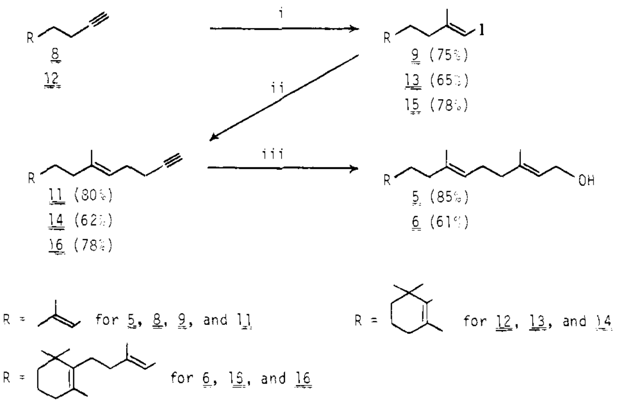
Scheme II[a]



[a] (i) Me_3Al (2 equiv)–Cl_2ZrCp_2 (0.2 equiv) in $(CH_2Cl)_2$, room temperature and then I_2 (1.2 equiv) in THF, 0 °C; (ii) $Me_3SiC{\equiv}CCH_2CH_2ZnCl$ (1 equiv), $Pd(PPh_3)_4$ (0.05 equiv) in THF, room temperature, 3–6 h and then $KF{\cdot}2H_2O$ (3 equiv) in DMF; (iii) Me_3Al (2 equiv)–Cl_2ZrCp_2 (0.2 equiv) in $(CH_2Cl)_2$, room temperature, evaporation, *n*-BuLi (1 equiv) and then $(CH_2O)_n$ in THF.

ylation of 4-bromo-1-butyne (*n*-BuLi and Me_3SiCl) followed by treatment with a mixture of Mg (1.5 equiv) and anhydrous $ZnCl_2$ (1 equiv) in refluxing THF (3-4 h).[13] The organozinc reagent **10** and **9** were mixed with $Pd(PPh_3)_4$ (0.05 equiv) to give the desired cross-coupled product in 90% GLC yield. Significantly, no other peaks were present in any more than trace amounts. The crude cross-coupled product was treated with $KF{\cdot}2H_2O$ (three times), dissolved in DMF[14] at room temperature to give **11**, bp 57–58 °C (0.5 mmHg), in 80% yield from **9** (procedure ii). The stereoisomeric purity of **11** was ≥98% based on its GLC and NMR examination, and its overall purity was >95%. Without further purification **11** was subjected to the second carbometalation followed by ate complexation and treatment with paraformaldehyde, as previously described[15] (procedure iii). Examination of the crude product by GLC (Carbowax 20M) and ^1H NMR indicated the formation of ~95% pure (*E,E*)-farnesol (**5**) in 91% yield (85% isolated). Purification by column chromatography (Florisil, 20:1 benzene–AcOEt) gave **5** which was both stereochemically and regiochemically ≥98% pure.

One distinctly attractive feature of the methodology herein reported is that the two-step cycle consisting of procedures i and ii can readily be repeated for the construction of long-chain 1,5-diene skeletons. Thus no major difficulty was encountered in synthesizing **6** by applying twice the two-step cycle consisting of procedures i and ii. Here again the overall process is estimated to be ≥98% stereoselective. Minor apparently regioisomeric byproducts (<5–10%) in crude **16** (Scheme II) were readily separated by column chromatography (Florisil, hexane). The tetraenol **6** was obtained from **16** via procedure iii (80% by NMR). After simple column chromatography (Florisil, 20:1 hexane–AcOEt) **6** was isolated in 61% yield as an essentially pure single isomer (^1H and ^{13}C NMR and TLC).

Acknowledgments. We thank the National Science Foundation, the National Institutes of Health, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also thank Matthey Bishop, Inc., for a generous loan of palladium compounds.

Supplementary Material Available: Experimental data for compounds **5**, **6**, **9**, **11**, and **13–16** (1 page). Ordering information is given on any current masthead page.

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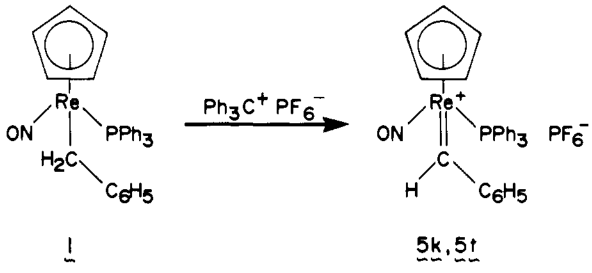
Unprecedented Regiospecificity and Stereospecificity in Reactions of $Ph_3C^+PF_6^-$ with Rhenium Alkyls of the Formula $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2R)$

Sir:

With a single exception,[1] the abstraction or elimination of α-hydrides from transition metal alkyls has been observed only when β-hydrides are absent.[2] In this communication, we report that the rhenium alkyls $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)$ (**1**), $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_3)$ (**2**), and $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_2CH_3)$ (**3**) each react with $Ph_3C^+PF_6^-$ to afford isolable cationic alkylidene complexes $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)({=}CHR)]^+PF_6^-$ in high yields, despite the presence of β-hydrides in **2** and **3**. Furthermore, a novel addition–elimination cycle is utilized to demonstrate that $Ph_3C^+PF_6^-$ stereospecifically abstracts one diastereotopic α-hydride over the other.

Alkyls **1–3** were isolated in 60–80% yields from the reactions of C_6H_5Li, CH_3Li, and CH_3CH_2MgCl, respectively, with the previously described[3] methylidene complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)]^+PF_6^-$ (**4**).[4] Treatment of **1** in CD_2Cl_2 with 1.1 equiv of $Ph_3C^+PF_6^-$ at −70 °C resulted in the immediate formation of benzylidene complex **5k** (eq i), as evidenced by ^1H NMR resonances at δ 16.08 (s, 1 H) and 5.89 (s, 5 H). When the solution was warmed to 10–20 °C, **5k** began to disappear as a new benzylidene complex, **5t**, formed. After solvent removal, **5t** could be isolated in 70–80% yield by crystallization from $CHCl_3$–petroleum ether (30–60 °C).[6] In the solid state, **5t** proved stable to 215 °C.

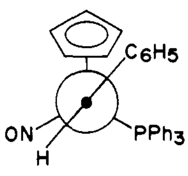
(i)



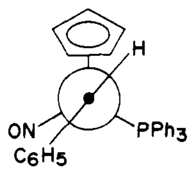
k ⇒ kinetic

t ⇒ thermodynamic

The most plausible explanation for the above observations is that **5** can exist as two geometric isomers owing to restricted rotation about the rhenium-benzylidene bond.[7] Although exact structures cannot be assigned with certainty, Hückel MO calculations on related complexes predict eclipsing of the alkylidene ligand with the nitrosyl group.[8] Since we observed eclipsing of the nitrosyl ligand with the plane of the formyl ligand in the solid-state structure of (η-C_5H_5)Re(NO)(PPh_3)(CHO),[9] we presently favor geometries I and II (Newman projections down the rhenium–alkylidene axis) for **5k** and **5t**, respectively. CPK molecular models indicate I to be considerably more strained than II.



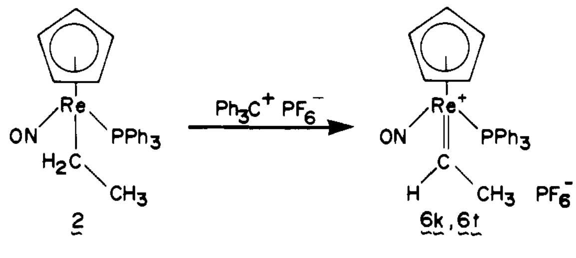
I



II

Treatment of **2** in CD_2Cl_2 with 1.5 equiv of $Ph_3C^+PF_6^-$ at −70 °C resulted, much to our surprise, in the clean and immediate formation of ethylidene complex **6k** (eq ii).[10] At 10–20 °C, **6k** diminished as **6t** appeared. After 4 h at room temperature, <1% **6k** remained. Upon crystallization, mixtures of **6t** and **6k** were obtained (60–75% yields, 90:10–50:50 ratios).[10]

(ii)

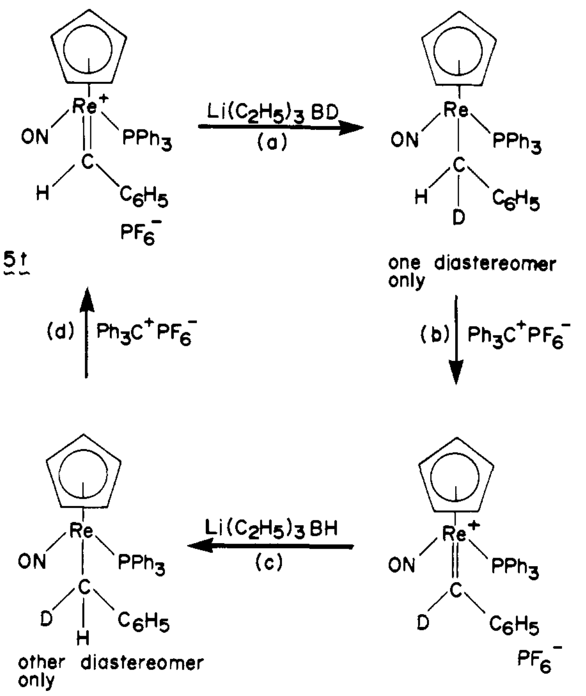


To verify that **6k** and **6t** are α-hydride abstraction products, (η-C_5H_5)Re(NO)(PPh_3)(CD_2CH_3) (**2**-α-d_2) was synthesized.[11] Upon treatment with $Ph_3C^+PF_6^-$, [(η-C_5H_5)Re(NO)(PPh_3)(=$CDCH_3$)]$^+PF_6^-$ (**6**-α-d_1)[12] formed exclusively.

The secondary β-hydrides of **3** might be expected to be more prone toward abstraction than the primary β-hydrides of **2**. However, reaction of **3** in CD_2Cl_2 with 1.5 equiv of $Ph_3C^+PF_6^-$ at −70 °C cleanly yielded the *n*-propylidene complex [(η-C_5H_5)Re(NO)(PPh_3)(=$CHCH_2CH_3$)]$^+PF_6^-$ (**7k**).[13] At 20 °C, **7k** diminished as **7t** formed.[13] Crystallization afforded a 77% yield of a 90:10 **7t**–**7k** mixture.

Experiments were conducted to test the stereospecificity of these reactions. First, **5t** was reacted with $Li(C_2H_5)_3BD$, resulting in the formation of **1**-α-d_1 (70–80% isolated yields), a compound with two chiral centers. The ^1H NMR spectrum of this material in CD_2Cl_2 [δ 3.41 (br d, $J_{^{31}P-^{1}H} = 8$, $J_{^{2}H-^{1}H} \le 2$ Hz)] indicated one of the two diastereotopic hydrogens normally present[3] in **1** to be completely absent (step a, Scheme I). When this **1**-α-d_1 was reacted with $Ph_3C^+PF_6^-$ as described above for **1**-d_0, **5k**-d_1 and then **5t**-d_1 were formed *exclusively*.[14] The mass spectrum of the Ph_3CH formed in this reaction indicated Ph_3CD to be present at natural abundance level. After isolation, **5t**-d_1 was reacted with $Li(C_2H_5)_3BH$, yielding **1**-α-d_1, but with the absolute configuration at carbon opposite the isomer described above [^1H NMR ($CDCl_3$) δ 2.87 (d, $J_{^{31}P-^{1}H} = 3$ Hz)]. After reaction with $Ph_3C^+PF_6^-$ and warming, **5t** was regenerated (step d, Scheme I). Relative areas of the C_5H_5 and benzylidene ^1H NMR resonances showed ≃6% **5t**-d_1 to be present. This indicates the average stereoselectivity of the four steps in Scheme I to be on the order of 98%. However, we believe that a kinetic isotope effect adversely affects the outcome of the final step d and constitutes the principal loss of specificity.

Scheme I. An Organometallic Walden-Type Cycle



To summarize, the above data indicate that (a) only one of two diastereotopic α-hydrides of **1** is prone to abstraction by $Ph_3C^+PF_6^-$ and (b) triethyl borohydride attacks specifically one face of the benzylidene ligand of **5t**. As a final probe, **5k** was prepared from **1** in situ at −70 °C and treated with $Li(C_2H_5)_3BD$. The **1**-α-d_1 formed was a 92:8 mixture of diastereomers; the configuration at carbon in the major product was *opposite* that obtained from **5t** and $Li(C_2H_5)_3BD$. Thus **5k** and **5t** undergo preferred nucleophilic attack on the same benzylidene face.

Several aspects of the preceding reactions merit discussion. First, geometric isomers arising from metal–carbon multiple bonding have not, to our knowledge, been previously observed. Secondly, the regiospecificity evidenced in the reactions of **2** and **3** with $Ph_3C^+PF_6^-$ supports the growing feeling that α-hydride eliminations and/or abstractions may be more common in catalysis than previously supposed.[15] However, with isoelectronic (η-C_5H_5)Fe(CO)$_2$-alkyl complexes, β-hydride abstraction by $Ph_3C^+PF_6^-$ has been unequivocally demonstrated.[16] We believe it possible that an electron-transfer step might alter the selection rules for α- vs. β-hydride abstraction. Finally, transformations of the type depicted in Scheme I establish a remarkable degree of control by a chiral metal center on the development of stereochemistry at an adjacent carbon. Since other nucleophiles can be expected to react similarly to $Li(C_2H_5)_3BH$, and stereospecific methods for metal-alkyl bond cleavages have been developed for related systems,[17] important extensions of these reactions in asymmetric organic synthesis can be anticipated.

Acknowledgment. We are grateful to the Department of Energy for financial support and to Mr. V. K. Wong and Dr. W.-K. Wong for experimental observations related to the chemistry described herein. William A. Kiel thanks the Regents of the University of California for a fellowship.

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(3) Wong, W.-K.; Tam, W.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979,** *101*, 5440.

(4) Alkyl 1 has been reported previously.[3] Data for **2**:[5] ^1H NMR ($CDCl_3$) δ 7.54–7.22 (m, 15 H), 4.92 (s, 5 H), 2.10 (m, 1 H): 1.68 (m, 1 H), 1.58 (distorted t, 3 H); ^{13}C NMR ($CDCl_3$) 89.5, 26.0, −17.4 ppm, and phenyl carbons; IR (CH_2Cl_2) ν_{NO} 1614 cm^{-1}; mp 220 °C dec. 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. Data for **3**:[5] ^1H NMR (CD_2Cl_2) δ 7.57–7.38 (m, 15 H), 4.92 (s, 5 H), 2.03–1.64 (m, 4 H), 0.83 (t, J = 7 Hz, 3 H); ^{13}C NMR (acetone-d_6) 90.3, 35.3, 20.5, −5.9 ppm, and phenyl carbons; IR (CH_2Cl_2) ν_{NO} 1618 cm^{-1}; mp 184–185 °C; mass spectrum (16 eV) *m/e* 587 (M^+, ^{187}Re, 100%).

(5) ^1H NMR spectra were recorded at 200 MHz and ^{13}C NMR spectra were recorded at 50.32 MHz on a spectrometer provided by a NSF departmental instrument grant (CHE76-05926). Probe temperatures were ambient unless noted and chemical shifts were measured relative to $(CH_3)_4Si$.

(6) (a) Data for **5t**:[5] ^1H NMR ($CDCl_3$) δ 15.30 (s, 1 H), 7.52–7.18 (m, 20 H), 6.06 (s, 5 H); ^{13}C NMR (acetone-d_8) 289.0, 101.2 ppm, and phenyl carbons; IR (CH_2Cl_2) ν_{NO} 1708 cm^{-1}; mp 215 °C dec. (b) We have not been able to obtain solvent-free analytically pure crystals of the alkylidene complexes reported herein. However, **5t** and **6t** react with $Li(C_2H_5)_3BH$ to afford high yields of **1** and **2**, respectively, which have been microanalyzed.

(7) Restricted rotation about the rhenium–methylidene bond of **4** is evident from its ^1H NMR spectrum.[3] For the isolation of an isoelectronic and isostructural benzylidene complex *without* the observation of geometric isomers, see Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977,** *99*, 6099.

(8) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979,** *101*, 592.

(9) Wong, W.-K.; Tam, W.; Strouse, C. E.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.*, **1979,** 530. The dihedral angle is ~4.4°.

(10) ^1H NMR of **6k** (CD_2Cl_2, −70 °C)[5] δ 16.27 (q, J = 8 Hz, 1 H), 5.92 (s, 5 H), 2.68 (d, J = 8 Hz, 3 H); phenyl protons overlap with Ph_3CH in the reaction mixture. Data for **6t**:[5,6b] ^1H NMR (CD_2Cl_2) δ 15.82 (q, J = 8 Hz, 1 H), 7.62–7.28 (m, 15 H), 5.94 (s, 5 H), 2.53 (d, J = 8 Hz, 3 H); ^{13}C NMR (acetone-d_6) 310.7, 100.7, 44.0 ppm, and phenyl carbons; IR (CH_2Cl_2) ν_{NO} 1720 cm^{-1}: mp 165 °C dec.

(11) (a) The reaction of $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+PF_6^-$ with $LiAlD_4$ or $NaBD_4$ afforded $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(CD_3)$, which was reacted with $Ph_3C^+PF_6^-$ at −70 °C to yield **4**-α-d_2. Subsequent addition of CH_3Li gave **2**-α-d_2. (b) It is significant that the triphenylmethane accompanying the preparation of **4**-α-d_2[11a] was found to be an ~96:4 mixture of Ph_3CD and Ph_3CH by mass spectrometry. Hence $Ph_3C^+PF_6^-$ may competitively abstract H^- from nondeuterated ligands or other sources. Therefore the presence of small amounts of Ph_3CH when only Ph_3CD is expected cannot be taken as evidence against specificity.

(12) (a) Data for **6t**-α-d_1:[5] ^1H NMR (CD_2Cl_2): δ 7.62–7.30 (m, 15 H), 5.94 (s, 5 H), 2.52 (s, 3 H); ^{13}C NMR identical with that of **6t**-d_0[10] except deuterated carbon was absent owing to increased relaxation time. (b) A 79% yield of an ~96:4 Ph_3CD–Ph_3CH mixture (mass spectrometric determination) was also isolated from this reaction.[11b]

(13) Data for **7k**:[5] ^1H NMR (CD_2Cl_2, −70 °C) δ 15.98 (t, J = 8 Hz, 1 H), 5.94 (s, 5 H), 3.22–3.18 (m, 1 H), 2.63–2.55 (m, 1 H), 0.87 (t, J = 7 Hz, 1 H); phenyl protons overlap with Ph_3CH in the reaction mixture. Data for **7t**:[5,6b] ^1H NMR (CD_2Cl_2) δ 15.55 (t, J = 8 Hz, 1 H), 7.62–7.30 (m, 15 H), 5.93 (s, 5 H), 3.29–3.06 (m, 1 H), 2.74–2.52 (m, 1 H), 0.79 (t, J = 7 Hz, 3 H); ^{13}C NMR (acetone-d_6) 315.5, 100.7, 51.5, 12.6 ppm, and phenyl carbons; IR (CH_2Cl_2) ν_{NO} 1718 cm^{-1}; mp 120 °C dec.

(14) ^1H NMR (CD_2Cl_2):[5] **5k**-d_1, δ 5.89 (s), no benzylidene proton; **5t**-d_1, δ 6.08 (s), no benzylidene proton.

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(17) See: Bock, P. L.; Boschetto, D. J.; Rasmussen, J. R.; Demers, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974,** *96*, 2814. Slack, D. M.; Baird, M. C. *Ibid.* **1976,** *98*, 5539. Miles, S. L.; Miles, D. L.; Bau, R.; Flood, T. C. *Ibid.* **1978,** *100*, 7278, and references therein.

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Metal Atom to Cluster to Bulk Transformations. Electron Spin Resonance Studies of Silver Atoms in Rare Gas Matrices at 12 K. Quantum Size Effect

Sir:

The controlled clustering of silver atoms in a wide variety of matrices has directed attention to the general question of the fundamental interrelationship between metal cluster nuclearity and molecular and bulk properties, as seen through the eye of various spectroscopies. A number of groups have recently examined the optical absorption spectra of very small silver clusters generated by matrix cryochemical methods and have used the appearance of a surface plasma absorption as one criterion for establishing the onset of bulk silver microcrystalline properties, from that of molecular silver cluster behavior.[1-3] Although the nuclearity determination above six silver atoms is not yet firmly established, a relatively smooth conversion from a one-electron molecular eigenstate cluster picture into that of conduction band bulk-like character is emerging from this "optical-electronic" image of the very early stages of silver nucleation.[1-3]

Along with the optical absorption measurements of the embryonic stages of silver cluster growth, we have also recently conducted a series of ESR measurements, in a designed attempt to collect complementary structural and electronic information for the paramagnetic species present in the silver cluster system. It is the purpose of this communication to report that, by simultaneously monitoring the optical and ESR spectra for Ag/inert gas samples deposited onto a sapphire rod,[12] it is possible to establish that the onset of collective electronic excitations in silver clusters around a nuclearity of ~6–13 atoms[1,2,3] is accompanied in the ESR spectrum by the appearance of a conduction electron spin resonance (C ESR) whose band width and g-shift behavior provides one of the few, direct experimental verifications of "quantum size effects" in very small metal particles.[4]

At high silver concentrations in Ar or Kr matrices (1:10^{2-3}), or after extensive matrix annealing or photoaggregation[1] of matrices dilute in silver (1:10^{3-4}), the samples showed only *weak* ESR lines corresponding to the hyperfine components of isolated $^{107}Ag/^{109}Ag$ atoms[5] (nuclear spin $I = 1/2$ in both cases, with roughly equal natural isotopic abundances), as well as a resonance around the free electron value of $g = 2$, whose intensity, band width, and associated fine structure depended on the matrix preparation and pretreatment mentioned above (Figure 1). According to earlier ESR studies of small metal particles,[6] it would appear that this latter resonance is a composite of two contributions: (i) sharp lines associated with a range of silver aggregates with molecular cluster properties (four to six atoms suggested optically),[1,2,3] rather than metal microcrystallite properties, and (ii) a broader C ESR line ascribable to small silver microcrystallites on which the sharp lines (i) are superimposed. The temperature dependence of these ESR spectra indicate that silver atomic features decay to 0 in Ar at ~30–35 K, while the resonances associated with molecular silver clusters disappear at ~40–45 K, leaving behind the broader, small-particle C ESR. This type of behavior seems to be mirroring the metal atom to cluster to bulk transformations observed in the corresponding optical spectra.[1-3]

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