowed to slowly warm to room temperature. After an additional 2 h of stirring, solvents were removed by rotary evaporation. The residue was taken up in benzene and filtered. The benzene was removed by rotary evaporation to give a yellow oil contaminated with a white solid. The oil was extracted with CH_2Cl_2 and filtered to remove the solid. The CH_2Cl_2 was pumped off to give 0.510 g (1.23 mmol, 96%) of $(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(CO_2CH_3)$ (**5**) as a yellow oil: ^1H NMR (δ, $CDCl_3$) 5.41 (s, C_5H_5), 3.56 (s, OCH_3), 1.70 (d, $J_{^1H\text{-}^{31}P} = 10.4$ Hz, PMe_3).

The **5** thus isolated was taken up in CH_2Cl_2 (30 mL) and cooled to −78 °C. Then 0.900 mL of 1.7 M C_6H_5MgBr (1.53 mmol) in ether was added dropwise. The solution was allowed to warm to room temperature, and after an additional hour solvents were removed by rotary evaporation. The residue was taken up in THF (30 mL) and 12 mL of 1.0 M $BH_3\cdot THF$ in THF (12 mmol) was added. The reaction was refluxed for 2 h, after which the THF was removed under oil pump vacuum. The resulting residue was transferred to a glovebox for the remaining workup. The residue was extracted with benzene and filtered through silica gel. The benzene was pumped off, and the resulting dark orange oil was chromatographed on a 2.5 × 13 cm silica gel column with 3:1 CH_2Cl_2/hexanes. Collection of the orange band and solvent

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removal gave 0.084 g (0.190 mmol, 15% from 4) of 7 as an orange oil: IR (cm^{-1}, CH_2Cl_2) $\nu_{N\equiv O}$ 1630 (s); ^1H NMR (δ, $CDCl_3$) 7.30–6.80 (m's, C_6H_5), 4.87 (s, C_5H_5), 3.22 (dd, $J_{^1H_\alpha-^1H_{\alpha'}} = 11.3$ Hz, $J_{^1H_\alpha-^{31}P} = 7.4$ Hz, ReCH), 2.72 (dd, $J_{^1H_{\alpha'}-^1H_\alpha} = 11.3$ Hz, $J_{^1H_{\alpha'}-^{31}P} = 3.6$ Hz, ReCH), 1.65 (d, $J_{^1H-^{31}P} = 9.7$ Hz, PMe_3); ^{13}C NMR (ppm, $CDCl_3$) phenyl carbons at 158.87, 127.59, 126.97, and 121.82, 88.17 (C_5H_5), 19.38 (d, $J_{^{13}C-^{31}P} = 35.5$ Hz, PMe_3), –7.97 (d, $J_{^{13}C-^{31}P} = 4.5$ Hz, $ReCH_3$).

Generation and Reactions of $[(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(=CH_2)]^+PF_6^-$. A septum-capped NMR tube was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(CH_3)$ (0.0148 g, 0.040 mmol) and CD_2Cl_2 (0.350 mL). The NMR tube was cooled to –78 °C whereupon 0.0176 g (0.045 mmol) of $Ph_3C^+PF_6^-$ in 0.150 mL of CD_2Cl_2 was added via gas-tight syringe. The tube was quickly transferred to a –70 °C NMR probe. The formation of a methylidene complex was evident (δ 15.36 (br t), 14.88 (br d, $=CH_2$), 6.23 (s, C_5H_5)) as well as a byproduct (δ 5.62) (1:2 ratio). A preparative reaction was similarly conducted in a Schlenk flask using 0.195 g (0.524 mmol) of $(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(CH_3)$ in 20 mL of CH_2Cl_2 and 0.244 g (0.629 mmol) of $Ph_3C^+PF_6^-$. The methylidene solution was stirred for 0.5 h, and then 0.500 mL of 2 M C_6H_5Li in C_6H_6/ether (1.00 mmol) was added dropwise. The solution turned from light yellow to orange and was allowed to warm to room temperature. Solvent was removed under oil pump vacuum and the residue transferred to a glovebox for the remaining workup. The residue was taken up in CH_2Cl_2 and filtered through silica gel. The CH_2Cl_2 was pumped off, and the resulting orange oil was chromatographed on a 2.5 × 14 cm silica gel column with 3:1 CH_2Cl_2/hexanes. Collection of the orange band and solvent removal gave 0.099 g (~40%) of a 3:1 mixture of 7 and $(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(CH_3)$, as determined by integration of the C_5H_5 ^1H NMR resonances.

Preparation of *ac*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(=CHC_6H_5)]^+PF_6^-$ (13t). **A.** A septum-capped NMR tube was charged with 7 (0.039 g, 0.087 mmol) and CD_2Cl_2 (0.350 mL) and was cooled to –78 °C. Then $Ph_3C^+PF_6^-$ (0.041 g, 0.105 mmol) in CD_2Cl_2 (0.350 mL) was added, and the tube was quickly transferred to a –70 °C NMR probe. Benzylidene **13t** had formed cleanly: δ 14.76 (s, Re=CH), 6.24 (s, C_5H_5), 5.61 (s, Ph_3CH), 1.70 (d, $J_{^1H-^{31}P} = 11.4$ Hz, PMe_3). No evidence for isomerization was noted upon warming, although resolution improved. The CD_2Cl_2 was removed via oil pump vacuum and replaced with $CDCl_3$. This solution was heated for 3 h at 60 °C without apparent isomerization. **B.** A –78 °C solution of 7 (0.084 g, 0.187 mmol) in CH_2Cl_2 (15 mL) was treated with solid $Ph_3C^+PF_6^-$ (0.087 g, 0.224 mmol). The solution was stirred at –78 °C for 20 min and was then allowed to warm to room temperature. Solvent was removed under oil pump vacuum, and the remaining dark yellow oily residue was washed with hexanes, dissolved in CH_2Cl_2, and filtered. Hexanes was added to the filtrate, but crystallization could not be induced. Solvents were removed under vacuum to give 0.071 g (0.128 mmol, 69%) of **13t** as a yellow oil: IR (cm^{-1}, CH_2Cl_2) $\nu_{N\equiv O}$ 1704 (s); ^1H NMR (δ, CD_2Cl_2) 14.89 (d, $J_{^1H-^{31}P} = 1.2$ Hz, Re=CH), 7.85–7.47 (d,t,t pattern, C_6H_5) 6.26 (s, C_5H_5), 1.70 (d, $J_{^1H-^{31}P} = 11.6$ Hz, PMe_3); ^{13}C NMR (ppm, acetone-d_6) 283.81 (d, $J_{^{13}C-^{31}P} = 7.3$ Hz, Re=C), phenyl carbons at 152.99, 134.27, 131.74, and 130.62, 100.33 (C_5H_5), 18.71 (d, $J_{^{13}C-^{31}P} = 41.5$ Hz, PMe_3).

Photolysis of 13t. A septum-capped 5-mm NMR tube was charged with **13t** (0.081 g, 0.137 mmol) and CD_2Cl_2 (0.500 mL). The solution was freeze–thaw–degassed three times, and a N_2 atmosphere was admitted. The tube was placed in a large Pyrex test tube partially filled with acetone, and the test tube was in turn placed in a large unsilvered Pyrex Dewar charged with a dry ice/acetone bath. A Hanovia 450-W lamp was suspended in a water-cooled quartz immersion well and placed adjacent to the Dewar such that ca. 5 cm separated the lamp from the sample tube. The tube was irradiated for 4 h at –78 °C and then quickly transferred to a –70 °C NMR probe. A (44 ± 1):(56 ± 1) **13k**/**13t** mixture had been generated. ^1H NMR (δ): **13k**, at 15.80 (s, Re=CH), 6.16 (s, C_5H_5); **13t**, at 14.80 (br s, Re=CH), 6.29 (s, C_5H_5). The sample was warmed to room temperature. A ^1H NMR spectrum taken 0.5 h later showed only **13t**.

Reaction of 13t with $Li(C_2H_5)_3BD$. To a –78 °C solution of **13t** (0.040 g, 0.068 mmol) in CH_2Cl_2 (10 mL) was added dropwise 0.081 mL of 1.0 M $Li(C_2H_5)_3BD$ in THF (0.081 mmol). The solution was allowed to warm to room temperature, whereupon solvents were removed under oil pump vacuum. The residue was transferred to a glovebox and chromatographed on a 13 × 2.5 cm silica gel column in 3:1 CH_2Cl_2/hexanes. The orange band was collected and the solvent removed to give 0.021 g (0.047 mmol, 69%) of $(\eta^5\text{-}C_5H_5)Re(NO)(PMe_3)(CHDC_6H_5)$ (7-α-d_1) as an orange oil. The relative areas of the H_α ^1H NMR resonances at δ 3.20 and 2.71 were (77 ± 1):(23 ± 1).

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2(2\text{-}C_6H_4CH_3))$ (8). To a –78 °C solution of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$[9] (0.300 g, 0.537 mmol) in CH_2Cl_2 (30 mL) was added solid $Ph_3C^+PF_6^-$ (0.250 g, 0.644 mmol). The resulting yellow solution was stirred at –78 °C for 0.5 h, and then 1.5 mL of 0.75 M $o\text{-}CH_3C_6H_4MgBr$ in THF (1.12 mmol) was added dropwise. Solvent was then removed under oil pump vacuum as the reaction was allowed to warm to room temperature. The resulting residue was extracted with benzene and filtered through a 5-cm silica gel plug. Benzene was removed from the bright orange filtrate, and the residue was chromatographed on a 18 × 2.5 cm silica gel column with 1:1 CH_2Cl_2/hexanes. The orange band was collected, concentrated to a residue and recrystallized from CH_2Cl_2/hexanes to give 0.182 g (0.281 mmol, 52%) of 8 as small orange crystals: mp 179–182 °C dec; IR (cm^{-1}, CH_2Cl_2) $\nu_{N\equiv O}$ 1624 (s); ^1H NMR (δ, CD_2Cl_2) 7.45–6.76 (m's, phenyl, 19 H), 4.72 (s, C_5H_5), 3.09 (very br s, $ReCH_2$), 2.20 (s, CH_3); ^{13}C NMR (ppm, $CDCl_3$) phenyl carbons at 156.87 (d, $J_{^{13}C-^{31}P} = 4.3$ Hz), 136.05 (d, $J = 50.9$ Hz), 133.97, 133.62 (d, $J = 10.4$ Hz), 130.09, 129.95, 128.38 (d, $J = 10.2$ Hz), 127.99, 124.93, and 122.01, 90.58 (C_5H_5), 20.28 (CH_3), –6.23 (d, $J = 4.3$ Hz, ReC_α); mass spectrum (70 eV), *m*/*e* (relative intensity) 649 (M^+, ^{187}Re, 18), 544 ($M^+ - CH_2C_6H_4CH_3$, 100), 387 ($M^+ - PPh_3$, 27), 262 ($^+PPh_3$, 30).

Preparation of *ac*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CH(2\text{-}C_6H_4CH_3))]^+PF_6^-$ (11t). **A.** A septum-capped NMR tube was charged with 8 (0.021 g, 0.032 mmol) and CD_2Cl_2 (0.350 mL) and was cooled to –78 °C. Then $Ph_3C^+PF_6^-$ (0.015 g, 0.038 mmol) in CD_2Cl_2 (0.150 mL) was added, and the tube was quickly transferred to a –70 °C NMR probe. A ca. 50:50 ratio of xylylidenes **11t** (δ 15.72, 6.09, 1.86) and **11k** (δ 16.41, 5.86, 2.37) had cleanly formed. The tube was warmed in the NMR probe. As **11k** diminished, **11t** increased. After 45 min at room temperature, only **11t** remained. **B.** To a –78 °C solution of 8 (0.092 g, 0.142 mmol) in CH_2Cl_2 (20 mL) was added solid $Ph_3C^+PF_6^-$ (0.066 g, 0.170 mmol). The solution was stirred at –78 °C for 0.5 h and was allowed to warm to room temperature. After 2 h at room temperature, solvent was removed under oil pump vacuum. The remaining dark residue was filtered through a 5-cm silica gel plug with CH_2Cl_2. This operation required 1000–1500 mL of CH_2Cl_2 to ensure complete extraction of **11t** from the silica gel. The CH_2Cl_2 was removed from the filtrate by rotary evaporation. The resulting yellow oil was taken up in CH_2Cl_2 and carefully layered with hexane. Small yellow leafs of **11t** formed (0.056 g, 0.071 mmol, 50%): mp 245–250 °C dec; IR (cm^{-1}, CH_2Cl_2) $\nu_{N\equiv O}$ 1715 (s); ^1H NMR (δ, CD_2Cl_2) 15.76 (s, Re=CH), 7.55–7.00 (m, phenyls), 6.07 (s, C_5H_5), 1.88 (s, CH_3); ^{13}C NMR (ppm, acetone-d_6) 287.48 (d, $J_{^{13}C-^{31}P} = 9.8$ Hz, Re=CH), phenyl carbons at 152.63, 134.45, 134.36, 133.97 (d, $J_{^{13}C-^{31}P} = 9.9$ Hz), 133.33, 133.12, 131.59, 130.31 (d, $J = 11.9$ Hz), 130.21 (d, $J = 61.2$ Hz), and 128.09, 101.22 (C_5H_5), 20.21 (CH_3). Anal. Calcd for $C_{31}H_{28}F_6NOP_2Re$: C, 46.97; H, 3.56. Found: C, 46.73; H, 3.66.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2(2,4,6\text{-}C_6H_2(CH_3)_3))$ (9). To a –78 °C solution of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (0.404 g, 0.724 mmol) in CH_2Cl_2 (40 mL) was added solid $Ph_3C^+PF_6^-$ (0.338 g, 0.871 mmol). The resulting yellow solution was stirred at –78 °C for 20 min, and then 2.0 mL of 0.7 M mesitylmagnesium bromide in THF (1.4 mmol) was added dropwise. Solvent was then removed under oil pump vacuum as the reaction was allowed to warm to room temperature. The resulting residue was extracted with benzene and filtered through a 5-cm silica gel plug. Benzene was removed from the bright orange filtrate, and the residue was chromatographed on a 20 × 2.5 cm silica gel column with 1:1 CH_2Cl_2/hexanes. The orange band was collected. Solvent was removed under vacuum to give 0.384 g (0.568 mmol, 78%) of 9 as an orange powder: mp 215–216 °C dec; IR (cm^{-1}, CH_2Cl_2) $\nu_{N\equiv O}$ 1623 (s); ^1H NMR (δ, CD_2Cl_2, 25 °C) 7.55–7.13 (m, C_6H_5), 6.68 (s, $2,4,6\text{-}C_6\mathbf{H}_2(CH_3)_3$), 4.55 (s, C_5H_5), 3.20 (dd, $J_{^1H_{\alpha S}-^1H_{\alpha R}} = 11.9$ Hz, $J_{^1H_{\alpha S}-^{31}P} = 8.9$ Hz, $ReCH_S$), 2.64 (dd, $J_{^1H_{\alpha R}-^1H_{\alpha S}} = 11.9$ Hz, $J_{^1H_{\alpha R}-^{31}P} = 1.5$ Hz, 1 H, $ReCH_R$), 2.18 (s, 4-CH_3), 2.12 (br s, 2,6-CH_3); ^{13}C NMR (ppm, $CDCl_3$, 25 °C) phenyl carbons at 152.10 (d, $J_{^{13}C-^{31}P}$ = 2.7 Hz), 136.06 (d, J = 51.1 Hz), 133.60 (d, J = 9.5 Hz), 133.07 (br s), 130.32, 130.05, and 128.34 (d, J = 9.5 Hz), 90.35 (C_5H_5), 20.97 (2,6-CH_3), 20.62 (4-CH_3), −11.28 (d, J = 4.1 Hz, ReC_α); mass spectrum (16 eV), m/e (relative intensity) 677 (M^+, ^{187}Re, 31), 544 ($M^+ - CH_2C_6H_2(CH_3)_3$, 100), 415 ($M^+ - PPh_3$, 33), 262($^+PPh_3$, 28). Anal. Calcd for $C_{33}H_{33}NOPRe$: C, 58.56; H, 4.91. Found: C, 58.77; H, 5.02.

Variable Temperature ^{1}H NMR Spectra of 9. The data in Figure 1 were treated as follows.[13] The ortho CH_3 and meta H $\Delta\nu$ were determined to be 85.43 and 17.27 Hz, respectively. The coalescence formula gave k_c (s^{-1}) of 189.7 (248 K) and 38.4 (236 K), respectively. The equation $\Delta G_c^\ddagger = 4.57T_c\,(10.32 + \log T_c/k_c)$ was applied and gave values of 11.8 and 12.0 kcal/mol. The ortho CH_3 (270 K), meta H (248 K), and ortho CH_3 (236 K) line widths were corrected for field inhomogeneties by substracting the $(CH_3)_4Si$ line width. This gave values of 12.78, 5.48, and 14.12 Hz, respectively. Application of the fast exchange approximation to the first two and the slow exchange approximation to the last gave k (s^{-1}) of 83.2, 85.5, and 44.4, respectively. These yielded $\Delta G^\ddagger$ of 12.1, 12.2, and 11.9 kcal/mol.

Preparation of *ac*-[(η-C_5H_5)Re(NO)(PPh_3)(=CH(2,4,6-$C_6H_2(CH_3)_3$))]$^+PF_6^-$ (12t). A. A septum-capped NMR tube was charged with **9** (0.017 g, 0.025 mmol) and CD_2Cl_2 (0.350 mL) and was cooled to −78 °C. Then $Ph_3C^+PF_6^-$ (0.011 g, 0.028 mmol) in CD_2Cl_2 (0.150 mL) was added, and the tube was quickly transferred to a −70 °C NMR probe. Resonances were broad, but some **12t** (δ 15.93 and 6.12) was evident. The sample was warmed to room temperature. Broadening diminished, but no evidence for geometric isomerization was observed. **B.** To a −78 °C solution of **9** (0.152 g, 0.225 mmol) in CH_2Cl_2 (20 mL) was added solid $Ph_3C^+PF_6^-$ (0.106 g, 0.273 mmol). The solution was allowed to warm to room temperature and was stirred for an additional hour. Solvent was then removed under oil pump vacuum, and the residue was washed with hexanes and ether. The yellow powder that remained was extracted with $CHCl_3$. Hexanes was added until cloud point was reached. The solution was filtered and stored in a freezer overnight. Small yellow prisms of **12t** formed (0.037 g, 0.045 mmol, 20%): mp 215 °C dec; IR (cm^{-1}, CH_2Cl_2) $\nu_{N=O}$ 1730 (s); ^{1}H NMR (δ, $CDCl_3$) 16.11 (br s, Re=CH), 7.53–7.10 (m's, C_6H_5), 6.75 (s, 2,4,6-$C_6H_2(CH_3)_3$), 6.14 (s, C_5H_5), 2.30 (s, 4-CH_3), 1.92 (s, 2,6-CH_3); ^{13}C NMR (ppm, acetone-d_6) 294.62 (d, $J_{^{13}C-^{31}P}$ = 7.3 Hz, Re=CH), phenyl carbons at 152.00, 141.28, 135.17, 134.01 (d, $J_{^{13}C-^{31}P}$ = 9.8 Hz), 133.28, 132.21, 130.58 (d, J = 61.0 Hz), 130.44 (d, J = 12.2 Hz), and 130.12, 101.52 (C_5H_5), 21.10 (4-CH_3), 20.67 (2,6-CH_3). Anal. Calcd for $C_{33}H_{22}F_6NOP_2Re$: C, 48.30; H, 3.93. Found: C, 48.07; H, 4.03.

Photolysis of 12t. Rate of Isomerization of 12k to 12t. A septum-capped NMR tube was charged with **12t** (0.10 g, 0.012 mmol) and CD_2Cl_2 (0.500 mL) and was degassed and photolyzed as described above for **13t**. The tube was quickly transferred to a −70 °C NMR probe. A (55 ± 2):(45 ± 2) **12k**/**12t** mixture had been generated. ^{1}H NMR (δ, −70 °C): **12k**, at 16.22 (s, Re=CH), 5.86 (s, C_5H_5); **12t**, at 15.93 (br s, Re=CH), 6.14 (s, C_5H_5); data at −24.5 °C (Figure 3) **12k**, at 16.15, 6.82 (2,4,6-$C_6H_2(CH_3)_3$), 5.79, 2.25 (4-CH_3), 1.71 (2,6-CH_3); **12t**, at 15.92, 6.76, 6.09, 2.28, 1.88. Rate data were collected for $2.0t_{1/2}$ at −15.0, −20.1, and −24.5 °C and for $1.0t_{1/2}$ at −20.0 and −30.0 °C. Rate constants and activation parameters were calculated as previously described.[3]

Reaction of 12t with Li(C_2H_5)$_3$BD. To a −78 °C solution of **12t** (0.031 g, 0.038 mmol) in CH_2Cl_2 (10 mL) was added dropwise 0.050 mL of 1.0 M $Li(C_2H_5)_3BD$ in THF (0.050 mmol). The solution was warmed to room temperature, and solvent was removed under oil pump vacuum. The residue was chromatographed on a 13 × 2.5 cm silica gel column with 1:1 CH_2Cl_2/hexanes. The orange band was collected and the solvent removed to give 0.020 g (0.030 mmol, 78%) of (*SS*,*RR*)-**9**-α-d_1 as an orange solid. The ^{1}H NMR spectrum ($CDCl_3$) was identical with that of **9** except for the H_α resonances: δ 2.69 (br s, $w_{1/2}$ = 4.9 Hz), 3.20 absent.

Reaction of (*SS*,*RR*)-9-α-d_1 with $Ph_3C^+PF_6^-$. A septum-capped NMR tube was charged with (*SS*,*RR*)-**9**-α-d_1 (0.020 g, 0.030 mmol) and CD_2Cl_2 (0.300 mL) and cooled to −78 °C. Then $Ph_3C^+PF_6^-$ (0.013 g, 0.034 mmol) in CD_2Cl_2 (0.200 mL) was added, and the reaction was ^{1}H NMR monitored analogously to preparation A of **12t** above. The sample was warmed to room temperature, and the Re=CH and C_5H_5 resonances of **12t** were integrated. The integral heights (18 and 88 mm) indicated the product to be ≳98% **12t**-d_0.

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Registry No. **4**, 89727-22-0; **5**, 89727-23-1; **7**, 89727-24-2; 7-α-d_1, 89727-25-3; **8**, 89727-26-4; **9**, 89727-27-5; (*SS*,*RR*)-**9**-α-d_1, 89727-28-6; **11k**, 89824-58-8; **11t**, 89727-30-0; **12k**, 89824-60-2; **12t**, 89727-32-2; **13k**, 89824-62-4; **13t**, 89727-34-4; [(η^5-C_5H_5)Re(NO)(CO)$_2$]$^+BF_4^-$, 31960-40-4; $C_6H_5I^+$-O^-, 536-80-1; (η^5-C_5H_5)Re(NO)(PMe_3)(CH_3), 80668-22-0; C_6H_5Br, 108-86-1; [(η^5-C_5H_5)Re(NO)(PMe_3)(=CH_2)]$^+PF_6^-$, 89727-36-6; (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3), 71763-18-3; $Li(C_2H_5)_3BD$, 74540-86-6; o-$CH_3C_6H_4Br$, 95-46-5; 2,4,6-$C_6H_2(CH_3)_3Br$, 576-83-0.