Synthesis and Properties of [(η-C5H5)Re(NO)(PPh3)(=CHC6H5)]+PF6-: A Benzylidene Complex That Is Formed by a Stereospecific α-Hydride Abstraction, Exists as Two Geometric Isomers, and Undergoes Stereospecific Nucleophilic Attack

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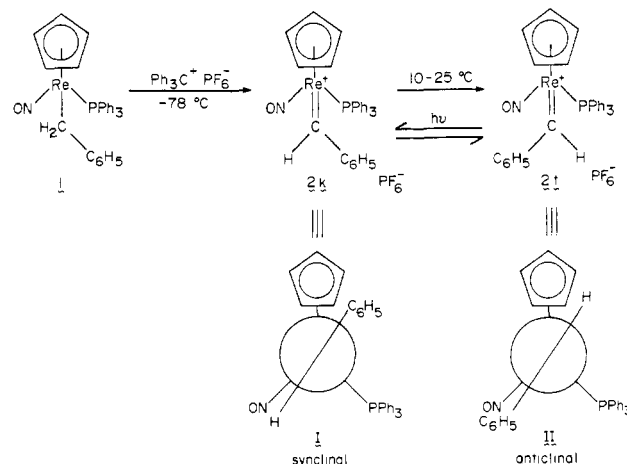
Abstract: Reaction of (η-C5H5)Re(NO)(PPh3)(CH2C6H5) (1) with Ph3C+PF6- at -78 °C gives the benzylidene *sc*-[(η-C5H5)Re(NO)(PPh3)(=CHC6H5)]+PF6- (**2k**), which isomerizes upon warming ($t_{1/2}$ = 17 min at 29.5 °C, $\Delta H^{\ddagger}$ = 20.9 ± 0.4 kcal/mol, $\Delta S^{\ddagger}$ = -3.8 ± 0.2 eu) to a new Re=C geometric isomer, *ac*-[(η-C5H5)Re(NO)(PPh3)(=CHC6H5)]+PF6- (**2t**). The **2t/2k** equilibrium mixture is ≥99:1, but irradiation between -78 and -20 °C establishes a (55 ± 3):(45 ± 3) photostationary state. The structures of **2t** and **2k** are confirmed by X-ray crystallography (**2t**) and extended Hückel MO calculations. Nucleophiles (Nu) Li(C2H5)3BD, CH3Li, CH3CH2MgBr, C6H5CH2MgCl, PMe3, and CH3ONa attack **2t** to give diastereomerically pure adducts (η-C5H5)Re(NO)(PPh3)(CHNuC6H5), in which a new chiral center is stereospecifically generated. The same nucleophiles react stereoselectively with **2k**, affording adducts in (generally) 92-95:8-5 diastereomer ratios. The minor diastereomers from **2k** are identical with the products from **2t**. Thus nucleophilic attack upon **2t** and **2k** occurs preferentially from the same direction. An X-ray structure of (*SS,RR*)-(η-C5H5)Re(NO)(PPh3)(CH(CH2C6H5)C6H5) (**5t**, from C6H5CH2MgCl attack upon **2t**) establishes this direction to be antiperiplanar to the PPh3. When (*SS,RR*)-(η-C5H5)Re(NO)(PPh3)(CHDC6H5) (**1**-α-d_1-t; from Li(C2H5)3BD attack upon **2t**) is treated with Ph3C+PF6-, exclusive H- abstraction occurs to give first **2k**-α-d_1 and then **2t**-α-d_1. When (*SR,RS*)-(η-C5H5)Re(NO)(PPh3)(CHDC6H5) (**1**-α-d_1-k; from Li(C2H5)3BH attack upon **2t**-α-d_1 or Li(C2H5)3BD attack upon **2k**) is treated with Ph3C+PF6-, preferential (92:8) D- abstraction occurs to give undeuterated **2k** and (subsequently) **2t**. These data (after an isotope effect correction) indicate that the *pro-R* α-hydrogen of **1** is abstracted by Ph3C+PF6- essentially stereospecifically. Insights into this specificity are gained by 1H NMR, extended Hückel MO calculations, and the chemospecific and stereospecific abstraction of CH3O- from (η-C5H5)Re(NO)(PPh3)(CH(OCH3)C6H5) (*SR,RS*: **7t**; *SS,RR*: **7k**) by Ph3C+PF6-. A mechanism is proposed in which the least stable rotamer of **1** is the most reactive toward Ph3C+PF6-.

Introduction

During the last decade, the use of chiral transition-metal catalysts in asymmetric organic synthesis has received increasing attention.[4] Extremely useful *stoichiometric* reagents such as Sharpless' Ti(O-*i*-Pr)4/*t*-BuOOH/diethyl tartrate system for asymmetric epoxidation have also been developed.[5] However, understanding of the mechanistic basis for chirality transfer is still at a very formative stage. Some surprising results have been obtained from initial studies. For instance, the [Rh(*S,S*-chiraphos)S′2]+-catalyzed[6] asymmetric hydrogenation of prochiral enamides proceeds via the *less* stable of two diastereomeric olefin complexes.

We recently described syntheses of rhenium alkyls and alkylidenes of the formulas (η-C5H5)Re(NO)(PPh3)(CH2R) and [(η-C5H5)Re(NO)(PPh3)(=CHR)]+PF6-.[7] Both classes of compounds contain a pseudotetrahedral asymmetric rhenium and have been found to undergo unprecedented ligand-based stereospecific (or highly stereoselective) stoichiometric reactions. These transformations offer the opportunity to study the transfer of metal-centered chirality to carbon at a fundamental level and consequently have been the subject of detailed investigations in our laboratory.

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(4) (a) Kagan, H. B.; Fiund, J. C. *Top. Stereochem.* **1978**, *10*, 175. (b) Fryzuk, M. D.; Bosnich, B. *J. Am. Chem. Soc.* **1979**, *101*, 3043. (c) Valentine, D., Jr.; Scott, J. W. *Synthesis* **1978**, 329.

(5) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974.

(6) Chan, A. S. C.; Pluth, J. J.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 5952. Chua, P. S.; Roberts, N. K.; Bosnich, B.; Okrasinski, S. J.; Halpern, J. *J. Chem. Soc., Chem. Commun.* **1982**, 1278. Chiraphos = (*SS,RR*)-(C6H5)2PCH(CH3)CH(CH3)P(C6H5)2.

(7) Kiel, W. A.; Lin, G.-Y.; Gladysz, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 3299.

Scheme I. Syntheses and Interconversions of Isomeric Benzylidene Complexes[10]

In this paper, we present a full account of our work with the benzyl complex (η-C5H5)Re(NO)(PPh3)(CH2C6H5) (1) and the benzylidene complex [(η-C5H5)Re(NO)(PPh3)(=CHC6H5)]+PF6- (2).[7-9] As will be disclosed, three principal findings emerge from our *chemical* data:

(a) Reaction of (η-C5H5)Re(NO)(PPh3)(CH2C6H5) (1) with Ph3C+PF6- results in abstraction of only one of the two diastereotopic α hydrogens.

(b) The product from a, benzylidene 2, is generated initially as a "kinetic" Re=C geometric isomer (**2k**); at 10-25 °C, **2k** isomerizes to a "thermodynamic" geometric isomer (**2t**).

(8) Constable, A. G.; Gladysz, J. A. *J. Organomet. Chem.* **1980**, *202*, C21.

(9) McCormick, F. B.; Kiel, W. A.; Gladysz, J. A. *Organometallics* **1982**, *1*, 405.

Figure 1. Calculated E_{total} for $[(\eta\text{-}C_5H_5)Re(NO)(PH_3)(\!=\!CH_2)]^+$ as the $=\!CH_2$ ligand is rotated.

(c) Benzylidenes **2k** and **2t** undergo stereoselective and stereospecific attack, respectively, when treated with a variety of nucleophiles.

We then describe the use of physical and theoretical methods (two X-ray crystal structures; extended Hückel MO calculations) to precisely define the stereochemical relationships between the starting materials and products in a–c and to provide insight into the origins of stereocontrol.

Results

1. Synthesis and Structural Characterization of Benzylidene Complexes. The benzyl complex $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)\text{-}(CH_2C_6H_5)$ (**1**) was treated with 1.1 equiv of $Ph_3C^+PF_6^-$ in CD_2Cl_2 at $-78\ ^\circ C$. Proton NMR monitoring ($-70\ ^\circ C$) indicated the clean and immediate formation of a cationic benzylidene complex (**2k**; Scheme I),[10] as evidenced by a characteristic[11] low-field $Re\!=\!CH(C_6H_5)$ resonance (δ 16.08 (s, 1 H)) and a deshielded C_5H_5 resonance (δ 5.89 (s, 5 H)). When this solution was warmed to 10–25 $^\circ C$, **2k** began to disappear as a new benzylidene complex, **2t**, formed (δ 15.30 (s, 1 H), 6.06 (s, 5 H)). At room temperature, the equilibrium ratio of **2t**/**2k** was >99:1. After solvent removal and recrystallization, **2t** was isolated in 73–75% yields as yellow, air-stable powder or crystals (Experimental Section) which were stable to >200 $^\circ C$. Attempts to isolate **2k** by low-temperature crystallization gave only impure oils.

Additional experiments indicated **2k** and **2t** to be geometric isomers differing in the orientation of ligands about the $Re\!=\!C$ double bond. First, both **2k**[12] and **2t** reacted cleanly with Li-$(C_2H_5)_3BH$ to give **1**. This transformation established the benzylidene carbon to be electrophilic. Second, irradiation of CD_2Cl_2, CD_3CN, or $(CD_3)_2CO$ solutions of **2t** (Hanovia 450-W lamp, through Pyrex) between -78 and $-20\ ^\circ C$ afforded, after 3 h, clean (55 ± 3):(45 ± 3) photostationary states of **2t** and **2k**, as determined by ^1H NMR integration of the C_5H_5 resonances. These solutions were allowed to return to thermal equilibrium in the dark. A sample to which p-di-*tert*-butylbenzene had been added indicated >95% of the original **2t** to be present. Thus **2t** and **2k** can be photointerconverted analogously to $C\!=\!C$ double-bond geometric isomers.[9,13]

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(10) For the conversion of planar representations of rhenium complexes into three dimensional structures, we employ the convention shown in Scheme I for alkylidenes[8] and the following convention for alkyls:
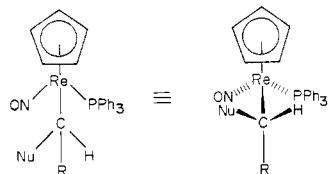
(11) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099.
(12) Unless otherwise noted, reactions of **2k** were conducted with material prepared in situ at $-78\ ^\circ C$.
(13) (a) Saltiel, J.; D'Agostino, J.; Megarity, E. D.; Metts, L.; Neuberger, K. R.; Wrighton, M.; Zafiriou, O. C. In "Organic Photochemistry"; Chapman, O. L., Ed.; Marcel Dekker: New York, 1973; Vol. 3, pp 1–113. (b) Saltiel, J.; Charlton, J. L. In "Rearrangements in Ground Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 25.

Figure 2. Stereoview of the molecular structure of $ac\text{-}[(\eta\text{-}C_5H_5)Re\text{-}(NO)(PPh_3)(\!=\!CHC_6H_5)]^+PF_6^-\cdot CHCl_3$ (**2t**·CHCl_3).

Table I. Selected Bond Lengths and Bond Angles in 2t·CHCl_3

atoms	dist, Å	atoms	angle, deg
Re–C1	1.949 (6)	Re–C1–C21	136.2 (5)
Re–P1	2.427 (2)	Re–C1–H1	117[b]
Re–N	1.761 (5)	N–Re–C1	99.8 (2)
Re–C_5H_5 [a]	2.333	P1–Re–N	91.0 (2)
N–O1	1.195 (7)	P1–Re–C1	93.2 (2)
C1–H1	0.98[b]	O1–N–Re	172.7 (5)
C1–C21	1.454 (9)		

[a] Average distance from Re to C_5H_5 carbons. [b] H1 was not refined.

Since geometric isomerism due to metal–carbon multiple bonding was without precedent, we turned to an MO analysis for additional insight. Extended Hückel MO calculations have been previously shown to accurately predict metal–alkylidene bonding geometries.[14] Computations on the parent model system[15] $[(\eta\text{-}C_5H_5)Re(NO)(PH_3)(\!=\!CH_2)]^+$ showed two degenerate energy minima, separated by a $\sim$19-kcal barrier, as the rhenium–methylidene bond was rotated through 360° (Figure 1). In the favored conformer, the $=\!CH_2$ plane eclipsed the (C)Re–N–O plane. Thus two *nondegenerate* minima, I and II (Scheme I; Newman projections down the benzylidene–rhenium bond) are expected as the benzylidene ligand in **2** is rotated through 360°.

Space-filling molecular models indicated II to be considerably less congested than I. In the former, the benzylidene phenyl ring eclipses the small NO ligand, whereas in the latter it is forced to reside between the bulky PPh_3 and medium-sized C_5H_5 ligand. Calculations on the model system $[(\eta\text{-}C_5H_5)Re(NO)(PH_3)(\!=\!CHC_6H_5)]^+$ indicated II to be more stable than I as long as the benzylidene phenyl ring was canted at least 25° with respect to the (C)Re–N–O plane (i.e., slightly out of conjugation with $Re\!=\!C$). This relieves a repulsive nonbonding interaction between the NO and an ortho proton of the benzylidene phenyl ring.

A definitive structural assignment for **2t** was made by X-ray crystallography. A suitable single crystal ($0.19\times0.20\times0.30$ mm; $CHCl_3$ monosolvate) was obtained by slow diffusion of petroleum ether (bp 30–60 $^\circ C$) into a $CHCl_3$ solution of **2t**. X-ray data were obtained at $-158\ ^\circ C$ by using monochromated Mo Kα (0.710 69 Å) radiation on a Syntex P$\bar{1}$ automatic diffractometer. The general techniques employed have been previously described.[16] The unit cell was found to be triclinic, space group $P\bar{1}$ ($Z = 2$), with lattice parameters $a = 8.984$ (5) Å, $b = 14.008$ (6) Å, $c = 13.965$ (7) Å, $\alpha = 109.06$ (4)°, $\beta = 101.92$ (4)°, $\gamma = 75.99$ (4)°. Of 5666 reflections with $2\theta < 50°$ collected, 5070 with $I \geq 3\sigma(I)$ were used in the final refinement. The positions of the Re and P(1) atoms were obtained from a three-dimensional Patterson map. Several least-squares refinements yielded all non-hydrogen atoms, including the $CHCl_3$, in the unit cell. Absorption corrections were then applied after which all hydrogens were located from a difference Fourier map. The rhenium, chlorine, fluorine, and

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(14) (a) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592. (b) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *Ibid.* **1979**, *101*, 585.
(15) (a) The isolation of the methylidene complex $[(\eta\text{-}C_5H_5)Re(NO)\text{-}(PPh_3)(\!=\!CH_2)]^+PF_6^-$ has been described in a separate publication.[15b] (b) Tam, W.; Lin, G.-Y.; Wong, W. K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.
(16) Strouse, J.; Layten, S. W.; Strouse, C. E. *J. Am. Chem. Soc.* **1977**, *99*, 562.

Benzylidine [(η-C₅H₅)Re(NO)(PPh₃)(=CHC₆H₅)]⁺PF₆⁻

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Table II. Rate Constants for the Re=C Bond Rotation
$2k \rightarrow 2t$ in CD_2Cl_2 [a]

entry	temp (±0.1 °C)	$10^5 k_{obsd}$, s⁻¹
1	29.5	69.2 ± 0.6
2	24.0	37.6 ± 0.6
3	19.0	20.5 ± 0.2
4	19.0	19.2 ± 0.2
5[b]	19.0	20.9 ± 0.3
6	14.0	11.5 ± 0.2
7	10.0	4.81 ± 0.10
8	10.0	6.93 ± 0.10
9	4.0	2.61 ± 0.03

[a] $[2k]_0 = 0.038 - 0.042$ M. Entries 1-5 were followed through $>2t_{1/2}$; others were followed through at least one $t_{1/2}$. See Experimental Section for further details. [b] 2k photochemically generated at -78 °C.

phosphorus atoms were refined with anisotropic temperature factors, and all other non-hydrogen atoms were refined with isotropic thermal parameters. All hydrogen atoms were held at positions indicated from the map with assigned isotropic thermal parameters. The final R index was 0.039 with $R_w = 0.049$.[17]

The molecular structure of 2t·CHCl₃ thus obtained is shown in Figure 2. The near eclipsing of the (C1)Re–N–O1 and H1–C1–C21 planes (torsion angle = 4.0 ± 0.7°) is evident. Thus 2t has the structure approximated by Newman projection II (Scheme I). Since the MO calculations indicate only *two* energy minima as rhenium–alkylidene bonds are rotated through 360°, 2k can confidently be assigned the structure I.

An exhaustive list of bond distances and angles in 2t·CHCl₃ and a crystal packing diagram are provided in the supplementary material. Important bond distances and angles are summarized in Table I. The P1–Re–N angle of 91.0 (2)° is expected based upon crystal structures of other, formally octahedral, (η-C₅H₅)ML₃ (M = Mn, Re) complexes.[18a] Hence the corresponding angles in Newman projections I–XIV (normally 120°) have been compressed. As anticipated by the calculations, the least-squares plane of the benzylidene phenyl ring (Figure 2) is canted 19.9 ± 0.8° with respect to the Re=C vector.

Benzylidene complexes 2k and 2t were further characterized by isomerization rate measurements and UV–visible spectroscopy. The first-order rate constant for equilibration of a (55 ± 3):(45 ± 3) 2t/2k photostationary state (in CD_2Cl_2) back to 2t was measured by ¹H NMR at 19 °C (entry 5, Table II). The k_{obsd} obtained was in good agreement with the k_{obsd} determined (19 °C) from 2k prepared in situ from (η-C₅H₅)Re(NO)(PPh₃)(CH₂C₆H₅) and Ph₃C⁺PF₆⁻ (entries 3 and 4, Table II). Hence, data obtained by the latter route can reliably be used to calculate activation parameters for rotation about rhenium–alkylidene bonds. Rate constants for 2k → 2t were measured from 4 °C ($t_{1/2}$ = 443 min) to 29.5 °C ($t_{1/2}$ = 17 min), as summarized in Table II. These yielded $\Delta H^{\ddagger} = 20.9 \pm 0.4$ kcal/mol and $\Delta S^{\ddagger} = -3.8 \pm 0.2$ eu.[18b]

The absorption spectrum of 2t displayed a λ_{max} at 365 nm (ϵ 13 000) in CH₃CN. A series of spectra (Figure 3) were recorded as a CH₂Cl₂ 2t/2k photostationary state was warmed from -78 °C to room temperature. An isosbestic point was evident as 2k isomerized to 2t. Its location indicates that λ_{max} for 2k is at a shorter wavelength than for 2t.

2. Stereochemistry of Nucleophilic Attack at Benzylidene Carbon. The exclusive formation of the less stable geometric
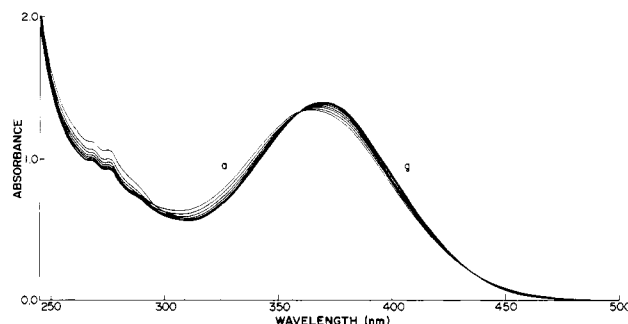
(17) All least-squares refinements computed the agreement factors R and R_w according to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w_i||F_o| - |F_c||^2/\Sigma w_i|F_o|^2]^{1/2}$, where F_o and F_c are the observed and calculated structure factors, respectively, and $w_i^{1/2} = 1/\sigma(F_o)$. The parameter minimized in all least-squares refinements was $\Sigma w_i||F_o| - |F_c||^2$.

(18) (a) Caulton, K. G. *Coord. Chem. Rev.* **1981**, *38*, 1. (b) A reviewer has raised the possibility of PPh₃ dissociation during the 2k → 2t isomerization. Free phosphines complex (with varying K_{eq}) to the benzylidene carbons of 2k and 2t, as shown with PMe₃ below. Thus isomerization rates comparable to those in Table I cannot be obtained in the presence of added PPh₃. However, when 0.5 equiv of P(p-C₆H₄CH₃)₃ is added to 2t at 25 °C, no [(η-C₅H₅)Re(NO)(P(p-C₆H₄CH₃)₃)(=CHC₆H₅)]⁺PF₆⁻ (independently synthesized analogously to 2t) forms.

Figure 3. Absorption spectra recorded as a (55 ± 3):(45 ± 3) 2t/2k mixture in CH₂Cl₂ (prepared by photolysis at -78 °C) was warmed to room temperature: initial spectrum, trace a; final spectrum, trace g.

isomer 2k upon reaction of 1 with Ph₃C⁺PF₆⁻ suggested to us that only one of the two diastereotopic α-hydrides underwent abstraction. The widely separated α-hydride ¹H NMR chemical shifts, δ 3.50 and 2.89 (CDCl₃; couplings: Table V), also hinted at the possibility of differential reactivity. Testing of this hypothesis required the synthesis of 1 with an α-deuterium label at either the *pro-R* or *pro-S* site. Obvious routes to such a substrate did not exist, so exploratory reactions of 2k and 2t with nucleophiles were conducted.

Benzylidene 2t was reacted with Li(C₂H₅)₃BD. Subsequently isolated was 1-α-d₁-t (92% yield), a compound with two chiral centers (see step a, Scheme III). The ¹H NMR spectrum of 1-α-d₁-t in CD₂Cl₂ (δ 3.41 (br d, $J_{^1H-^{31}P}$ = 8 Hz, $J_{^1H-^2H} \leq 2$ Hz)) indicated that one of the two diastereotopic hydrogens normally present in 1 was completely absent. Hence the addition of D⁻ to 2t occurred *stereospecifically* on one benzylidene face. As little as 1% of the other possible diastereomer would have been detected.

Authentic samples of the other 1-α-d₁ diastereomer, 1-α-d₁-k, were available by reaction of Li(C₂H₅)₃BD with 2k.[12] Reaction in this case was *stereoselective*; a (92 ± 1):(8 ± 1) mixture of 1-α-d₁-k/1-α-d₁-t was obtained. The ¹H NMR monitored reaction of 2k with Li(C₂H₅)₃BD was complete within 3 min at -73 °C. Since the rate constants in Table II indicate that no 2k → 2t isomerization occurs on this time scale, the lack of stereospecificity must be ascribed to a small amount of Li(C₂H₅)₃BD attack upon a second benzylidene face of 2k.
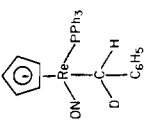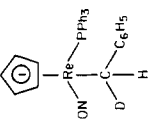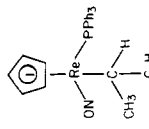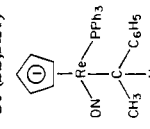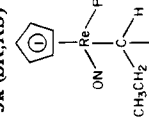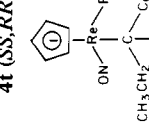
The possibility of crystallographically determining the direction of Li(C₂H₅)₃BD attack upon 2t was considered. However, a neutron diffraction structure is required to distinguish H from D, and sufficiently large crystals of 1-α-d₁-t could not be grown. Fortunately, 2t underwent similar stereospecific attack (as assayed by ¹H NMR spectroscopy of the reaction mixtures prior to any crystallizations) with nucleophiles CH₃Li, CH₃CH₂MgBr, C₆H₅CH₂MgCl, PMe₃, and CH₃ONa. Diastereomerically pure adducts (η-C₅H₅)Re(NO)(PPh₃)(CH(CH₃)C₆H₅) (3t), (η-C₅H₅)Re(NO)(PPh₃)(CH(CH₂CH₃)C₆H₅) (4t), (η-C₅H₅)Re(NO)(PPh₃)(CH(CH₂C₆H₅)C₆H₅) (5t), [(η-C₅H₅)Re(NO)(PPh₃)(CH(PMe₃)C₆H₅)]⁺PF₆⁻ (6t), and (η-C₅H₅)Re(NO)(PPh₃)(CH(OCH₃)C₆H₅) (7t) were subsequently isolated in 75–90% yields. Benzylidene isomer 2k was *stereoselectively* attacked by these nucleophiles.[12] The predominantly formed diastereomer (3k–7k) was in each case *opposite* to the one obtained from 2t. Diastereomer ratios were assayed by ¹H NMR spectroscopy in situ and/or prior to any workup crystallizations: 3k/3t, (94 ± 1):(6 ± 1); 4k/4t, (95 ± 1):(5 ± 1); 5k/5t, (94 ± 1):(6 ± 1); 6k/6t, (94 ± 1):(6 ± 1); 7k/7t, (78–85):(22–15). Complexes 3k–7k could be obtained in pure form by fractional crystallization. Spectroscopic properties of 3–7 are summarized in Table III.
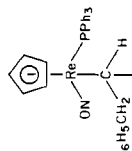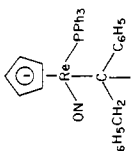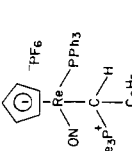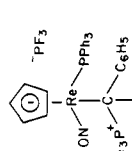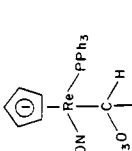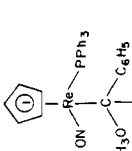
The preceding data constitute compelling evidence that Li(C₂H₅)₃BD, CH₃Li, CH₃CH₂MgBr, C₆H₅CH₂MgCl, PMe₃, and CH₃ONa each attack 2t from the same direction. The effective bulk of Li(C₂H₅)₃BD should be considerably greater than that of an isolated D⁻. Thus it seems highly unlikely that Li(C₂H₅)₃BD would stereospecifically attack one benzylidene face of 2t (see projection II, Scheme I), while R⁻, Me₃P, and CH₃O⁻ nucleophiles stereospecifically attack the other. Furthermore, the dominant

Table III. Spectroscopic Data and Configurational Assignments of Diastereomeric Rhenium Complexes Formed by Nucleophilic Attack upon Benzylidenes 2t and 2k

complex and configuration (Re,C)	IRνNO (CH$_2$Cl$_2$), cm^{-1}	^{1}H NMR ^{a,b} δ			^{13}C NMR ^{b,c} ppm		
		Re–CH	C$_5$H$_5$	other	Re–C	C$_5$H$_5$	other
1-α-d$_1$-t (SS,RR)	1624	3.48 (d, 1 H), $J_{^1\text{H}-^{31}\text{P}}$ = 8.0 Hz	4.74 (s, 5 H)	Ph (m, 20 H), 6.86–7.50			
1-α-d$_1$-k (SR,RS)	1622	2.87 (d, 1 H), $J_{^1\text{H}-^{31}\text{P}}$ = 3.0 Hz	4.74 (s, 5 H)	Ph (m, 20 H), 6.83–7.49			
3t (SS,RR)	1633	3.94 (d of quartet, 1 H), $J_{^1\text{H}\alpha-^1\text{H}\beta}$ = 7.3 Hz; $J_{^1\text{H}\alpha-^{31}\text{P}}$ = 4.4 Hz	4.61 (s, 5 H)	CH$_3$ (d, 3 H), 1.49, $J_{^1\text{H}\beta-^1\text{H}\alpha}$ = 7.3 Hz; Ph (m, 20 H), 6.90–7.40	6.34, d, $J_{^{13}\text{C}-^{31}\text{P}}$ = 3.7 Hz	91.50	CH$_3$, 28.46; Ph 121.71, 125.54, 127.36, 128.38, d, $J_{^{13}\text{C}-^{31}\text{P}}$ = 9.8 Hz, 129.98, 133.57, d, J = 9.8 Hz, 136.58, d, J = 51.3 Hz^d
3k (SR,RS)	1638	3.96 (pseudoquintet, 1 H), $J_{^1\text{H}\alpha-^1\text{H}\beta}$ = 6.8 Hz, $J_{^1\text{H}\alpha-^{31}\text{P}}$ = 6.5 Hz	4.73 (s, 5 H)	CH$_3$ (d, 3 H), 1.91, $J_{^1\text{H}\beta-^1\text{H}\alpha}$ = 6.8 Hz; Ph (m, 20 H), 6.70–7.40	7.68, d, $J_{^{13}\text{C}-^{31}\text{P}}$ = 3.7 Hz	91.46	CH$_3$, 32.48; Ph 122.02, 126.00, 127.36, 128.26, d, $J_{^{13}\text{C}-^{31}\text{P}}$ = 9.8 Hz, 129.95, 133.70, d, J = 11.0 Hz, 136.53, d, J = 51.3 Hz^d
4t (SS,RR)	1634	3.79 (m, 1 H), $J_{^1\text{H}\alpha-^{31}\text{P}}$ = 5.1 Hz, $J_{^1\text{H}\alpha-^1\text{H}\beta}$ = 4.9 Hz, $J_{^1\text{H}\alpha-^1\text{H}\beta'}$ = 10.5 Hz	4.68 (s, 5 H)	CH$_3$ (dd, 3 H) 0.37, $J_{^1\text{H}\gamma-^1\text{H}\beta}$ = $J_{^1\text{H}\gamma-^1\text{H}\beta'}$ = 7.0 Hz; CHβHβ' (m, 2 H), 1.72; Ph (m, 20 H), 6.40–7.40	16.90^e	90.68	CH$_3$, 16.90; CH$_2$, 35.40; Ph 121.59, 126.13, 127.32, 128.26, d, $J_{^{13}\text{C}-^{31}\text{P}}$ = 9.9 Hz, 129.91, 133.64, d, J = 10.4 Hz, 136.21, d, J = 51.2 Hz, 159.44
4k (SR,RS)	1632	3.49 (pseudoquintet, 1 H), $J_{^1\text{H}\alpha-^{31}\text{P}}$ = 5.0 Hz, $J_{^1\text{H}\alpha-^1\text{H}\beta}$ = 5.0 Hz, $J_{^1\text{H}\alpha-^1\text{H}\beta'}$ = 10.0 Hz	4.73 (s, 5 H)	CH$_3$ (dd, 3 H), 0.51, $J_{^1\text{H}\gamma-^1\text{H}\beta}$ = $J_{^1\text{H}\gamma-^1\text{H}\beta'}$ = 7.1 Hz; CHβHβ' (m, 2 H), 2.10, $J_{^1\text{H}\beta-^1\text{H}\beta'}$ = 13.3 Hz; Ph (m, 20 H), 6.60–7.36	17.79, d,	91.36	CH$_3$, 17.13; CH$_2$, 39.52; Ph 122.03, 127.28, 128.17, d, $J_{^{13}\text{C}-^{31}\text{P}}$ = 10.9 Hz, 129.92, 133.68, 133.78, d, J = 10.3 Hz, 136.34, d, J = 50.0 Hz, 159.15

Compound	IR	^{1}H (CHα)	Cp	other ^{1}H	^{13}C (carbene)	Cp	other ^{13}C
5t (SS,RR)	1640	4.47 (ddd, 1 H), $J_{^1H_\alpha-^{31}P}$ = 4.5 Hz, $J_{^1H_\alpha-^1H_\beta}$ = 13.2 Hz, $J_{^1H_\alpha-^1H_{\beta'}}$ = 3.7 Hz	4.78 (s, 5 H)	H$_\beta$ (dd, 1 H), 2.88, $J_{^1H_\beta-^1H_{\beta'}}$ = 13.7 Hz, $J_{^1H_\beta-^1H_\alpha}$ = 13.2 Hz; H$_{\beta'}$ (dd, 1 H), 3.21, $J_{^1H_{\beta'}-^1H_\beta}$ = 13.7 Hz, $J_{^1H_{\beta'}-^1H_\alpha}$ = 3.7 Hz; Ph (m's, 25 H), 6.43–7.52, CH$_2$Cl$_2$ solvate, 5.28	14.91, d, $J_{^{13}C-^{31}P}$ = 4.0 Hz	90.88	CH$_2$, 48.40; Ph 121.64, 124.55, 126.27, 127.05, 127.38, 128.21, 128.48, d, $J_{^{13}C-^{31}P}$ = 10.8 Hz, 129.99, 133.64, d, J = 9.5 Hz, 136.10, d, J = 50.2 Hz, 145.19, 158.48, CH$_2$Cl$_2$ solvate 53.39
5k (SR,RS)	1636	3.82 (ddd, 1 H), $J_{^1H_\alpha-^{31}P}$ = 4.6 Hz, $J_{^1H_\alpha-^1H_\beta}$ = 4.7 Hz, $J_{^1H_\alpha-^1H_{\beta'}}$ = 11.5 Hz	4.72 (s, 5 H)	H$_\beta$H$_{\beta'}$ (m, 2 H); H$_\beta$, 3.35,^{f} H$_{\beta'}$, 3.46, $J_{^1H_\beta-^1H_{\beta'}}$ = 13.5 Hz; Ph (m's, 25 H), 6.39–7.42	16.62, d, $J_{^{13}C-^{31}P}$ = 4.3 Hz	91.55	CH$_2$, 52.26, d, $J_{^{13}C-^{31}P}$ = 2.6 Hz; Ph 122.12, 124.29, 127.11, 127.21, 127.59, 128.29, d, $J_{^{13}C-^{31}P}$ = 8.9 Hz, 130.03, 133.80, d, J = 10.9 Hz, 136.09, d, J = 50.9 Hz, 146.26, 158.26
6t (SR,RS)	1639	4.47 (dd, 1 H),^{g} $J_{^1H-^{31}PMe_3}$ = 23.4 Hz, $J_{^1H-^{31}PPh_3}$ = 1.4 Hz	5.23 (s, 5 H)^g	PMe$_3$, (d, 9 H), 1.66,^{g} $J_{^1H-^{31}P}$ = 12.6 Hz; Ph (m's, 20 H), 6.87–7.46	−11.29, d,^{g} $J_{^{13}C-^{31}P}$ = 31.8 Hz	93.73^g	PMe$_3$, 13.26, d,^{g} $J_{^{13}C-^{31}P}$ = 56.2 Hz; Ph 125.94, 129.58, d, $J_{^{13}C-^{31}P}$ = 9.8 Hz, 129.82, 131.57, 134.50, d, J = 12.2 Hz, 137.25, d, J = 53.7 Hz, 149.57
6k (SS,RR)	1654	4.03 (dd, 1 H),^{g} $J_{^1H-^{31}PMe_3}$ = 17.4 Hz, $J_{^1H-^{31}PPh_3}$ = 4.6 Hz	5.30 (s, 5 H)^g	PMe$_3$, (d, 9 H), 1.61,^{g} $J_{^1H-^{31}P}$ = 12.4 Hz; phenyl (m's, 20 H), 6.85–7.50	1.90, d,^{h} $J_{^{13}C-^{31}P}$ = 30.8 Hz	92.38^g	PMe$_3$, 12.04, d,^{g} $J_{^{13}C-^{31}P}$ = 55.6 Hz; Ph 126.81, d, $J_{^{13}C-^{31}P}$ = 4.1 Hz, 129.74, 129.84, d, J = 10.9 Hz, 130.86, d, J = 6.8 Hz, 131.81, 134.52, d, J = 9.5 Hz, 134.71, d, J = 52.9 Hz, 144.90, d, J = 4.1 Hz
7t (SR,RS)	1630	5.97, d, 1 H, $J_{^1H-^{31}P}$ = 5.4 Hz	4.66 (s, 5 H)	OCH$_3$, (s, 3 H), 2.55; Ph (m, 20 H), 6.90–7.58	65.60, d, $J_{^{13}C-^{31}P}$ = 7.2 Hz	91.33	CH$_3$O, 59.62; Ph 122.50, 123.29, 127.44, 128.20, d, $J_{^{13}C-^{31}P}$ = 10.8 Hz, 129.84, 133.94, d, J = 10.9 Hz, 136.84, d, J = 51.6 Hz, 157.63
7k (SS,RR)	1639	5.75, d, 1 H, $J_{^1H-^{31}P}$ = 2.4 Hz	4.89 (s, 5 H)	OCH$_3$, (s, 3 H), 2.67; phenyl (m, 20 H), 6.82–7.88	68.38, d, $J_{^{13}C-^{31}P}$ = 5.4 Hz	91.19	CH$_3$O, 58.77; Ph 123.64, 124.96, 127.39, 128.02, d, $J_{^{13}C-^{31}P}$ = 10.2 Hz, 129.72, 133.64, d, J = 10.9 Hz, 136.32, d, J = 51.6 Hz, 155.28

^{a} 200 MHz. ^{b} In CDCl$_3$ and referenced to internal (CH$_3$)$_4$Si unless otherwise noted. ^{c} 50 MHz. ^{d} ipso C–C$_6$H$_5$ carbon (ca. 159 ppm) outside of spectrum width employed. ^{e} Obscured by CH$_3$ (16.9 ppm); spectrum in 50:50 CDCl$_3$/C$_6$D$_6$ shows one resonance of doublet. ^{f} Chemical shifts assigned by computer simulation of multiplet. ^{g} Spectrum recorded in CD$_3$CN. ^{h} Resonance obscured by CD$_3$CN; value obtained in acetone-d_6.
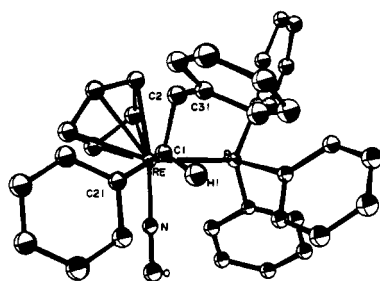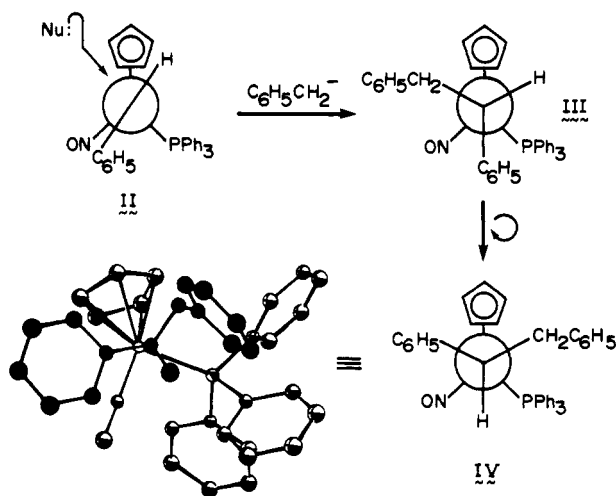
Figure 4. Stereoview of the molecular structure of (SS,RR)-$(\eta$-$C_5H_5)Re(NO)(PPh_3)(CH(CH_2C_6H_5)C_6H_5)\cdot CH_2Cl_2$ ($5t\cdot CH_2Cl_2$).

Scheme II. Assignment of the Direction of Nucleophilic Attack upon **2t**

Table IV. Selected Bond Lengths and Bond Angles in $5t\cdot CH_2Cl_2$

atoms	dist, Å	atoms	angle, deg
Re–C1	2.215 (4)	Re–C1–C2	115.7 (2)
Re–P1	2.337 (1)	Re–C1–C21	107.8 (3)
Re–N1	1.747 (3)	C1–C2–C31	114.0 (3)
Re–C$_5$H$_5$[a]	2.301	C2–C1–C21	114.7 (3)
N1–O1	1.216 (4)	N1–Re–C1	90.6 (1)
C1–C2	1.539 (5)	P1–Re–N1	90.0 (1)
C1–C21	1.502 (5)	P1–Re–C1	93.6 (1)
C2–C31	1.512 (5)	O1–N1–Re	178.3 (3)

[a] Average distance from Re to C$_5$H$_5$ carbons.

production of opposite diastereomers from **2k** requires that these nucleophiles approach I and II from the same "direction".[19] Thus an X-ray structure determination of any of **3t–7t** or **3k–7k** allows configurations to be assigned to all diastereomers.

Suitable crystals of **3t** could not be grown, but single crystals of **5t** (as a CH$_2$Cl$_2$ monosolvate) were obtained by layering a CH$_2$Cl$_2$ solution with hexane. Since these crystals lost CH$_2$Cl$_2$ upon standing at room temperature, the one selected for X-ray analysis (0.20 × 0.25 × 0.40 mm) was isolated and mounted immediately prior to data collection (–158 °C, Mo Kα irradiation as described above). The unit cell was found to be monoclinic, space group $P2_1/c$ ($Z = 4$), with lattice parameters $a = 12.027$ (4) Å, $b = 16.083$ (6) Å, $c = 18.446$ (6) Å, $\beta = 110.57$ (2)°. Of 6441 reflections with $2\theta < 50°$ collected, 5309 with $I \geq 3\sigma(I)$ were used in the final refinement. Positions of all atoms, including the solvate CH$_2$Cl$_2$, were located as outlined for **2t·CHCl$_3$** above. The rhenium, chlorine, and phosphorus atoms were refined with anisotropic temperature factors, and all other non-hydrogen atoms were refined with isotropic thermal parameters. Hydrogen atoms were held at positions indicated from the difference Fourier map with assigned thermal parameters. The final R index was 0.025 with $R_w = 0.038$.[17]

The molecular structure of **5t·CH$_2$Cl$_2$** thus obtained is shown in Figure 4. The enantiomer of the structure in Figure 4 is of course present in the unit cell as well. Absolute configurations at the chiral centers in **5t** are therefore (Re, C) S,S (Figure 4) and R,R.

The configuration of **5t** indicates that it is formed by C$_6$H$_5$-CH$_2$MgCl attack upon the *si*-benzylidene face, antiperiplanar to the PPh$_3$, as shown in Scheme II. The initially generated conformer, III, is however not the one found in the crystal. Rather, a 120° Re–C rotation occurs which orients the –CH$_2$C$_6$H$_5$ substituent between the C$_5$H$_5$ and PPh$_3$ ligands (IV, Scheme II). By
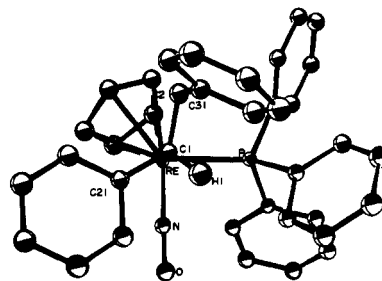
assumption of an identical direction[19] of attack for the other nucleophiles (vide supra), configurations are assigned to the chiral centers in **1-α-d_1-t**, **1-α-d_1-k**, **3t–7t**, and **3k–7k** as summarized in Table III.

An exhaustive list of bond distances and angles in **5t·CH$_2$Cl$_2$** and a crystal packing diagram are provided in the supplementary material. Important bond distances and angles are summarized in Table IV. The Re–C1–C21 plane was found to make a 92.7 ± 0.5° angle with the least-squares plane of the Re–CHRC$_6$H$_5$ phenyl ring.

3. Stereochemistry of Hydride Abstraction from $(\eta$-C$_5$H$_5)$-Re(NO)(PPh$_3$)(CH$_2$C$_6$H$_5$). With the absolute configurations of the enantiomers comprising **1-α-d_1-t** established, the stereochemistry of the reaction of **1-α-d_1-t** with Ph$_3$C$^+$PF$_6^-$ could be definitively probed. Proton NMR monitoring at –70 °C (Scheme III, step b) indicated the *exclusive* formation of H$^-$ abstraction product **2k-α-d_1** and then, upon warming (step b'), **2t-α-d_1**. Byproduct Ph$_3$CH was isolated. Its mass spectrum indicated Ph$_3$CD to be present at natural abundance level.
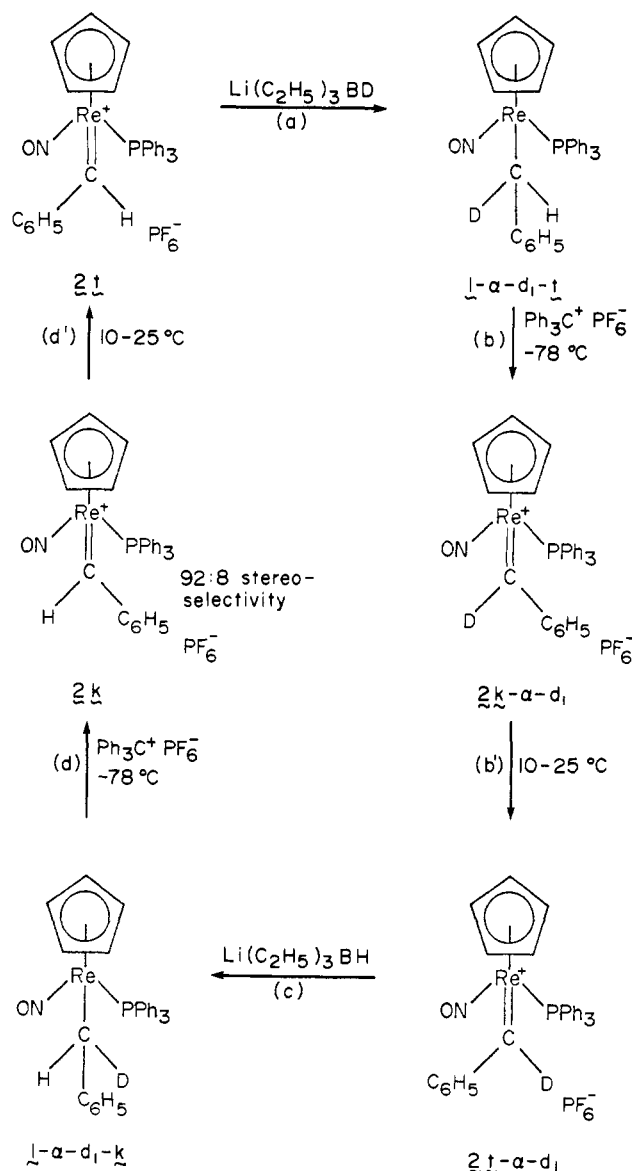
To ensure that the unusual stereospecificity of step b was not due to an extraordinary kinetic isotope effect, a closed stereochemical cycle was constructed. Thus, isolated **2t-α-d_1** was treated with Li(C$_2$H$_5$)$_3$BH (Scheme III, step c); **1-α-d_1-k** formed stereospecifically. As little as 1% of **1-α-d_1-t** would have been detected. These results evidence a remarkable degree of metal-mediated stereocontrol over the first three steps (a, b, b', c) of the cycle.

The **1-α-d_1-k** from step c (Scheme III) was treated with Ph$_3$C$^+$PF$_6^-$ (step d). Proton NMR monitoring indicated the formation of **2k** (D$^-$ abstraction product) and then, upon warming (step d'), **2t**. However, some Ph$_3$CH was evident by ^{1}H NMR. Careful integration of Re=CHC$_6$H$_5$ and C$_5$H$_5$ resonances (both in situ and after isolation) indicated the product from step d' to be a (92 ± 2):(8 ± 2) **2t-α-d_0/2t-α-d_1** mixture. The triphenylmethane by product was isolated; mass spectral analysis indicated a (89 ± 1):(11 ± 1) Ph$_3$CD/Ph$_3$CH mixture.[20] Thus, on the order of 8–10% H$^-$ abstraction occurs in step d.

The unusual features of Scheme III are more evident when viewed in Newman projection form (Scheme IV). In advance of any experiment, it would not have been surprising if D$^-$ abstraction from **1-α-d_1-t** (V) had occurred (i.e., a "quasi-microscopic reverse" of D$^-$ attack). Instead, H$^-$ loss occurs, corresponding to

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(19) We define "direction" or "side" with reference to the rhenium ligands in I and II. Nucleophilic attack upon the benzylidene carbon from a direction anti to the PPh$_3$ would constitute *re* face attack in I but *si* face attack in II.

(20) The Ph$_3$CD/Ph$_3$CH ratio may underestimate stereoselectivity in reactions involving predominant deuterium abstraction. For instance, we find the triphenylmethane generated by reaction of Ph$_3$C$^+$PF$_6^-$ with $(\eta$-C$_5$H$_5)$-Re(NO)(PPh$_3$)(CD$_3$) to be a (96 ± 1):(4 ± 1) Ph$_3$CD/Ph$_3$CH mixture. We attribute part of the Ph$_3$CH to side reactions involving nondeuterated ligands and/or adventitious H$^-$ sources.
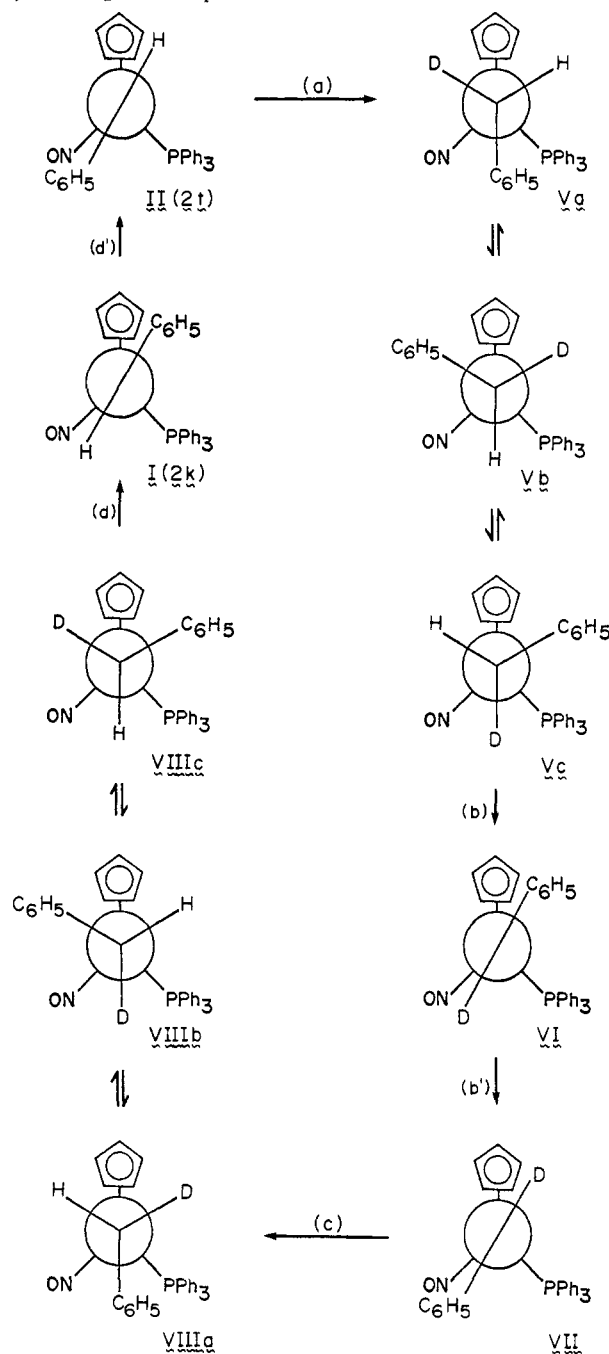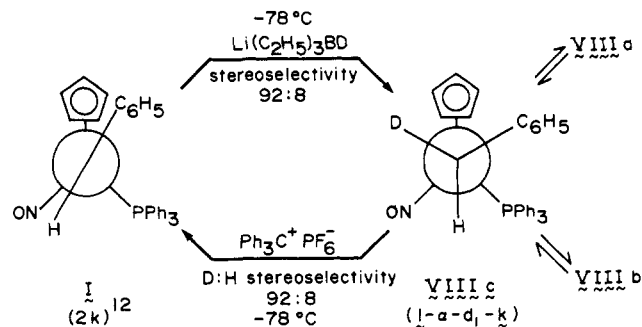
Benzylidine [(η-C₅H₅)Re(NO)(PPh₃){═CHC₆H₅}]⁺PF₆⁻

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Scheme III. An Organometallic Walden-Type Cycle ("Long" Cycle)

Scheme IV. Newman Projections of Species Involved in Scheme III, Including All 1-α-d₁ Rotamers

abstraction of the *pro-R* α-hydride from (η-C₅H₅)Re(NO)-(PPh₃)(CH₂C₆H₅) (1). Possible rationales for this reactivity will be presented in the Discussion.

A "short" cycle, interconverting **2k** and **1-α-d₁-k** as shown in Scheme V, is implicit in the reactions described above. The simplicity of Scheme V vis-à-vis the complexity of Scheme IV can be explained as follows, without reference to mechanism. When the cycle is started with **2k** (Scheme V), D⁻ is delivered into what would be the *pro-R* position of **1**. Hence D⁻ is abstracted in the subsequent step with Ph₃C⁺PF₆⁻. However, when the cycle is started with **2t** (Scheme IV), D⁻ is delivered into what would be the *pro-S* position of **1**. Hence H⁻ is abstracted in the subsequent step with Ph₃C⁺PF₆⁻.

4. Additional Experiments Related to Reaction Stereocontrol. Further experiments were conducted to provide insight into Schemes I–V. First, the α-proton J_{31P-1H} in the ¹H NMR spectrum of **1** in CDCl₃ were examined as a function of temperature. The data shown in Table V were obtained. Couplings measured in CD₂Cl₂ were similar. As will be described in the Discussion, $J_{31P-1H_α}$ values have been previously correlated to conformer populations (e.g., Va–c) in (η-C₅H₅)Fe(CO)(PX₃)(CH₂R) systems.[21]

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(21) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 4292.

Scheme V. A "Short" Cycle

Second, the dissymmetry of the Hückel orbitals with respect to the Re═CHR plane (which could provide an *electronic* basis for the nonequivalent reactivities of the two diastereotopic al-

Table V. Variation of ^{31}P–^{1}H and ^{1}H–^{1}H NMR Coupling Constants (Hz)^{b} in $(\eta$-C$_5$H$_5$)Re(NO)(PPh$_3$)(CH$_2$C$_6$H$_5$) with Temperature^{a}

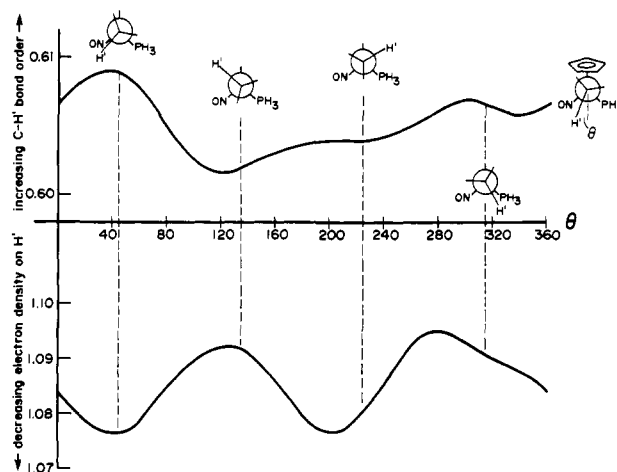| temp, K	$J_{^{31}P-^{1}H_\alpha}$	$J_{^{31}P-^{1}H_\alpha'}$	$J_{^{1}H_\alpha-^{1}H_\alpha'}$
320	7.64	3.16	11.70
310	7.74	3.10	11.70
300	7.86	3.04	11.72
290	7.88	2.92	11.72
280	7.81	2.83	11.73
270	7.92	2.75	11.72
260	7.90	2.60	11.75
250	7.82	2.32	11.70
240	7.78	2.26	11.72

^{a} In CDCl$_3$; data are the average of two runs. ^{b} Spectra were recorded at 0.061 Hz/data point. Low-temperature coupling constants are less accurate than the others due to peak broadening.
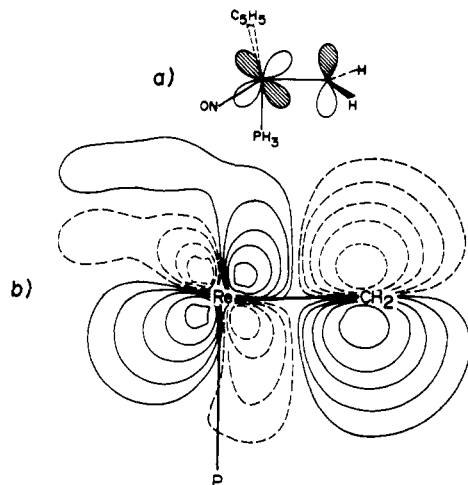
Figure 5. LUMO of $[(\eta$-C$_5$H$_5$)Re(NO)(PH$_3$)(=CH$_2$)]$^{+}$: (a) schematic; (b) contour diagram (for $\Psi = \pm0.20, \pm0.15, \pm0.10, \pm0.05, \pm0.01$) in P–Re–C plane.

kylidene faces) was examined. In the model compound $[(\eta$-C$_5$H$_5$)Re(NO)(PH$_3$)(=CH$_2$)]$^{+}$, the LUMO was found to be the d–p π antibonding combination. This orbital should command the major interaction with the incoming nucleophile, but as shown in Figure 5, it is *symmetrical* with respect to the Re=CH$_2$ plane. A model nucleophile, H^{-}, was placed 2 Å from the methylidene in $[(\eta$-C$_5$H$_5$)Re(NO)(PH$_3$)(=CH$_2$)]$^{+}$. The total energy indicated a slight preference for an approach antiperiplanar (over synperiplanar) to the PH$_3$.

Third, properties of the model alkyl $(\eta$-C$_5$H$_5$)Re(NO)-(PH$_3$)(CH$_3$) were also probed via extended Hückel MO calculations. The barrier to rotation about the Re–CH$_3$ bond was found to be $\sim$3 kcal/mol, with a staggered conformation (hydrogen antiperiplanar to C$_5$H$_5$) as energy minimum. As the Re–CH$_3$ bond was rotated, no particular weakening (bond-order decrease) of any C–H bond was noted. One C–H bond of the Re–CH$_3$ group (C–H') was elongated from 1.09 to 1.40 Å in order to more closely resemble a hydride abstraction transition state. Now as the Re–CH$_2$H' bond was rotated, a significant weakening of the C–H' bond (and increase of electron density on H') occurred when it was antiperiplanar to the PH$_3$ ligand (see Figure 6).

Finally, reactions of **7t** and **7k** with Ph$_3$C^{+}PF$_6^{-}$ were also investigated.^{8} When **7t** was treated with Ph$_3$C^{+}PF$_6^{-}$ at −78 °C in a ^{1}H NMR monitored reaction, **2t** was observed to form exclusively. Thus CH$_3$O^{-} is chemospecifically^{22} and stereospecifically abstracted. Coupled with the reaction of **2t** and NaOCH$_3$ described above, this reaction completes a second "short cycle", as shown in Scheme VI. Similarly, when a 90:10 **7k**/**7t** mixture was treated with Ph$_3$C^{+}PF$_6^{-}$ at −78 °C, a 90:10 **2k**/**2t** mixture

(22) Trost, B. M.; Salzmann, T. N. *J. Am. Chem. Soc.* **1973**, *95*, 6840. See footnote 12.

Figure 6. Calculated change in C–H' bond order and electron density on H' as the Re–C σ bond in $(\eta$-C$_5$H$_5$)Re(NO)(PH$_3$)(CH$_2$H') is rotated through 360° (C–H' = bond arbitrarily elongated to 1.4 Å).

Scheme VI. "Short" Cycles Involving CH$_3$O^{-} Addition/Abstraction
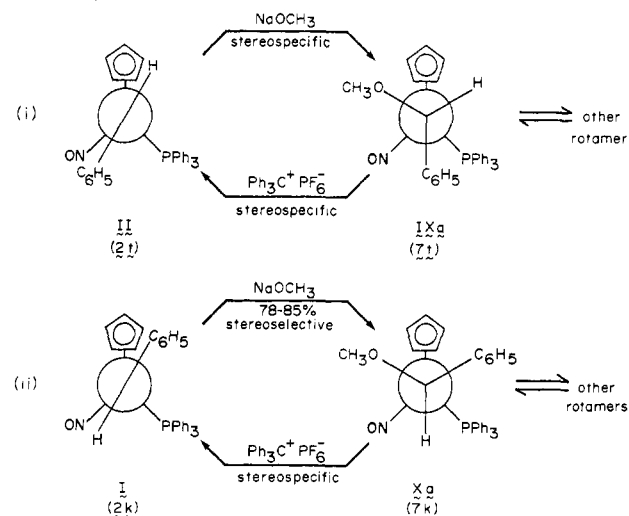
formed. Thus CH$_3$O^{-} is stereospecifically abstracted from **7k**, closing the other short cycle in Scheme VI. These data require that $^{-}$OCH$_3$ attack and $^{-}$OCH$_3$ abstraction occur from the same "side"^{19} of the complex.

Discussion

1. Benzylidene Complexes: Structure and Bonding. To our knowledge, the existence of geometric isomers due to metal–carbon multiple bonding is without precedent. Commonly used terms for distinguishing geometric isomers (cis/trans; Z/E) are clearly inadequate for **2k** and **2t**. According to IUPAC nomenclature,^{23} I (**2k**) and II (**2t**) are unambiguously designated as synclinal (sc) and anticlinal (ac), respectively.

Absolute configurations at rhenium are assigned according to the Baird–Sloan modification of the Cahn–Ingold–Prelog priority rules.^{24} The C$_5$H$_5$ ligand is considered to be a pseudoatom of atomic number 30. Hence all figures in this paper have have an S-rhenium configuration.

As has been observed with other metals and unsaturated ligands,^{14} extended Hückel calculations accurately predict rhenium alkylidene bonding geometries. The optimal alkylidene position

(23) *Pure Appl. Chem.* **1976**, *45*, 11. See section E-5.6, p 24. A synclinal conformer of **2** is one in which the highest priority^{24} groups on Re(C$_5$H$_5$) and C(C$_6$H$_5$) define a 60 ± 30° torsion angle. An anticlinal conformer is one in which the highest priority groups define a 120 ± 30° torsion angle.

(24) (a) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598. (b) Sloan, T. *Top. Stereochem.* **1981**, *12*, 1.

Benzylidine [(η-C₅H₅)Re(NO)(PPh₃){=CHC₆H₅}]⁺PF₆⁻

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is obtained when the empty p orbital of the carbene fragment (counted as neutral) maximally overlaps the highest occupied d orbital of the metal fragment. In a d⁶ metal fragment such as $(\eta\text{-}C_5H_5)Mn(CO)_2$, which has a plane of symmetry, the highest occupied d orbital would be in a *horizontal* plane in the Newman projections perspectives utilized in this paper.[14] Accordingly, the X-ray crystal structure of $(\eta\text{-}C_5H_5)Mn(CO)_2(=C(CH_3)_2)$ (Mn=C distance = 1.868 Å) shows that the alkylidene plane *bisects* the C_5H_5 ring.[25] In $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)^+$ (and related isoelectronic metal fragments), no symmetry is maintained and the highest occupied d orbital rotates into a plane containing the Re–P bond (compare to Figure 5),[14] resulting in alkylidene geometries I and II.

The crystal structures of three benzylidene complexes, $(\eta\text{-}C_5H_5)_2Ta(CH_2C_6H_5)(=CHC_6H_5)$,[26] $(\eta\text{-}C_5Me_5)Ta(CH_2C_6H_5)_2(=CHC_6H_5)$,[27] and $(\eta\text{-}C_5H_5)_2W=CHC_6H_5$,[28] have been previously reported. Since these all contain third-row metals, their bonding features may be closely compared to **2t**. For the first and third complexes, $M=C_\alpha\text{–}C_{ipso}$ bond angles are reasonably close to those expected for sp² carbons (135, 133°), and $M=C_\alpha$ bond lengths are 2.07 and 2.05 Å, respectively. However, $(\eta\text{-}C_5Me_5)Ta(CH_2C_6H_5)_2(=CHC_6H_5)$ is a 14-electron complex, so the benzylidene ligand adopts a "T" shaped[29] geometry ($\angle Ta=C_\alpha\text{–}C_{ipso} = 160°$, with a proposed $\angle Ta=C_\alpha\text{–}H$ of ca. 90°) to help relieve the electron deficiency. A short $Ta=C_\alpha$ distance of 1.88 Å was also noted. Benzylidene **2t** is an 18-electron complex, and accordingly its $\angle Re=C_\alpha\text{–}C_{ipso}$ of 136° more closely resembles the former class of complexes. The $^+Re=C_\alpha$ distance in **2t**, 1.949 (6) Å, is intermediate between the two types of complexes. The bond contraction vis-à-vis $(\eta\text{-}C_5H_5)_2W=CHC_6H_5$ may be due to the positive charge on rhenium.

Together with the X-ray structure of the formyl $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$ (**8**),[30] this study marks the first time that accurate metal–carbon bond lengths have been determined for a homologous series of alkyl, formyl, and alkylidene complexes.[31] As shown below, the $Re–C_\alpha$ distances decrease as the π-acceptor capabilities of the ligands increase. The $Re–C_\alpha$ distance in formyl **8** is closer to that of benzylidene **2t** than it is to alkyl **5t**. This supports our previous conclusion[15b,30] that a dipolar alkylidene-like resonance form $^+Re=C(H)O^-$ makes a substantial contribution to the ground state of **8**.
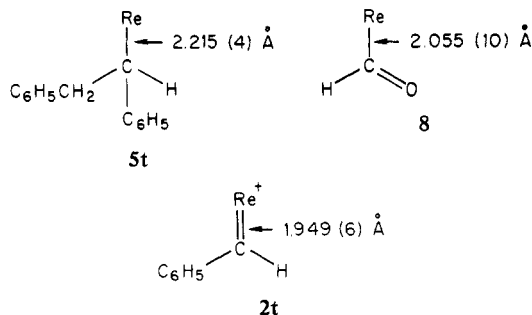
The activation parameters for **2k** → **2t** isomerization contain a component arising from steric interactions. In view of recent data on homologous vinylidene complexes $[(\eta\text{-}C_5H_5)Re(NO)\text{-}$
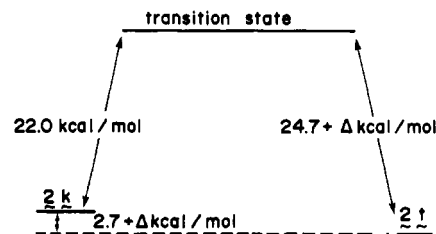
Figure 7. ΔG and $\Delta G^\ddagger$ for the interconversion of **2k** and **2t** at 25 °C.

$(PPh_3)(=C=CRR')]^+$, where steric effects should be attenuated,[32] we estimate the d–p π bond strength in **2** to be on the order of 15 ± 2 kcal/mol. A Re=CH₂ rotational barrier (which also should involve minimal steric interactions) has not yet been obtained for $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$, but the fact that no coalescence of the =CH₂ ¹H NMR resonances occurs at 27 °C bounds $\Delta G^\ddagger_{27}$ as >15 kcal/mol.[15b]

Rotational barriers of other electrophilic alkylidene complexes have proven to be much lower.[33] For instance, $\Delta G^\ddagger$ for =CH₂ rotation in $[(\eta\text{-}C_5H_5)Fe(PPh_2CH_2CH_2PPh_2)(=CH_2)]^+CF_3SO_3^-$ is only (despite strong donor ligands and the absence of good π-acceptor ligands on iron) 10.4 ± 0.1 kcal/mol over the temperature range of –65 to –14 °C.[33a] This probably reflects intrinsic differences in first-row vs. third-row metal–ligand π-bond strengths. Rotational barriers of two unstable W=CH₂ complexes, $[(\eta\text{-}C_5H_5)W(CO)_2(PPh_3)(=CH_2)]^+AsF_6^-$ and $[(\eta\text{-}C_5H_5)W(CO)_2(PEt_3)(=CH_2)]^+AsF_6^-$, have been determined to be 8.3 ± 0.1 and 9.0 ± 0.1 kcal/mol, respectively.[33b] These low values may result from the presence of two good π-accepting CO ligands on each tungsten. Schrock has measured the Ta=CH–C₆H₅ rotational barrier (which interconverts enantiomers) of the *nucleophilic* benzylidene complex $(\eta\text{-}C_5H_5)_2Ta(CH_2C_6H_5)(=CHC_6H_5)$.[26] A $\Delta G^\ddagger$ of 19.2 ± 0.2 kcal/mol, comparable to that observed for other tantalum alkylidene complexes,[26] was determined.

Alkylidene complexes of the formula $[(\eta\text{-}C_5H_5)Fe(CO)(PPh_3)(=CHR)]^+$, which are expected[14] to be isostructural with **2** and its aliphatic homologues, have been extensively studied by Brookhart.[11,34] The fact that these have not been observed to exist in two geometric isomeric forms (despite in some cases having been generated from diastereomeric $(\eta\text{-}C_5H_5)Fe(CO)(PPh_3)(CH(OCH_3)R)$ complexes at –78 °C) is understandable in view of the above rotational barrier data.

Although ¹H NMR indicates that ≤1% of **2k** is in equilibrium with **2t** at 25 °C, we do not believe that K_{eq} is significantly greater than 99.[35] For instance, aliphatic homologues of **2**, such as propylidene $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH_2CH_3)]^+PF_6^-$, exist as (91 ± 2):(9 ± 2) equilibrium mixtures of anticlinal and synclinal isomers. If the **2t**/**2k** K_{eq} is assumed to be slightly greater than 99, then $\Delta G_{25} = -2.7 - \Delta$ kcal/mol, where Δ is a small increment. From $\Delta H^\ddagger$ (20.9 ± 0.4 kcal/mol) and $\Delta S^\ddagger$ (–3.8 ± 0.2 eu), a $\Delta G^\ddagger_{25}$ of 22.0 kcal/mol can be calculated. This enables the construction of the energy diagram shown in Figure 7.

The 365-nm absorption in the UV–visible spectrum of **2t** (Figure 3) is possibly a n → π* transition involving a LUMO of the type in Figure 5.[14] It is absent in aliphatic homologues such as the cream-colored propylidene $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH_2CH_3)]^+PF_6^-$.[9] These undergo analogous photoisomerization but exhibit only an extended tail into the visible region. The mechanism of the photoisomerization **2t** → **2k** is presently under study.[9] In view of the wealth of metal alkylidene ground-state chemistry, many intriguing possibilities exist for metal

(25) Friedrich, P.; Besl, G.; Fischer, E. O.; Huttner, G. *J. Organomet. Chem.* **1977**, *139*, C68.

(26) Schrock, R. R.; Messerle, L. W.; Wood, C. D.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 3793.

(27) Messerle, L. W.; Jennische, P.; Schrock, R. R.; Stucky, G. *J. Am. Chem. Soc.* **1980**, *102*, 6744.

(28) Marsella, J. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 5596.

(29) Goddard, R. J.; Hoffmann, R.; Jemmis, E. D. *J. Am. Chem. Soc.* **1980**, *102*, 7667.

(30) Wong, W.-K.; Tam, W.; Strouse, C. E.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1979**, 530.

(31) (a) An X-ray crystal structure of optically pure (–)-*R*-(η-C₅H₅)Re-(NO)(PPh₃)(CH₂C₆H₅) has also been completed and will be described in a separate publication.[31b] The Re–C$_\alpha$ bond distance was found to be 2.203 (8) Å. (b) Merrifield, J. H.; Strouse, C. E.; Gladysz, J. A. *Organometallics*, in press.

(32) Wong, A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4948.

(33) (a) Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. *J. Am. Chem. Soc.* **1980**, *102*, 1203. (b) Kegley, S. E.; Brookhart, M.; Husk, G. R. *Organometallics* **1982**, *1*, 760.

(34) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1981**, *103*, 979.

(35) When crystals of optically pure **2t** are dissolved, a slight mutarotation occurs. This sensitive criterion suggests the presence of small equilibrium concentrations of **2k**.[31b]

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alkylidene *excited-state* chemistry.

2. Benzylidenes 2t and 2k: Stereochemistry of Nucleophilic Attack. While the LUMO of the model system [(η-C$_5$H$_5$)Re-(NO)(PH$_3$)(=CH$_2$)]$^+$ reveals no distortion with respect to the Re=C plane (Figure 5), such dissymmetries are usually minute. Dissymmetries in the π system of organic alkenes and carbonyl compounds (measured by the mixing of s and p coefficients) are usually on the order of magnitude of 10^{-3} (ratio of s to p) but nonetheless predict the stereochemical course of addition reactions.[36] While our findings do not exclude electronic effects from contributing to the stereospecific attack of nucleophiles upon 2t (for instance, the participation of low-lying antiperiplanar σ^* orbitals in nucleophilic attack upon organic π systems is well documented,[37] and we did calculate an energetic preference for H$^-$ approach antiperiplanar to the Re–PH$_3$ bond), more elaborate calculations are required to probe this point.

In view of the above, we ascribe the stereospecificity of nucleophilic attack upon 2t primarily to steric effects. As can easily be seen in Figure 2, the *re* face of the benzylidene ligand is shielded by the bulky PPh$_3$ ligand. Thus nucleophilic attack occurs on the *si* face, as indicated by the molecular structure of 5t (Figure 2 and Scheme II). The ca. 90° angle of the Re–C1–C21 plane in 5t with the adjacent phenyl ring suggests a hyperconjugative interaction. This may be a factor in the crystallization of 5t in rotamer IV.

It is not uncommon for the less stable of two isomers to exhibit slightly lower reaction stereoselectivity. Hence the 92–95% stereoselectivity generally observed in nucleophilic attack upon 2k is understandable. As noted previously, nucleophilic attack upon 2t and 2k occurs preferentially from the same direction.[19]

There are at least two important general factors that can influence the stereochemistry of alkylidene attack: (a) the alkyl group in Re=CHR; (b) the size of the phosphine. Experimental details of these studies will be reported separately, but two key results will be summarized here.[38]

First, the ethylidene complex[7] [(η-C$_5$H$_5$)Re(NO)(PPh$_3$)(=CHCH$_3$)]$^+$PF$_6^-$ exists as a (90 ± 2):(10 ± 2) equilibrium mixture of anticlinal[23] (e.g., II) and synclinal (e.g., I) geometric isomers. Upon reaction with Li(C$_2$H$_5$)$_3$BD, a (89 ± 2):(11 ± 2) mixture of diastereomers of (η-C$_5$H$_5$)Re(NO)(PPh$_3$)(CHDCH$_3$) is produced. We therefore conclude that the size of the Re=CHR alkyl group does not significantly influence the direction of nucleophilic attack.

Second, the PMe$_3$ complex (η-C$_5$H$_5$)Re(NO)(PMe$_3$)-(CH$_2$C$_6$H$_5$) has been prepared. When (η-C$_5$H$_5$)Re(NO)-(PMe$_3$)(CH$_2$C$_6$H$_5$) is treated with Ph$_3$C$^+$PF$_6^-$ in CD$_2$Cl$_2$ at –78 °C, a single geometric isomer of [(η-C$_5$H$_5$)Re(NO)(PMe$_3$)(=CHC$_6$H$_5$)]$^+$PF$_6^-$ forms. No isomerization is observed upon warming to room temperature or heating to 60 °C in CDCl$_3$. Subsequent reaction of [(η-C$_5$H$_5$)Re(NO)(PMe$_3$)(=CHC$_6$H$_5$)]$^+$PF$_6^-$ with Li(C$_2$H$_5$)$_3$BD at –78 °C yields (η-C$_5$H$_5$)Re(NO)(PMe$_3$)(CHDC$_6$H$_5$) as a (77 ± 1):(23 ± 1) mixture of diastereomers. Thus a bulky phosphine is necessary for high stereoselectivity.

3. Stereochemistry of the Reactions of Rhenium Alkyls with Ph$_3$C$^+$PF$_6^-$. The data in Schemes III–V show that Ph$_3$C$^+$PF$_6^-$ preferentially abstracts the hydride or deuteride corresponding to the *pro-R* α hydrogen of 1. A deuterium isotope effect would be expected to enhance the stereoselectivity of step b (>99:1) in Schemes III and IV while diminishing the stereoselectivity of step d ((92 ± 2):(8 ± 2)). If a k_H/k_D in the 4–7 range is assumed,

the intrinsic stereoselectivity for *pro-R* α-hydride abstraction from 1 is on the order of 99–98:1–2. We now consider the mechanistic implications of this selectivity.

An important question is whether the Re–C rotamers of 1 (or Va–c, VIIIa–c, Scheme IV) are rapidly interconverting on the time scale of the reaction of 1 with Ph$_3$C$^+$PF$_6^-$. A variety of methods have been used to probe rotational barriers about transition-metal–carbon σ bonds.[21,39] Values in the 3–6 kcal/mol range have generally been obtained for L$_n$M–CH$_3$ complexes, in reasonable agreement with that calculated above for (η-C$_5$H$_5$)-Re(NO)(PH$_3$)(CH$_3$). More congested transition-metal alkyls (such as (η-C$_5$H$_5$)Fe(CO)$_2$[C(SCH$_3$)$_3$], $\Delta G^\ddagger \cong 8.7$ kcal/mol)[39b] have rotational barriers approaching 10 kcal/mol. However, there is no evidence for any coalescence phenomena in the 200-MHz ^{1}H NMR spectrum of 1 as the temperature is varied from 50 to –85 °C.

Baird has addressed the question of metal–carbon σ-bond rotation in (η-C$_5$H$_5$)Fe(CO)(PPh$_3$)(CH$_2$C$_6$H$_5$),[21] which is isostructural with 1. If the α-hydrogen $J_{^{31}P-^1H}$ 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 $J_{^{31}P-^1H_\alpha}$. Baird in fact noted that the $J_{^{31}P-^1H_\alpha}$ varied smoothly with temperature. Our similar experiment with 1 (Table V) shows that one $J_{^{31}P-^1H_\alpha}$ shifts smoothly with temperature, while the other fluctuates over the narrow range of 7.64–7.92 Hz. The geminal coupling constants, $J_{^1H_\alpha-^1H_{\alpha'}}$, which should change only minutely with temperature, are included (Table V) to provide an idea of the intrinsic scatter in the data. Thus it is clear that rotamers of 1 interconvert over the temperature range examined.

From the assumption that $J_{^{31}P-^1H_\alpha}$ = 17 ± 1 Hz when the phosphorus is antiperiplanar to hydrogen and 0 ± 1 Hz when the phosphorus is gauche to hydrogen, Baird concluded (by extrapolating his data to absolute zero) that the rotamer of (η-C$_5$H$_5$)-Fe(CO)(PPh$_3$)(CH$_2$C$_6$H$_5$) corresponding to Va/VIIIa (Scheme IV) is the thermodynamically most stable. A similar analysis of our data with 1 (Table V) suggests that Va and Vb (or VIIIa and VIIIb) type rotamers are of approximately equal energies. In *crystalline* 1, only a Vb (or VIIIb) type rotamer is present.[31b] The most important conclusion, for our purposes, from this and Baird's study—and one that we think is reasonable on intuitive grounds alone—is that Vc (or VIIIc) type rotamers are the *least* stable. These force a phenyl ring to reside between the bulky PPh$_3$ and C$_5$H$_5$ ligands.

Hence, in the absence of evidence to the contrary, we assume that rotamers of 1 rapidly interconvert at –78 °C and that any are available for reaction with Ph$_3$C$^+$PF$_6^-$. We now consider two classes of mechanisms for the reactions of rhenium alkyls with Ph$_3$C$^+$PF$_6^-$: (a) "conventional" mechanisms which have analogy in C=C double-bond-forming reactions, and (b) "new" mechanisms which are without established precedent.

We visualize the abstraction of an X$^-$ group from (η-C$_5$H$_5$)-Re(NO)(PPh$_3$)(CHXR) by Ph$_3$C$^+$PF$_6^-$ as being closely related to the second step of an E1cB elimination reaction (eq i).[40] As

(i)
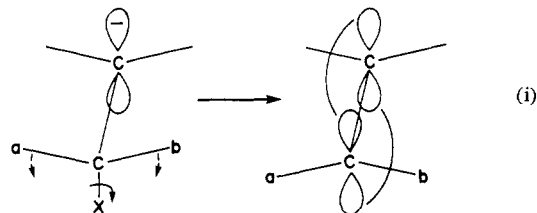
(36) (a) Klein, J. *Tetrahedron Lett.* **1973**, 4307; *Tetrahedron* **1974**, *30*, 3349. (b) Nguyen, Trong Anh; Eisenstein, O.; Lefour, J. M.; Tran Huu Dau, M. E. *J. Am. Chem. Soc.* **1973**, *95*, 6146. (c) Liotta, C. L. *Tetrahedron Lett.* **1975**, 519. (d) Liotta, C. L.; Burgess, E. M. *J. Org. Chem.* **1981**, *46*, 1703. (e) Inagaki, S.; Fukui, K. *Chem. Lett.* **1974**, 509. (f) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4054. (g) Eisenstein, O.; Klein, J.; Lefour, J. M. *Tetrahedron* **1979**, *35*, 225.

(37) (a) Nguyen, Trong Anh; Eisenstein, O. *Nouv. J. Chim.* **1977**, *1*, 61. (b) Huet, J.; Maroni-Barnaud, Y.; Nguyen, Trong Anh; Seyden-Penne, J. *Tetrahedron Lett.* **1976**, 159. (c) Caramella, P.; Rondan, N. G.; Paddon-Row, M. N.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 2438.

(38) Kiel, W. A. Ph.D. Thesis, UCLA, 1982.

(39) (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.

(40) (a) Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry", 2nd ed.; Harper and Row: New York, 1981; pp 530–556 and references therein. (b) For related lone-pair effects in organic reactions, see: Deslongchamps, P. *Tetrahedron* **1975**, *31*, 2463. Wolfe, S. *Acc. Chem. Res.* **1972**, *5*, 102.

Scheme VII. Possible "Elimination-Type" Transition States for Abstraction of X⁻ from (η-C₅H₅)Re(NO)(PPh₃)(CHXR) by Ph₃C⁺ PF₆⁻
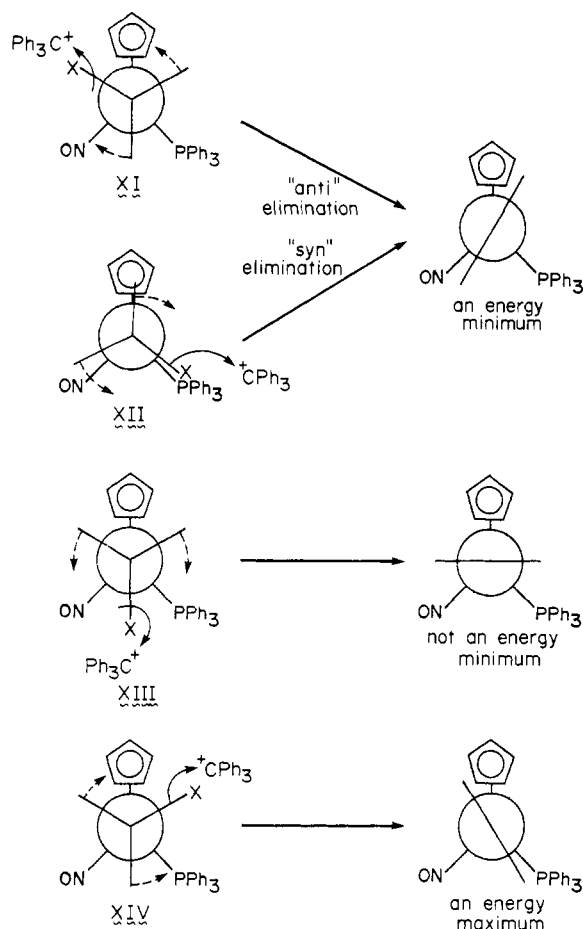
shown, a lone pair assists in the departure of leaving group X⁻; X⁻ departs in a periplanar fashion such that as the carbon is rehybridized from sp³ to sp², substituents a and b move toward their new energy minima. Other transition-state structures are of much higher energy.[40]

As previously noted, (η-C₅H₅)Re(NO)(PPh₃)(CHXR) alkyls have a high-lying d orbital "lone pair" on rhenium. Thus in Scheme VII, we consider transition states that are related to eq i. In the first two, XI and XII, the rhenium fragment lone pair is positioned to anchimerically assist the departure of X⁻, and the concomitant rehybridization of the alkyl carbon leads directly to the product ground-state geometry. Both of these features are absent in transition states XIII and XIV (and their eclipsed variants), and hence they are rejected.

Transition state XI is an "anti" elimination with respect to PPh₃, whereas XII is a "syn" elimination. These can be distinguished on stereochemical grounds. Consider the "short" CH₃O⁻ addition/elimination cycles in Scheme VI. It can be readily seen that only the "anti" transition state converts IXa (**7t**) to II (**2t**), and Xa (**7k**) to I (**2k**). The "syn" transition state (XII) would give alkylidene geometric isomers *opposite* to those observed.

Turn next to Scheme V, the "short" D⁻ addition/elimination cycle. Again, an "anti" deuteride elimination from **1-α-d₁-k** (transition state XI utilizing rotamer VIIIc) affords the principal product, **2k**. No "syn" deuteride elimination, which would yield **2t**, occurs. This is in qualitative agreement with the calculations on (η-C₅H₅)Re(NO)(PH₃)(CH₂H') (CH' = elongated CH bond), which indicated a slight bond weakening when H' was antiperiplanar to PPh₃ (Figure 6).

Consider the possibility of an anti *hydride* (H⁻) abstraction in Scheme V. Such a reaction would have to occur via rotamer VIIIa (shown in Scheme IV) and would result in a product (**2t-α-d₁**) other than the one observed. However, as noted above, rotamer

VIIIa is significantly more stable than VIIIc. Therefore, if the "anti" elimination mechanism (transition state XI, Scheme VII) for hydride abstraction is correct, *the least stable rotamer of* **1** *is the most kinetically reactive one.*

We turn finally to Scheme IV, the "long" D⁻ addition/elimination cycle. It is again clear that only "anti" elimination can lead to the observed products. In each case, the least stable **1-α-d₁** rotamer (Vc, VIIIc) is the most reactive toward Ph₃C⁺PF₆⁻.

Hence we have formulated a mechanism for X⁻ group abstraction from (η-C₅H₅)Re(NO)(PPh₃)(CHXR) alkyls that is consistent with all of the observed data. Are there others? We consider a variation in which electron transfer occurs (from Re to Ph₃C⁺) prior to X loss to be likely. The Ph₃C⁺ is of course very bulky, and the close approach to X shown in XI–XIV may not be realistic. Since our suggestion of this possibility,[7] Cooper has obtained evidence for radical cation intermediates in the abstraction of α hydrides from (η-C₅H₅)₂W(CH₃)₂ by Ph₃C⁺.[41] Also, distinctly different mechanisms might appear in time that equally well fit our observations. We have considered the possibility of Ph₃C⁺–nitrosyl coordination. While this would alter the relative sizes of the rhenium ligands, we do not presently see any reason why it would yield energetically more favorable reaction pathways or better explain our results.

At the present level of sophistication, our proposed mechanism does not address the reason *why* the least stable rotamer of **1** is the most reactive toward Ph₃C⁺PF₆⁻. If the kinetic product were **2t** instead of **2k**, "product development control" could be invoked. However, since the least stable rotamer affords the *less* stable of two possible isomeric products, there must be some unique means of transition-state stabilization available to Vc → **2k-α-d₁** (and VIIIc → **2k**) but not Va → **2t** (and VIIIa → **2t-α-d₁**).[42] For instance, attractive interactions between η-C₅H₅ rings and neighboring phenyls have been previously observed crystallographically.[43] However, these are not in evidence in any of the X-ray structures (**2t·CHCl₂, 5t·CH₂Cl₂, (−)-R-1**[31b]) we have completed to date. Furthermore, aliphatic homologues of **1** behave similarly toward Ph₃C⁺PF₆⁻.[7] While 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,[44] we know of no example exactly analogous (nondissociative equilibria; Curtin–Hammett conditions;[42] exclusive operation of one pathway) to the case in hand.

4. Concluding Remarks. This study has served to define many conceptual analogies between C=C double bonds and Re=C double bonds. However, rhenium, unlike carbon, can form a *fifth* bond and remain (pseudo) tetrahedral. This adds extra dimensions of structure and reactivity.

The ability of rhenium to form a fifth bond is critical to the excellent stereocontrol in the reaction of **1** with Ph₃C⁺PF₆⁻ and the reactions of **2t** and **2k** with nucleophiles. In aldehydes and ketones with *adjacent* chiral centers, nucleophilic attack upon the >C=O bond (neither terminus of which is itself chiral) commonly occurs with 30–90% diastereoselectivity.[45] In the case of **2t** and

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(42) (a) This is most readily seen by superimposing two energy–reaction coordinate diagrams onto Figure 7. From Baird's data,[21] it can be estimated that the Vc/VIIIc type rotamers are at most 1 kcal/mol higher in energy than the Va/VIIIa type rotamers. When energy curves connecting the former to **2k** and the latter to **2t** are drawn, the Curtin–Hammett principle[42b–d] requires that the transition state leading to **2k** be placed at a *lower* position on the energy axis (Figure 7) than the transition state leading to **2t**. (b) Carey, F. A.; Sundberg, R. J. "Advanced Organic Chemistry. Part A: Structure and Mechanisms"; Plenum: New York, 1977; pp 168–170. (c) Seeman, J. I.; Sanders, E. B.; Farone, W. A. *Tetrahedron* **1980**, *36*, 1173. (d) Seeman, J. I. *Chem. Rev.*, in press.

(43) Brunner, H.; Agrifoglio, G.; Bernal, I.; Creswick, M. W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 641 and references therein. Bernal, I.; Creswick, M.; Brunner, H.; Agrifoglio, G. *J. Organomet. Chem.* **1980**, *198*, C4.

(44) Such behavior may be relatively common in homogeneous catalysis. For instance, the direct oxidative addition of H₂ to RhCl(PPh₃)₃ can occur, but addition of H₂ to RhCl(PPh₃)₂ (generated in small quantities by PPh₃ dissociation) is at least 10⁴ times faster. Halpern, J.; Wong, C. S. *J. Chem. Soc., Chem. Commun.* **1973**, 629.

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2k, the rhenium terminus of Re=C< is chiral, and diastereoselectivities of 90–100% are observed. Benzylidenes **2t** and **2k** have two principal elements of stereoisomerism: (i) a center of chirality; (ii) an unsymmetrically substituted multiple bond.[46] Conversion of **2t** and **2k** to **3–7** entails the stereospecific or stereoselective conversion of the second element[46] (which contains rhenium) to a new chiral center (which does not contain rhenium). The presence of large (PPh₃), medium (C₅H₅), and small (NO) ligands on rhenium, coupled with a strong rhenium-carbon π bond to lock the benzylidene geometry, provides a steric basis for the chirality transfer. There is a strong conceptual parallel to Cram's rule[45] and related models for asymmetric induction.[37a]

While the reactions described herein do not provide a basis for new *catalytic* asymmetric syntheses, stoichiometric metal–carbon bond-cleavage reactions can be anticipated[47] to give chiral organic molecules such as C₆H₅CHDBr and C₆H₅CHDT in high optical yields. This topic will be the subject of future reports from our laboratory. We also emphasize the close interplay of theory and experiment that guided this work.[48] Additional predictions of extended Hückel MO calculations in organorhenium chemistry are presently under study.

Experimental Section

General Information. All reactions were conducted under an atmosphere of dry N₂. Chromatographies were conducted in air unless noted. Hexanes were distilled from potassium metal, and CH₂Cl₂ was distilled from P₂O₅. Benzene, CHCl₃, and other solvents were commercial reagent grade and simply degassed with N₂ prior to use. CD₂Cl₂ and CD₃CN were degassed and distilled from P₂O₅. Other deuterated solvents were used without purification unless noted.

IR spectra were recorded on a Perkin-Elmer Model 521 spectrometer. ¹H NMR and ¹³C NMR spectra were (unless otherwise noted) recorded at ambient probe temperature on a Bruker WP-200 spectrometer at 200 and 50 MHz, respectively, and referenced to internal (CH₃)₄Si. UV-vis spectra were recorded on a Cary 219 spectrophotometer. Mass spectra were obtained on an AEI-M59 instrument. Melting points were recorded on a Büchi Schmeltzpunktbestimmungsapparat and were not corrected. Microanalyses were conducted by Galbraith.

Starting Materials. (η-C₅H₅)Re(NO)(PPh₃)(CH₃) was prepared as previously described.[15b] Ph₃C⁺PF₆⁻ was purchased from Aldrich and Columbia Organic Chemicals and stored under N₂ in the refrigerator. Over the course of these investigations the quality of the Ph₃C⁺PF₆⁻ varied considerably. It was found that recrystallization of Ph₃C⁺PF₆⁻ from CH₂Cl₂/benzene or from CH₂Cl₂/ether under N₂ gave pure Ph₃C⁺PF₆⁻ (50–60% recovery).[49] C₆H₅Li (2 M in C₆H₆/ether), Li(C₂H₅)₃BD (1 M in THF), and CH₃CH₂MgBr (3 M in Et₂O) were purchased from Aldrich; C₆H₅CH₂MgCl (1.8 M in THF) and CH₃Li· LiBr complex (1.4 M in THF) were purchased from Alfa. Except for the CH₃Li,[50] these were used without standardization. PMe₃ was obtained from Strem Chemicals and used without purification.

Preparation of (η-C₅H₅)Re(NO)(PPh₃)(CH₂C₆H₅) (1). The following procedure is similar to the one developed by Wong and Tam.[51] To a 100-mL Schlenk flask was added 0.517 g (0.926 mmol) of (η-C₅H₅)-Re(NO)(PPh₃)(CH₃) and 50 mL of CH₂Cl₂. The resulting orange solution was then cooled to –78 °C, and 0.396 g (1.020 mmol) of Ph₃C⁺-PF₆⁻ was added as a solid. After the reaction mixture was stirred for 30 min at –78 °C (during which time a yellow solution formed), 0.700 mL of C₆H₅Li (2 M in benzene/ether) was added dropwise. The reaction mixture was stirred at –78 °C for an additional 15 min and then allowed to warm to room temperature. The solvent was then removed by rotary evaporation. The residue was taken up in benzene and filtered through a 2-in. silica gel plug. The benzene was removed by rotary evaporation to give an orange solid. Overnight recrystallization from CH₂Cl₂/hexanes in a freezer gave fine orange crystals of **1**, which were collected by filtration, washed with hexanes, and dried (0.483 g, 0.761 mmol, 82%): mp 180–182 °C; ¹³C NMR (ppm, CDCl₃) 90.56, –3.94 (d, $J_{^{13}C-^{31}P}$ = 4.8

Hz), phenyl carbons at 133.68 (d, $J_{^{13}C-^{31}P}$ = 9.7 Hz), 130.07 (d, J = 3.2 Hz), 128.41 (d, J = 9.7 Hz), 127.61, 127.23, 121.90, ipso phenyl carbons not observed; other data,[51] IR (cm⁻¹, CH₂Cl₂) $\nu_{N\equiv O}$ 1626 s; ¹H NMR (CDCl₃) δ 7.09–7.49 (m, 20 H), 4.74 (d, $J_{^1H-^{31}P}$ = 1.0 Hz, 5 H), 3.50 (dd, $J_{^1H-^1H'}$ = 11.8 Hz, $J_{^1H-^{31}P}$ = 7.9 Hz, 1 H), 2.89 (dd, $J_{^1H'-^1H}$ = 11.8 Hz, $J_{^1H'-^{31}P}$ = 2.8 Hz, 1 H). Anal. Calcd for C₃₀H₂₇NOPRe: C, 56.67; H, 4.29; N, 2.21; P, 4.88. Found: C, 56.84; H, 4.32; N, 2.14; P, 5.06.

Preparation of *ac*-[(η-C₅H₅)Re(NO)(PPh₃)(=CHC₆H₅)]⁺PF₆⁻ (2t). To a 100-mL Schlenk flask was added 0.302 g (0.477 mmol) of (η-C₅H₅)Re(NO)(PPh₃)(CH₂C₆H₅) (1) and 30 mL of CH₂Cl₂. The resulting orange solution was cooled to –78 °C and 0.203 g (0.524 mmol) of Ph₃C⁺PF₆⁻ was added as a solid. The resulting yellow solution was stirred at –78 °C for 30 min and then allowed to warm to room temperature. After an additional 2 h, hexanes (20 mL) were added (to inhibit oiling upon concentration), and both solvents were removed under an oil pump vacuum. The resulting solid was washed with hexanes and then small portions of ether. An off-yellow powder was obtained. Recrystallization from CH₂Cl₂/hexanes (freezer) gave 0.278 g (0.358 mmol, 75%) of **2t** as a yellow powder, mp 225–230 °C dec. Alternatively, diffusion of petroleum ether (bp 30–60 °C) into a CHCl₃ solution of **2t** afforded bright yellow crystals of the monosolvate **2t·CHCl₃** (0.312 g, 0.348 mmol, 73%): mp 215 °C dec; ¹H NMR (CDCl₃) δ 15.30 (s, 1 H), 7.52–7.18 (m, 20 H), 6.06 (s, 5 H); ¹³C NMR (ppm, CDCl₃) 288.6 (Re=C), phenyl carbons at 151.8, 133.9, 133.0 (d, $J_{^{13}C-^{31}P}$ = 11.9 Hz), 132.2, 131.9, 129.5 (d, $J_{^{13}C-^{31}P}$ = 10.2 Hz), 129.1, 127.9 (ipso PPh₃ carbons, portion of doublet with other portion likely obscured by 129.1-ppm resonance), C₅H₅ at 99.6; ¹³C NMR (CD₂Cl₂, in situ, for comparison to **2k** chemical shifts below) 287.4, 100.0; IR (cm⁻¹, CH₂Cl₂) $\nu_{N\equiv O}$ 1708 s.

Preparation of *sc*-[(η-C₅H₅)Re(NO)(PPh₃)(=CHC₆H₅)]⁺PF₆⁻ (2k). Preparative-scale syntheses of **2k** were conducted as described above for **2t**. In each case, solutions were stirred for 0.5 h at –78 °C before reaction. Spectroscopic-scale syntheses were conducted at –78 °C as described below for the isomerization rate measurements. ¹H NMR (CD₂Cl₂) δ 16.08 (s, 1 H), 7.52–7.18 (m, 20 H), 5.89 (s, 5 H); ¹³C NMR (ppm, CD₂Cl₂, –63 °C) 280.5, 98.5, phenyl carbons obscured by Ph₃CH.

Photolysis of 2t. The following experiment is representative: To a septum-capped 5-mm NMR tube was added **2t** (0.0290 g, 0.0370 mmol), p-di-*tert*-butylbenzene standard (0.0022 g, 0.012 mmol), and acetone-d_6 (dried over 4A molecular sieves). The tube was then subjected to five freeze–pump–thaw degassing cycles, and a ¹H NMR spectrum (including integrals of the **2t** and standard resonances) was recorded. The tube was then placed in a large Pyrex test tube partially filled with acetone and the test tube in turn placed in a large unsilvered Pyrex Dewar containing a dry ice/acetone cooling bath. A Hanovia 450-W lamp was suspended in a quartz immersion well and placed adjacent to the Dewar such that ca. 5 cm separated the lamp from the sample. After 3 h of irradiation at –78 °C, the NMR tube was transferred to a Varian T-60 spectrometer (ambient probe temperature; previously tuned to **2t** in acetone-d_6) and five spectra of the C₅H₅ region (**2t**, δ 6.42; **2k**, δ 6.30) were recorded in rapid succession (negligible isomerization; see Table II). The relative integrals were averaged and indicated a (57 ± 1):(43 ± 1) **2t/2k** ratio. The sample was allowed to stand overnight at room temperature in the dark. Integration of the **2t** vs. p-di-*tert*-butylbenzene resonances indicated >95% of the original **2t** to be present.

Rates of Isomerization: 2k → 2t. To a septum-capped NMR tube was added 0.0148–0.0168 g of (η-C₅H₅)Re(NO)(PPh₃)(CH₂C₆H₅) (1) in 0.300 mL of CD₂Cl₂. The NMR tube was then cooled to the temperature of data collection (Table II), whereupon 1.2 equiv of Ph₃C⁺PF₆⁻ in 0.200 mL of CD₂Cl₂ was added via gas-tight syringe. The NMR tube was then quickly transferred to a NMR probe that had been preequilibrated to the appropriate temperature. Disappearance of **2k** was monitored by integration of the δ 16.08 resonance. Standard ln (integral) vs. time plots yielded the data in Table II. $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were obtained from ln (k_{obsd}/T) vs. $1/T$ plots.

Preparation of (SS,RR)-(η-C₅H₅)Re(NO)(PPh₃)(CHDC₆H₅) (1-α-d_1-t). Benzylidene **2t** (0.154 g, 0.198 mmol) was dissolved in 20 mL of CH₂Cl₂ in a 100-mL Schlenk flask and cooled to –78 °C. Then 0.220 mL (0.220 mmol) of Li(C₂H₅)₃BD (1.0 M in THF) was added dropwise. The solution was allowed to warm to room temperature and the solvent removed under oil pump vacuum. The resulting orange residue was extracted with benzene and filtered through a 2-in. silica gel plug. The benzene was removed and the residue recrystallized from CH₂Cl₂/hexanes to give **1-α-d_1-t** as an orange solid (0.116 g, 0.183 mmol, 92%), mp 220–222 °C dec. Spectral data: Tables III and VI.

Preparation of (SR,RS)-(η-C₅H₅)Re(NO)(PPh₃)(CHDC₆H₅) (1-α-d_1-k). A. To a –78 °C solution of **2k** (prepared from 0.187 mmol of **1** as described above) was added dropwise 0.280 mL of Li(C₂H₅)₃BD (1.0 M in THF). After 15 min at –78 °C, the reaction was allowed to warm to room temperature while solvent was simultaneously removed under oil

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Benzylidine [(η-C₅H₅)Re(NO)(PPh₃){=CHC₆H₅}]⁺PF₆⁻

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Table VI. Summary of 16-eV Mass Spectral Data

com-plex	ions, m/e for ^{187}Re (% of base peak)				
	M⁺	M⁺ − R	M⁺ − PPh₃	PPh₃⁺	other
1-α-d_1-t	636 (47.8)	544 (100)	374 (20.9)	262 (41.5)	
1-α-d_1-k	636 (40.4)	544 (100)	374 (27.3)	262 (62.3)	
3t	649 (6.4)	544 (73.5)	387 (25.8)	262 (100)	359 (13.8)
3k	649 (5.7)	544 (72.1)	387 (29.2)	262 (100)	359 (11.5)
4t	663 (6.8)	544 (82.1)	401 (21.4)	262 (100)	359 (14.4)
4k	663 (9.2)	544 (100)	401 (6.6)	262 (12.1)	359 (27.1)
5t	not observed^a	544 (29.9)	463 (28.7)	262 (100)	634^b (1.2) 359 (40.5)
5k	725 (3.9)	544 (51.1)	463 (28.1)	262 (100)	634^b (6.5) 359 (29.5)
7t	665 (1.1)	544 (100)	not observed	262 (81.1)	635^c (21.7) 373 (14.3)

^{a} The absence of a M⁺ ion for **5t** but not **5k** may be a consequence of the different probe temperatures used: **5t**, 210 °C; **5k**, 190 °C. ^{b} M⁺ − CH₂C₆H₅. ^{c} M⁺ − NO.

pump vacuum. The residue was extracted with benzene and filtered through a 2-in. silica gel plug. The benzene was removed by rotary evaporation and the orange solid ¹H NMR assayed. Integration of the ReC*H*DC₆H₅ resonances indicated a (92 ± 2):(8 ± 2) ratio of **1-α-d_1-k** to **1-α-d_1-t**. Recrystallization from CH₂Cl₂/hexanes gave 0.096 g (0.151 mmol, 80%) of (predominantly) **1-α-d_1-k**.

B. Diastereomerically pure **1-α-d_1-k** was prepared by the reaction of Li(C₂H₅)₃BH with **2t-α-d_1** (preparation below) in a procedure analogous to the one above for **1-α-d_1-t**. Spectral data are given in Tables III and VI.

Preparation of (SS,RR)-(η-C₅H₅)Re(NO)(PPh₃)(CH(CH₃)C₆H₅) (3t). Benzylidene **2t** (0.306 g, 0.393 mmol) was dissolved in 40 mL of CH₂Cl₂ in a Schlenk flask and cooled to −78 °C. Then 0.320 mL of CH₃Li (1.4 M in ether) was added dropwise. The solution turned orange and was allowed to warm to room temperature. Solvent was removed under oil pump vacuum. The resulting residue was extracted with benzene and filtered through a 2-in. silica gel plug. The benzene was removed by rotary evaporation, and the orange solid that remained was chromatographed on a 13 × 2.5 cm silica gel column (1:1 CH₂Cl₂/hexanes). The orange band was collected, and solvent was removed under oil pump vacuum to give 0.214 g (0.330 mmol, 84%) of **3t** as an orange powder, mp 237–240 °C dec. Spectroscopic data are given in Tables III and VI.

Preparation of (SS,RR)-(η-C₅H₅)Re(NO)(PPh₃)(CH(CH₂CH₃)C₆H₅) (4t). Benzylidene **2t** (0.105 g, 0.135 mmol) was dissolved in 20 mL of CH₂Cl₂ in a Schlenk flask and cooled to −78 °C. Then 0.180 mL of CH₃CH₂MgBr (3 M in THF) was added dropwise. After 15 min at −78 °C, the reaction was allowed to warm to room temperature while solvent was simultaneously removed under oil pump vacuum. The residue was extracted with benzene and filtered through a 2-in. silica gel plug. The benzene was removed by rotary evaporation, and the resulting orange oil was chromatographed on a 13 × 2.5 cm silica gel column (1:1 CH₂Cl₂/hexanes). The orange band was collected, and solvent was removed under oil pump vacuum to give 0.078 g (0.118 mmol, 87%) of **4t** as an orange powder, mp 183–185 °C dec. Spectroscopic data are given in Tables III and VI.

Preparation of (SS,RR)-(η-C₅H₅)Re(NO)(PPh₃)(CH-(CH₂C₆H₅)C₆H₅) (5t). Benzylidene **2t** (0.309 g, 0.397 mmol) was dissolved in 40 mL of CH₂Cl₂ in a Schlenk flask and cooled to −78 °C. Then 0.330 mL of C₆H₅CH₂MgCl (1.8 M in THF) was added dropwise. After 20 min at −78 °C, the reaction was allowed to warm to room temperature while solvent was simultaneously removed under oil pump vacuum. The residue was extracted with benzene and filtered through a 2-in. silica gel plug. The benzene was removed by rotary evaporation, and the resulting orange oil was chromatographed on a 13 × 2.5 cm silica gel column (1:1 CH₂Cl₂/hexanes). The orange band was collected, and solvent was removed under oil pump vacuum to give 0.259 g (0.358

mmol, 90%) of **5t** as an orange powder, mp 222–225 °C dec. Spectroscopic data are given in Tables III and VI.

Preparation of (SR,RS)-[(η-C₅H₅)Re(NO)(PPh₃)(CH-(PMe₃)C₆H₅)]⁺PF₆⁻ (6t). Benzylidene **2t** (0.116 g, 0.149 mmol) was dissolved in 20 mL of CH₂Cl₂ in a Schlenk flask and cooled to −78 °C. Then 0.030 mL (0.022 g, 0.295 mmol) of PMe₃ was added. The resulting orange solution was stirred for 5 min at −78 °C. The reaction was then allowed to warm to room temperature while solvent was simultaneously removed under oil pump vacuum.[52] The resulting solid was taken up in CH₂Cl₂; hexanes were then layered onto this solution. On standing, orange needles of **6t** formed. These were collected by filtration and dried (0.105 g, 0.123 mmol, 82%), mp 229–230 °C dec. Spectroscopic data are given in Table III.

Preparation of (SR,RS)-(η-C₅H₅)Re(NO)(PPh₃)(CH(OCH₃)C₆H₅) (7t). To a solution of **1** (0.385 g, 0.609 mmol) in dry CH₂Cl₂ (30 mL) at −78 °C was added solid Ph₃C⁺PF₆⁻ (0.334 g, 0.861 mmol). The resulting mixture was stirred for 30 min and then allowed to warm to room temperature. After 4 h at room temperature, a CH₃ONa solution prepared from Na (0.64 g, 27.8 mmol) and anhydrous CH₃OH (15 mL) was added. The resulting mixture was stirred for 20 min, whereupon the solvent was removed under reduced pressure. The residue was extracted with CH₂Cl₂[52] and recrystallized from CH₂Cl₂/hexanes to give yellow crystals of **7t** (0.299 g, 0.452 mmol, 74%), mp 169–172 °C dec. Spectroscopic data are given in Tables III and VI. Anal. Calcd for C₃₁H₂₉NO₂PRe: C, 56.01; H, 4.40; N, 2.11; P, 4.66. Found: C, 55.81; H, 4.47; N, 2.34; P, 4.61.

Preparation of (SR,RS)-(η-C₅H₅)Re(NO)(PPh₃)(CH(CH₃)C₆H₅) (3k). To a −78 °C solution of **2k** (prepared from 0.160 mmol of **1** as described above) was added dropwise 0.350 mL of CH₃Li (1.4 M in ether). After 5 min at −78 °C (during which time the solution turned from yellow to orange), the reaction was allowed to warm to room temperature while solvent was simultaneously removed under oil pump vacuum. The residue was extracted with benzene/CH₂Cl₂ (1:1) and filtered through a 2-in. silica gel plug. The solvent was removed and the residue chromatographed on a 13 × 2.5 cm silica gel column (1:1 CH₂Cl₂/hexanes). The orange band was collected. Solvent removal afforded an orange powder (0.0893 g, 0.138 mmol, 86%), mp 186–188 °C dec, which was shown by ¹H NMR (C₅H₅ resonances) to be a (94 ± 1):(6 ± 1) **3k/3t** mixture.[53] Spectroscopic data are given in Tables III and VI.

Preparation of (SR,RS)-(η-C₅H₅)Re(NO)(PPh₃)(CH-(CH₂CH₃)C₆H₅) (4k). To a −78 °C solution of **2k** (prepared from 0.300 mmol of **1** as described above) was added dropwise 0.400 mL of CH₃C-H₂MgBr (3.0 M in ether). After 5 min at −78 °C, the reaction was allowed to warm to room temperature while solvent was simultaneously removed under oil pump vacuum. The residue was extracted with benzene and filtered through a 2-in. silica gel plug in a glovebox. The benzene was removed under oil pump vacuum, and the resulting residue was chromatographed on a 13 × 2.5 cm silica gel column (1:1 CH₂Cl₂/hexanes). The orange band was collected. Solvent removal afforded an orange powder (0.100 g, 0.150 mmol, 50%), mp 172–175 °C dec, which was shown by ¹H NMR (C₅H₅ resonances) to be a (94 ± 1):(6 ± 1) **4k/4t** mixture.[53] Spectroscopic data are given in Tables III and VI.

Preparation of (SR,RS)-(η-C₅H₅)Re(NO)(PPh₃)(CH-(CH₂C₆H₅)C₆H₅) (5k). To a −78 °C solution of **2k** (prepared from 0.160 mmol of **1** as described above) was added dropwise 0.180 mL of C₆H₅-CH₂MgCl (1.8 M in THF). After 15 min at −78 °C, the reaction was allowed to warm to room temperature while solvent was simultaneously removed under oil pump vacuum. The residue was extracted with benzene and filtered through a 2-in. silica gel plug in a glovebox. The benzene was removed under oil pump vacuum, and the resulting oil was chromatographed on a 13 × 2.5 cm silica gel column (1:1 CH₂Cl₂/hexanes). The orange band was collected. Solvent removal afforded an orange powder (0.095 g, 0.132 mmol, 82%), mp 194–197 °C dec, which was shown by ¹H NMR (C₅H₅ resonances) to be a (94 ± 1):(6 ± 1) **5k/5t** mixture.[53] Spectroscopic data are given in Tables III and VI.

Preparation of (SS,RR)-[(η-C₅H₅)Re(NO)(PPh₃)(CH-(PMe₃)C₆H₅)]⁺PF₆⁻ (6k). To a −78 °C solution of **2k** (prepared from 0.165 mmol of **1** as described above) was added 0.020 mL (0.014 g, 0.197 mmol) of PMe₃. After 15 min at −78 °C, the reaction was allowed to warm to room temperature while solvent was simultaneously removed under oil pump vacuum. The residue was taken up in CH₂Cl₂. Dia-

(52) ¹H NMR analysis was conducted at this stage to assay diastereomer purity. All **t** isomers were ≥99% pure.

(53) Recrystallization of this mixture from CH₂Cl₂/hexanes over the course of several days in the freezer afforded pure **k** isomer. For **3k**, it was necessary to halt the crystallization after 10–20% recovery in order to prevent cocrystallization of **3t**.

stereomerically pure **6k** was obtained as an orange powder (0.099 g, 0.116 mmol, 70%), mp 122–123 °C dec, by allowing ether to slowly diffuse into this solution in a freezer. Spectroscopic data are given in Table III.

An ^{1}H NMR monitored experiment (see isomerization rate studies) was conducted on a 0.024 mmol scale in CD$_2$Cl$_2$ at –78 °C. Addition of 0.005 mL (0.049 mmol) of PMe$_3$ to **2k** gave an orange solution, which upon warming to room temperature was shown by integration of the C$_5$H$_5$ resonances to be a (94 ± 1):(6 ± 1) **6k/6t** mixture.

Preparation of (SS,RR)-(η-C$_5$H$_5$)Re(NO)(PPh$_3$)(CH(OCH$_3$)C$_6$H$_5$) (7k). To a –78 °C solution of **2k** (prepared from 0.350 mmol of **1** as described above) was added a solution of CH$_3$ONa generated from Na (0.20 g, 8.7 mmol) and anhydrous CH$_3$OH (8 mL). After 10 min at –78 °C, the reaction was allowed to warm to room temperature while solvent was simultaneously removed under oil pump vacuum. The resulting residue was extracted with benzene (ca. 200 mL) and dried over MgSO$_4$. Solvent was removed from the filtrate; ^{1}H NMR analysis of the residue indicated a (78 ± 1):(22 ± 1) **7k/7t** ratio. Diffusion recrystallization of the residue from CH$_2$Cl$_2$/hexanes in the freezer gave orange prisms (0.079 g, 0.119 mmol, 35%), which were shown by ^{1}H NMR (C$_5$H$_5$ resonances) to be a (90 ± 1):(10 ± 1) **7k/7t** mixture, mp 155–172 °C dec.[53] Spectroscopic data are given in Table III. Anal. Calcd for C$_{31}$H$_{29}$NO$_2$PRe: C, 56.01; H, 4.40. Found: C, 55.93; H, 4.51.

A ^{1}H NMR monitored experiment (see isomerization rate studies) was conducted on a 0.019 mmol scale in CD$_2$Cl$_2$ at –78 °C. A CD$_3$ONa solution that was generated from Na (0.018 g, 0.782 mmol) and CD$_3$OD (0.300 mL) was added to **2k**. Reaction was complete within 3 min as assayed by a ^{1}H NMR spectrum at –70 °C. A (85 ± 1):(15 ± 1) **7k-d_3/7t-d_3** mixture formed.

Reaction of 1-α-d_1-t with Ph$_3$C$^+$PF$_6$$^-$. Preparation of 2t-$\alpha$-$d_1$. To a 100-mL Schlenk flask were added 0.211 g (0.332 mmol) of **1-α-d_1-t** and 20 mL of CH$_2$Cl$_2$. The resulting solution was cooled to –78 °C, and 0.135 g (0.349 mmol) of Ph$_3$C$^+$PF$_6$$^-$ was added as a solid. The resulting yellow solution was stirred at –78 °C for 30 min and then allowed to warm to room temperature. After an additional 30 min, solvent was removed under oil pump vacuum. The residue was extracted with hexanes to recover the triphenylmethane. The hexanes were removed from the extracts via rotary evaporation, and the residue was recrystallized from hot 95% ethanol. Fluffy white crystals of triphenylmethane (0.059 g, 0.241 mmol, 73%) were obtained. Analysis of the m/e 244:245 peak ratio in the 16-eV mass spectrum (including comparison to an authentic sample) indicated a natural abundance Ph$_3$CH/Ph$_3$CD ratio.

The residue remaining after hexane extraction was taken up in CH$_2$Cl$_2$ and filtered through a 2-in. silica gel plug. The CH$_2$Cl$_2$ was then removed by rotary evaporation, and the residue was diffusion recrystallized from CHCl$_3$/petroleum ether (bp 35–60 °C). Yellow prisms of **2t-α-d_1·CHCl$_3$** formed, which were collected by filtration and dried (0.195 g, 0.217 mmol, 65%; mp 215 °C, dec).[54]

A ^{1}H NMR monitored reaction in CD$_2$Cl$_2$ was conducted analogously to the immediately following experiment and showed the sequential formation of **2k-α-d_1** (δ 5.89) and **2t-α-d_1** (δ 6.08).

Reaction of 1-α-d_1-k with Ph$_3$C$^+$PF$_6$$^-$. To a septum-capped NMR tube was added 0.020 g (0.032 mmol) of diastereomerically pure **1-α-d_1-k** in 0.400 mL of CD$_2$Cl$_2$. The tube was then cooled to –78 °C, whereupon 0.0134 g (0.035 mmol) of Ph$_3$C$^+$PF$_6$$^-$ in 0.150 mL of CD$_2$Cl$_2$ was added via gas-tight syringe. The tube was quickly transferred to a –73 °C NMR probe. A spectrum indicated the complete consumption of **1-α-d_1-k** and the presence of **2k** (δ 16.08, 5.89) and some Ph$_3$CH (δ 5.59). Upon warming to room temperature in the NMR probe, **2k** disappeared as **2t** appeared. After several hours at room temperature, the $^+$Re═CHC$_6$H$_5$ (δ 15.30) and C$_5$H$_5$ (δ 6.05) resonances of **2t** were integrated repeatedly. From these data, a (92 ± 2):(8 ± 2) ratio of **2t-α-d_0/2t-α-d_1** was calculated.

The contents of the NMR tube were applied to a preparative silica gel TLC plate, which was then eluted with 90:10 ethyl acetate/hexanes. The UV-active triphenylmethane band (R_f ~0.7) was isolated and extracted with CH$_2$Cl$_2$. The eluent was concentrated to a residue, which was then recrystallized from hot 95% ethanol to give pure triphenylmethane. Analysis of the m/e 244:245 peak ratio in the 16 eV mass spectrum indicated a (89 ± 1):(11 ± 1) Ph$_3$CD/Ph$_3$CH ratio. The origin of the TLC plate was extracted with CH$_2$Cl$_2$. The extract was concentrated to a residue, which was then diffusion recrystallized from CHCl$_3$/petroleum ether (bp 35–60 °C). Yellow crystals of **2t·CHCl$_3$** (0.017 g,

0.019 mmol, 59%) were obtained. The **2t-α-d_1** content was assayed as described in the preceding paragraph (with identical results).

Reaction of 7t with Ph$_3$C$^+$PF$_6$$^-$. To a septum-capped NMR tube was added 0.016 g (0.024 mmol) of **7t** in 0.300 mL of CD$_2$Cl$_2$. The tube was then cooled to –78 °C, whereupon 0.010 g (0.025 mmol) of Ph$_3$C$^+$PF$_6$$^-$ in 0.140 mL of CD$_2$Cl$_2$ was added via gas-tight syringe. The tube was quickly transferred to a –65 °C NMR probe. A ^{1}H NMR spectrum indicated the exclusive formation of **2t** and Ph$_3$COCH$_3$ (δ 2.91). A small amount of starting **7t** remained. No products derived via hydride abstraction from **7t**[8] formed. A small resonance at ca. δ 3.3 was tentatively assigned to CH$_3$OCH$_3$ byproduct.

Reaction of 7k with Ph$_3$C$^+$PF$_6$$^-$. To a septum-capped ^{1}H NMR tube was added 0.020 g (0.030 mmol) of a 90:10 **7k/7t** mixture in 0.300 mL of CD$_2$Cl$_2$. The tube was then cooled to –78 °C, whereupon 0.018 g (0.046 mmol) of Ph$_3$C$^+$PF$_6$$^-$ in 0.150 mL of CD$_2$Cl$_2$ was added via gas-tight syringe. The tube was quickly transferred to a –70 °C NMR probe. A ^{1}H NMR spectrum indicated the formation of a (90 ± 1):(10 ± 1) ratio of **2k/2t** and Ph$_3$COCH$_3$ (δ 2.91). No other organometallic products were present; a very small δ 3.3 resonance was noted.

Calculations. All calculations were of the extended Hückel type,[55] with a weighted H_{ij} formula.[56] The ligand geometry about rhenium was assumed to be octahedral, and the following distances (Å) were used as input: Re–C, 2.10; Re–N, 1.78; N–O, 1.19; Re–P, 2.36; Re–C$_5$H$_5$ (distance to carbon), 2.33; C–C (C$_5$H$_5$), 1.40; C–H, 1.09; P–H, 1.44. Standard parameters were employed for carbon, nitrogen, oxygen, and hydrogen.[55] Those utilized for the other atoms were as follows: Re 6s, H_{ii} = –9.36 eV, ζ = 2.398; Re 6p, H_{ii} = –5.96 eV, ζ = 2.372; Re 5d, H_{ii} = –12.66 eV, ζ = 5.343 (coefficient = 0.6359) and 2.277 (coefficient = 0.5677); P 3s, H_{ii} = –18.6 eV, ζ = 1.6; P 3p, H_{ii} = –14 eV, ζ = 1.6. The model nucleophile, H$^-$, was given H_{ii} = –10 eV and ζ = 1.3.

Supplementary Material Available: Figure 8, numbering of atoms in ac-[(η-C$_5$H$_5$)Re(NO)(PPh$_3$)(═CHC$_6$H$_5$)]$^+$PF$_6$$^-$·CHCl$_3$ (**2t·CHCl$_3$**); Figure 9, crystal packing diagram of **2t·CHCl$_3$** as viewed down axis A; Table VII, summary of crystallographic data for **2t·CHCl$_3$**; Table VIII, bond and short interatomic distances in **2t·CHCl$_3$**; Table IX, bond angles in **2t·CHCl$_3$**; Table X, atomic coordinates of **2t·CHCl$_3$** (atoms refined isotropically); Table XI, atomic coordinates of **2t·CHCl$_3$** (atoms refined anisotropically); Table XII, calculated and observed structure factors for **2t·CHCl$_3$**; Figure 10, numbering of atoms in (SS,RR)-(η-C$_5$H$_5$)Re(NO)(PPh$_3$)(CH(CH$_2$C$_6$H$_5$)C$_6$H$_5$)· CH$_2$Cl$_2$ (**5t·CH$_2$Cl$_2$**); Figure 11, crystal packing diagram of **5t·CH$_2$Cl$_2$** as viewed down axis A; Table XIII, summary of crystallographic data for **5t·CH$_2$Cl$_2$**; Table XIV, bond and short interatomic distances in **5t·CH$_2$Cl$_2$**; Table XV, bond angles in **5t·CH$_2$Cl$_2$**; Table XVI, atomic coordinates of **5t·CH$_2$Cl$_2$** (atoms refined isotropically); Table XVII, atomic coordinates of **5t·CH$_2$Cl$_2$** (atoms refined anisotropically); Table XVIII, calculated and observed structure factors for **5t· CH$_2$Cl$_2$** (65 pages). Ordering information is given on any current masthead page.

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(54) It should be noted that the sequence (η-C$_5$H$_5$)Re(NO)(PPh$_3$)-(CD$_3$)^{7,15b} → **1-α-d_2** → [**2k-α-d_1**] → **2t-α-d_1** (all by procedures analogous to those given for unlabeled compounds above) constitutes a considerably easier and more direct synthesis of **2t-α-d_1**.

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(56) Ammeter, J. H.; Bürgi, H. B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.