Regiospecific and Stereospecific Reactions of $Ph_3C^+PF_6^-$ with Rhenium Alkyls $(\eta-C_5H_5)Re(NO)(PPh_3)(R)$. α- vs. β-Hydride Abstraction

William A. Kiel,[1a] Gong-Yu Lin,[1a] Gerardo S. Bodner,[1b] and J. A. Gladysz*[1a,b,2]

Contribution from the Departments of Chemistry, University of Utah, Salt Lake City, Utah 84112, and University of California, Los Angeles, California 90024.
Received December 20, 1982

Abstract: Alkyls $(\eta-C_5H_5)Re(NO)(PPh_3)(R)$ (**2**, R = CH_2CH_3; **3**, R = $CH_2CH_2CH_3$; **4**, R = $CH_2CH_2CH_2CH_2CH_3$; **5**, R = $CH_2CH(CH_3)_2$; **6**, R = $CH_2C(CH_3)_3$; **8**, R = $CH(CH_3)_2$) are synthesized in 49-82% yields by Grignard or alkyllithium attack upon the appropriate $[(\eta-C_5H_5)Re(NO)(PPh_3)(=CHR')]^+PF_6^-$ precursor. The acyl $(\eta-C_5H_5)Re(NO)(PPh_3)(COCH_2C_6H_5)$ is prepared from $(\eta-C_5H_5)Re(NO)(PPh_3)(CO_2CH_3)$ and $C_6H_5CH_2MgBr$ (80%) and is reduced with excess BH_3 to alkyl $(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2CH_2C_6H_5)$ (**9**, 64%). These alkyls, and previously synthesized (*SS,RR*)-$(\eta-C_5H_5)Re(NO)(PPh_3)(CH(CH_3)C_6H_5)$ ((*SS,RR*)-**7**) and (*SR,RS*)-**7**, are treated with $Ph_3C^+PF_6^-$ at -78 °C, and the regiochemistry and stereochemistry of hydride abstraction is examined. Results obtained by use of appropriately labeled deuterated substrates are as follows: $Ph_3C^+PF_6^-$ abstracts the *pro-R* α-hydride of **2**-**4** to give alkylidenes *sc*-$[(\eta-C_5H_5)Re(NO)(PPh_3)(=CHR')]^+PF_6^-$ (**10k**, R' = CH_3; **11k**, R' = CH_2CH_3; **12k**, R' = $CH_2CH_2CH_2CH_3$). Upon warming to 10-25 °C, these equilibrate to (90 ± 2):(10 ± 2) mixtures of *ac* (**10t**-**12t**) and *sc* Re=C geometric isomers. For **10k** → **10t**, $\Delta H^\ddagger$ = 17.4 ± 0.5 kcal/mol and $\Delta S^\ddagger$ = -7.3 ± 2.0 eu. $Ph_3C^+PF_6^-$ abstracts the β-hydride from **5** to give $[(\eta-C_5H_5)Re(NO)(PPh_3)(H_2C=C(CH_3)_2)]^+PF_6^-$ (**13**) but does not appear to abstract hydride from **6**. $Ph_3C^+PF_6^-$ abstracts β-hydrides from (*SS,RR*)-**7** and (*SR,RS*)-**7** to give (*RR,SS*)-$[(\eta-C_5H_5)Re(NO)(PPh_3)(H_2C=CHC_6H_5)]^+PF_6^-$ ((*RR,SS*)-**14**) and (*RS,SR*)-**14**, respectively. $Ph_3C^+PF_6^-$ preferentially abstracts β-hydrides from the *pro-R* methyl group of **8** to give a (92 ± 1):(8 ± 1) mixture of (*RR,SS*)-$[(\eta-C_5H_5)Re(NO)(PPh_3)(H_2C=CHCH_3)]^+PF_6^-$ ((*RR,SS*)-**15**) and (*RS,SR*)-**15**. $Ph_3C^+PF_6^-$ abstracts the *pro-R* α- and both β-hydrides from **9** to give *sc*-$[(\eta-C_5H_5)Re(NO)(PPh_3)(=CHCH_2C_6H_5)]^+PF_6^-$ (**16k**, 63%), (*RR,SS*)-**14** (18%), and (*RS,SR*)-**14** (18%). Ethylidene **10k** is stereospecificially attacked by $Li(C_2H_5)_3BD$, $C_6H_5CH_2MgBr$, C_6H_5MgBr, and PMe_3 to give (*SR,RS*)-**2**-α-d_1, (*SS,RR*)-$(\eta-C_5H_5)Re(NO)(PPh_3)(CH(CH_2C_6H_5)CH_3)$ ((*SS,RR*)-**17**), (*SS,RR*)-**7** and (*SS,RR*)-$[(\eta-C_5H_5)Re(NO)(PPh_3)(CH(^+PMe_3)CH_3)]PF_6^-$ ((*SS,RR*)-**18**), respectively. Reaction of the **10t**/**10k** equilibrium mixture with $Li(C_2H_5)_3BD$, $C_6H_5CH_2MgBr$, and PMe_3 gives corresponding adducts as (10 ± 2):(90 ● 2) diastereomer mixtures. The protons of **10t**/**10k** exchange with acetone-d_6 without added catalyst.

Introduction

Reactions of β-carbon-hydrogen bonds play a pivotal role in the chemistry of transition-metal alkyls.[3] Of these, the thermal "β-hydride elimination", $L_nMCH_2CH_2R \rightarrow L_nMH + H_2C{=}CHR$, has been the most thoroughly studied.[4] The initial steps of catalytic olefin hydrogenation closely approximate the microscopic reverse of this elimination.[5] The reaction of $L_nMCH_2CH_2R$ with $Ph_3C^+PF_6^-$ to give olefin complex $L_nM^+(H_2C{=}CHR)$ and Ph_3CH[6] is a common bimolecular transformation which involves the β-C-H bond.

Reactions of α-carbon-hydrogen bonds of transition-metal alkyls are much less common.[3,7] Initially discovered examples involved substrates in which β-C-H bonds were absent. Only a few cases exist of α-C-H bond reactivity when β-C-H bonds are present.[8] These are of special interest, since olefin metathesis (initiation)[9] and possibly some olefin polymerizations[8c,10] involve key α-C-H bond activation steps.[11]

We recently communicated the synthesis of chiral rhenium alkyls of the formula $(\eta-C_5H_5)Re(NO)(PPh_3)(R)$.[12] When R = $-CH_2CH_3$ and $-CH_2CH_2CH_3$, these underwent regiospecific α-hydride abstraction upon treatment with $Ph_3C^+PF_6^-$ to give alkylidenes $[(\eta-C_5H_5)Re(NO)(PPh_3)(=CHCH_3)]^+PF_6^-$ (**10**) and $[(\eta-C_5H_5)Re(NO)(PPh_3)(=CHCH_2CH_3)]^+PF_6^-$ (**11**), respectively. In this paper, we examine the reactions of $Ph_3C^+PF_6^-$ with a series of structurally diverse $(\eta-C_5H_5)Re(NO)(PPh_3)(R)$ alkyls[13] and thereby map the structural parameters which influence α/β regioselectivity. In a second facet of this study, we probe the *stereochemistry* of the reactions of $Ph_3C^+PF_6^-$ with $(\eta-C_5H_5)Re(NO)(PPh_3)(R)$. As will be disclosed, $Ph_3C^+PF_6^-$ exhibits a remarkable ability to discriminate between diastereotopic -H or -R groups in these hydride abstraction reactions.

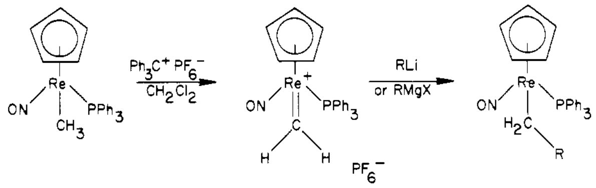
Results

I. Preparation of Alkyls $(\eta-C_5H_5)Re(NO)(PPh_3)(R)$. Primary rhenium alkyls $(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2R)$ were generally synthesized by the reaction of methylidene $[(\eta-C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$ (**1**)[14] with alkyllithium or Grignard reagents (eq 1). In most cases, **1** was generated (and used) in situ in CH_2Cl_2 at -78 °C by the reaction of $(\eta-C_5H_5)Re(NO)(PPh_3)(CH_3)$ with $Ph_3C^+PF_6^-$. Alkyls **2**-**6** (eq 1) were isolated as orange

(1) (a) University of California. (b) University of Utah.
(2) To whom correspondence should be addressed at the Department of Chemistry, University of Utah, Salt Lake City, UT 84112. Fellow of the Alfred P. Sloan Foundation (1980-1984) and Camille and Henry Dreyfus Teacher-Scholar Grant Recipient (1980-1985).
(3) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; Chapter 12.
(4) (a) Whitesides, G. M.; Gaasch, J. F.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 5258. (b) Reger, D. L.; Culbertson, E. C. *Ibid.* **1976**, *98*, 2789. (c) Kazlauskas, R. J.; Wrighton, M. S. *Ibid.* **1982**, *104*, 6005.
(5) James, B. R. *Adv. Organomet. Chem.* **1979**, *17*, 319.
(6) (a) Green, M. L. H.; Nagy, P. L. I. *J. Organomet. Chem.* **1963**, *1*, 58. (b) Laycock, D. E.; Hartgerink, J.; Baird, M. C. *J. Org. Chem.* **1980**, *45*, 291 and references therein. (c) Mink, R. I.; Welter, J. J.; Young, P. R.; Stucky, G. D. *J. Am. Chem. Soc.* **1979**, *101*, 6928.
(7) (a) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. (b) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Chem. Rev.* **1976**, *76*, 219. (c) Schrock, R. R.; Parshall, G. W. *Ibid.* **1976**, *76*, 243. (d) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1121. (e) Hayes, J. C.; Pearson, G. D. N.; Cooper, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 4648.
(8) (a) Sanders, A.; Bauch, T.; Magatti, C. V.; Lorenc, C.; Giering, W. P. *J. Organomet. Chem.* **1976**, *107*, 359. (b) Fellmann, J. D.; Schrock, R. R.; Traficante, D. D. *Organometallics* **1982**, *1*, 481. (c) Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 2331. (d) Hayes, J. C.; Cooper, N. J. *Ibid.* **1982**, *104*, 5570.
(9) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449.
(10) Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Chem. Commun.* **1978**, 604.
(11) Theoretical studies: (a) Goddard, R. J.; Hoffmann, R.; Jemmis, E. D. *J. Am. Chem. Soc.* **1980**, *102*, 7667. (b) Reetz, M. T.; Stephan, W. *J. Chem. Res., Synop.* **1981**, 44.
(12) Kiel, W. A.; Lin, G.-Y.; Gladysz, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 3299.
(13) (a) A detailed study of the reaction of $Ph_3C^+PF_6^-$ with $(\eta-C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)$ is reported separately.[13b] (b) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865.
(14) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

0002-7863/83/1505-4958$01.50/0

crystals or powders in 50–82% yields. Small amounts of (η-C_5H_5)Re(NO)(PPh_3)(CH_3) accompanied the formation of **5** and **6**, even when isolated **1** was employed.



(1)

1

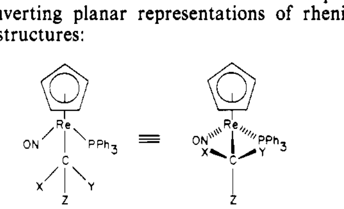
2:	R = CH_3;	77%
3:	R = CH_2CH_3;	82%
4:	R = $CH_2CH_2CH_2CH_3$;	70%
5:	R = $CH(CH_3)_2$;	52%
6:	R = $C(CH_3)_3$;	50%

Secondary rhenium alkyls (η-C_5H_5)Re(NO)(PPh_3)(CHRR′) were prepared by the reaction of alkyllithium reagents R′Li with substituted alkylidenes [(η-C_5H_5)Re(NO)(PPh_3)(=CHR)]$^+PF_6^-$. The synthesis of the (*SS*,*RR*) and (*SR*,*RS*) diastereomers[15] of (η-C_5H_5)Re(NO)(PPh_3)($CH(CH_3)C_6H_5$) ((*SS*,*RR*)-**7**, (*SR*,*RS*)-**7**) by CH_3Li attack upon benzylidene [(η-C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]$^+PF_6^-$ has been previously described.[13b] Isopropyl complex (η-C_5H_5)Re(NO)(PPh_3)($CH(CH_3)_2$) (**8**) was synthesized in 49% yield by the reaction of CH_3Li with ethylidene [(η-C_5H_5)Re(NO)(PPh_3)(=$CHCH_3$)]$^+PF_6^-$ (**10**). The somewhat low yield of **8** may be due to competing deprotonation of **10** to the vinyl complex (η-C_5H_5)Re(NO)(PPh_3)(CH=CH_2).[16]

Phenethyl complex (η-C_5H_5)Re(NO)(PPh_3)($CH_2CH_2C_6H_5$) (**9**) was isolable in at best 20% yield from the reaction of $C_6H_5CH_2Li$ or $C_6H_5CH_2MgBr$ with **1** in CH_2Cl_2. It is perhaps surprising that **9** (or even **2–6**, eq 1) is obtained at all, since CH_2Cl_2 is normally too reactive a solvent for RLi or RMgX additions. Methylidene **1** is not soluble in Grignard-inert solvents such as hydrocarbons or ethers. To avoid these problems, the alternative synthesis of **9** shown in eq 2 was devised. The readily available, benzene-soluble "methyl ester" (η-C_5H_5)Re(NO)(PPh_3)(CO_2CH_3)[17] was treated with $C_6H_5CH_2MgBr$. The crystalline, yellow-organge acyl (η-C_5H_5)Re(NO)(PPh_3)($COCH_2C_6H_5$) was subsequently isolated in 80% yield. Reduction of this acyl with excess BH_3·THF[14,18] gave alkyl **9** in 64% yield.

Alkyls **2–9** were characterized by ^1H NMR, ^{13}C NMR, IR, and mass spectrometry. These data are summarized in Tables I and II.

(15) (a) The absolute configuration at rhenium is specified first and is assigned according to the Baird/Sloan modification of the Cahn-Ingold-Prelog priority rules.[15b,c] By this system, the η-C_5H_5 ligand is considered to be a pseudoatom of atomic number 5 × 6 = 30. We employ the following convention for converting planar representations of rhenium alkyls into three-dimensional structures:

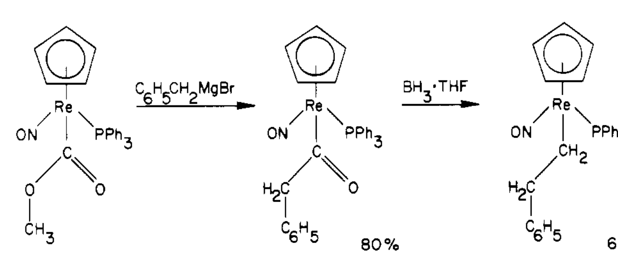


Hence all alkyl complexes in this manuscript have an *S* configuration at rhenium. Note however that an olefin complex of the same relative configuration would be *R*, since η^2-RR′C=CH″R‴ (12) > NO (7). The ligand-based element of chirality in the styrene and propylene complexes is designated *R* or *S* following the convention of Paiaro and Panunzi:[15d] the complex is drawn in its metallocyclopropane resonance form and the Cahn–Ingold–Prelog rules are applied to the "new" asymmetric carbon. We thank a reviewer and Dr. Kurt Loening (Chemical Abstracts Service) for their assistance with this point of nomenclature. (b) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598. (c) Sloan, T. *Top. Stereochem.* **1981**, *12*, 1. (d) Paiaro, G.; Panunzi, A. *J. Am. Chem. Soc.* **1964**, *86*, 5148.

(16) The synthesis and some very unusual properties of this class of compounds (which react with rhenium alkylidene complexes) will be reported shortly: Hatton, W. G.; Gladysz, J. A. *J. Am. Chem. Soc.*, submitted for publication.

(17) Merrifield, J. H.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1204.

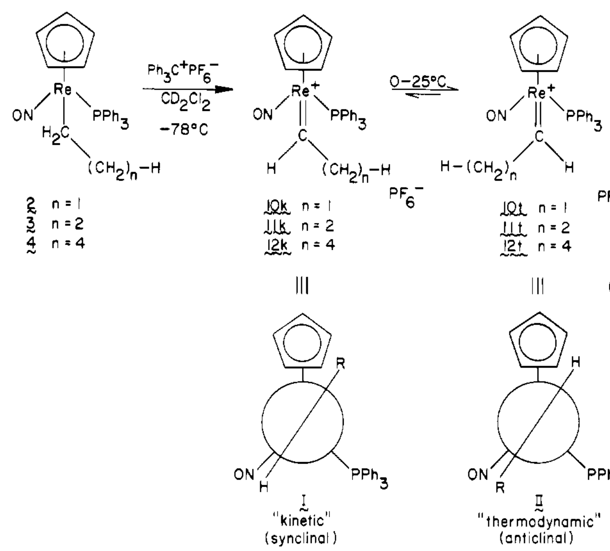
(18) Van Doorn, J. A.; Masters, C.; Volger, H. C. *J. Organomet. Chem.* **1976**, *105*, 245.



(2)

9

II. Regiochemistry of the Reaction of Alkyls (η-C_5H_5)Re(NO)(PPh_3)(R) with $Ph_3C^+PF_6^-$. Unbranched primary alkyls **2–4** were treated with 1.1 equiv of $Ph_3C^+PF_6^-$ at −78 °C in CD_2Cl_2. Proton NMR monitoring (−70 °C) showed the immediate, quantitative, *regiospecific* formation of alkylidenes [(η-C_5H_5)Re(NO)(PPh_3)(=$CHCH_3$)]$^+PF_6^-$ (**10k**), [(η-C_5H_5)Re(NO)(PPh_3)(=$CHCH_2CH_3$)]$^+PF_6^-$ (**11k**), and [(η-C_5H_5)Re(NO)(PPh_3)(=$CHCH_2CH_2CH_2CH_3$)]$^+PF_6^-$ (**12k**) (eq 3). When **10k–12k** were warmed to 0–25 °C in CD_2Cl_2, they diminished as ^1H NMR resonances ascribable to *new* alkylidene complexes (**10t–12t**) appeared. By analogy to structures established for benzylidene [(η-C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]$^+PF_6^-$,[13b] the two forms of **10–12** are assigned as *geometric isomers* which differ in substituent orientation about the Re=C bond. The **k** ("kinetic") isomers have the *synclinal* (*sc*) conformation I (Newman projection down the C=Re bond) and the **t** ("thermodynamic") isomers have the less congested *anticlinal* (*ac*) conformation II.[19]



(3)

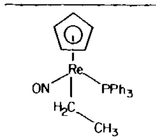
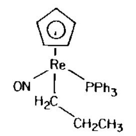
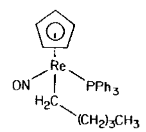
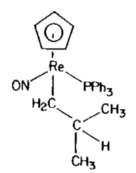
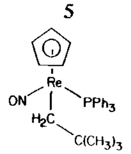
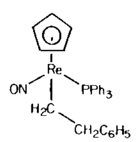
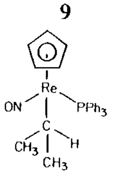
The equilibrium **k/t** ratios were measured by ^1H NMR and found to be (90 ± 2):(10 ± 2) for **10t/10k** and **12t/12k** and (91 ± 2):(9 ± 2) for **11t/11k**. Recrystallized products were obtained in 75% (**10**), 78% (**11**), and 56% (**12**) yields. When these were dissolved in CD_2Cl_2 at −78 °C, **t/k** ratios were within a few percent of the equilibrium values.

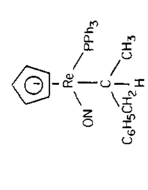
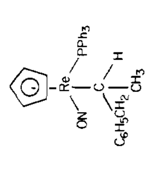
The rate of isomerization of **10k** to **10t** was measured at temperatures ranging from −15 to +14 °C, as summarized in Table III. These data yielded the activation parameters $\Delta H^{\ddagger}$ = 17.4 ± 0.5 kcal/mol and $\Delta S^{\ddagger}$ = −7.3 ± 2.0 eu.

A sample of (η-C_5H_5)Re(NO)(PPh_3)(CD_2CH_3) (**2**-α-d_2) was synthesized from CH_3Li and [(η-C_5H_5)Re(NO)(PPh_3)(=CD_2)]$^+PF_6^-$ (**1**-α-d_2).[11,12b] Reaction of **2**-α-d_2 with $Ph_3C^+PF_6^-$ gave exclusively [(η-C_5H_5)Re(NO)(PPh_3)(=$CDCH_3$)]$^+PF_6^-$ (**10**-α-d_1). Thus hydride abstraction from **2** occurs regiospecifically and without intervening 1,2-hydride migration. The triphenylmethane byproduct was isolated and found by mass spectrometry

(19) A synclinal alkylidene conformer is one in which the highest priority[15] groups on Re(C_5H_5) and C(alkyl) define a 60 ± 30° torsion angle. An anticlinal conformer is one in which the highest priority groups define a 120 ± 30° torsion angle. Identical terminology can be used to designate olefin complex rotamers. See section E-5.6, p 24: *Pure Appl. Chem.* **1976**, *45*, 11.

Table I. Spectroscopic Data on Rhenium Alkyls $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(R)$

alkyl complex	IR, ν_{NO} (cm^{-1}, CH_2Cl_2)	^1H NMR,[a,b] δ: Re–CH_α	^1H NMR,[a,b] δ: C_5H_5	^1H NMR,[a,b] δ: other	^{13}C NMR,[b,c] ppm: Re–C_α	^{13}C NMR,[b,c] ppm: C_5H_5	^{13}C NMR,[b,c] ppm: other
 **2**	1614	H_α (m, 1 H), 1.68; $H_{\alpha'}$ (m, 1 H), 2.10	4.92 (s, 5 H)	CH_3 (dd, 3 H), 1.58 ($J_{^1H_\beta-^1H_\alpha} = J_{^1H_\beta-^1H_{\alpha'}}$ = 6.6 Hz); phenyl (m, 15 H), 7.54–7.72	−17.52 (s)[d]	89.48	CH_3, 25.98, phenyl, 128.19 (d, $J_{^{13}C-^{31}P}$ = 10.5 Hz), 129.82, 133.59 (d, J = 10.4 Hz), 136.67 (d, J = 49.6 Hz)
 **3**	1618	H_α (m, overlap with H_β)	4.92 (s, 5 H)	CH_3 (t, 3 H), 0.83 ($J_{^1H_\gamma-^1H_\beta}$ = 7.0 Hz); H_α and H_β (m, 4 H), 1.64–2.03; phenyl (m, 15 H), 7.38–7.57	−6.16 (d, $J_{^{13}C-^{31}P}$ = 5.2 Hz)	89.50	CH_3, 20.04; C_β, 34,71; phenyl, 128.18 (d, $J_{^{13}C-^{31}P}$ = 10.3 Hz), 129.84, 133.63 (d, J = 10.4 Hz), 136.66 (d, J = 50.5 Hz)
 **4**	1621	H_α (overlap with alkyl protons), $H_{\alpha'}$ (m, 1 H), 2.08	4.89 (s, 5 H)	CH_3 (t, 3 H), 0.83 ($J_{^1H_\epsilon-^1H_\delta}$ = 7.0 Hz); 1.20 (m, 4 H); 1.70 (m, 3 H); phenyl (m, 15 H), 7.35–7.43	9.30 (d, $J_{^{13}C-^{31}P}$ = 4.5 Hz)	89.49	C_β–C_ϵ, 14.32, 22.42, 37.93, 41.39; phenyl, 128.17 (d, $J_{^{13}C-^{31}P}$ = 10.4 Hz), 129.79, 133.64 (d, J = 10.4 Hz), 136.72 (d, J = 52.1 Hz)
 **5**	1620	H_α (m, overlap with H_β), $H_{\alpha'}$ (m, 1 H), 2.03	4.89 (s, 5 H)	CH_3 (d, 6 H), 0.91 ($J_{^1H_\gamma-^1H_\beta}$ = 5.8 Hz); H_α and H_β (m, 2 H), 1.77; phenyl (m, 15 H), 7.17–7.56	2.61 (d, $J_{^{13}C-^{31}P}$ = 5.4 Hz)	89.70	CH_3's, 25.82, 28.09; C_β, 39.14 (d, $J_{^{13}C-^{31}P}$ = 2.7 Hz), phenyl, 128.18 (d, J = 9.5 Hz), 129.86, 133.71 (d, J = 9.5 Hz), 136.60 (d, J = 51.5 Hz)
 **6**	1621	H_α (d, 1 H), 1.77 ($J_{^1H_\alpha-^1H_{\alpha'}}$ = 12.8 Hz), $H_{\alpha'}$ (dd, 1 H), 2.60 ($J_{^1H_{\alpha'}-^1H_\alpha}$ = $J_{^1H_{\alpha'}-^{31}P}$ = 12.8 Hz)	4.91 (s, 5 H)	CH_3 (s, 9 H), 0.91; phenyl (m, 15 H), 7.26–7.37	8.00 (d, $J_{^{13}C-^{31}P}$ = 4.1 Hz)	89.74	CH_3, 33.89; C_β, 38.57 (d, $J_{^{13}C-^{31}P}$ = 2.3 Hz); phenyl, 128.20 (d, J = 10.5 Hz), 129.89 (d, J = 1.9 Hz), 133.85 (d, J = 10.6 Hz) 136.55 (d, J = 51.5 Hz)
 **9**	1624	H_α (m, overlap with H_β)	4.90 (s, 5 H)	H_α and H_β, 1.91 (m, 1 H), 2.96 (m, 2 H); phenyl (m's, 20 H), 7.01–7.23 and 7.36–7.42	−7.30 (d, $J_{^{13}C-^{31}P}$ = 5.2 Hz)	89.59	C_β, 47.79; phenyl, 124.63, 127.93, 128.24 (d, $J_{^{13}C-^{31}P}$ = 10.6 Hz), 129.91, 133.64 (d, J = 10.7 Hz), 136.55 (d, J = 51.6 Hz), 149.27
 **8**	1625	2.78 (m, 1 H)	4.90 (s, 5 H)	CH_3 (d, 3 H), 1.14 ($J_{^1H_\beta-^1H_\alpha}$ = 7.0 Hz); CH_3' (d, 3 H), 1.65 ($J_{^1H_{\beta'}-^1H_\alpha}$ = 7.0 Hz); phenyl (m, 15 H), 7.37–7.40	2.14 (d, $J_{^{13}C-^{31}P}$ = 4.1 Hz)	90.19	CH_3's, 33.26, 36.63; phenyl 128.18 (d, $J_{^{13}C-^{31}P}$ = 9.5 Hz), 129.79, 133.64 (d, J = 10.9 Hz), 136.66 (d, J = 51.4 Hz)

 (SS,RR)-17	1622	3.16 (m, 1 H)	4.93 (s, 5 H)	CH_3 (d, 3 H), 0.97 ($J_{^1H-^1H_\alpha}$ = 7.2 Hz); H_β (dd, 1 H), 2.75 ($J_{^1H_\beta-^1H_{\beta'}}$ = 13.0 Hz, $J_{^1H_\beta-^1H_\alpha}$ = 10.2 Hz); $H_{\beta'}$ (dd, 1 H), 3.16 ($J_{^1H_{\beta'}-^1H_\beta}$ = 13.0 Hz, $J_{^1H_{\beta'}-^1H_\alpha}$ = 4.0 Hz); phenyl (m's, 20 H), 7.02-7.42	4.92 (d, $J_{^{13}C-^{31}P}$ = 3.7 Hz)	90.20	CH_3, 28.56; CH_2, 56.11; phenyl, 124.56, 127.54, 128.18 (d, $J_{^{13}C-^{31}P}$ = 9.4 Hz), 128.97, 129.84, 133.59 (d, J = 9.8 Hz), 136.29 (d, J = 51.3 Hz), 146.21
 (SR,RS)-17	1626	2.99 (m, 1 H)	4.97 (s, 5 H)	CH_3 (d, 3 H), 1.40 ($J_{^1H-^1H_\alpha}$ = 6.7 Hz); H_β (dd, 1 H), 2.05 ($J_{^1H_\beta-^1H_{\beta'}}$ = $J_{^1H_\beta-^1H_\alpha}$ = 12.8 Hz); $H_{\beta'}$ (dd, 1 H), 3.06 ($J_{^1H_{\beta'}-^1H_\beta}$ = 12.8 Hz, $J_{^1H_{\beta'}-^1H_\alpha}$ = 3.0 Hz); phenyl (m's, 20 H), 6.35 and 7.02-7.43	5.45 (d, $J_{^{13}C-^{31}P}$ = 4.0 Hz)	89.93	CH_3, 31.39; CH_2, 53.71; phenyl, 124.68, 127.54, 128.36 (d, $J_{^{13}C-^{31}P}$ = 8.8 Hz), 129.87, 133.72 (d, J = 10.7 Hz), 136.20 (d, J = 50.4 Hz), 145.88

[a] 200 MHz. [b] In $CDCl_3$ and referenced to internal $(CH_3)_4Si$. [c] 50 MHz. [d] Broad singlet with line width ~ 5 Hz.

Table II. 16-eV Mass Spectra of Rhenium Alkyls $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(R)$

complex	ions, m/e for ^{187}Re (% of base peak) M$^+$	$M^+ - R$	PPh_3^+	other
2 (R = CH_2CH_3)	573 (100)	544 (18.9)	262 (46.8)	545 (24.4)[a] 467 (11.0)[b] 263 (41.2)
3 (R = $CH_2CH_2CH_3$)	587 (100)	544 (27.6)	262 (78.4)	545 (53.9)[a] 467 (20.4)[b] 263 (71.8)
4 (R = $(CH_2)_4CH_3$)	615 (90.4)	544 (28.9)	262 (100)	545 (54.3)[a] 467 (19.1)[b] 263 (82.1)
5 (R = $CH_2CH(CH_3)_2$)	601 (100)	544 (56.7)	262 (61.5)	545 (76.0)[a] 467 (57.4)[b] 399 (36.8) 263 (83.3)
6 (R = $CH_2C(CH_3)_3$)	615 (35.3)	544 (12.0)	262 (36.0)	558 (100)[c] 263 (7.1)
8 (R = $CH(CH_3)_2$)	587 (41.6)	544 (70.6)	262 (71.9)	545 (100)[a] 467 (48.2)[b] 263 (98.9)
9 (R = $CH_2CH_2C_6H_5$)	649 (44.6)	544 (14.9)	262 (58.4)	558 (100)[c] 545 (47.3)[a] 467 (31.5)[b] 387 (16.4) 263 (47.9)

[a] Tentatively assigned as $[(C_5H_5)Re(NO)(PPh_3)(H)]^+$; intensity not corrected for $M^+ - R$ (m/e 544) isotope peak. [b] Assigned as $M^+ - R - C_6H_5$ based upon spectra of $P(C_6D_5)_3$-labeled samples. [c] Assigned as $[(C_5H_5)Re(NO)(PPh_3)(CH_2)]^+$.

Table III. Rate Constants for the Re=C Bond Rotation **10k** → **10t** in CD_2Cl_2

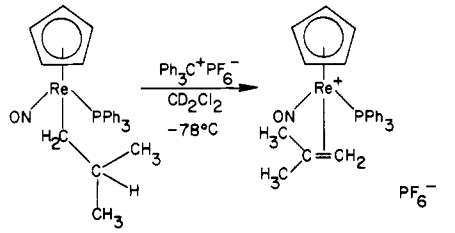
entry	temp, ±0.2 °C	10^4k_1,[a] s^{-1}
1	14.0	76.6 ± 7.0
2	9.0	42.1 ± 2.5
3	4.0	26.3 ± 0.9
4	−1.0	15.3 ± 1.5
5	−5.0	7.39 ± 0.20
6	−11.0	3.60 ± 0.30
7	−15.0	2.38 ± 0.24

[a] The forward rate constant, k_1, was obtained by plotting log $([\mathbf{10k}]_{equil} - [\mathbf{10k}]_t)$ vs. time. The variable k_{-1} was eliminated from the slope, $-0.4343\,(k_1 + k_{-1})$, by substituting k_1/K: Capellos, C.; Bielski, B. H. J. "Kinetic Systems"; Wiley: New York, 1972; Chapter 8.

to be a (96 ± 1):(4 ± 1) Ph_3CD/Ph_3CH mixture. The small amount of Ph_3CH cannot be taken as evidence against regioselectivity, since similar quantities of Ph_3CH are also formed in the reaction of $Ph_3C^+PF_6^-$ with $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CD_3)$.[13b] We believe that the bulk of the Ph_3CH arises from adventitious H^- sources and/or impurities in the $Ph_3C^+PF_6^-$.

A 50:50 mixture of **2** and **2**-α-d_2 was treated with 0.20 equiv (20 mol %) of $Ph_3C^+PF_6^-$ at −78 °C. The resulting triphenylmethane byproduct was isolated and found to be a (82 ± 2):(18 ± 2) Ph_3CH/Ph_3CD mixture (average of two runs). To ensure that this competition experiment gave a reasonably quantitative measure of the primary deuterium isotope effect, three controls were conducted. First, triphenylmethane was isolated from an identical, side-by-side reaction of **2**-α-d_2 and $Ph_3C^+PF_6^-$ (0.20 equiv). A (91 ± 2):(9 ± 2) Ph_3CD/Ph_3CH ratio was found (average of two runs). Second, 0.20 equiv of a (88 ± 1):(12 ± 1) Ph_3CD/Ph_3CH mixture was added to a **10t**/**10k** thermodynamic mixture in CH_2Cl_2. After 22 h, the triphenylmethane was recovered and found to be a (87 ± 1):(13 ± 1) Ph_3CD/Ph_3CH mixture. Third, no detectable H/D exchange (<4%) occurred between **10t**/**10k** and **2**-α-d_2 (each 0.022 M) over the course of 10 h at 25 °C in CH_2Cl_2. These observations establish the integrity of the Ph_3CD and **2**-α-d_2 labels in the competition experiment. Hence k_H/k_D is in the range 2–4.

Reaction of $Ph_3C^+PF_6^-$ with the isobutyl alkyl **5** (eq 4) was examined next. Proton NMR monitoring (−70 °C) showed the immediate and quantitative formation of isobutylene complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}C(CH_3)_2)]^+PF_6^-$ (**13**). A bench top reaction gave **13** as cream crystals in 70% yield. Byproduct Ph_3CH was isolated from the reaction of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CD_2CH(CH_3)_2)$ (**5**-α-d_2) with $Ph_3C^+PF_6^-$. Mass spectral analysis indicated Ph_3CD to be present at natural abundance level. Thus **13** is formed via a regiospecific β-hydride abstraction.

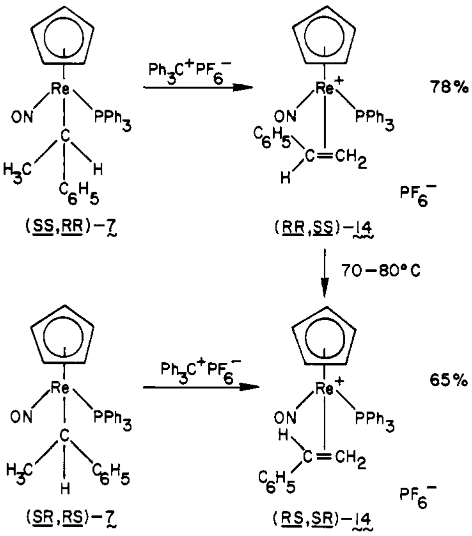


(4)

5 13

Reaction of the neopentyl complex $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C(CH_3)_3)$ (**6**) with $Ph_3C^+PF_6^-$ was ^{1}H NMR monitored at −70 °C. Extensive peak broadening was observed, but no alkylidene products could be detected. Triphenylmethane was detected in some reactions, but it was not consistently formed.

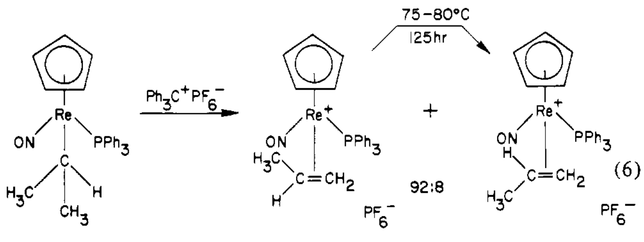
Reactions of the secondary rhenium alkyls with $Ph_3C^+PF_6^-$ were investigated next. Reaction of diastereometrically pure (*SS*,*RR*)-$(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH(CH_3)C_6H_5)$ ((*SS*,*RR*)-**7**) with $Ph_3C^+PF_6^-$ gave (as assayed in situ) a diastereomerically pure styrene complex (eq 5). As will be rationalized in the Discussion, the structure of this β-hydride abstraction product was assigned as (*RR*,*SS*)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHC_6H_5)]^+PF_6^-$ ((*RR*,*SS*)-**14**).[15] Subsequent $CHCl_3$/ether recrystallization gave (*RR*,*SS*)-**14** as yellow crystals in 78% yield.



(5)

Similarly, reaction of (*SR*,*RS*)-**7** (eq 5) with $Ph_3C^+PF_6^-$ gave exclusively the other styrene complex diastereomer (*RS*,*SR*)-**14**. A sample of (*RR*,*SS*)-**14** was heated in CD_3CN at 70–80 °C. After 24 h, a ca. 1:2:1 mixture of (*RR*,*SS*)-**14**/(*RS*,*SR*)-**14**/$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(NCCD_3)]^+PF_6^-$ [20] had formed. Continued heating resulted in the complete disappearance of (*RR*,*SS*)-**14**, and after ca. 50 h only the CD_3CN complex was present. Thus (*RS*,*SR*)-**14** is the more stable styrene complex diastereomer.

Reaction of the isopropyl complex $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH(CH_3)_2)$ (**8**) with $Ph_3C^+PF_6^-$ also gave β-hydride abstraction (eq 6). Proton NMR analysis of the crude reaction mixture showed a (92 ± 1):(8 ± 1) mixture of diastereomeric propylene complexes which were assigned (as described in the Discussion) the structures (*RR*,*SS*)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH_3)]^+PF_6^-$ ((*RR*,*SS*)-**15**) and (*RS*,*SR*)-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCH_3)]^+PF_6^-$ ((*RS*,*SR*)-**15**), respectively.[15] Byproduct Ph_3CH was isolated from the reaction of $Ph_3C^+PF_6^-$ with $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CD(CH_3)_3)$ (**8**-α-d_1). Mass spectral analysis showed Ph_3CD was present at natural abundance level.

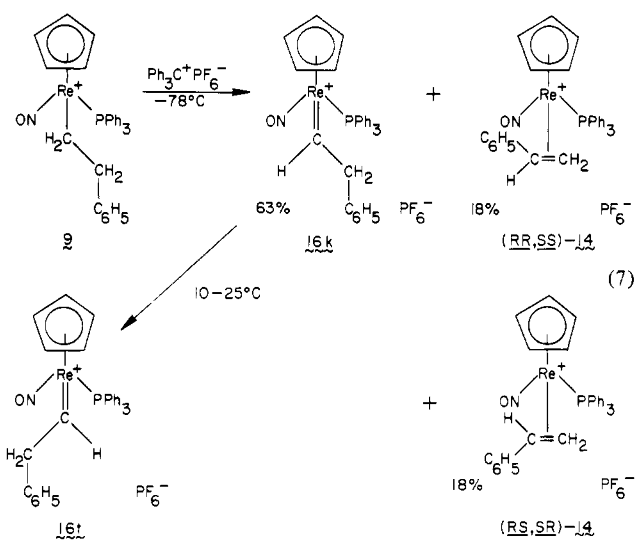


(6)

8 (RR,SS)-15 (RS,SR)-15

Diastereomerically pure (*RR*,*SS*)-**15** was obtained by recrystallizing the eq 4 reaction mixture from $CHCl_3$/ether (yellow prisms, 72%). A sample of (*RR*,*SS*)-**15** was heated for 125 h at 75–80 °C in CH_3CN. Proton NMR analysis of an aliquot of this sample indicated that a ca. 79:12:9 mixture of (*RS*,*SR*)-**15**/(*RR*,*SS*)-**15**/$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(NCCH_3)]^+PF_6^-$ had formed. Workup and $CHCl_3$/ether recrystallization gave a (95 ± 1):(5 ± 1) (*RS*,*SR*)-**15**/(*RR*,*SS*)-**15** mixture. Thus (*RS*,*SR*)-**15** is the more stable propylene complex diastereomer.

Reaction of the β-phenethyl complex $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_2C_6H_5)$ (**9**) with $Ph_3C^+PF_6^-$ (CD_2Cl_2, −78 °C) was monitored by ^{1}H NMR at −63 °C (eq 7). The α-hydride abstraction product alkylidene *sc*-$[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH_2C_6H_5)]^+PF_6^-$ (**16k**) formed in 63% yield. The β-hydride abstraction products, styrene complexes (*RR*,*SS*)-**14** and (*RS*,*SR*)-**14**, were present in 18% yield each. Upon warming to room temperature, a new alkylidene geometric isomer (**16t**) formed as **16k** disappeared. Extensive decomposition of **16t** occurred over several hours at 25 °C.



(7)

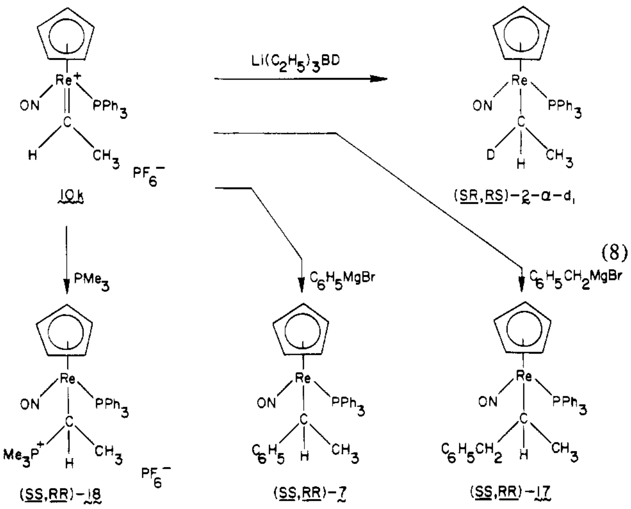
Cationic alkylidene and olefin complexes **10**–**15** were characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy. These data are summarized in Table IV. The NMR spectral properties of the olefin complexes closely resemble those of related iron complexes.[21]

(20) Merrifield, J. H.; Lin, G-Y.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.*, in press.

(21) Characteristic upfield shifts of the olefin ^{1}H and ^{13}C NMR chemical shifts are observed, and the larger olefinic $^3J_{^1H-^1H}$ are assigned as J_{trans}, as established in the following studies of $[(\eta\text{-}C_5H_5)Fe(CO)(L)(HRC{=}CR'R'')]^+$: (a) L = CO: Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495. Laycock, D. E.; Baird, M. C. *Inorg. Chim. Acta* **1980**, *42*, 263. (b) L = PPh_3: Reger, D. L.; Coleman, C. J.; McElligott, P. J. *J. Organomet. Chem.* **1979**, *171*, 73. (c) L = $P(OPh_3)_3$: Reger, D. L.; Coleman, C. J. *Inorg. Chem.* **1979**, *18*, 3155.

III. Origin of Diastereoselectivity in the Reactions of Alkyls (η-C_5H_5)Re(NO)(PPh_3)(R) with $Ph_3C^+PF_6^-$. In most of the preceding reactions of alkyls (η-C_5H_5)Re(NO)(PPh_3)(R) with $Ph_3C^+PF_6^-$, one of two possible products formed stereospecifically. Furthermore, the less stable diastereomer was often the kinetic product. In order to obtain substrates which were appropriately labeled to test the origins of this diastereoselectivity, we examined the reaction of ethylidene **10** with a series of nucleophiles.

Ethylidene **10k** was treated with $Li(C_2H_5)_3BD$ at −78 °C. Ethyl complex **2**-α-d_1 was subsequently isolated in 70% yield. The δ 2.10 ^1H NMR resonance normally present in **2** (Table I) was not detected (≤1% of normal intensity) in this material. As will be rationalized in the Discussion, the (*SR,RS*) configurations were assigned to this **2**-α-d_1 diastereomer.



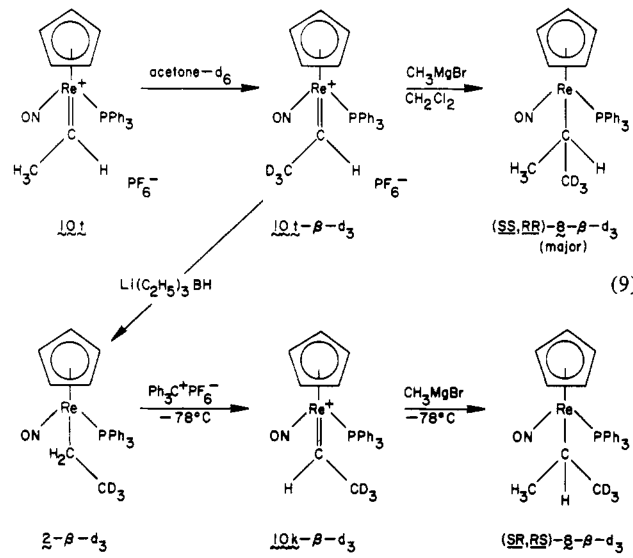
(8)

Reactions of **10k** with $C_6H_5CH_2MgBr$, C_6H_5MgBr, and PMe_3 were similarly stereospecific, as assyed by ^1H NMR of the reaction mixture either in situ or prior to any recrystallizations. Adducts (*SS,RR*)-(η-C_5H_5)Re(NO)(PPh_3)(CH($CH_2C_6H_5$)CH_3) ((*SS,RR*)-**17**), (*SS,RR*)-**7**, and (*SS,RR*)-[(η-C_5H_5)Re(NO)(PPh_3)(CH($^+PMe_3$)CH_3)]PF_6^- ((*SS,RR*)-**18**) were obtained in 53%, 76%, and 70% yields, respectively (eq 8). Spectral properties of **17** are included in Table I, and those of **18** are given in the Experimental Section.

An identical series of reactions were attempted with the (90 ± 2):(10 ± 2) **10t**/**10k** thermodynamic mixture. In each case, the major diastereomer formed was the opposite of the one obtained in eq 8. Reaction with $Li(C_2H_5)_3BD$ gave a (89 ± 2):(11 ± 2) (*SS,RR*)-**2**-α-d_1/(*SR,RS*)-**2**-α-d_1 mixture, as assayed by the relative areas of the two H_α NMR resonances. Addition of $C_6H_5CH_2MgCl$ gave a (91 ± 2):(9 ± 2) (*SR,RS*)-**17**/(*SS,RR*)-**17** mixture (84% yield), as assayed by the relative areas of the two C_5H_5 ^1H NMR resonances. Similarly, PMe_3 gave a (90 ± 2):(10 ± 2) (*SR,RS*)-**18**/(*SS,RR*)-**18** mixture (74% yield). However, no adduct was obtained when C_6H_5MgBr was added to the **10t**/**10k** thermodynamic mixture.

A route to **10**-β-d_3 was sought in order that the two diastereomers of **8**-β-d_3 might be synthesized. Surprisingly, the β-protons of a **10t**/**10k** equilibrium mixture exchanged with acetone-d_6 without added catalyst (eq 9). Over the course of 4 days at room temperature, 81–>98% deuterium incorporation could be achieved. Reaction of a 81% labeled **10t**-β-d_3/**10k**-β-d_3 thermodynamic mixture with CH_3MgBr gave a (91 ± 2):(9 ± 2) (*SS,RR*)-**8**-β-d_3/(*SR,RS*)-**8**-β-d_3 mixture (eq 9). Addition of $Li(C_2H_5)_3BH$ to a >98% labeled **10t**-β-d_3/**10k**-β-d_3 mixture afforded 2-β-d_3. Sequential treatment of **2**-β-d_3 with $Ph_3C^+PF_6^-$ (−78 °C) and CH_3MgBr gave diastereomerically pure (*SR,RS*)-**8**-β-d_3 (eq 9).

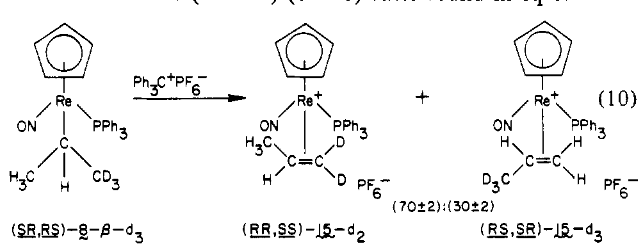
The stereochemistry of the reaction of **2** with $Ph_3C^+PF_6^-$ was examined by using the α-d_1-labeled substrates. Treatment of (*SR,RS*)-**2**-α-d_1 with $Ph_3C^+PF_6^-$ in CD_2Cl_2 at −78 °C gave a (98 ± 2):(2 ± 2) **10k**-α-d_0/**10k**-α-d_1 mixture, as assayed by careful integration of the C_5H_5 and residual Re=C*H*CH_3 ^1H NMR



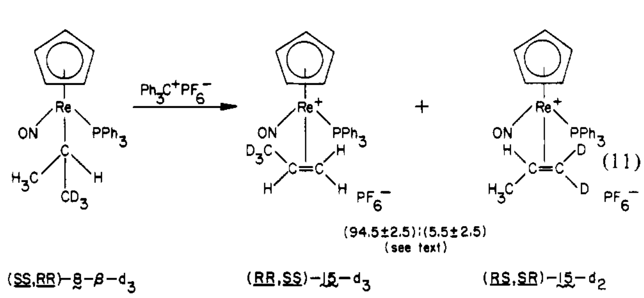
(9)

resonances. Similarly, reaction of the (89 ± 2):(11 ± 2) (*SS,RR*)-**2**-α-d_1/(*SR,RS*)-**2**-α-d_1 mixture with $Ph_3C^+PF_6^-$ gave a (89 ± 2):(11 ± 2) **10k**-α-d_1/**10k**-α-d_0 mixture. These data indicate that the hydride (or deuteride) in the *pro-R* α-position of **2** is preferentially abstracted.

The stereochemistry of the reaction of **8** with $Ph_3C^+PF_6^-$ was examined using the β-d_3-labeled substrates. As shown in eq 10, reaction of >98% labeled, diastereomerically pure (*SR,RS*)-**8**-β-d_3 with $Ph_3C^+PF_6^-$ gave the diastereomeric propylene complexes (*RR,SS*)-**15**-d_2 and (*RS,SR*)-**15**-d_3. Close examination of the ^1H NMR spectrum showed that the C=CH_2 resonances normally found for (*RR,SS*)-**15** and the −CH_3 resonance normally found for (*RS,SR*)-**15** were absent. The (70 ± 2):(30 ± 2) product ratio differed from the (92 ± 1):(8 ± 1) ratio found in eq 6.



(10)

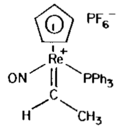
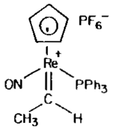
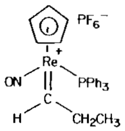
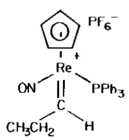
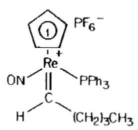
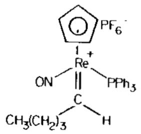
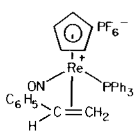


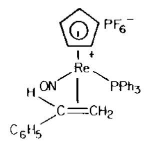
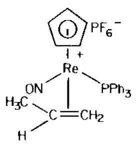
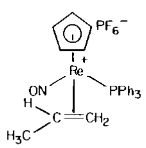
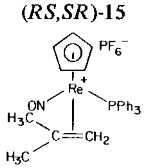
(11)

Reaction of the 81% labeled (91 ± 2):(9 ± 2) (*SS,RR*)-**8**-β-d_3/(*SR,RS*)-**8**-β-d_3 mixture with $Ph_3C^+PF_6^-$ gave (*RR,SS*)-[(η-C_5H_5)Re(NO)(PPh_3)(H_2C=$CHCD_3$)]$^+PF_6^-$ ((*RR,SS*)-**15**-d_3) as the major product. This was accompanied by much smaller amounts of (*RS,SR*)-[(η-C_5H_5)Re(NO)(PPh_3)(D_2C=$CHCH_3$)]$^+PF_6^-$ ((*RS,SR*)-**15**-d_2) and the products (from (*SR,RS*)-**8**-β-d_3) shown in eq 10. The total ratio of (*RR,SS*)-**15**/(*RS,SR*)-**15** diastereomers was (92 ± 2):(8 ± 2). After the contribution of eq 10 was subtracted, it was calculated that the primary products from (*SS,RR*)-**8**-β-d_3—(*RR,SS*)-**15**-d_3 and (*RS,SR*)-**15**-d_2—had formed in a (94.5 ± 2.5):(5.5 ± 2.5) ratio (eq 11).

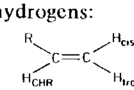
These data indicate that hydride (or deuteride) is preferentially abstracted from the *pro-R* methyl group of **8**. An isotope effect

Table IV. Spectroscopic Data on Alkylidene and Olefin Complexes

complex	IR,[a] ν_{NO} (cm^{-1})	^1H NMR,[b,c] δ			^{13}C NMR,[d,e] ppm		
		Re–C*H*	C_5H_5	other	Re–*C*	C_5H_5	other
 **10k**		16.27[f] (q, 1 H, $J_{^1H_\alpha-^1H_\beta}$ = 8.0 Hz)	5.92 (s, 5 H)	CH_3 (d, 3 H), 2.68 ($J_{^1H_\beta-^1H_\alpha}$ = 8.0 Hz); phenyl obscured by Ph_3CH			
 **10t**	1720	15.82 (q, 1 H, $J_{^1H_\alpha-^1H_\beta}$ = 8.0 Hz)	5.94 (s, 5 H)	CH_3 (d, 3 H), 2.53 ($J_{^1H_\beta-^1H_\alpha}$ = 8.0 Hz); phenyl (m, 15 H) 7.28–7.62	310.71 (br s)	100.72	CH_3, 44.00; phenyl, 130.08 (d, $J_{^{13}C-^{31}P}$ = 10.8 Hz), 133.00, 133.83 (d, J = 11.9 Hz), ipso carbon not observed
 **11k**		15.98[f] (dd, 1 H, $J_{^1H_\alpha-^1H_\beta}$ = $J_{^1H_\alpha-^1H_{\beta'}}$ = 8.0 Hz)	5.94 (s, 5 H)	H_β (m, 1 H), 2.59; $H_{\beta'}$ (m, 1 H), 3.20; CH_3 (dd, 3 H), 0.87 ($J_{^1H_\gamma-^1H_\beta}$ = $J_{^1H_\gamma-^1H_{\beta'}}$ = 7.1 Hz); phenyl obscured by Ph_3CH			
 **11t**	1718	15.55 (dd, 1 H, $J_{^1H_\alpha-^1H_\beta}$ = $J_{^1H_\alpha-^1H_{\beta'}}$ = 8.0 Hz)	5.93 (s, 5 H)	H_β (m, 1 H), 2.64; $H_{\beta'}$ (m, 1 H), 3.18; CH_3 (dd, 3 H), 0.79 ($J_{^1H_\gamma-^1H_\beta}$ = $J_{^1H_\gamma-^1H_{\beta'}}$ = 7.1 Hz); phenyl (m's, 15 H), 7.30–7.62	315.54 (br s)	100.67	CH_3, 12.59; C_β, 51.46; phenyl, 130.53 (d, $J_{^{13}C-^{31}P}$ = 11.6 Hz), 133.37, 134.17 (d, J' = 11.6 Hz), ipso carbon not observed
 **12k**		16.00[f] (dd, 1 H, $J_{^1H_\alpha-^1H_\beta}$ = $J_{^1H_\alpha-^1H_{\beta'}}$ = 8.7 Hz)	5.93 (s, 5 H)	H_β (m, 1 H), 2.67; $H_{\beta'}$ (m, 1 H), 3.09; H_γ–H_δ (m, 4 H), 1.30–1.08; CH_3 (dd, 3 H), 0.81 ($J_{^1H_\epsilon-^1H_\delta}$ = $J_{^1H_\epsilon-^1H_{\delta'}}$ = 6.9 Hz), phenyl obscured by Ph_3CH			
 **12t**	1722	15.61 (dd, 1 H, $J_{^1H_\alpha-^1H_\beta}$ = $J_{^1H_\alpha-^1H_{\beta'}}$ = 7.6 Hz)	5.93 (s, 5 H)	H_β (m, 1 H), 3.20; $H_{\beta'}$ (m, 1 H), 2.47; H_γ–H_δ (m, 4 H), 1.27–1.00; CH_3 (dd, 3 H), 0.79 ($J_{^1H_\epsilon-^1H_\delta}$ = $J_{^1H_\epsilon-^1H_{\delta'}}$ = 6.8 Hz); phenyl (m's, 15 H), 7.27–7.67	314.82 (d, $J_{^{13}C-^{31}P}$ = 7.3 Hz)	99.13	C_ϵ–C_γ, 13.54, 22.28, 29.90; C_β, 57.55; phenyl, 129.65 (d, $J_{^{13}C-^{31}P}$ = 63.5 Hz), 129.62 (d, J = 12.2 Hz), 132.46, 132.92 (d, J = 12.2 Hz)
 ***(RR,SS)*-14**	1732[g]	H_{cis} (ddd, 1 H),[h] 2.68 ($J_{^1H_c-^1H_t}$ = 5.0 Hz, $J_{^1H_c-^1H_{HCR}}$ = 14.0 Hz, $J_{^1H_c-^{31}P}$ = 3.5 Hz); H_{trans} (ddd, 1 H), 3.15 ($J_{^1H_t-^1H_c}$ = 5.0 Hz, $J_{^1H_t-^1H_{HCR}}$ = 9.0 Hz, $J_{^1H_t-^{31}P}$ = 14.0 Hz); H_{HCR} (dd, 1 H), 4.84 ($J_{^1H_{HCR}-^1H_c}$ = 14.0 Hz, $J_{^1H_{HCR}-^1H_t}$ = 9.0 Hz)	5.27 (d, 5 H $J_{^1H-^{31}P}$ = 0.6 Hz)	phenyl, 7.22–7.47 and 7.55–7.67 (m's, 20 H)	CH_2, 32.65 (d, $J_{^{13}C-^{31}P}$ = 5.4 Hz); *C*RH, 54.05 (s)	100.92	phenyl, 128.20 (b), 129.20, 129.90, 130.63 (d, $J_{^{13}C-^{31}P}$ = 10.8 Hz), 131.57,[i] 133.27, 134.32 (d, J = 10.9 Hz), 143.19

 (*RS,SR*)-14	1733	H_{cis} (ddd, 1 H),[h] 2.55 ($J_{^1H_c-^1H_t}$ = 5.0 Hz, $J_{^1H_c-^1H_{HCR}}$ = 11.0 Hz, $J_{^1H_c-^{31}P}$ = 5.0 Hz); H_{trans} (ddd, 1 H), 3.12 ($J_{^1H_t-^1H_c}$ = 5.0 Hz, $J_{^1H_t-^1H_{HCR}}$ = 11.0 Hz, $J_{^1H_t-^{31}P}$ = 11.0 Hz); H_{HCR} (ddd, 1 H), 5.67 ($J_{^1H_{HCR}-^1H_c}$ = 11.0 Hz, $J_{^1H_{HCR}-^1H_t}$ = 11.0 Hz, $J_{^1H_{HCR}-^{31}P}$ = 2.2 Hz)	5.84 (d, 5 H, $J_{^1H-^{31}P}$ = 0.6 Hz)	phenyl, 7.01–7.08 and 7.28–7.68 (m's, 20 H)	CH_2, 33.76 (d, $J_{^{13}C-^{31}P}$ = 6.8 Hz); CRH, 49.14 (s)	98.79	phenyl, 127.92, 128.54, 129.25, 130.57 (d, $J_{^{13}C-^{31}P}$ = 10.9 Hz), 131.54 (d, J = 59.7 Hz), 133.29, 134.34 (d, J = 10.9 Hz), 141.24
 (*RR,SS*)-15	1727	H_{cis} (ddd, 1 H),[h,j] 2.02 ($J_{^1H_c-^1H_t}$ = 4.0 Hz, $J_{^1H_c-^1H_{HCR}}$ = 14.0 Hz, $J_{^1H_c-^{31}P}$ = 4.0 Hz); H_{trans} (ddd, 1 H), 3.00 ($J_{^1H_t-^1H_c}$ = 4.0 Hz, $J_{^1H_t-^1H_{HCR}}$ = 9.0 Hz, $J_{^1H_t-^{31}P}$ = 14.0 Hz); H_{HCR} (m, 1 H), 3.64	5.65[j] (s, 5 H)	CH_3[j] (d, 3 H), 2.27 ($J_{^1H_{CH_3}-H_{HCR}}$ = 6.0 Hz); phenyl, 7.26–7.37 and 7.56–7.61 (m's, 15 H)	CH_2, 39.46 (d, $J_{^{13}C-^{31}P}$ = 5.1 Hz), CRH, 50.70 (s)	99.05	CH_3, 24.42; phenyl, 130.49 (d, $J_{^{13}C-^{31}P}$ = 10.9 Hz), 133.16 (d, J = 2.5 Hz), 134.32 (d, J = 10.7 Hz), ipso carbon not observed
 (*RS,SR*)-15	1724	H_{trans}, H_{cis} (m, 2 H),[h,j] 2.45; H_{HCR} (m, 1 H), 4.55	5.71[j] (s, 5 H)	CH_3[j] (d, 3 H), 2.08 ($J_{^1H_{CH_3}-^1H_{HCR}}$ = 6.0 Hz); phenyl, 7.32–7.42 and 7.53–7.60 (m's, 15 H)	CH_2, 40.27 (d, $J_{^{13}C-^{31}P}$ = 5.9 Hz); CRH, 47.02 (s)	98.09	CH_3, 23.02; phenyl, 130.50 (d, $J_{^{13}C-^{31}P}$ = 11.5 Hz), 132.24,[i] 133.12, 134.28 (d, J = 9.7 Hz)
 13	1723	H_{gem} (dd, 1 H),[k] 2.44 ($J_{^1H_{gem}-^1H_{gem'}}$ = 3.5 Hz, $J_{^1H_{gem}-^{31}P}$ = 5.2 Hz); $H_{gem'}$ (dd, 1 H), 2.77 ($J_{^1H_{gem'}-^1H_{gem}}$ = 3.5 Hz; $J_{^1H_{gem'}-^{31}P}$ = 13.0 Hz)	5.64[k] (s, 5 H)	CH_3 (s, 3 H),[k] 2.07; CH_3' (s, 3 H), 2.26; phenyl, 7.26–7.40 and 7.55–7.60 (m's, 15 H)	CH_2, 45.52 (d, $J_{^{13}C-^{31}P}$ = 5.5 Hz); $C(CH_3)_2$, 71.11 (s)	99.22	CH_3's, 31.99, 32.65; phenyl 130.44 (d, $J_{^{13}C-^{31}P}$ = 10.8 Hz), 131.30 (d, J = 59.7 Hz), 133.18 (d, J = 2.6 Hz), 134.41 (d, J = 9.5 Hz)

[a] Alkylidene complexes in CH_2Cl_2; olefin complexes in CH_3CN. [b] 200 MHz. [c] Alkylidene complexes in CD_2Cl_2 (k isomers at −70 °C) and olefin complexes in CD_3CN unless noted; referenced to internal $(CH_3)_4Si$. [d] 50 MHz. [e] Alkylidene complexes in $(CD_3)_2CO$ and olefin complexes in CD_3CN; referenced to internal $(CH_3)_4Si$. [f] When the k alkylidene isomers are warmed, resolution improves and $J_{^1H-^{31}P}$ ~ 2.0 Hz is observable. [g] ν_{NO} (CH_2Cl_2) = 1735 cm^{-1}. [h] Labeling of monosubstituted olefin hydrogens:



[i] Part of ipso carbon doublet; other portion obscured. [j] In $CDCl_3/CD_2Cl_2$ (1:1). The C_5H_5 resonances for (*RR,SS*)-15 and (*RS,SR*)-15 in CD_3CN are at δ 5.68 (d, J = 0.6 Hz) and δ 5.71 (d, J = 0.5 Hz), respectively. [k] In $CDCl_3$.

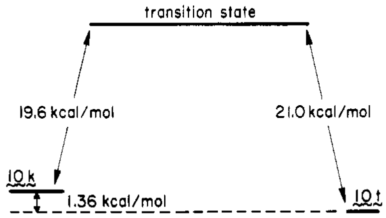


Figure 1. ΔG and ΔG* for the interconversion of **10k** and **10t** at 25 °C.

can account for the shifts in product ratios upon going from eq 6 to eq 10 and 11.

A sample of (*SS*,*RR*)-(η-C_5H_5)Re(NO)(PPh_3)(CH(CD_3)C_6H_5) ((*SS*,*RR*)-**7**-β-d_3) was synthesized by C_6H_5Li attack upon **10k**-β-d_3. A 50:50 mixture of (*SS*,*RR*)-**7** and (*SS*,*RR*)-**7**-β-d_3 was treated with 0.20 equiv (20 mol %) of $Ph_3C^+PF_6^-$ at −78 °C. The resulting triphenylmethane byproduct was isolated and found to be a (86 ± 2):(14 ± 2) Ph_3CH/Ph_3CD mixture. Triphenylmethane was isolated from an identical, side-by-side control reaction of (*SS*,*RR*)-**7**-β-d_3 with $Ph_3C^+PF_6^-$. A (89 ± 1):(11 ± 1) Ph_3D/Ph_3CH ratio was found. Hence the primary kinetic isotope effect, k_H/k_D, is in the range 3–4.

Discussion

1. Primary Rhenium Alkyls (η-C_5H_5)Re(NO)(PPh_3)(CH_2R). Although primary alkyls **2**–**6** (eq 1) can be synthesized in good yields, some (η-C_5H_5)Re(NO)(PPh_3)(CH_3) accompanies the formation of **5** and **6**. No other alkyl or alkylidene byproducts were found. This suggests that $(CH_3)_2CHLi$ and $(CH_3)_3CLi$ can donate hydride to **1**. Hydride-transfer side reactions are commonly encountered in Grignard and alkyllithium additions.[11b,22] Since the "methyl ester" (η-C_5H_5)Re(NO)(PPh_3)(CO_2CH_3) (eq 2) is easily prepared from [(η-C_5H_5)Re(NO)(PPh_3)(CO)]$^+BF_4^-$ and CH_3ONa,[18] and subsequent RMgX addition gives acyls (η-C_5H_5)Re(NO)(PPh_3)(COR) in high yields,[23] we now favor the route shown in eq ii for the synthesis of many primary rhenium alkyls.

2. Alkylidene Complexes: Structure and Bonding. The bonding geometries and relative stabilities of benzylidenes *ac*-[(η-C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]$^+PF_6^-$ (**t**) and *sc*-[(η-C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]$^+PF_6^-$ (**k**) have been established by X-ray crystallography and Hückel MO calculations.[13b] As shown in eq 3, we assume that the bonding and relative stabilities of alkylidenes **10t**/**10k**, **11t**/**11k**, and **12t**/**12k** are similar. The (η-C_5H_5)Re(NO)(PPh_3)$^+$ fragment HOMO is a d orbital which is bisected by the Re–P bond and perpendicular to the Re–NO bond. Thus **10**–**12** adopt conformations which maximize overlap of the alkylidene p orbital with this HOMO (see Figure 3).

The activation parameters for the ethylidene isomerization **10k** → **10t**, $\Delta H^\ddagger$ = 17.4 ± 0.5 kcal/mol and $\Delta S^\ddagger$ = −7.3 ± 2.0 eu, are somewhat less than those for the corresponding benzylidene isomerization, $\Delta H^\ddagger$ = 20.9 ± 0.4 kcal/mol and $\Delta S^\ddagger$ = −3.8 ± 0.2 eu.[13b] We attribute most of the $\Delta H^\ddagger$ decrease to a diminished steric barrier. The vinylidene Re=C bond rotation *ac*-[(η-C_5H_5)Re(NO)(PPh_3)(=C=C(CH_3)C_6H_5)]$^+SO_3F^-$ → *sc*-[(η-C_5H_5)Re(NO)(PPh_3)(=C=C(CH_3)C_6H_5)]$^+SO_3F^-$ was found to have $\Delta H^\ddagger$ = 15.7 ± 1.7 kcal/mol and $\Delta S^\ddagger$ = −9.8 ± 5.5 eu.

The **10k** → **10t** activation parameters yield $\Delta G^\ddagger_{25°C}$ = 19.6 ± 1.1 kcal/mol. Since the equilibrium concentrations of **10k** and **10t** are known, the free energy diagram in Figure 1 can be constructed. The equilibrium concentrations of **10k** and **11k** were slightly underestimated in earlier communications.[12,24]

Aliphatic L_nM=CHR complexes are a very rare class of compounds. The first ethylidene complex (η-C_5H_5)$_2$Ta(CH_3)(=$CHCH_3$) was isolated by Sharp and Schrock.[25] Electrophilic alkylidenes (η-C_5H_5)$_2$W(=$CHCH_3$) and [(η-C_5H_5)Fe(CO)(PPh_3)(=CHR)]$^+CF_3SO_3^-$ (R = CH_3, CH_2CH_3) have been spectroscopically characterized by Caulton[26] and Brookhart and Husk.[27]

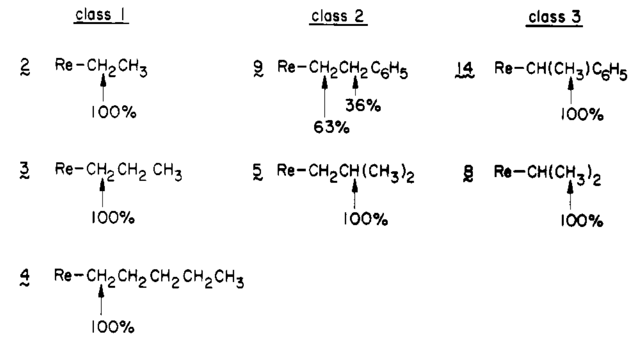


Figure 2. Summary of regiochemistry of hydride abstraction from (η-C_5H_5)Re(NO)(PPh_3)(R) by $Ph_3C^+PF_6^-$.

3. Stereochemistry of Nucleophilic Attack upon Ethylidenes 10k and 10t. In order to mechanistically analyze the reactions of diastereomeric alkyls (η-C_5H_5)Re(NO)(PPh_3)(CHRR′) with $Ph_3C^+PF_6^-$, the configuration at each chiral center must be established. We previously executed an X-ray crystal structure which demonstrated that nucleophiles preferentially attack both geometric isomers of benzylidene [(η-C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]$^+PF_6^-$ from a direction anti to the bulky PPh_3. The product of CH_3Li attack upon **t** benzylidene *ac*-[(η-C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]$^+PF_6^-$ was thus established to be (*SS*,*RR*)-**7**. We now find that the same diastereomer of **7** is obtained by C_6H_5MgBr attack upon **10k** (eq 8). This can only be true if C_6H_5MgBr approaches anti to the PPh_3 of **10k**. We make the key generalization that all nucleophiles (Nu) preferentially attack **10k** and **10t** anti to the PPh_3 and assign configurations accordingly (eq 8, 9).[15] An important expected (and observed) consequence is that **10k** and **10t** afford opposite (η-C_5H_5)Re(NO)(PPh_3)(CHRNu) diastereomers.

Reaction of ethylidene **10k** with nucleophiles gives (η-C_5H_5)Re(NO)(PPh_3)(CH(CH_3)Nu) adducts in ≥99:1 diastereomer ratios, whereas reaction of the corresponding **k** benzylidene *sc*-[(η-C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]$^+PF_6^-$ with identical nucleophiles gives (η-C_5H_5)Re(NO)(PPh_3)(CH(C_6H_5)Nu) adducts in (92–95):(8–5) diatereomer ratios.[13b] We are presently unable to account for the lower benzylidene stereoselectivity. Since reaction of nucleophiles with the (90 ± 2):(10 ± 2) **10t**/**10k** equilibrium mixture gives (η-C_5H_5)Re(NO)(PPh_3)(CH(CH_3)Nu) adducts in ca. 90:10 diastereomer ratios, attack upon **10t** is also likely ≳98% stereoselective. We do not at present have a means of preparing **10t** free of **10k**.

Fortunately, the acidic β protons of **10**[16] are not abstracted by most carbon and hydride nucleophiles. Only in the **10t**/C_6H_5MgBr reaction was the anticipated adduct ((*SR*,*RS*)-**7**)[13b] not detected. The high stereoselectivity with which new C_α chiral centers are formed foreshadows potentially broad utility for [(η-C_5H_5)Re(NO)(PPh_3)(=CHR)]$^+$ reagents in asymmetric organic synthesis.[17]

4. Regiochemistry of the Reactions of Rhenium Alkyls with $Ph_3C^+PF_6^-$. With the configurations of all rhenium alkyls employed in this study established, we now address the regiochemistry of hydride abstraction. Our data are summarized in Figure 2. For each class of alkyl substrate, deuterium labeling was used to rigorously establish the site of hydride loss.

The potential β-hydride abstraction product of **2**, ethylene complex [(η-C_5H_5)Re(NO)(PPh_3)(H_2C=CH_2)]$^+PF_6^-$, has been independently synthesized.[20] It is thermally stable and would have been easily detected. The potential α-hydride abstraction product

(22) (a) March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1978; pp 836–840. (b) Reetz, M. T.; Stephan, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 44.
(23) Wong, A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4948.
(24) McCormick, F. B.; Kiel, W. A.; Gladysz, J. A. *Organometallics* **1982**, *1*, 405.
(25) Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43.
(26) Marsella, J. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 5596.
(27) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258.

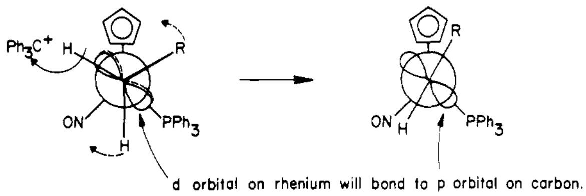
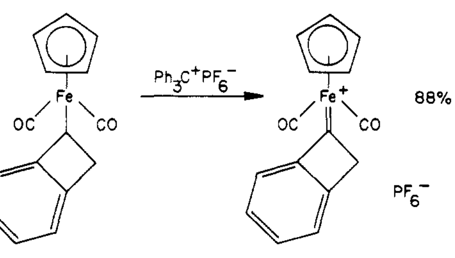


Figure 3. A possible transition state for α-hydride abstraction from $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2R)$ by $Ph_3C^+PF_6^-$.

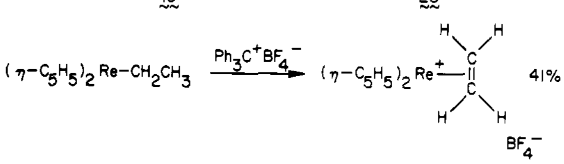
of **5**, isobutylidene $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHCH(CH_3)_2)]^+PF_6^-$, has been independently synthesized.[16] Although it rearranges to isobutylene complex **13** above −10 °C, it would have been detected by ^1H NMR monitoring.

Several L_nMR/Ph_3C^+ reactions discovered by other researchers are particularly relevant to Figure 2. First, Giering found that benzocyclobutene complex **19** (eq 12) gave benzocyclobutylidene **20** upon treatment with $Ph_3C^+PF_6^-$.[8a] Deuterium labeling and an independent synthesis of the potential β-hydride abstraction product $[(\eta\text{-}C_5H_5)Fe(CO)_2(\eta^2\text{-benzocyclobutene})]^+PF_6^-$ rigorously showed eq 12 to be an α-hydride abstraction. This is the only previously demonstrated abstraction of an α-hydride from an alkyl ligand containing β-hydrides. Stucky obtained rhenium ethylene complex $[(\eta\text{-}C_5H_5)_2Re(H_2C{=}CH_2)]^+BF_4^-$ (**21**) in 41% yield from the reaction of $(\eta\text{-}C_5H_5)_2ReCH_2CH_3$ with $Ph_3C^+BF_4^-$ (eq 13).[6c] Although **21** appears to be a β-hydride abstraction product, no labeling experiments were reported. Finally, Cooper treated $(\eta\text{-}C_5H_5)_2W(CH_2CH_3)(CD_3)$ (**22**) with $Ph_3C^+PF_6^-$.[8d] Product **24**, derived from α deuteride abstraction, formed as outlined in eq 14. The same product formed when the 17-electron species $[(\eta\text{-}C_5H_5)_2W(CH_2CH_3)(CD_3)]^+PF_6^-$ (**23**) was treated with $Ph_3C\cdot$. This indicates that electron transfer is the initial step of the reaction of **22** with $Ph_3C^+PF_6^-$.



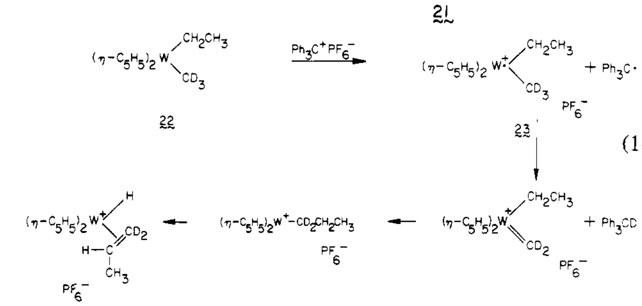
(12)

19 **20**



(13)

21

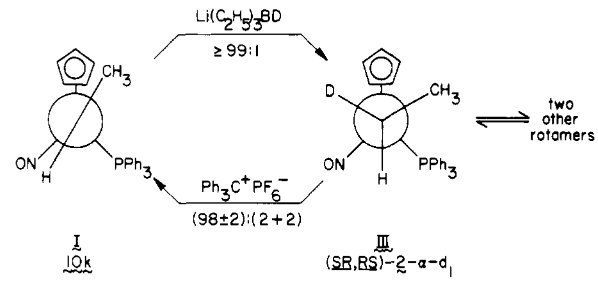


(14)

5. Stereochemistry of the Reactions of Rhenium Alkyls with $Ph_3C^+PF_6^-$. Stereochemical data enable geometric constraints to be placed upon transition states. We now attempt to interpret the diastereoselectivity often encountered in the preceding reactions of rhenium alkyls with $Ph_3C^+PF_6^-$.

The exclusive formation of the less stable geometric isomer **10k** upon reaction of ethyl **2** with $Ph_3C^+PF_6^-$ suggests that only one of the two diastereotopic α-hydrides is abstracted. Accordingly, reactions of the two diastereomers of **2**-α-d_1 with $Ph_3C^+PF_6^-$ show that the *pro-R* α-hydride is essentially exclusively abstracted.

Two reactions can be combined to create the stereochemical cycle shown in eq 15. As determined above, deuteride attacks I (**10k**) anti to the PPh_3. Three rotamers of product (*SR,RS*)-**2**-α-d_1 exist. In order to convert (*SR,RS*)-**2**-α-d_1 to kinetic product **10k**, $Ph_3C^+PF_6^-$ must abstract deuteride from a direction anti to PPh_3. Since III is the only rotamer which has deuteride anti to PPh_3, it (or a skewed variant) must be the one which reacts with $Ph_3C^+PF_6^-$.



(15)

Identical conclusions were reached regarding interconversions of benzyl $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)$, benzylidenes $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHC_6H_5)]^+PF_6^-$, and their α-deuterated homologues.[13b] Since III has the methyl group situtated between the two largest ligands PPh_3 and C_5H_5, it is likely the least stable (*SR,RS*)-**2**-α-d_1 rotamer.[13b] We are at present unable to account for its greater reactivity.

We assert that the abstraction of hydride anti to PPh_3 should also be favored on electronic grounds. In this orientation, the rhenium fragment HOMO is able to anchimerically assist the departure of hydride, as shown in Figure 3. The −R and −H substituents move toward their new energy minima, and d–p π bonding is maximized in the transition state. We have previously noted the close correspondence of Figure 3 with the second step of the E1cB elimination mechanism.[13b]

The reactions shown in eq 5 entail the stereospecific conversion of a center of chirality (C_α) to a new element of stereoisomerism (styrene *si* or *re* face coordination).[15] Abstraction of β-hydrides from metal alkyls by $Ph_3C^+PF_6^-$ has been shown to occur antiperiplanar to the M–C_α bond.[28–30] Theoretical studies support these experimental results.[11b] Product stereochemistry in eq 5 has been assigned accordingly. The formation of diastereomers opposite of the ones observed in eq 5 would constitute an inversion of configuration at C_α.

We assert that the rhenium fragment HOMO should also anchimerically assist the departure of β-hydrides and suggest the transition states for styrene complex formation shown in Figure 4.[31] Product rotamers with the geometries V ⇌ VI and VIII ⇌ IX are expected, since these maximize overlap of the rhenium HOMO with the empty olefin π* orbital. Accordingly, the X-ray crystal structure of the formaldehyde complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}O)]^+PF_6^-$ shows that the Re—C=O plane virtually eclipses the Re—PPh_3 bond (∠15°). The bulkier $H_2C{=}$ end of $H_2C{=}O$ is anti to the PPh_3.[32]

The more stable $H_2C{=}CHR$ complex rotamers would be expected to have their bulkier $RHC{=}$ termini anti to the PPh_3, as in VI and IX in Figure 4. Hence transition states IV and VII lead to the less stable rotamers. We have not yet been able to observe discrete rotamers of **14** or any related olefin complex. Since olefin complex *diastereomer* interconverion (eq 5, 6) is relatively facile (70–80 °C), we believe that rotamer intercon-

(28) Slack, D.; Baird, M. C. *J. Chem. Soc., Chem. Commun.* **1974**, 701.
(29) Hannon, S. J.; Traylor, T. G. *J. Org. Chem.* **1981**, *46*, 3645.
(30) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333.
(31) Our convention for converting planar representations of diastereomeric olefin complexes (eq 5–7, 10, 11) into three-dimensional structures is as follows: (*RR,SS*)-**14** (eq 5) ≡ VI (Figure 4) and (*RS,SR*)-**14** ≡ IX.
(32) Buhro, W. E.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A.; McCormick, F. B.; Etter, M. C. *J. Am. Chem. Soc.* **1983**, *105*, 1056.

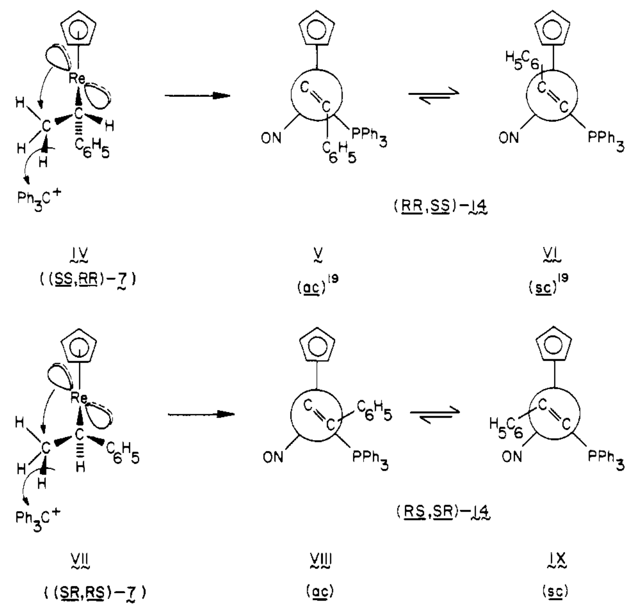


Figure 4. Possible transition states for the formation of styrene complexes **14**.

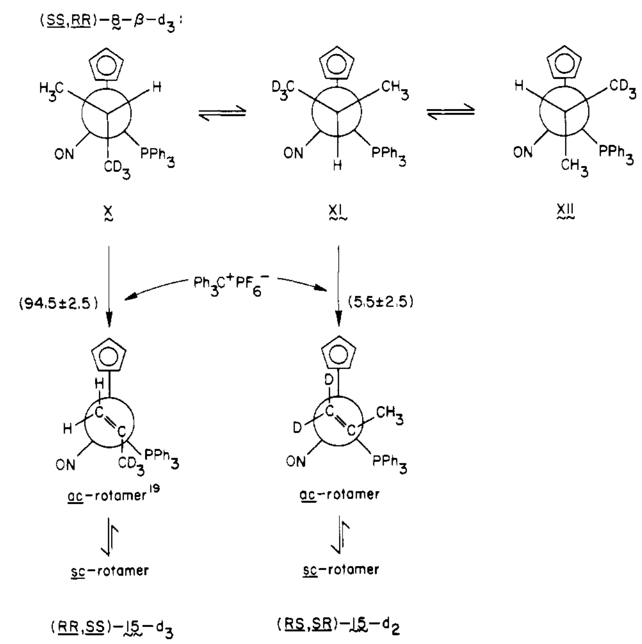
version should be rapid at room temperature. Typical $\Delta G^{\ddagger}$ for rotation about metal–olefin bonds are 8.0 kcal/mol for $[(\eta\text{-}C_5H_5)Fe(CO)(P(OPh)_3)(H_2C{=}CH_2)]^+BF_4^-$,[33] 10 kcal/mol for $[(\eta\text{-}C_5H_5)Fe(CO)(PPh_3)(H_2C{=}CH_2)]^+PF_6^-$,[33] and 12.8 kcal/mol for $(\eta\text{-}C_5H_5)Fe(CO)(SnPh_3)(H_2C{=}CH_2)$.[34]

Both styrene complex rotamers VI and IX have their $=CHC_6H_5$ termini anti to the PPh_3. However, in the former the phenyl ring points toward the medium sized C_5H_5 ligand, whereas in the latter it points toward the small NO ligand. We propose that this difference accounts for the greater thermodynamic stability of styrene complex diastereomer (*RS,SR*)-**14**.[31]

An alternative to transition state IV (or VII) would utilize the d orbital lobe syn to PPh_3 and an eclipsed Re–C rotamer (CH_3 syn to PPh_3). This would afford the more stable olefin complex rotamer directly. However, then $Ph_3C^+PF_6^-$ would have to approach syn to the bulky PPh_3. We have never observed an attacking reagent to preferentially approach syn to the PPh_3.[13b,16,23]

The predominant formation of the less stable propylene complex diastereomer in eq 6 suggests that $Ph_3C^+PF_6^-$ preferentially abstracts hydride from one of the two diastereotopic methyl groups of **8**. The diastereomeric **8**-β-d_3 substrates in eq 10 and 11 show that the *pro-R* methyl group is more reactive. The same reasoning used to assign product structures in eq 5 predicts that β-hydride abstraction from (*SR,RS*)-**8**-β-d_3 (eq 10) will give (*RR,SS*)-**15**-d_2, whereas β-deuteride abstraction from (*SR,RS*)-**8**-β-d_3 will give (*RS,SR*)-**15**-d_3. Assignments are similarly made for eq 11 and then for the unlabeled propylene complexes in eq 6. We rationalize the relative diastereomer stabilities in the same manner as was done for the styrene complexes.

Analysis of eq 11 in terms of a Figure 4 mechanism is given in eq 16. Rotamer X yields the predominant kinetic product, whereas sterically more congested XI leads to the minor kinetic product. Rotamer XIII is unreactive, since the rhenium fragment HOMO cannot efficiently anchimerically assist hydride departure. The product isotope effects in eq 6, 10, and 11 are reasonably close to the *product* isotope effect of 2.5 observed by Baird in the reaction of $(\eta\text{-}C_5H_5)Fe(CO)_2(CHDCHDC_6H_5)$ with $Ph_3C^+PF_6^-$ and the *kinetic* isotope effect, $k_H/k_D = 3.7$, observed by Traylor in the reactions of $(CH_3)_3SnCH(CH_3)CH_2CH_3$ and $(CH_3)_3SnCH(CH_3)CHDCH_3$ with $Ph_3C^+BF_4^-$.[28,29] We are unaware of any nonenzymatic process which discriminates between diastereotopic gem-dimethyl groups as efficiently as eq 6.



6. Mechanistic Basis for the Regiochemistry of Hydride Abstraction. There are two limiting modes of hydride transfer from $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(R)$ alkyls to $Ph_3C^+PF_6^-$: concerted or via an intermediate electron-transfer step to give radical cation $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(R)]^{+\cdot}PF_6^-$ and $Ph_3C\cdot$. Although we have depicted the former mechanism in Figure 3, the latter mechanism would, as required by the deuterium labeling experiments, have a similar gross geometry. Furthermore, the rhenium fragment HOMO in $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(R)]^{+\cdot}$ would be the same as in the precursor alkyl. Similarly, there is no compelling reason to alter the β-hydride abstraction transition-state geometries in Figure 4 as a result of an initial electron-transfer step.

The structural parameters which influence hydride abstraction regiochemistry can be summarized from Figure 2 as follows. Unbranched aliphatic alkyls (class 1) give exclusively α-hydride abstraction. However, when C_β is substituted such that an incipient carbonium ion would be stabilized (class 2), β-hydride abstraction can compete (**9**) or dominate (**5**). Secondary rhenium alkyls (class 3) give exclusively β-hydride abstraction. In these cases, approach of Ph_3C^+ or $Ph_3C\cdot$ to H_α would be more hindered. No well-defined hydride abstraction products are obtained from the congested neopentyl alkyl $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C(CH_3)_3)$ (**6**).

The regiochemistry of hydride abstraction can potentially be influenced by thermodynamic factors. For isobutyl complex **5**, we know that the kinetic hydride abstraction product **13** is also the thermodynamic product.[16] However, we do not know the relative stabilities of, for instance, ethylidene **10** and the corresponding ethylene complex. Several examples of 1,2-hydrogen shifts which convert cationic alkylidene complexes ($L_nM^+{=}C(CH_3)_2$, $L_nM^+{=}CHCH_2CH_3$) to cationic olefin complexes have recently been found.[16,27,35] However, it should be kept in mind that the kinetic products in Figures 3 and 4 are *not* the thermodynamically favored alkylidene complex isomers or olefin complex rotamers. Some interesting relevant equilibria have recently been reported by Schrock. Neopentyl ethylene complex $Ta(CH_2C(CH_3)_3)(H_2C{=}CH_2)(Cl)_2(PMe_3)_2$ and neopentylidene ethyl complex $Ta({=}CHC(CH_3)_3)(CH_2CH_3)(Cl)_2(PMe_3)_2$ were found to exist as a 1:1 tautomeric mixture. Hence in this system, the thermodynamics of α-hydride elimination from neopentyl and β-hydride elimination from ethyl are approximately equal.[7b] Remarkably, a living ethylene polymerization catalyst, Ta-

(33) Reger, D. L.; Coleman, C. J. *Inorg. Chem.* **1979**, *18*, 3270.
(34) Faller, J. W.; Johnson, B. V.; Schaeffer, C. D., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 1395. See also: Mann, B. E. In "Comprehensive Organometallic Chemistry"; Wilkinson, S., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 3, pp 105–108.
(35) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761.

$(=CH(CH_2CH_2)_nC(CH_3)_3)(H)(I)_2(PMe_3)_2$, has been shown to rest in an alkylidene hydride state.[8c] This suggests, but does not prove, that α-hydride elimination from the precursor alkyl is thermodynamically preferred over β-hydride elimination.

Previous studies of L_nMR/Ph_3C^+ β-hydride abstractions have not considered in detail the possibility of initial electron transfer.[28,29] However, the observation of a substantial *kinetic* deuterium isotope effect in Traylor's $(CH_3)_3SnCH(CH_3)CH_2CH_3/Ph_3C^+PF_6^-$ study[28] does, as emphasized by Kochi,[36] exclude electron transfer as an *initial and rate determining* step. In view of the k_H/k_D of 3–4 from the *(SS,RR)*-**7**/*(SS,RR)*-**7**-β-d_3/$Ph_3C^+PF_6^-$ competition experiment, the same conclusion may be drawn for β-hydride abstraction from $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(R)$ alkyls. However, the possibility of an initial, preequilibrium electron transfer remains. In important related work, Ashby has obtained compelling evidence that Grignard reagents transfer β-hydrides to dimesityl ketone via a tight, solvent-caged radical pair.[37] Similar reactivity was shown by other ketones with low reduction potentials (<−2.0 V).

The elegant studies of Cooper,[7e,8d] summarized in eq 14, provide direct evidence that L_nMR/Ph_3C^+ α-hydride abstractions can proceed via initial electron transfer. The ability to trap and independently synthesize radical cations such as **23**, and convert them to α-hydrogen abstraction products with $Ph_3C\cdot$, excludes nearly all other mechanistic possibilities. Although we have obtained preliminary NMR and ESR evidence for the presence of radical species during $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(R)/Ph_3C^+PF_6^-$ reactions, we have so far been unable to synthesize authentic samples of $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(R)]^{+\cdot}$ radical cations.[38] Since related radical cations $[(\eta\text{-}C_5H_5)Fe(L)(L')(R)]^{+\cdot}$ have been generated,[39] we are confident that this difficulty will eventually be overcome. However, the k_H/k_D of 2–4 from the **2**/**2**-α-d_2/$Ph_3C^+PF_6^-$ competition experiments excludes electron transfer as an initial and rate-determining step in our α-hydride abstractions.

In attempting to rationalize why regiospecific β-hydride abstraction is observed in nearly all other L_nMR/Ph_3C^+ reactions, we initially speculated that $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(R)$ alkyls might be more easily oxidized than first-row counterparts such as $(\eta\text{-}C_5H_5)Fe(CO)(L)(R)$ (L = PPh_3, CO)[40] and that prior electron transfer might be uniquely associated with α-hydrogen loss. Equation 12 would be an understandable exception in that the β-hydride abstraction transition state would have considerable benzocyclobutene-like character. Alkyl $(\eta\text{-}C_5H_5)Fe(CO)_2(CH_2CH_2CO_2CH_3)$, in which β-hydride abstraction would similarly be electronically unfavorable, has been reported not to react with $Ph_3C^+PF_6^-$ at all.[6b] Since class 2 substrates in Figure 2 would have stabilized incipient β-carbonium ions, two-electron β-hydride abstraction would be able to compete with α-hydride abstraction. Steric factors would then be invoked to explain β-hydride abstraction from class 3 substrates. While this rationale accounts for all results obtained to date, we believe that it is premature to discount the possibility of prior electron transfer in β-hydride abstractions. The demanding experiments required to definitively address these points are being pursued in a coordinated effort in our Utah laboratories[2] and Professor John Cooper's laboratory at Harvard.

Conclusion

This study has mapped the structural features which control the regiochemistry of hydride abstraction by $Ph_3C^+PF_6^-$ from alkyls $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(R)$. Accurate predictions can now be made regarding the reactivity of yet unsynthesized rhenium alkyls. Detailed transition-state models for α- and β-hydride abstraction have been proposed.

This study has also provided additional examples of the striking ability of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)$ systems to paticipate in stereospecific and/or highly stereoselective reactions. The rhenium chirality is efficiently transferred to new, ligand-based centers or elements of chirality. Since these complexes are now readily available in optically active form,[17] important applications in asymmetric synthesis will soon be forthcoming.

Experimental Section

General procedures employed for this study were identical with those given in a previous paper.[13b]

Starting Marterials. Alkyls $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$,[14] *(SS,RR)*-**7**, and (SR,RS)-**7**,[12] and ester $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO_2CH_3)$[17] were prepared as previously described. $Ph_3C^+PF_6^-$ was purchased from Aldrich and Columbia Organic and was stored under N_2 in the refrigerator. Over the course of this study the quality of the $Ph_3C^+PF_6^-$ varied considerably. Recrystallization from CH_2Cl_2/benzene or CH_2Cl_2/ether under N_2 was found to give pure $Ph_3C^+PF_6^-$ (50–60% recovery).[41] Reagents CH_3MgBr (3 M in ether), CH_3CH_2MgBr (3 M in ether), $BH_3\cdot THF$ (1 M in THF), and $NaBD_4$ were purchased from Aldrich. Alkyls $CH_3CH_2CH_2CH_2Li$ (1.3 M in hexane) and $C_6H_5CH_2MgCl$ (1.8 M in THF) were purchased from Alfa. Alkyls $(CH_3)_2CHLi$ (1.4 M in pentane) and $(CH_3)_3CLi$ (1.9 M in pentane) were purchased from Orgmet, Inc. All Grignard and organolithium reagents were used without standardization. PMe_3 was obtained from Strem Chemicals and used without purification.

Preparation of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_3)$ (2). To a −78 °C solution of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (0.504 g, 0.0903 mmol) in 50 mL of CH_2Cl_2 was added 0.393 g (0.988 mmol) of Ph_3C^+ PF_6^-. The resulting yellow solution was stirred for 30 min at −78 °C, and then 1.8 mL of CH_3Li (1.0 M in ether) was added dropwise. After 15 min, the dark orange solution was allowed to warm to room temperature. The CH_2Cl_2 was removed by rotary evaporation, and the residue was taken up in CH_2Cl_2/benzene and filtered through silica gel. The orange filtrate was rotovapped to dryness and the residue recrystallized from CH_2Cl_2/hexanes. This gave 0.397 g (0.694 mmol, 77%) of **2** as orange flakes, mp 220 °C dec. Spectroscopic data: Tables I and II. Anal. Calcd for $C_{25}H_{25}NOPRe$: C, 52.44; H, 4.40; N, 2.44; P, 5.41. Found: C, 52.19; H, 4.41; N, 2.30; P, 5.19.

Preparation of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_2CH_3)$ (3). To a −78 °C solution of $(\eta\text{-}C_5kH_5)Re(NO)(PPh_3)(CH_3)$ (0.355 g, 0.636 mmol) in 40 mL of CH_2Cl_2 was added 0.296 g (0.763 mmol) of $Ph_3C^+PF_6^-$. The resulting yellow solution was stirred for 20 min at −78 °C, and 0.850 mL of CH_3CH_2MgBr (3 M in ether) was then added dropwise. After 10 min, an oil pump vacuum was applied and the solvents were removed as the orange solution was allowed to warm to room temperature. 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 silica gel column with 1:1 CH_2Cl_2/hexanes. The orange band was collected and gave 0.306 g (0.522 mmol, 82%) of **3** as an orange powder, mp 184–185 °C dec. Spectroscopic data: Tables I and II.

Preparation of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_2CH_2CH_2CH_3)$ (4). To a −78 °C solution of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (0.300 g, 0.537 mmol) in 30 mL of CH_2Cl_2 was added 0.250 g (0.644 mmol) of $Ph_3C^+PF_6^-$. The resulting yellow solution was stirred for 20 min at −78 °C, and then 0.490 mL of $CH_3CH_2CH_2CH_2Li$ (1.3 M in hexanes) was added dropwise. After 15 min, the orange solution was allowed to warm to room temperature. The solvents were removed under oil pump vacuum, and the residue was extracted with benzene. The extracts were filtered through a 2-in. silica gel plug, and the benzene was removed by rotary evaporation. The resulting orange oil was taken up in hexanes and stored in a freezer overnight. Orange crystals of **4** formed and were isolated by filtration (0.231 g, 0.376 mmol, 70%; mp 135–137 °C). Spectroscopic data: Tables I and II.

Preparation of $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH(CH_3)_2)$ (5). To 20 mL of CH_2Cl_2 at −78 °C was added 0.239 g (0.340 mmol) of isolated $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+PF_6^-$ (**1**).[13] Then 0.490 mL of $(CH_3)_2CHLi$ (1.4 M in pentane) was added dropwise. The reaction mixture was stirred for 30 min at −78 °C, during which time it turned orange. Analysis by silica gel TLC showed spots corresponding to both $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ and the new alkyl **5**. The reaction was allowed to warm to room temperature, whereupon the solvents were removed under oil pump vacuum. The residue was extracted with

(36) Klingler, R. J.; Mochida, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6626.

(37) Ashby, E. C.; Goel, A. B. *J. Am. Chem. Soc.* **1981**, *103*, 4983.

(38) Kiel, W. A.; Wong, A.; Bodner, G., unpublished results.

(39) Magnuson, R. H.; Zulu, S.; T'sai, W.-M.; Giering, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6887. See also: Treichel, P. M.; Molzahn, D. C.; Wagner, K. P. *J. Organomet. Chem.* **1979**, *174*, 191.

(40) For instance, $(\eta\text{-}C_5H_5)Re(CO)_3$ is easier to oxidize than $(\eta\text{-}C_5H_5)Mn(CO)_3$: Denisovich, L. I.; Zakarin, N. V.; Gubin, S. P.; Ginzburg, A. G. *J. Organomet. Chem.* **1975**, *101*, C43.

(41) Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *J. Am. Chem. Soc.*, in press.

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 silica gel column with 3:1 CH_2Cl_2/hexanes. The first orange fraction was collected and gave 0.107 g (0.178 mmol, 52%) of **5** as an orange powder. Alkyl **5** was subsequently recrystallized from CH_2Cl_2/hexanes; mp 222–225 °C dec. Spectroscopic data: Tables I and II.

Preparation of (η-C_5H_5)Re(NO)(PPh_3)($CH_2C(CH_3)_3$) (6). To 20 mL of CH_2Cl_2 at −78 °C was added 0.213 g (0.303 mmol) of isolated [(η-C_5H_5)Re(NO)(PPh_3)(=CH_2)]$^+PF_6^-$ (**1**).[13] Then 0.240 mL of $(CH_3)_3CLi$ (1.9 M in pentane) was added dropwise. The reaction mixture was stirred for 30 min at −78 °C, during which time it turned bright orange. Analysis by silica gel TLC (3:1 CH_2Cl_2/hexanes) showed spots corresponding to both (η-C_5H_5)Re(NO)(PPh_3)(CH_3) (R_f 0.31) and the new alkyl **6** (R_f 0.41). The reaction mixture was allowed to warm to room temperature, whereupon the solvents were 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 oil was chromatographed on a silica gel column with 3:1 CH_2Cl_2/hexanes. The first orange fraction was collected and gave 0.093 g (0.151 mmol, 50%) of **6** as an orange powder. Alkyl **6** was subsequently recrystallized from hexanes; mp 187–190 °C. Spectroscopic data: Tables I and II.

Preparation of (η-C_5H_5)Re(NO)(PPh_3)($CH(CH_3)_2$) (8). A solution of 0.102 g (0.142 mmol) of [(η-C_5H_5)Re(NO)(PPh_3)(=$CHCH_3$)]$^+PF_6^-$ (**10**; see synthesis below) in 20 mL of CH_2Cl_2 was cooled to −78 °C, and 0.400 mL of CH_3Li (1.4 M in THF) was added dropwise. Alternatively, CH_3MgBr was used. The resulting orange solution was stirred for 20 min at −78 °C. The solvents were then removed under oil pump vacuum while the reaction was allowed to warm. The resulting orange residue was extracted with benzene and filtered through a 2-in. silica gel plug. The benzene was removed by rotary evaporation to give an orange oily solid which was dissolved in hexanes and stored in a freezer overnight. This gave 0.041 g (0.070 mmol) of **8** as orange-red crystals, mp 175–178 °C. Spectroscopic data: Tables I and II.

Preparation of (η-C_5H_5)Re(NO)(PPh_3)($COCH_2C_6H_5$). To a 25 °C solution of (η-C_5H_5)Re(NO)(PPh_3)(CO_2CH_3) (0.128 g, 0.212 mmol) in 20 mL of benzene was added dropwise 0.180 mL of $C_6H_5CH_2MgCl$ (1.8 M in THF). After 15 min, the solution had turned from bright yellow to orange. Solvents were then removed under oil pump vacuum. The residue was taken up in acetone and filtered through a 3-in. silica gel plug. Acetone was removed from the resulting yellow solution by rotary evaporation. The residue was taken up in benzene and crystallized by subsequent diffusion addition of hexane. Thus obtained were bright yellow-orange needles (0.112 g, 0.169 mmol, 80%) of (η-C_5H_5)Re(NO)(PPh_3)($COCH_2C_6H_5$): mp 223–226 °C dec; IR (cm^{-1}, CH_2Cl_2) $\nu_{N\equiv O}$ 1647 (s), $\nu_{C=O}$ 1555 (m); ^1H NMR (δ, $CDCl_3$) 7.56–7.05 (m's, 20 H), 5.03 (s, 5 H), 4.15 (d, $J_{^1H-^1H'}$ = 12.6 Hz, 1 H), 3.18 (d, $J_{^1H'-^1H}$ = 12.6 Hz, 1 H).

Preparation of (η-C_5H_5)Re(NO)(PPh_3)($CH_2CH_2C_6H_5$) (9). A. To a 25 °C solution of (η-C_5H_5)Re(NO)(PPh_3)($COCH_2C_6H_5$) (0.075 g, 0.113 mmol) in 20 mL of THF was added 3.0 mL of BH_3·THF (1 M in THF). The solution was refluxed for 4.5 h, during which time the color changed from yellow to orange. The THF was removed by rotary evaporation, and the residue was extracted with benzene and filtered through a 2-in. silica gel plug. The benzene was removed, and the remaining orange solid was chromatographed on a silica gel column in 1:1 CH_2Cl_2/hexanes. The orange band was collected and gave 0.047 g (0.072 mmol, 64%) of **9** as an orange powder, mp 222–224 °C dec. Spectroscopic data: Tables I and II.

B. To 20 mL of CH_2Cl_2 at −78 °C was added 0.200 g (0.285 mmol) of isolated [(η-C_5H_5)Re(NO)(PPh_3)(=CH_2)]$^+PF_6^-$ (**1**).[13] Then 0.398 mL of $C_6H_5CH_2MgCl$ (1.8 M in THF) was added dropwise. After 15 min, the reaction mixture was allowed to warm to room temperature. Solvents were removed under oil pump vacuum, and the residue was taken up in CH_2Cl_2/benzene and filtered through a silica gel plug. Workup as in A gave 0.037 g (0.057 mmol, 20%) of **9**.

Generation of *sc*-Alkylidenes 10k, 11k, and 12k. For a typical spectroscopic scale experiment, 0.035 mmol of **2–4** was dissolved in 0.350 mL of CD_2Cl_2 in a septum-capped NMR tube. The tube was cooled to −78 °C, and 1.1 equiv of $Ph_3C^+PF_6^-$ in 0.200 mL of CD_2Cl_2 was slowly injected. The tube was shaken and quickly transferred to a −73 °C NMR probe, and the data compiled in Table I were recorded.

To obtain the isomerization rates in Table III, **10k** was generated at the temperature of the rate measurement. The disappearance of **10k** and the appearance of **10t** were monitored by integration of the CH_3 ^1H NMR resonances.

Preparative scale syntheses of **10k–12k** were effected as described in the following experimentals. In each case, solutions were stirred for at least 20 min at −78 °C before reaction.

Preparation of [(η-C_5H_5)Re(NO)(PPh_3)(=$CHCH_3$)]$^+PF_6^-$ (10t/10k Equilibrium Mixture). To a −78 °C solution of **2** (0.314 g, 0.549 mmol) in 30 mL of CH_2Cl_2 was added 0.234 g (0.604 mmol) of $Ph_3C^+PF_6^-$. The reaction was kept at −78 °C for 0.5 h and became yellow. The solution was allowed to warm to room temperature and was kept at room temperature for an additional hour. Hexanes (10–15 mL) was then added, and the solvents were removed under oil pump vacuum to give an off-white powder. The powder was washed with hexanes and several small portions of ether. This material was pure by ^1H NMR spectroscopy and unsolvated and was used for most subsequent **10t/10k** experiments. The powder was taken up in $CHCl_3/CH_2Cl_2$ and crystallized by subsequent diffusion addition of ether. Thus obtained was 0.311 g (0.410 mmol, 75%) of (90 ± 2):(10 ± 2) **10t/10k**·(0.5$CHCl_3$) as greenish yellow leafs, mp 165 °C dec. Spectroscopic data for **10t**: Table IV. Anal. Calcd for $C_{25}H_{24}F_6NOP_2Re$ + 0.5$CHCl_3$: C, 39.30; H, 3.16; N, 1.79; P, 7.93. Found: C, 39.59; H, 3.35; N, 1.73; P, 7.68.

Preparation of [(η-C_5H_5)Re(NO)(PPh_3)(=$CHCH_2CH_3$)]$^+PF_6^-$ (11t/11k Equilibrium Mixture). To a −78 °C solution of **3** (0.129 g, 0.220 mmol) in 20 mL of CH_2Cl_2 was added 0.115 g (0.296 mmol) of $Ph_3C^+PF_6^-$. The reaction was kept at −78 °C for 10 min and became yellow. The solution was allowed to warm to room temperature and was kept at room temperature for an additional 2 h. The CH_2Cl_2 was then removed under oil pump vacuum, and the residue was washed with hexanes. The residue was taken up in $CHCl_3$. Subsequent addition of hexanes gave a white powder which was again taken up in $CHCl_3$ and crystallized by diffusion addition of hexanes. Thus obtained was 0.123 g (0.172 mmol, 78%) of (91 ± 2):(9 ± 2) **11t/11k**, mp 120 °C dec. Spectroscopic data for **11t**: Table IV.

Preparation of [(η-C_5H_5)Re(NO)(PPh_3)(=$CHCH_2CH_2CH_2CH_3$)]$^+PF_6^-$ (12t/12k Equilibrium Mixture). To a −78 °C solution of **4** (0.159 g, 0.259 mmol) in 20 mL of CH_2Cl_2 was added 0.120 g (0.309 mmol) of $Ph_3C^+PF_6^-$. The reaction was kept at −78 °C for 10 min and became bright yellow. The solution was allowed to warm to room temperature and was kept at room temperature for an addition 2 h. Hexanes (10 mL) was then added, and the solvents were removed under oil pump vacuum. The resulting cream powder was washed with hexanes and ether, dissolved in CH_2Cl_2, and layered with hexanes. This solution was stored in a freezer overnight, whereupon 0.110 g (0.145 mmol, 56%) of (90 ± 2):(10 ± 2) **12t/12k** formed as light yellow crystals, mp 172 °C dec. Some decomposition occurred during the recrystallization. Spectroscopic data for **12t**: Table IV.

Preparation of [(η-C_5H_5)Re(NO)(PPh_3)(H_2C=$C(CH_3)_2$)]$^+PF_6^-$ (13). To a −78 °C solution of **5** (0.081 g, 0.135 mmol) in 15 mL of CH_2Cl_2 was added 0.062 g (0.160 mmol) of $Ph_3C^+PF_6^-$. The resulting solution was stirred at −78 °C for 15 min and was then allowed to warm to room temperature. Hexanes (10 mL) was added, and the solvents were removed under oil pump vacuum. The residue was washed with hexanes followed by small amounts of ether. The residue was taken up in $CHCl_3/CH_2Cl_2$ and crystallized by diffusion addition of ether. Cream crystals of **13** (0.070 g, 0.094 mmol, 70%) were collected by filtration; mp 197–199 °C (dec with gas evolution). Spectroscopic data: Table IV.

Preparation of (*RR*,*SS*)-[(η-C_5H_5)Re(NO)(PPh_3)(H_2C=CHC_6H_5)]$^+PF_6^-$ ((*RR*,*SS*)-14). To a −78 °C solution of (*SS*,*RR*)-**7** (0.062 g, 0.095 mmol) in 15 mL of CH_2Cl_2 was added 0.045 g (0.116 mmol) of $Ph_3C^+PF_6^-$. The resulting solution was stirred at low temperature for 15 min. Then hexanes (10 mL) was added, an oil pump vacuum was applied, and the solvents were removed as the reaction was allowed to warm to room temperature. This gave an off-white powder which was washed with large amounts of hexanes and assayed by ^1H NMR for product diastereomer purity. The powder was taken up in $CHCl_3$ and crystallized by diffusion addition of ether. Yellow crystals of (*RR*,*SS*)-**14** (0.059 g, 0.074 mmol, 78%) were collected by filtration; mp 245–247 °C (dec with gas evolution). Spectroscopic data: Table IV.

Preparation of (*RS*,*SR*)-[(η-C_5H_5)Re(NO)(PPh_3)(H_2C=CHC_6H_5)]$^+PF_6^-$ ((*RS*,*SR*)-14). To a −78 °C solution of (*SR*,*RS*)-**7** (0.203 g, 0.313 mmol) in 20 mL of CH_2Cl_2 was added 0.134 g (0.344 mmol) of $Ph_3C^+PF_6^-$. The resulting solution was stirred at low temperature for 30 min. Then hexanes (20 mL) was added, an oil pump vacuum was applied, and the solvents were removed as the reaction was allowed to warm to room temperature. This gave a light yellow solid which was washed with hexanes and assayed by ^1H NMR for product diastereomer purity. The solid was taken up in CH_3CN and crystallized by diffusion addition of ether. Yellow crystals of (*RS*,*SR*)-**14** (0.162 g, 0.204 mmol, 65%) were collected by filtration; mp 252–258 °C (dec with gas evolution). Spectroscopic data: Table IV.

Preparation of (*RR*,*SS*)-[(η-C_5H_5)Re(NO)(PPh_3)(H_2C=$CHCH_3$)]$^+PF_6^-$ ((*RR*,*SS*)-15). To a −78 °C solution of **8** (0.059 g, 0.101 mmol) in 15 mL of CH_2Cl_2 was added 0.047 g (0.121 mmol) of $Ph_3C^+PF_6^-$. The resulting solution was stirred at low temperature for 10 min. Then hexanes (10 mL) was added, an oil pump vacuum was applied, and the solvents were removed as the reaction was allowed to warm to room temperature. This gave a yellow solid which was washed with hexanes and assayed by ^{1}H NMR for the product diastereomer ratio (eq 6; a δ 5.43 impurity (ca. 13%) was also present). The solid was taken up in $CHCl_3$ and crystallized by diffusion addition of ether. Yellow prisms of (*RR,SS*)-**15** (0.053 g, 0.073 mmol, 72%) were collected by filtration; mp 200–202 °C (dec with gas evolution). Spectroscopic data: Table IV.

Preparation of (*RS,SR*)-[(η-C_5H_5)Re(NO)(PPh_3)(H_2C=$CHCH_3$)]$^+$$PF_6^-$ ((*RS,SR*)-15). A septum-capped test tube was charged with (*RR,SS*)-**15** (0.063 g, 0.086 mmol) and CH_3CN (3.0 mL). The solution was freeze–thaw degassed three times. The tube was heated in a 77 ± 3 °C oil bath for 125 h. Solvent was removed under oil pump vacuum, and the residue was analyzed by ^{1}H NMR (see Results). The residue was taken up in $CHCl_3$ and crystallized by diffusion addition of ether. Yellow needles of (95 ± 1):(5 ± 1) (*RS,SR*)-**15**/(*RR,SS*)-**15** were collected by filtration; mp 227 °C (dec with gas evolution). Spectroscopic data for (*RS,SR*)-**15**: Table IV.

Reaction of 9 with Ph_3C^+ PF_6^-. Generation of [(η-C_5H_5)Re(NO)(PPh_3)(=$CHCH_2C_6H_5$)]$^+$$PF_6^-$ (16). A septum-capped NMR tube was charged with **9** (0.0266 g, 0.041 mmol) and CD_2Cl_2 (0.300 mL) and was cooled to −78 °C. Then $Ph_3C^+PF_6^-$ (0.019 g, 0.049 mmol) in CD_2Cl_2 (0.200 mL) was added via gas-tight syringe. The tube contents were mixed and transferred to a −63 °C NMR probe. The reaction was monitored at 20 °C intervals as the probe was warmed from −63 to +25 °C. At 25 °C, the reaction had turned very dark, and a considerable amount of white precipitate (insoluble in CH_2Cl_2, CH_3CN, and acetone) was present: ^{1}H NMR data (δ, CD_2Cl_2) **16k** (−63 °C), 15.87 (ddd, $J_{^1H_\alpha-^{31}P}$ = 2.0 Hz, $J_{^1H_\alpha-^1H_\beta}$ = 8.5 Hz, $J_{^1H_\alpha-^1H_{\beta'}}$ = 8.5 Hz, 1 H), 6.07 (s, 5 H), 4.34 (dd, $J_{^1H_\beta-^1H_\alpha}$ = 8.5 Hz, $J_{^1H_\beta-^1H_\beta}$ = 14.4 Hz, 1 H), 3.95 (dd, $J_{^1H_{\beta'}-^1H_\alpha}$ = 8.5 Hz, $J_{^1H_\beta-^1H_{\beta'}}$ = 14.4 Hz, 1 H), **16t** (25 °C), 15.41 (dd, $J_{^1H_\alpha-^1H_\beta}$ = 9.8 Hz, $J_{^1H_\alpha-^1H_{\beta'}}$ = 6.1 Hz, 1 H), 5.89 (s, 5 H), 4.66 (dd, $J_{^1H_\beta-^1H_{\beta'}}$ = 15.6 Hz, $J_{^1H_\beta-^1H_\alpha}$ = 9.9 Hz, 1 H), 3.25 (dd, $J_{^1H_{\beta'}-^1H_\beta}$ = 15.6 Hz, $J_{^1H_{\beta'}-^1H_\alpha}$ = 6.2 Hz). Product ratios are given in eq 7, and ^{1}H NMR data on **14** are given above.

Preparation of (*SS,RR*)-(η-C_5H_5)Re(NO)(PPh_3)(CH($CH_2C_6H_5$)-CH_3) ((*SS,RR*)-17). To a −78 °C solution of **2** (0.076 g, 0.133 mmol) in 15 mL of CH_2Cl_2 was added 0.063 g (0.162 mmol) of $Ph_3C^+PF_6^-$. The solution was stirred for 20 min at −78 °C, and then 0.150 mL of $C_6H_5CH_2MgCl$ (1.8 M in THF) was added dropwise. The solution turned orange immediately and was allowed to warm to room temperature, whereupon 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 remaining orange oil was chromatographed in 1:1 CH_2Cl_2/hexanes on a 13 × 2.5 cm silica gel column. The entire orange band was collected. Solvent removal gave 0.047 g (0.071 mmol, 53%) of (*SS,RR*)-**17**, mp 193–195 °C dec. Spectroscopic data: Tables I and II.

Preparation of (*SR,RS*)-(η-C_5H_5)Re(NO)(PPh_3)(CH($CH_2C_6H_5$)-CH_3) ((*SR,RS*)-17). To a −78 °C solution of an equilibrium **10t/10k** mixture (0.084 g, 0.117 mmol) in 15 mL of CH_2Cl_2 was added dropwise 0.130 mL of $C_6H_5CH_2MgCl$ (1.8 M in THF). The solution was stirred for 10 min at −78 °C, and then an oil pump vacuum was applied and the solvents were removed as the reaction was allowed to warm to room temperature. The resulting residue was extracted with benzene and filtered through a 2-in. silica gel plug. The benzene was removed to give oily orange crystals which were taken up in 1:1 CH_2Cl_2/hexanes and chromatographed on a 13 × 2.5 cm silica gel column. The entire orange band was collected. Solvent removal under oil pump vacuum gave 0.065 g (0.098 mmol, 84%) of a (91 ± 1):(9 ± 1) (*SR,RS*)-**17**/(*SS,RR*)-**17** (^{1}H NMR analysis) mixture as an orange powder, mp 125–128 °C. Spectroscopic data: Tables I and II.

Preparation of (*SS,RR*)-[(η-C_5H_5)Re(NO)(PPh_3)(CH($^+PMe_3$)-CH_3)]PF_6^- ((*SS,RR*)-18). To a −78 °C solution of **2** (0.106 g, 0.185 mmol) in 20 mL of CH_2Cl_2 at −78 °C was added 0.088 g (0.227 mmol) of $Ph_3C^+PF_6^-$. The yellow solution was stirred for 20 min at −78 °C, and then PMe_3 (0.020 mL, 0.197 mmol) was added dropwise. After an additional 15 min at −78 °C, the solution was allowed to warm to room temperature. Solvent was removed under oil pump vacuum, and the residue was extracted with CH_3CN. Ether was added to the CH_3CN, and the solvents were removed to give an orange powder which was washed with ether. Thus obtained was 0.102 g (0.128 mmol, 70%) of (*SS,RR*)-**18**: mp 224–227 °C dec; IR (cm^{-1}, CH_2Cl_2) $\nu_{N≡O}$ 1648 (s); ^{1}H NMR (δ, $CDCl_3$) 7.54–7.38 (m's, 15 H), 5.24 (s, 5 H), 2.90 (m, 1 H), 1.60 (d, $J_{^1H-^{31}P}$ = 12.7 Hz, 9 H), 1.08 (dd, $J_{^1H_\beta-^1H_\alpha}$ = 7.6 Hz, $J_{^1H_\beta-^{31}PMe_3}$ = 22.5 Hz, 3 H), C_5H_5 in CD_2Cl_2 at δ 5.19; ^{13}C NMR (ppm, acetone-d_6) 134.36 (d, $J_{^{13}C-^{31}P}$ = 9.9 Hz), 131.75 (s), 129.79 (d, J = 9.7 Hz) (ipso carbon not observed), 92.27 (s), 21.12 (s, C*C*H_3), 11.03 (PCH_3, d, J = 54.2 Hz), −13.82 (C_α, d, $J_{^{13}C-^{31}PMe_3}$ = 29.3 Hz).

A ^{1}H NMR monitored reaction was conducted at −78 °C as described above with **10k** generated from 0.012 g (0.021 mmol) of **2** and 0.009 g (0.023 mmol) of $Ph_3C^+PF_6^-$ in CD_2Cl_2. Following the addition of PMe_3 (0.002 mL, 0.020 mmol), no (*SR,RS*)-**18** was detected.

Preparation of (*SR,RS*)-[(η-C_5H_5)Re(NO)(PPh_3)(CH($^+PMe_3$)-CH_3)]PF_6^- ((*SR,RS*)-18). A 15-mL CH_2Cl_2 solution of an equilibrium **10t/10k** mixture was cooled to −78 °C, and 0.016 mL (0.157 mmol) of PMe_3 was added dropwise. The solution turned orange immediately and was allowed to warm to room temperature. Solvent was removed under vacuum to give an orange solid which was washed with ether and dried under vacuum. Thus obtained was 0.085 g (0.107 mmol, 74%) of a (92 ± 1):(8 ± 1) (*SR,RS*)-**18**/(*SS,RR*)-**18** mixture (^{1}H NMR analysis): mp 225–230 °C dec; data on (*SR,RS*)-**18**, IR (cm^{-1}, CH_2Cl_2) $\nu_{N≡O}$ 1643 (s); ^{1}H NMR (δ, CD_2Cl_2) 7.52–7.31 (m's, 15 H), 5.23 (s, 5 H), 2.85 (dq, $J_{^1H_\alpha-^1H_\beta}$ = 7.4 Hz, $J_{^1H_\alpha-^{31}PMe_3}$ = 20.6 Hz, 1 H), 1.63 (d, $J_{^1H-^{31}P}$ = 12.6 Hz, 9 H), 1.33 (dd, $J_{^1H_\beta-^1H_\alpha}$ = 7.4 Hz, $J_{^1H_\beta-^{31}PMe_3}$ = 22.9 Hz, 3 H); ^{13}C NMR (ppm, acetone-d_6) 137.52 (d, $J_{^{13}C-^{31}P}$ = 51.4 Hz), 134.39 (d, J = 9.7 Hz), 131.53 (s), 129.58 (d, J = 9.8 Hz), 92.95 (s), 24.01 (C*C*H_3, d, $J_{^{13}C-^{31}PMe_3}$ = 4.9 Hz), 11.21 (PCH_3, d, $J_{^{13}C-^{31}PMe_3}$ = 54.0 Hz), −21.09 (C_α, d, $J_{^{13}C-^{31}PMe_3}$ = 25.4 Hz).

A ^{1}H NMR monitored reaction was conducted at −78 °C as described above with 0.010 g (0.014 mmol) of **10t/10k** in CD_2Cl_2. Following the addition of PMe_3 (0.002 mL, 0.020 mmol), a (88 ± 1):(12 ± 1) ratio of (*SR,RS*)-**18**/(*SS,RR*)-**18** was observed.

Preparation of (*SR,RS*)-(η-C_5H_5)Re(NO)(PPh_3)(CHDCH_3) ((*SR,RS*)-2-α-d_1). To a −78 °C solution of **2** (0.082 g, 0.143 mmol) in 15 mL of CH_2Cl_2 at −78 °C was added 0.066 g (0.170 mmol) of $Ph_3C^+PF_6^-$. The solution was stirred for 20 min at −78 °C, and then Li(C_2H_5)$_3$BD (0.300 mL, 1.0 M in THF) was added dropwise. The solution turned orange. An oil pump vacuum was applied, and the solvents were removed as the reaction was allowed to warm to room temperature. The resulting residue was extracted with CH_2Cl_2/benzene and filtered through a silica gel plug. The solvent was removed by rotary evaporation, and the resulting orange oil was chromatographed on a 13 × 2.5 cm silica gel column with 1:1 CH_2Cl_2/hexanes. The orange band was collected. Solvent removal under oil pump vacuum gave 0.057 g (0.099 mmol, 70%) of (*SR,RS*)-**2**-α-d_1 as an orange powder. ^{1}H NMR: as for **2** (Table I), but no δ 2.10 resonance.

Preparation of (*SS,RR*)-(η-C_5H_5)Re(NO)(PPh_3)(CHDCH_3) ((*SS,RR*)-2-α-d_1). To a −78 °C solution of an equilibrium **10t/10k** mixture (0.201 g, 0.281 mmol) in 15 mL of CH_2Cl_2 was added dropwise 0.320 mL of Li(C_2H_5)$_3$BD (1.0 M in THF). The solution was stirred for 15 min at −78 °C and then allowed to warm to room temperature. Solvent was removed under oil pump vacuum, and the residue was extracted with CH_2Cl_2/benzene and filtered through a 2-in. silica gel plug. The solvent was removed, and the resulting orange oil was recrystallized from CH_2Cl_2/hexanes to give 0.080 g (0.139 mmol, 50%) of a (89 ± 2):(11 ± 2) (*SS,RR*)-**2**-α-d_1/(*SR,RS*)-**2**-α-d_1 mixture (as determined from the relative integration of the diastereotopic H_α).

Reactions of 2-α-d_1 with $Ph_3C^+PF_6^-$. The following experiment is representative. A septum-capped NMR tube was charged with (*SR,RS*)-**2**-α-d_1 (0.015 g, 0.026 mmol) and CD_2Cl_2 (0.350 mL). The tube was cooled to −78 °C, and $Ph_3C^+PF_6^-$ (0.012 g, 0.031 mmol) in CD_2Cl_2 (0.250 mL) was added via gas tight syringe. The tube was quickly transferred to a −70 °C NMR probe. A ^{1}H NMR spectrum showed that **10k** had formed. Integration of the Re=CH and CH_3 resonances indicated a **10k**-α-d_0/**10k**-α-d_1 ratio of ≳99:1. The sample was warmed to room temperature. A similar integration indicated a **10t**-α-d_0/**10t**-α-d_1 ratio of ≳97:3.

Preparation of [(η-C_5H_5)Re(NO)(PPh_3)(=$CHCD_3$)]$^+$$PF_6^-$ (10-β-d_3). A Schlenk flask was charged with 0.375 g (0.523 mmol) of an equilibrium **10t/10k** mixture and 4.0 mL of acetone-d_6. The solution was stirred for 4 days at room temperature, whereupon solvent was removed under oil pump vacuum. The residue was taken up in $CHCl_3$/CH_2Cl_2 and crystallized by subsequent diffusion addition of ether. This gave 0.300 g (0.394 mmol, 75%) of **10**-β-d_3·0.5 $CHCl_3$ as off yellow plates. Deuterium incorporation ranged from 81% to >98%.

Other Experiments Utilizing Deuterated Rhenium Complexes. Synthesis of and experiments with other deuterated complexes were conducted as outlined in the Results using procedures analogous to those given for the undeuterated complexes. Full details are given elsewhere.[42] Representative experiments follow.

To a −78 °C solution of **2**-α-d_2 (0.104 g, 0.181 mmol) in 20 mL of CH_2Cl_2 was added 0.077 g (0.199 mmol) of $Ph_3C^+PF_6^-$. The resulting bright yellow solution was stirred at −78 °C for 15 min and then allowed to warm to room temperature. After 1 h at room temperature, solvent was removed under oil pump vacuum and the residue was extracted with hexanes. The hexanes were removed by rotary evaporation, and the residue was recrystallized from hot 95% ethanol. Triphenylmethane (0.055 g, 0.143 mmol, 79%) was obtained as white fluffly crystals. The

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

mass spectrum (70 eV) of this material showed a 40.6:100 m/e 244:245 ratio. That for authentic Ph_3CD is 40.3:100. A Ph_3CD/Ph_3CH ratio of (96 ± 1):(4 ± 1) was calculated. The residue remaining after the hexanes extraction was taken up in $CHCl_3$. Ethylidene **10** was isolated by a procedure similar to the one given above. The H_α ^1H NMR resonance was absent, and the H_β ^1H NMR resonance (δ 2.52) was a singlet.

A septum-capped NMR tube was charged with **5**-α-d_2 (0.027 g, 0.044 mmol) and CD_2Cl_2 (0.350 mL). The tube was cooled to −78 °C, and $Ph_3C^+PF_6^-$ (0.019 g, 0.049 mmol) in CD_2Cl_2 (0.200 mL) was slowly added. After a thorough shaking, the tube was quickly transferred to a −73 °C NMR probe. A ^1H NMR spectrum showed the clean formation of **13**-d_2; no olefinic protons were detectable. The sample was warmed to room temperature, which allowed (as a result of slight chemical shift changes) the detection of Ph_3CH (δ 5.54). Solvent was removed from the reaction mixture, and the residue was applied to a silica gel preparative TLC plate. Elution with 1:4 ethyl acetate/hexanes gave a UV-active band with a R_f of ca. 0.7. Triphenylmethane (0.014 g, 0.036 mmol, 82%) was isolated from this band. Its 70-eV mass spectrum gave a 100:18.6 m/e 244:245 ratio, which was identical with that observed in commercial Ph_3CH.

A septum-capped NMR tube was charged with **2** (0.0101 g, 0.0176 mmol), **2**-α-d_2 (0.0104 g, 0.0180 mmol), and CH_2Cl_2 (0.300 mL). The tube was freeze–thaw degassed three times and cooled to −78 °C. Then 0.100 mL of a 0.071 M solution of $Ph_3C^+PF_6^-$ in CH_2Cl_2 (0.0071 mmol, 0.20 equiv) was added via gas-tight syringe. The reaction was kept at −78 °C for 0.5 h and then allowed to warm to room temperature over the course of 3 h. The content of the NMR tube were applied to a preparative TLC plate, and the triphenylmethane was isolated as described in the preceding paragraph. Analysis of the m/e 244:245 ratio in the 70-eV mass spectrum indicated a (84 ± 1):(16 ± 1) Ph_3CH/Ph_3CD ratio.

A septum-capped NMR tube was charged with (*SS,RR*)-**7** (0.0089 g, 0.0137 mmol), (*SS-RR*)-**7**-β-d_3 (0.0092 g, 0.0141 mmol), and CH_2Cl_2 (0.300 mL). The tube was freeze–thaw degassed three times and cooled to −78 °C. Then 0.100 mL of a 0.056 M solution of $Ph_3C^+PF_6^-$ in CH_2Cl_2 (0.0056 mmol, 0.20 equiv) was added via gas-tight syringe. The reaction was kept at −78 °C for 0.5 h and then allowed to warm to room temperature over the course of 3 h. The contents of the NMR tube were applied to a preparative TLC plate and the triphenylmethane was isolated as described above. Analysis of the m/e 244:245 ratio in the 70-eV mass spectrum indicated a (86 ± 1):(14 ± 1) Ph_3CH/Ph_3CD ratio.

Acknowledgment. This investigation was supported by the Department of Energy (regiochemistry) and the NIH (Grant GM 29026-01; stereochemistry). FT NMR and mass spectral measurements made use of spectrometers obtained via NSF Departmental instrumentation grants and the University of Utah Institution Funds Committee. W.A.K. thanks the Regents of the University of California for a Fellowship.

Registry No. 1, 71763-23-0; **2**, 74540-90-2; **2**-α-d_2, 74540-81-1; (*SR,RS*)-**2**-α-d_1, 85926-89-2; (*SS,RR*)-**2**-α-d_1, 85955-96-0; **3**, 74540-91-3; **4**, 85926-72-3; **5**, 85926-73-4; **5**-α-d_2, 85939-48-6; **6**, 85926-74-5; (*SS,RR*)-**7**, 82399-54-0; (*SR,RS*)-**7**, 82374-39-8; **8**, 85956-36-1; **9**, 85926-75-6; **10k**, 74540-80-0; **10t**, 74561-66-3; **10k**-α-d_1, 85955-98-2; **10t**-α-d_1, 85956-00-9; **10**-β-d_3, 85926-91-6; **11k**, 74540-85-5; **11t**, 74561-68-5; **12k**, 85926-77-8; **12t**, 85955-88-0; **13**, 85926-83-6; (*RR,SS*)-**14**, 85926-79-0; (*RS,SR*)-**14**, 85955-90-4; (*RR,SS*)-**15**, 85926-81-4; (*RS,SR*)-**15**, 85955-92-6; **16k**, 85926-85-8; **16t**, 85956-02-1; (*SS,RR*)-**17**, 85926-86-9; (*SR,RS*)-**17**, 85955-93-7; (*SS,RR*)-**18**, 85926-88-1; (*SR,RS*)-**18**, 85955-95-9; (η-C_5H_5)Re(NO)(PPh_3)(CH_3), 71763-18-3; (η-C_5H_5)Re(NO)(PPh_3)($COCH_2C_6H_5$), 82582-48-7; (η-C_5H_5)Re(NO)(PPh_3)(CO_2CH_3), 82293-79-6; $Ph_3C^+PF_6^-$, 437-17-2; $Li(C_2H_5)_3BD$, 74540-86-6; $C_6H_5CH_2Br$, 100-39-0; C_6H_5Br, 108-86-1; PMe_3, 594-09-2.

Are the Silacyclopentadienyl Anion and the Silacyclopropenyl Cation Aromatic?

Mark S. Gordon,* Philip Boudjouk, and Freidun Anwari

Contribution from the Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105. *Received October 25, 1982*

Abstract: Stabilization energies attributable to aromaticity in the silacyclopentadienyl anion and the silacyclopropenyl cation were found to be small in the former and absent in the latter when calculated from bond-separation reactions employing 3-21G and STO-2G basis sets. The silacyclopentadienyl anion is approximately 25% as aromatic as the all-carbon analogue whereas silabenzene is more than 80% as aromatic as benzene. The introduction of diffuse functions into the basis sets has only a small effect on these results. The silacyclopropenyl cation is actually destabilized but strain is probably a key factor in the comparison. Also found was that the STO-2G basis set gives geometries and relative energies consistent with those of a larger basis set and that the semiempirical INDO method may be useful for predicting the structures of larger systems for which geometry optimizations even with STO-2G may be too time consuming.

The long-standing interest on the part of chemists in isolating and characterizing unsaturated silicon has dramatically increased in intensity in the past 10 years.[1] With the exception of a few papers,[2] however, relatively little attention has been paid to the subject of aromatic silicon. From a computational point of view, part of the reason for this is that the size of aromatic systems prevents extensive ab initio calculations with large basis sets.

The present paper has two goals: to investigate the possibility of aromaticity in two simple silacyclo ions and to assess potentially time-saving approaches to larger systems. The $4n + 2$ π electron network in the cyclopentadienyl anion is isoelectronic with that in benzene, and the six π electrons are spread symmetrically among the five carbons in the ion. As a result, one might expect substantial delocalization stabilization in the latter. Silabenzene is apparently nearly as aromatic as benzene;[2b] thus, similar comments presumably apply to the silacyclopentadienyl anion. In the latter system, however, the symmetry is partially destroyed, so the negative charge need not be spread evenly throughout the mol-

(1) L. E. Gusel'nikov and N. S. Nametkin, *Chem. Rev.*, **1979**, *79*, 531.
(2) (a) T. J. Barton and D. S. Banasiak, *J. Am. Chem. Soc.*, **1977**, *99*, 5199; T. J. Barton and G. T. Burns, *ibid.*, **1978**, *100*, 5199; H. Bock, A. Bowling, B. Solouki, T. J. Barton, and G. T. Burns, *ibid.*, **1980**, *102*, 429; C. L. Kreil, D. L. Chapman, G. T. Burns, and T. J. Barton, *ibid.*, **1980**, *102*, 841; G. Maier, G. Mihm, and H. P. Reisenhauer, *Angew. Chem.*, **1980**, *92*, 58 [*Angew. Chem., Int. Ed. Engl.*, **1980**, 19, 52]; B. Solouki, P. Rosmos, H. Bock, and G. Maier, *Angew. Chem.*, **1980**, *92*, 56 [*Angew. Chem., Int. Ed. Engl.*, **1980**, *19*, 51]; T. J. Barton and M. Vuper, *J. Am. Chem. Soc.*, **1981**, *103*, 6788. (b) H. B. Schlegel, B. Coleman, and M. Jones, *ibid.*, **1978**, *100*, 6499; P. H. Blustin, *J. Organomet. Chem.*, **1979**, *166*, 21.

0002-7863/83/1505-4972$01.50/0