suspect that inclusion of some electron correlation will dramatically improve the results, as it has been documented for the other situations.[37] Secondly, the optimized value of the Ta–benzene rotation angle, ϕ, is certainly too large. However, the potential energy surface around the optimized C_2 geometry was found to be extremely flat. In fact a single point calculation with ϕ set at the experimental value (15.6°) and fixing *all* other internal coordinates to their optimized values in 18 resulted in an energy expenditure of only 2.1 kcal/mol. Notice that the pattern of a short C(2)–C(3) (and C(5)–C(6)) distance compared to the others in 3 and reproduced in 18 is a direct result of the larger occupation of the a_1 π^* orbital on benzene compared to a_2 (see Figure 3). The a_1 orbital is bonding between C(2) and C(3), while it is antibonding between C(1)–C(2) and C(3)–C(4).

The peculiar twist-boat conformation in 3 is, therefore, tied to the hybridization presented in the $x^2 - y^2$ orbital on Ta along with the fact that the $1a_1$ molecular orbital in Figure 3 is doubly occupied, whereas $1a_2$ is occupied with a single electron. The substantial buckling of the arene ring and its C–C bond localization underscore the fact that there is extremely strong δ-type bonding between the arene and Ta in these complexes compared to the situation that exists for other 16–18-electron (η^6-arene)ML_n systems.[34,35] The addition of another electron to $1a_2$ should then cause the arene to return to planarity and greatly reduce the rotational barrier around the arene–Ta axis. A one-electron reduction of 3 is not particularly facile, as seen in its electrochemical reduction, which occurs at ca. −1.7 V vs Ag/AgCl. The reason for this is that strong π bonding exists between the alkoxide oxygen atoms and Ta. This is evidenced in the structure of 3 and the model calculations since the Ta–O–R angle (see Table V) is extremely large. Therefore, a 14-electron (η^6-arene)TaL_2 candidate is more feasible with a weaker π donor set on the auxiliary ligands. We shall explore work along these lines in the future.

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Supplementary Material Available: Textual presentation of data collection and reduction and structure solution and refinement, tables of the structure solution and crystallographic details for (η^6-C_6Et_6)$Ta(DIPP)_2$, atomic positional and thermal parameters, bond distances and angles, least-squares planes, dihedral angles, and ORTEP figures and full listings of the internal coordinates and total energies for (η^6-C_6H_6)$Ta(OH)_2$ (26 pages); tables of observed and calculated structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

(37) (a) Williamson, R. L.; Hall, M. B. *Int. J. Quantum Chem., Quantum. Chem. Symp.* **1987**, *21*, 503. (b) Taylor, T. E.; Hall, M. B. *Chem. Phys. Lett.* **1985**, *114*, 338. (c) Lüthi, H. P.; Siegbahn, P. E. M.; Almlöf, J.; Faegri, K., Jr.; Heiberg, A. *Ibid.* **1984**, *111*, 1. (d) Kang, S.-K.; Albright, T. A. Unpublished calculations.

Reactions of the Neohexyl Iodide Complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_2CH_2C(CH_3)_3)]^+BF_4^-$ and Nucleophiles: Stereochemistry of Carbon–Iodine Bond Cleavage in Highly Accelerated S_N2 Reactions

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Reaction of (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3), $ICH_2CH_2C(CH_3)_3$ (2), and HBF_4·OEt_2 in C_6H_5Cl gives neohexyl iodide complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_2CH_2C(CH_3)_3)]^+BF_4^-$ (3, 81%). Complex 3 and PPh_3 react (−40 °C, CD_2Cl_2) to give $[Ph_3PCH_2CH_2C(CH_3)_3]^+BF_4^-$ (7) and (η^5-C_5H_5)Re(NO)(PPh_3)(I) (6) in >99% spectroscopic yields. Complex 3 and $[Ph_3P{=}N{=}PPh_3]^+Br^-$ (PPN^+Br^-) react (−40 °C, CD_2Cl_2) to give $BrCH_2CH_2C(CH_3)_3$ (8) and 6 in 97–99% spectroscopic yields. Deuterated neohexyl halides *erythro*-$ICHDCHDC(CH_3)_3$ (*erythro*-2-d_2), *threo*-2-d_2, *erythro*-8-d_2, and *threo*-8-d_2 are prepared via (η^5-$C_5H_5)_2Zr(Cl)(X)$ compounds. The labeled complexes *erythro*-3-d_2 and *threo*-3-d_2 are synthesized, and analogous reactions with PPN^+Br^- and PPh_3 are conducted. Diastereomer ratios of the products 8-d_2 and 7-d_2, and all preceding deuterated compounds, are analyzed by 500-MHz $^1H\{^2H\}$ NMR spectroscopy. In all cases, the carbon–iodine bond in 3-d_2 is cleaved with essentially complete *inversion* of configuration at carbon.

Ten years ago, stable transition-metal complexes of alkyl halides were unknown. Since the pioneering 1982 study by Crabtree, the isolation of a variety of alkyl halide complexes has been reported.[1-7] Accordingly, there has been a surge of interest in the coordination chemistry of alkyl halide ligands.

(1) Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev.* **1990**, *99*, 89.

(2) (a) Crabtree, R. H.; Faller, J. W.; Mellea, M. F.; Quirk, J. M. *Organometallics* **1982**, *1*, 1361. (b) Burk, M. J.; Segmuller, B.; Crabtree, R. H. *Ibid.* **1987**, *6*, 2241. (c) Kulawiec, R. J.; Faller, J. W.; Crabtree, R. H. *Ibid.* **1990**, *9*, 745 and references therein.

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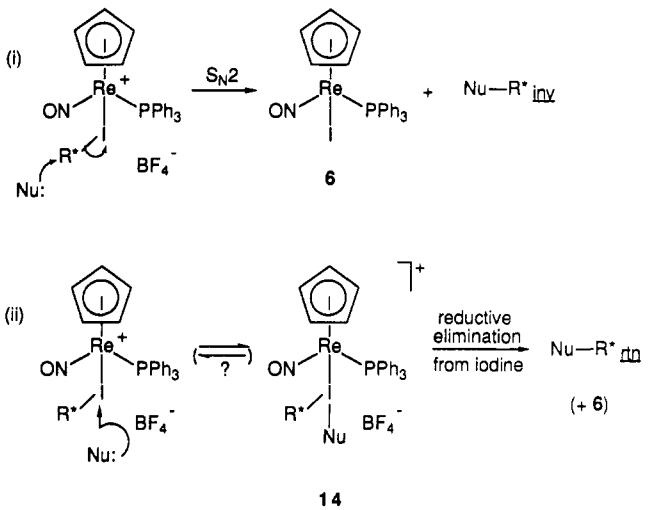
Scheme I. Possible Pathways for Nucleophilic Attack upon Coordinated Alkyl Iodides



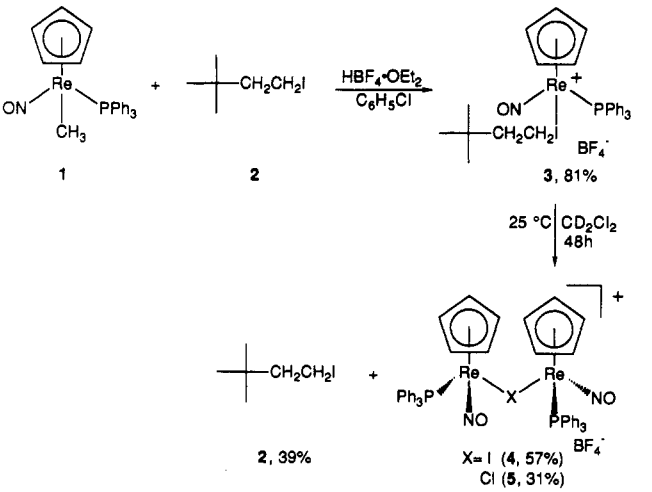
In a previous paper, we gave a detailed account of the synthesis, structure, and reactivity of primary alkyl iodide complexes of the formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_2R)]^+BF_4^-$.[5] We found that the binding of alkyl iodides to rhenium dramatically enhanced reactivity toward nucleophiles, thus providing superior (and chiral) alkylating agents. Rate accelerations of $(3.3 \pm 1.3) \times 10^5$ were measured for the reaction of PPh_3 and coordinated ethyl iodide at 298 K. Crabtree and co-workers have found comparable rate enhancements with the iridium methyl iodide complex $[(H)_2Ir(PPh_3)_2(ICH_3)_2]^+X^-$ and ruthenium complexes $[(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)(IR)]^+X^-$ (R = CH_3, $CH(CH_3)_2$).[2b,c]

We have sought to probe the origin of the enhanced electrophilicity of coordinated alkyl halides. A theoretical study of the model compound $[(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(ICH_3)]^+$ has been conducted by Fenske and Czech.[6] The results show that the LUMO is to a large extent localized on *iodine*, opposite to the rhenium–iodine bond. This suggests that nucleophiles (Nu) might initially associate with the iodine, as shown in eq ii of Scheme I. Reductive elimination of product (NuR) from iodine could subsequently occur. This step would likely proceed with *retention* of configuration at carbon. Accordingly, we set out to synthesize and study the reactivity of alkyl iodide complexes in which the stereochemistry of carbon–iodine bond cleavage could be assayed.

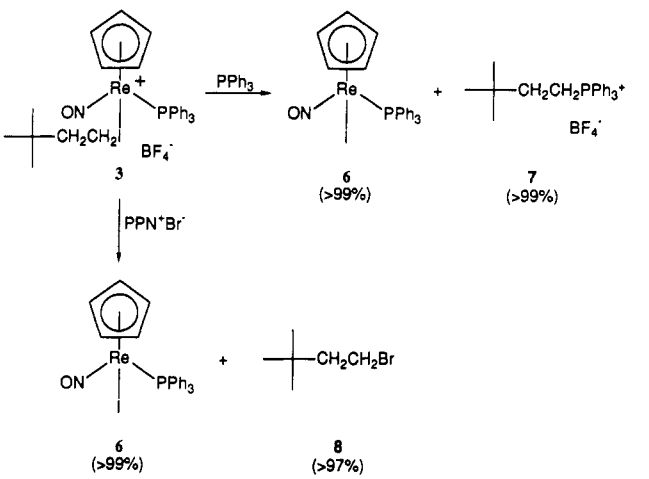
Results

1. Synthesis and Stability of a Neohexyl Iodide Complex. Methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (1)[8] and neohexyl iodide, $ICH_2CH_2C(CH_3)_3$ (2; 3 equiv), were dissolved in chlorobenzene at −40 °C (Scheme II). Then $HBF_4{\cdot}OEt_2$ was added (1.0 equiv).[9] Workup gave

Scheme II. Synthesis and Decomposition of Neohexyl Iodide Complex 3



Scheme III. Reactions of Neohexyl Iodide Complex 3 with Nucleophiles



the neohexyl iodide complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_2CH_2C(CH_3)_3)]^+BF_4^-$ (3) as a tan powder in 81% yield. Complex 3 was air and light sensitive and was stored under nitrogen at −10 °C.

Complex 3 was characterized by IR, NMR (^1H, ^{13}C, ^{31}P), and FAB mass spectroscopy (Experimental Section). General features resembled those found previously for other primary alkyl iodide complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_2R)]^+BF_4^-$.[5] In particular, the ICH_2 ^{13}C NMR resonance (26.1 ppm, CD_2Cl_2) showed a characteristic downfield shift (Δ24.7 ppm) from that of free neohexyl iodide (1.4 ppm, $CDCl_3$). By NMR spectroscopy, 3 appeared to be pure. However, in contrast to the primary alkyl iodide complexes reported earlier, satisfactory microanalyses were not obtained.

Complex 3 decomposed over the course of 48 h at room temperature in CD_2Cl_2 (Scheme II), as assayed by ^1H and ^{31}P NMR spectroscopy in the presence of an internal standard. A mixture of the previously characterized bridging iodide complex *RR,SS*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2I^+BF_4^-$ (4, 57%),[10] bridging chloride complex *SS,RR*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2Cl^+BF_4^-$ (5, 31%),[7a] and iodide $ICH_2CH_2C(CH_3)_3$ (2, 39%) formed. In separate

(3) (a) Colsman, M. R.; Newbound, T. D.; Marshall, L. J.; Noirot, M. D.; Miller, M. M.; Wulfsberg, G. P.; Frye, J. S.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 2349 and references therein. (b) Bown, M.; Water, J. M. *Ibid.* **1990**, *112*, 2442.

(4) Conroy-Lewis, F. M.; Redhouse, A. D.; Simpson, S. J. *J. Organomet. Chem.* **1989**, *366*, 357.

(5) Winter, C. H.; Veal, W. R.; Garner, C. M.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 4766.

(6) Czech, P. T.; Gladysz, J. A.; Fenske, R. F. *Organometallics* **1989**, *8*, 1806.

(7) (a) Fernández, J. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207. (b) Kowalczyk, J. J.; Agbossou, S. K.; Gladysz, J. A. *J. Organomet. Chem.* **1990**, *397*, 333.

(8) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

(9) In the absence of alkyl iodide, a chlorobenzene complex is generated under these conditions.[7b] Complex 3 can also be synthesized in CH_2Cl_2, but isolated yields are lower.

(10) Winter, C. H.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 219.

experiments, **4** and **5** were isolated. Their properties matched those of authentic samples.

2. Reactions of Neohexyl Iodide Complex 3 and Nucleophiles. Complex **3** and PPh_3 (1.6 equiv) were combined in CD_2Cl_2 at −40 °C in the presence of an internal standard (Scheme III). The solution was slowly warmed to room temperature. Carbon–iodine bond cleavage cleanly occurred to give iodide complex (η^5-C_5H_5)Re(NO)(PPh_3)(I) (**6**, >99%)[11] and the phosphonium salt $[Ph_3PCH_2CH_2C(CH_3)_3]^+BF_4^-$ (**7**, >99%), as assayed ^1H, ^{13}C, and ^{31}P NMR spectroscopy. The phosphonium salt **7** was a new compound. Thus, an authentic sample was prepared from PPh_3, neohexyl bromide $BrCH_2CH_2C(CH_3)_3$ (**8**), and $AgBF_4$, as described in the Experimental Section.

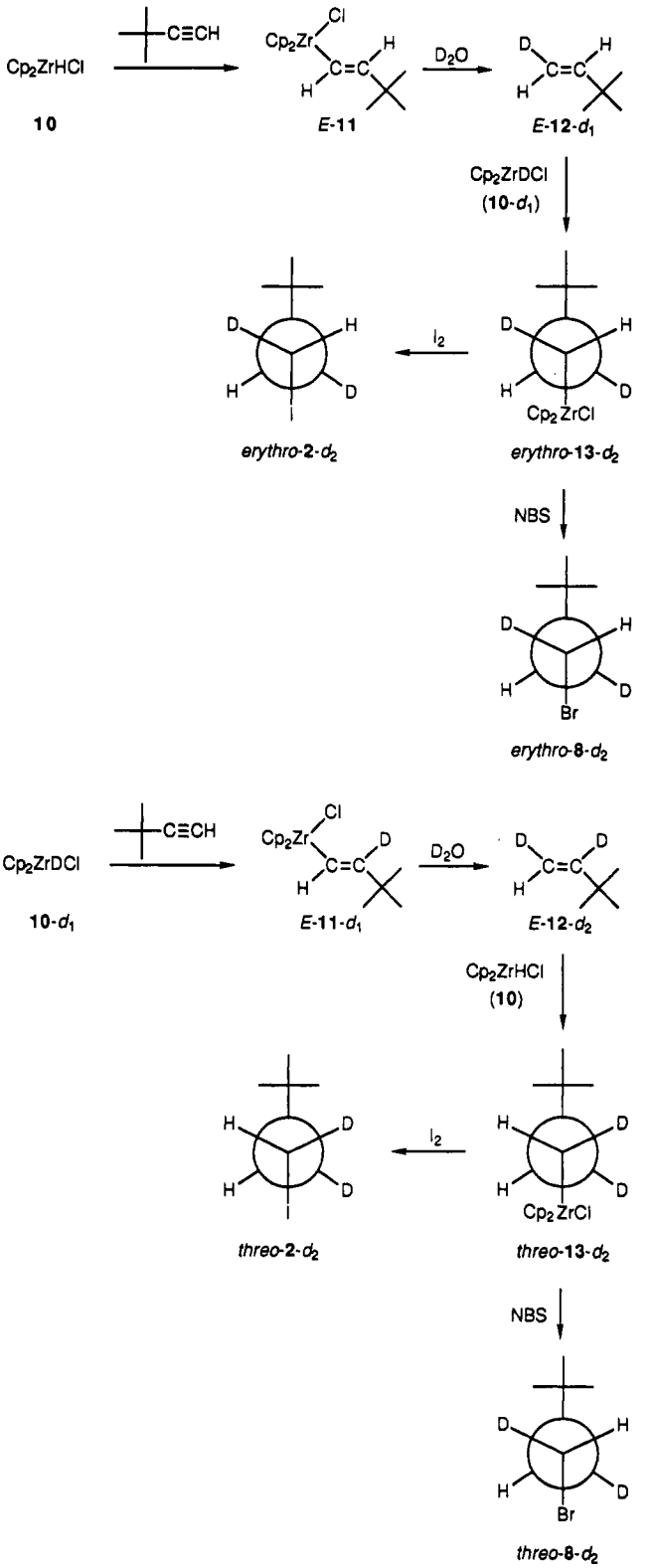
Complex **3** and PPN^+Br^- (1.2 equiv)[12] were combined in CD_2Cl_2 at −40 °C in the presence of an internal standard (Scheme III). After 12 h at −40 °C, ^1H, ^{13}C, and ^{31}P NMR spectra showed complete conversion to iodide complex **6** (>99%) and neohexyl bromide **8** (97%). The formation of **8** was also confirmed by GLC (97%). When an identical reaction was conducted at room temperature, some bromide complex (η^5-C_5H_5)Re(NO)(PPh_3)(Br) (**9**) was observed.

The ethyl iodide complex $[(\eta^5$-$C_5H_5)$Re(NO)(PPh_3)$(ICH_2CH_3)]^+BF_4^-$ has been previously shown to react with PPh_3 analogously to **3**.[5] Rates have been measured in $CDCl_3$ over the temperature range 218–243 K, and a second-order rate law established. A qualitative reactivity comparison to **3** was sought. Thus, rates of reaction of **3** and PPh_3 were measured in CD_2Cl_2 at 238 K ([**3**] = 0.0527 M, [PPh_3] = 0.0527 M) and 222 K ([**3**] = 0.0379 M, [PPh_3] = 0.0676 M).[13] The second-order rate constants (2.96 ± 0.03 M^{-1} s^{-1} and 0.47 ± 0.03 M^{-1} s^{-1}) were approximately 6 times less than those of the ethyl iodide complex at corresponding temperatures.

3. Synthesis of Dideuterioneohexyl Iodides (2-*d*$_2$). Several elegant mechanistic studies have made use of *erythro*- and *threo*-1,2-dideuterioneohexyl iodide, ICHDCHDC$(CH_3)_3$ (**2**-d_2), to determine the stereochemistry of carbon–iodine bond cleavage reactions.[14] The vicinal ^1H NMR coupling constants ($^3J_{HH}$) of erythro isomers of XCHDCHDC$(CH_3)_3$ compounds are commonly much greater than those of threo isomers.[15] Thus, inversion, retention, and racemization processes are easily distinguished.[16]

However, of the three syntheses of *erythro*-**2**-d_2 and *threo*-**2**-d_2 reported in the literature,[14a,c,17] only experimental procedures for the lengthiest have been described in detail.[14a] We elected to follow a shorter route utilizing zirconium-based reagents that was communicated by Schwartz some time ago.[17,18]

Scheme IV. Synthesis of *threo*- and *erythro*-Dideuterioneohexyl Derivatives



Schwartz has shown that the zirconium hydride (η^5-$C_5H_5)_2$Zr(Cl)(H) (**10**) adds to terminal alkynes RC≡CH with cis stereochemistry and very high regioselectivity to give (*E*)-vinylzirconium complexes *E*-(η^5-$C_5H_5)_2$Zr(Cl)-(CH=CHR).[17,18] Thus, HC≡CC$(CH_3)_3$ was reacted with

(11) Merrifield, J. H.; Fernández, J. M.; Buhro, W. E.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 4022.
(12) PPN^+ = $[Ph_3P{=}N{=}PPh_3]^+$.
(13) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw Hill: New York, 1981; pp 16–21.
(14) (a) Bock, P. L.; Boschetto, D. J.; Rasmussen, J. R.; Demers, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2814. (b) Collman, J. P.; Brauman, J. I.; Madonik, A. M. *Organometallics* **1986**, *5*, 310. (c) Madonik, A. M. Ph.D. Thesis, Stanford University, 1981.
(15) Since XCHD–CHDC$(CH_3)_3$ conformations in which the X and *tert*-butyl groups are anti will be preferred, H–C–C–H torsion angles will be ca. 180° in erythro isomers and 60° in threo isomers. The relationship $^3J_{HH}$(erythro) > $^3J_{HH}$(threo) then follows from the Karplus equation.
(16) Substrates such as ICHDCHDC$_6H_5$ offer the possibility of phenyl group participation and were thus avoided: Flood, T. C.; DiSanti, F. J. *J. Chem. Soc., Chem. Commun.* **1975**, 18.
(17) (a) Labinger, J. A.; Hart, D. W.; Seibert, W. E., III; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 3851. (b) Some procedures for analogous undeuterated compounds: Carr, D. B.; Schwartz, J. *Ibid.* **1979**, *101*, 3521. (c) See also: Nelson, J. E.; Bercaw, J. E.; Labinger, J. A. *Organometallics* **1989**, *8*, 2484.
(18) (a) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333. (b) Labinger, J. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, England, in press.

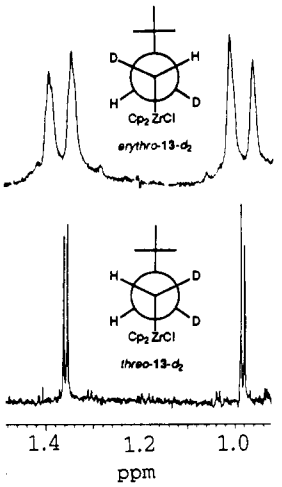


Figure 1. ^1H NMR spectra (CD_2Cl_2, ZrC*H*DC*H*D protons) of diastereomers of **13**-d_2: (top) 300-MHz ^1H NMR spectrum of *erythro*-**13**-d_2; (bottom) 500-MHz $^1H\{^2H\}$ NMR spectrum of *threo*-**13**-d_2.

both **10** and $(\eta^5\text{-}C_5H_5)_2Zr(Cl)(D)$ (**10**-d_1), as outlined in Scheme IV. Solvent removal gave crude vinylzirconium complexes $E\text{-}(\eta^5\text{-}C_5H_5)_2Zr(Cl)(CH{=}CHC(CH_3)_3)$ (*E*-**11**) and $E\text{-}(\eta^5\text{-}C_5H_5)_2Zr(Cl)(CH{=}CDC(CH_3)_3)$ (*E*-**11**-d_1), which were characterized by ^1H NMR spectroscopy (Experimental Section).

Complexes *E*-**11** and *E*-**11**-d_1 were treated with D_2O. Distillation gave the deuterioalkenes $E\text{-}CHD{=}CHC(CH_3)_3$ (*E*-**12**-d_1) and $E\text{-}CHD{=}CDC(CH_3)_3$ (*E*-**12**-d_2), respectively, in 71–72% yields (Scheme IV). These compounds were characterized by ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectra showed the level of deuteration to be >96% (no residual protium detected).

Schwartz has also established that the zirconium hydride **10** adds to terminal alkenes with cis stereochemistry and very high regioselectivity.[17,18] Thus, **10**-d_1 and *E*-**12**-d_1 were reacted (Scheme IV). Workup gave the dideuterioneohexyl complex *erythro*-$(\eta^5\text{-}C_5H_5)_2Zr(Cl)(CHDCHDC(CH_3)_3)$ (*erythro*-**13**-d_2) in 92% yield. A 300-MHz ^1H NMR spectrum indicated a high level of diastereomeric purity, as illustrated in Figure 1. The $^3J_{HH}$ value (13.0 Hz) was in good agreement with that reported earlier.[17a]

Next, **10** and *E*-**12**-d_2 were similarly reacted. Workup gave *threo*-$(\eta^5\text{-}C_5H_5)_2Zr(Cl)(CHDCHDC(CH_3)_3)$ (*threo*-**13**-d_2) in 91% yield. A 300-MHz ^1H NMR spectrum suggested high diastereomeric purity, but the vicinal couplings were poorly resolved due to deuterium broadening. Therefore a 500-MHz ^1H NMR spectrum was acquired with broad-band deuterium decoupling, as shown in Figure 1 (bottom). This gave a $^3J_{HH}$ value (3.6 Hz) that was close to that communicated previously[17a] and established a very high level of diastereomeric purity. In view of the improved resolution, all $XCHDCHDC(CH_3)_3$ compounds were analyzed by $^1H\{^2H\}$ NMR spectroscopy.

Dideuterioneohexyl iodides **2**-d_2 were subsequently sought. Previously, a number of zirconium alkyl complexes $(\eta^5\text{-}C_5H_5)_2Zr(Cl)(R)$ have been shown to react with iodine to give alkyl iodides RI.[17,18] Thus, a benzene solution of *erythro*-**13**-d_2 was frozen (−20 °C). Then a solution of iodine in THF was added, and the mixture was kept at 0–10 °C for 1 h. Workup gave *erythro*-**2**-d_2 as a colorless oil in 72% yield. A 500-MHz $^1H\{^2H\}$ NMR spectrum indicated a (85 ± 3):(15 ± 3) erythro:threo ratio.[19] Hence,

(19) The erythro:threo ratios (see spectra, Figures 2–6) were determined by both peak height and cut/weigh methods. Resolution enhancement was *not* used on the spectra thus analyzed.

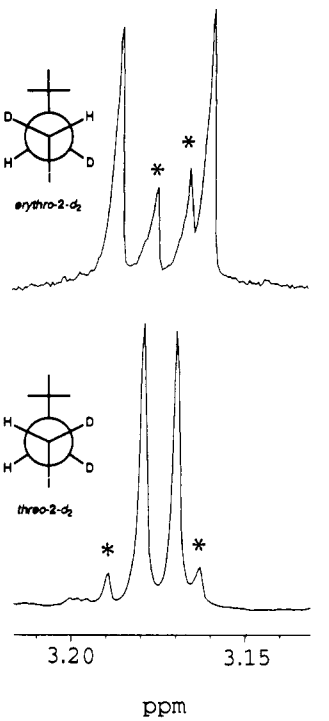


Figure 2. Representative 500-MHz $^1H\{^2H\}$ NMR spectra (CD_2Cl_2, IC*H*D protons) of diastereomers of **2**-d_2: (top) *erythro*-**2**-d_2 ((65 ● 3):(35 ± 3) erythro:threo* ratio); (bottom) *threo*-**2**-d_2 ((85 ± 3):(15 ± 3) threo:erythro* ratio).

a moderate decrease in diastereomeric purity accompanies the reaction. However, the configuration at carbon is predominantly retained, as reported earlier.[17a]

The stereochemistry of zirconium–carbon bond cleavage was found to be an extremely sensitive function of conditions. An analogous reaction of *erythro*-**13**-d_2 and iodine at room temperature gave **2**-d_2 that was a (65 ± 3):(35 ± 3) erythro:threo mixture. The corresponding 500-MHz $^1H\{^2H\}$ NMR spectrum is shown in Figure 2 (top). Reaction of *erythro*-**13**-d_2 and iodine in THF at −80 °C also gave **2**-d_2 that was a (65 ± 3):(35 ± 3) erythro:threo mixture. Better diastereoselectivity might be obtained in toluene at −80 °C, instead of benzene at 0–10 °C as used above. However, the volatile product **2**-d_2 would be difficult to separate from the higher boiling solvent.

Next, a frozen benzene solution of *threo*-**13**-d_2 and a THF solution of iodine were similarly combined. Workup gave *threo*-$ICHDCHDC(CH_3)_3$ (*threo*-**2**-d_2) as a colorless oil in 72% yield. A 500-MHz $^1H\{^2H\}$ NMR spectrum (Figure 2, bottom) indicated a (85 ± 3):(15 ± 3) threo:erythro ratio.

Authentic samples of dideuterioneohexyl bromides $BrCHDCHDC(CH_3)_3$ (**8**-d_2) were also sought. Thus, *erythro*-**13**-d_2 and *N*-bromosuccinimide (NBS) were reacted in benzene at 0–10 °C. Workup gave *erythro*-**8**-d_2 as a colorless oil in 82% yield. A 500-MHz $^1H\{^2H\}$ NMR spectrum (Figure 3, top) indicated a (95 ± 3):(5 ± 3) erythro:threo ratio.[19] A sample of *threo*-**8**-d_2 was analogously prepared. A 500-MHz $^1H\{^2H\}$ NMR spectrum (Figure 3, bottom) indicated a (92 ± 3):(8 ± 3) threo/erythro ratio.

4. Synthesis and Reactions of Dideuterioneohexyl Iodide Complexes. The samples of *erythro*-**2**-d_2 and *threo*-**2**-d_2 prepared above were reacted with $(\eta^5\text{-}C_5H_5)\text{-}Re(NO)(PPh_3)(CH_3)$ and $HBF_4{\cdot}OEt_2$ in procedures analogous to that in Scheme II. Workup gave the dideuterioneohexyl iodide complexes *erythro*-**3**-d_2 and *threo*-**3**-d_2, 500-MHz $^1H\{^2H\}$ NMR spectra of which are shown in Figure 4. Two points deserve emphasis. First,

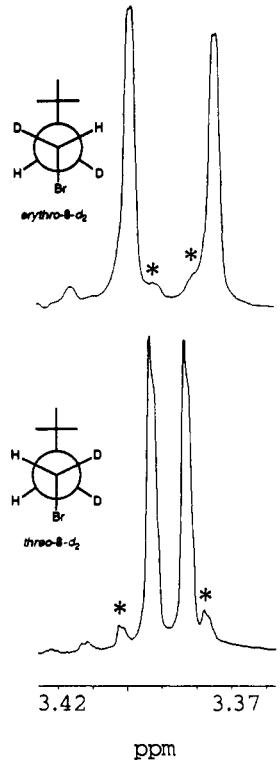


Figure 3. Representative 500-MHz $^1H\{^2H\}$ NMR spectra (CD_2Cl_2, BrC*H*D protons) of diastereomers of 8-d_2: (top) *erythro*-8-d_2 ((95 ± 3):(5 ± 3) erythro:threo* ratio); (bottom) *threo*-8-d_2 ((92 ± 3):(8 ± 3) threo:erythro* ratio).

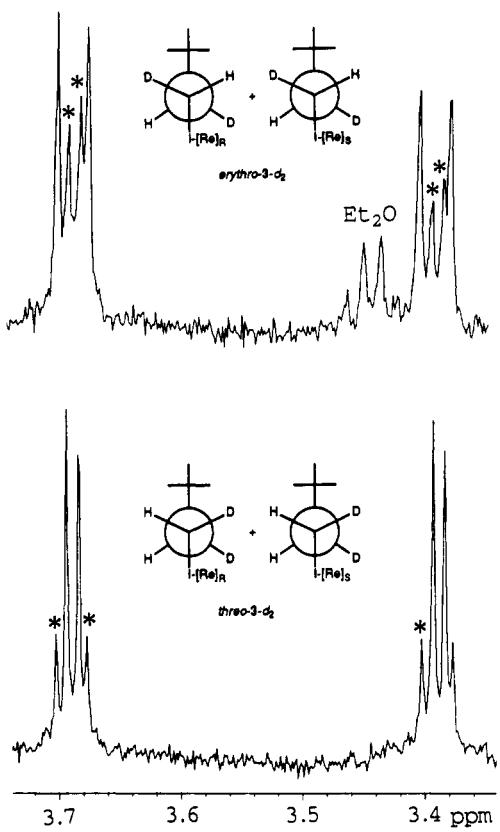


Figure 4. Representative 500-MHz $^1H\{^2H\}$ NMR spectra (CD_2Cl_2, ReIC*H*D protons) of diastereomers of 3-d_2: (top) *erythro*-3-d_2 ((65 ± 3):(35 ± 3) erythro:threo* ratio); (bottom) *threo*-3-d_2 ((85 ± 3):(15 ± 3) threo:erythro* ratio).

since the stereochemistry of carbon–iodine bond cleavage can be readily assayed with (85–65):(15–35) erythro:threo

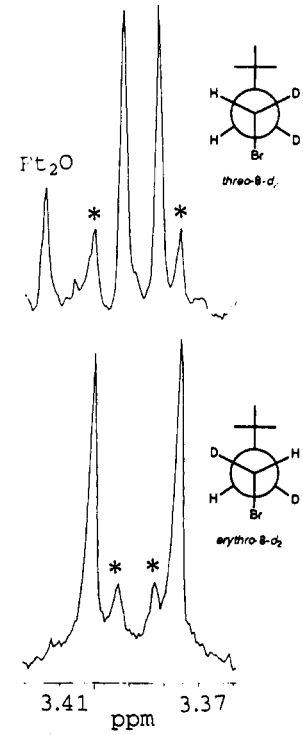
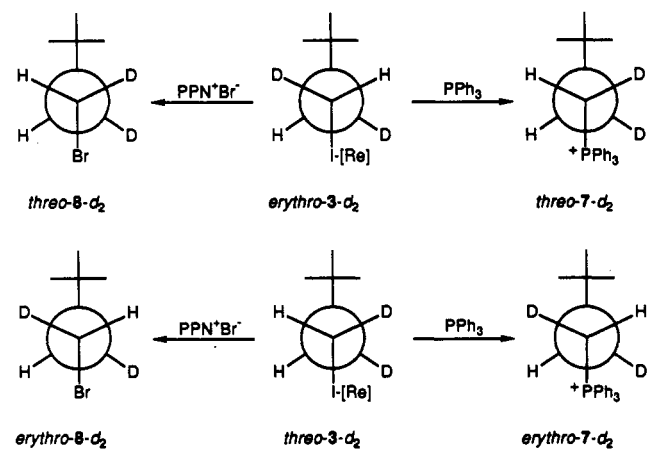


Figure 5. 500-MHz $^1H\{^2H\}$ NMR spectra (CD_2Cl_2, BrC*H*D protons) of diastereomers of 8-d_2 that have been prepared from 3-d_2: (top) *threo*-8-d_2 ((65 ± 3):(35 ± 3) threo:erythro* ratio); (bottom) *erythro*-8-d_2 ((85 ± 3):(15 ± 3) erythro:threo* ratio).

Scheme V. Reactions of Dideuterioneohexyl Iodide Complexes 3-d_2



mixtures, no special attempt was made to procure samples of 3-d_2 that were diastereomerically pure. Second, since the rhenium is a stereocenter, two sets of *erythro*-3-d_2 and *threo*-3-d_2 diastereomers are possible. These give distinct ^1H NMR resonances, as illustrated in Figure 4.

Next, *erythro*-3-d_2 ((65 ± 3):(35 ± 3) erythro:threo ratio) and PPN^+Br^- were reacted in a procedure analogous to that in Scheme III (Scheme V). The resulting dideuterioneohexyl bromide 8-d_2 was analyzed in situ by 500-MHz $^1H\{^2H\}$ NMR spectroscopy (Figure 5, top). A (65 ± 3):(35 ± 3) threo:erythro mixture formed. An identical reaction was conducted with *threo*-3-d_2 ((85 ± 3):(15 ± 3) threo:erythro ratio). Bromide 8-d_2 formed as a (85 ± 3):(15 ± 3) erythro:threo mixture (Figure 5, bottom). These data indicate that the carbon–iodine bond in 3-d_2 is cleaved by PPN^+Br^- with *inversion* of configuration at carbon.

Finally, *erythro*-3-d_2 ((65 ± 3):(35 ± 3) erythro:threo ratio) and PPh_3 were reacted in a procedure analogous to

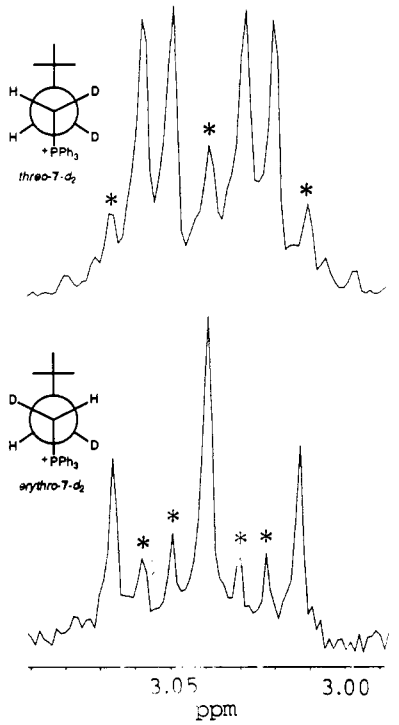


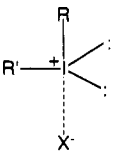
Figure 6. 500-MHz $^1H\{^2H\}$ NMR spectra (CD_2Cl_2, Ph_3PCHD protons) of diastereomers of **7-d_2** that have been prepared from **3-d_2**: (top) *threo*-**7-d_2** ((65 ± 5):(35 ± 5) threo:erythro* ratio); (bottom) *erythro*-**7-d_2** ((85 ± 5):(15 ± 5) erythro:threo* ratio).

that in Scheme III (Scheme V). The resulting dideuteriophosphonium salt **7-d_2** was analyzed in situ by 500-MHz $^1H\{^2H\}$ NMR spectroscopy (Figure 6, top). A (65 ± 5):(35 ± 5) threo:erythro mixture formed. Coupling of the PC*H*D proton to phosphorus ($^2J_{HP}$ = 13.4 Hz) was also evident. An identical reaction was conducted with *threo*-**3-d_2** ((85 ± 3):(15 ± 3) threo:erythro ratio). The salt **7-d_2** formed as a (85 ± 5):(15 ± 5) erythro:threo mixture (Figure 6, bottom). The coupling constants $^3J_{HH}$ and $^2J_{HP}$ were equal (13.4 Hz), giving an apparent triplet for the PC*H*D proton. These data indicate that the carbon–iodine bond in **3-d_2** is cleaved by PPh_3 with *inversion* of configuration at carbon.

Discussion

The erythro:threo ratios that can be extracted from Figures 1–6 are obviously subject to moderate error limits. However, the data clearly indicate that cleavage of the carbon–iodine bond in **3-d_2** by PPN^+Br^- and PPh_3 occurs with essentially complete *inversion* of configuration at carbon. All observations are consistent with a conventional S_N2 mechanism as shown in eq i of Scheme I. The alternative substitution pathway involving reductive elimination of product from the tricoordinate iodine species **14** (eq ii, Scheme I) can be excluded.

However, there is still the possibility that nucleophiles might *reversibly* associate with the iodine in **3**, as shown in the first step of eq ii in Scheme I. This would constitute a nonproductive equilibrium, with product subsequently arising by the slower S_N2 reaction in eq i. Some precedent is provided by the structures of iodonium salts $RR'I^+X^-$ (**15**).[20] The R and R′ groups commonly occupy axial and



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equatorial positions of a trigonal bipyramid, with R–I–R′ bond angles of ca. 95°. The anion X^- often loosely coordinates in the remaining axial position, forming a "secondary" bond of 2.4–2.9 Å.

In this context, it is of interest to compare the structures of **14** and **15** with those of alkyl iodide complexes. Crystal structures of three compounds—$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_2Si(CH_3)_3)]^+BF_4^-$, $[(\eta^5\text{-}C_5H_5)Ru(CNC(CH_3)_3)(PPh_3)(ICH_3)]^+PF_6^-$, and $[(H)_2Ir(PPh_3)_2(ICH_3)_2]^+SbF_6^-$—have been reported to date.[2b,4,5] These exhibit M–I–C bond angles of 102.5 (5), 104.9 (7), and 105.5 (4)/108.2 (5)°, respectively. In no case are close contacts of the weakly coordinating anions with the iodine observed. Thus, the bonding about iodine in these compounds does not appear to be very closely modeled by iodonium salts **15**. Nonetheless, note that the formation of adducts such as **14** would involve only a slight change of geometry at iodine.

Structural and theoretical data suggest that there is little back-bonding from filled metal orbitals to the vacant carbon–iodine σ^* orbital in alkyl iodide complexes.[1,2,4-6] Thus, the enhanced electrophilicity of coordinated alkyl halides is likely due to a combination of relatively straightforward factors. First, the carbon–halide bond dipole is increased. Second, attachment of an electrophile to a leaving group invariably gives a better leaving group.[21] Finally, neutral leaving groups have a much lower electrostatic attraction to the electrophile than anionic leaving groups.

In conclusion, we believe it likely that all metal complexes of structurally unexceptional primary alkyl halides[16] will react with nucleophiles with inversion of configuration at carbon. Future reports will focus on practical applications of the enhanced reactivity and the synthesis and chemistry of analogous secondary alkyl iodide complexes.[22]

Experimental Section

General Methods. All reactions were conducted under a dry N_2 atmosphere. IR spectra were recorded on a Mattson Polaris FT-IR spectrometer. NMR spectra were recorded on Varian XL-300 (^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$; CD_2Cl_2 or C_6D_6) and VXR-500 ($^1H\{^2H\}$; CD_2Cl_2) spectrometers. NMR chemical shift references: ^1H, residual $CHDCl_2$ or C_6D_5H (δ 5.32/7.15); ^{13}C, CD_2Cl_2 or C_6D_6 (53.8/128.0 ppm); ^{31}P, external 85% H_3PO_4 (0.00 ppm). Mass spectra were obtained on a VG 770 spectrometer. Analytical gas chromatography was conducted on a Hewlett Packard 5890 chromatograph utilizing a capillary column (crosslinked 5% phenyl methyl silicone, 25 m × 0.2 mm × 0.33 mm film) and a 0.6 mL/min helium flow. Melting points were determined in evacuated capillaries with a calibrated thermometer.[23]

Solvents and reagents were purified as follows: CH_2Cl_2 and C_6H_5Cl, distilled from P_2O_5; benzene, ether, and tetrahydrofuran, distilled from Na/benzophenone; hexane, distilled from sodium; methanol, distilled from Mg; CD_2Cl_2 and C_6D_6, distilled from CaH_2; $HBF_4{\cdot}OEt_2$ (Aldrich), standardized as described previously;[7a] PPh_3 (Aldrich), recrystallized from benzene; *N*-bromosuccinimide, $AgBF_4$, $HC{\equiv}CC(CH_3)_3$ (Aldrich) and Ph_3SiCH_3

(20) (a) Khotsianova, T. L. *Dolk. Akad. Nauk. SSSR* **1956**, *110*, 71. (b) Batchelor, R. J.; Birchall, R.; Sawyer, J. F. *Inorg. Chem.* **1986**, *25*, 1415. (c) Stang, P. J.; Surber, B. W.; Chen, Z.-C.; Roberts, K. A.; Anderson, A. G. *J. Am. Chem. Soc.* **1987**, *109*, 224. (d) Stang, P. J.; Arif, A. M.; Crittell, C. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 287.

(21) March, J. A. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; pp 310–315.

(22) Igau, A.; Gladysz, J. A. *Polyhedron*, in press.

(23) Tiers, G. V. D. *J. Chem. Educ.* **1990**, *67*, 258.

(Pfaltz & Bauer), used as received. Reagents $ICH_2CH_2C(CH_3)_3$ (**2**),[14b] $BrCH_2CH_2C(CH_3)_3$ (**8**),[14b] $(\eta^5\text{-}C_5H_5)Zr(H)(Cl)$ (**10**),[24] $(\eta^5\text{-}C_5H_5)Zr(D)(Cl)$ (**10-d_1**),[24] and PPN^+Br^-[12,25] were prepared by literature procedures.

Preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ICH_2CH_2C(CH_3)_3)]^+BF_4^-$ (3). A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (1;[8] 0.312 g, 0.558 mmol), C_6H_5Cl (4 mL), $ICH_2CH_2C(CH_3)_3$ (2; 0.350 mg, 0.261 mL, 1.67 mmol), and a stir bar. The solution was cooled to −40 °C (CH_3CN/dry ice), and $HBF_4{\cdot}OEt_2$ (0.106 mL, 0.558 mmol) was slowly added with stirring. The mixture was kept at −40 °C for 5 h, during which time some **3** precipitated. Hexane (20 mL) was then added, and the resulting powder was collected at −40 °C, washed with hexane (2 × 20 mL, −40 °C), CH_2Cl_2 (2 × 3 mL, −40 °C), and hexane (2 × 20 mL, −80 °C). The tan powder was dried under vacuum at room temperature in the dark to give **3** (0.381 g, 0.452 mmol, 81%), mp 145–150 °C dec. IR (cm^{-1}, KBr): ν_{NO} 1701 vs. ^1H NMR (δ, CD_2Cl_2, −40 °C): 7.54–7.28 (m, 3 C_6H_5), 5.60 (s, C_5H_5), 3.70 (m, IC*H*H′), 3.55 (m, ICH*H*′), 1.80 (m, ICHH′C*H*H′), 0.94 (s, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (ppm, CD_2Cl_2, −40 °C): 135.6 (d, J_{CP} = 10.9 Hz, *o*-Ph), 133.1 (d, J_{CP} = 56.4 Hz, *i*-Ph), 132.1 (d, J_{CP} = 2.4 Hz, *p*-Ph), 129.6 (d, J_{CP} = 11.0 Hz, *m*-Ph), 92.1 (s, C_5H_5), 46.8 (s, ICH_2CH_2), 33.2 (s, $C(CH_3)_3$), 29.0 (s, $C(CH_3)_3$), 26.1 (d, J_{CP} = 2.9 Hz, ICH_2). $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2, −40 °C): 11.98 (s). Mass spectrum ((+)-FAB (7 kV, Ar, 3-nitrobenzyl alcohol/$CHCl_3$), *m/z* (relative intensity), ^{187}Re): 756 (3^+, 39%), 671 ($3^+ - C_6H_{13}$, 36%), 544 ($3^+ - IC_6H_{13}$, 100%).

Decomposition of 3. The following experiment is representative. A 5-mm NMR tube was charged with **3** (0.0180 g, 0.0214 mmol), Ph_3SiCH_3 standard (0.0115 g, 0.0419 mmol), and CD_2Cl_2 (0.80 mL) and was capped with a septum. The tube was kept at room temperature, and ^1H and ^{31}P NMR spectra were periodically recorded. After 48 h, no **3** remained. The yields of *RR,SS*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2I^+BF_4^-$ (**4**, 0.0122 mmol, 57%), *SS,RR*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]_2Cl^+BF_4^-$ (**5**, 0.0066 mmol, 31%), and **2** (0.0083 mmol, 39%) were determined by integration of ^1H NMR resonances (C_5H_5, $C(CH_3)_3$) vs those of the standard. Product identities were confirmed by ^{31}P NMR spectroscopy (**4**, **5**) and GLC (**2**, 38%).

Reactions of 3 and Nucleophiles. Reaction A. A 5-mm NMR tube was charged with **3** (0.0244 g, 0.0290 mmol) and Ph_3SiCH_3 standard (0.0127 g, 0.0463 mmol) and was capped with a septum. The tube was cooled to −80 °C, and CD_2Cl_2 (0.80 mL) was added. Reference ^1H and ^{31}P NMR spectra were recorded at −40 °C. The sample was frozen in liquid N_2, and PPN^+Br^- (0.0210 g, 0.0340 mmol) was added. The sample was then kept at −40 °C for 12 h. Subsequently, ^1H and ^{31}P NMR spectra were recorded at room temperature. The yields of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$ (**6**, 0.0287 mmol, 99%) and $BrCH_2CH_2C(CH_3)_3$ (**8**, 0.0281 mmol, 97%; confirmed by GLC) were determined by integration of ^1H NMR resonances (C_5H_5, $C(CH_3)_3$) vs those of the standard.

Reaction B. An analogous reaction was conducted with **3** (0.0270 g, 0.0320 mmol), Ph_3SiCH_3 (0.0123 g, 0.0448 mmol), and PPh_3 (0.0136 g, 0.0519 mmol). The yields of **6** (0.0316 mmol, 99%) and $[Ph_3PCH_2CH_2C(CH_3)_3]^+BF_4^-$ (**7**, 0.0316 mmol, 99%) were similarly determined by ^1H NMR spectroscopy.

Preparation of $[Ph_3PCH_2CH_2C(CH_3)_3]^+BF_4^-$ (7). First, **8** and PPh_3 were reacted in a procedure analogous to that given for cyclohexyl bromide and PPh_3.[26] The product $[Ph_3PCH_2CH_2C(CH_3)_3]^+Br^-$ was recrystallized (CH_2Cl_2/ether) and characterized by NMR (all data similar to that of **7** below). A flask was then charged with $[Ph_3PCH_2CH_2C(CH_3)_3]^+Br^-$ (0.594 g, 1.39 mmol), $AgBF_4$ (0.325 g, 1.67 mmol), CH_3OH (25 mL), and a stir bar. The mixture was stirred for 15 min and was then poured through a 3-cm pad of Celite on a coarse glass frit. The solvent was removed from the filtrate by rotary evaporation. This gave **7** as a white microcrystalline powder, which was recrystallized from CH_2Cl_2/ether and dried under oil pump vacuum (0.567 g, 1.31 mmol, 94%), mp 189 °C dec. IR (cm^{-1}, KBr): ν_{BF} 1112 vs, 1056 vs, 1037 vs. ^1H NMR (δ, CD_2Cl_2, 25 °C): 7.90–7.64 (m, 3 C_6H_5), 3.07 (m, PCH_2), 1.54 (m, PCH_2CH_2), 0.98 (s, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (ppm, CD_2Cl_2): 135.6 (d, J_{CP} = 2.8 Hz, *p*-Ph), 133.6 (d, J_{CP} = 9.9 Hz, *m*-Ph), 130.8 (d, J_{CP} = 12.6 Hz, *o*-Ph), 118.0 (d, J_{CP} = 86.3 Hz, *i*-Ph), 35.8 (d, J_{CP} = 4.7 Hz, CCH_2C), 31.4 (d, J_{CP} = 14.0 Hz, $C(CH_3)_3$), 28.6 (s, $C(CH_3)_3$), 19.1 (d, J_{CP} = 52.6 Hz, PCH_2). $^{31}P\{^1H\}$ (ppm, CD_2Cl_2): 25.4 (s). Anal. Calcd for $C_{24}H_{28}BF_4P$: C, 66.25; H, 6.46. Found: C, 66.14; H, 6.45.

Preparation of *E*-CHD=CHC$(CH_3)_3$ (*E*-12-d_1). A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)_2Zr(H)(Cl)$ (**10**; 6.27 g, 24.3 mmol), CH_2Cl_2 (50 mL), and a stir bar and was cooled to 0 °C. Then $HC{\equiv}CC(CH_3)_3$ (2.39 g, 29.2 mmol) was added to the suspension. The mixture was stirred for 30 min, and solvent was removed to give crude *E*-$(\eta^5\text{-}C_5H_5)_2Zr(Cl)(CH{=}CHC(CH_3)_3)$ (*E*-**11**; 7.19 g, 19.4 mmol, 80%) as a pale yellow powder. ^1H NMR (δ, C_6D_6): 6.73 (d, J_{HH} = 18.6 Hz, ZrCCH), 5.96 (d, J_{HH} = 18.6 Hz, ZrCH), 1.08 (s, $C(CH_3)_3$). The powder was dissolved in toluene (40 mL) and cooled to 0 °C. A glass tube, fitted with a medium-porosity fritted disk, was connected between the reaction flask and a Schlenk flask. Then D_2O (0.50 mL, 27.5 mmol) was added to the reaction flask. The mixture was stirred for 1 h at 0 °C, during which time an abundant precipitate formed. The empty Schlenk flask was cooled in liquid N_2, and solvent was then transferred through the glass tube by use of a pressure differential. The product *E*-**12-d_1** was fractionally distilled (47 °C, 1 atm) from the Schlenk flask into a receiving flask that was cooled in liquid N_2 (1.47 g, 17.3 mmol, 71%). ^1H NMR (δ, C_6D_6): 5.81 (d, J_{HH} = 17.5 Hz, =CHD), 4.92 (d, J_{HH} = 17.5 Hz, =CHC), 0.93 (s, $C(CH_3)_3$).

Preparation of *erythro*-ICHDCHDC$(CH_3)_3$ (*erythro*-2-d_2). A Schlenk flask was charged with $(\eta^5\text{-}C_5H_5)_2Zr(D)(Cl)$ (**10-d_1**; 3.65 g, 14.1 mmol), C_6H_6 (50 mL), and a stir bar and was cooled to 0 °C. Then *E*-**12-d_1** (1.44 g, 16.9 mmol) was added. The mixture was stirred for 6 h at room temperature and became homogeneous when the reaction was complete. Solvent was removed in vacuo to give *erythro*-$(\eta^5\text{-}C_5H_5)_2Zr(Cl)(CHDCHDC(CH_3)_3)$ (*erythro*-**13-d_2**; 4.45 g, 13.0 mmol, 92%) as a pale yellow-orange powder. ^1H NMR (δ, CD_2Cl_2; Figure 1): 1.36 (d, J_{HH} = 13.0 Hz, ZrCHDC*H*D), 0.98 (d, J_{HH} = 13.0 Hz, ZrCHD), 0.81 (s, $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR (ppm, CD_2Cl_2): 113.0 (s, C_5H_5), 50.3 (t, J_{CD} = 18.1 Hz, CHD), 47.6 (t, J_{CD} = 18.8 Hz, CHD), 33.1 (s, $C(CH_3)_3$), 29.0 (s, $C(CH_3)_3$). The powder was dissolved in benzene (20 mL), and the solution was cooled to 0 °C. Then a solution of iodine (3.29 g, 13.0 mmol) in THF (20 mL) was added. The mixture was stirred for 30 min at 0–10 °C, and then solvents were removed by rotary evaporation at 0 °C. The residue was extracted with petroleum ether (bp 40–60 °C; 2 × 20 mL). The extract was passed through a short alumina column. Solvent was then removed under reduced pressure (0 °C, 20 Torr), and the residue was distilled (67 °C, 20 Torr, Kugelrohr) to give *erythro*-**2-d_2** as a colorless liquid (2.17 g, 10.1 mmol, 72%). $^1H\{^2H\}$ NMR (δ, CD_2Cl_2; Figure 2): 3.17 (d, J_{HH} = 13.1 Hz, ICHD), 1.89 (d, J_{HH} = 13.1 Hz, ICHDC*H*D), 0.91 (s, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (ppm, C_6D_6): 48.8 (t, J_{CD} = 19.9 Hz, CHD), 32.8 (s, $C(CH_3)_3$), 28.4 (s, $C(CH_3)_3$), 1.8 (t, J_{CD} = 22.8 Hz, ICHD).

Preparation of *E*-CHD=CDC$(CH_3)_3$ (*E*-12-d_2). A Schlenk flask was charged with **10-d_1** (7.13 g, 24.3 mmol), C_6H_6 (50 mL), and a stir bar and was cooled to 0 °C. Then $HC{\equiv}CC(CH_3)_3$ (2.71 g, 33.1 mmol) was added to the suspension. The mixture was stirred for 5 h, and solvent was removed to give crude *E*-$(\eta^5\text{-}C_5H_5)_2Zr(Cl)(CH{=}CDC(CH_3)_3)$ (*E*-**11-d_1**; 7.69 g, 22.6 mmol, 82%) as a pale yellow powder. ^1H NMR (δ, C_6D_6): 6.01 (t, J_{HD} = 3.1 Hz, ZrCH), 1.08 (s, $C(CH_3)_3$). The powder was dissolved in toluene (40 mL) and reacted with D_2O as described in the preparation of *E*-**12-d_1** above. An identical workup gave *E*-**12-d_2** (1.70 g, 19.8 mmol, 72%). ^1H NMR (δ, C_6D_6): 4.91 (t, J_{HD} = 2.6 Hz, =CHD), 0.95 (s, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (ppm, C_6D_6): 149.2 (t, J_{CD} = 22.8 Hz, =CDC), 108.8 (t, J_{CD} = 23.7 Hz, =CHD), 33.6 (s, $C(CH_3)_3$), 29.3 (s, $C(CH_3)_3$).

Preparation of *threo*-ICHDCHDC$(CH_3)_3$ (*threo*-2-d_2). Complex **10** (4.26 g, 16.5 mmol), C_6H_6 (60 mL), and *E*-**12-d_2** (1.44 g, 16.9 mmol) were reacted in a procedure analogous to that given for *erythro*-**2-d_2**. An identical workup gave *threo*-$(\eta^5\text{-}C_5H_5)_2Zr(Cl)(CHDCHDC(CH_3)_3)$ (*threo*-**13-d_2**; 5.17 g, 15.0 mmol, 91%) as a pale yellow-orange powder. $^1H\{^2H\}$ NMR (δ, CD_2Cl_2, Figure 1): 1.36 (d, J_{HH} = 3.6 Hz, ZrCHDC*H*D), 0.98 (d, J_{HH} = 3.6 Hz, ZrCHD), 0.81 (s, $C(CH_3)_3$). The powder was dissolved in benzene (20 mL) and reacted with iodine (3.89 g, 15.0 mmol) in THF (20

(24) Buchwald, S. L.; LaMaire, S. J.; Nielsen, R. B.; Watson, B. T.; King, S. M. *Tetrahedron Lett.* **1987**, *28*, 3895.
(25) Martinsen, A.; Songstad, J. *Acta Chem. Scand.* **1977**, *A31*, 645.
(26) Bestmann, H. J.; Kratzer, O. *Chem. Ber.* **1963**, *96*, 1899.

mL) in a procedure analogous to that given for *erythro*-**2**-d_2. An identical workup gave *threo*-**2**-d_2 as a colorless liquid (2.54 g, 11.9 mmol, 72%). $^1H\{^2H\}$ NMR (δ, CD_2Cl_2; Figure 2): 3.17 (d, J_{HH} = 4.6 Hz, ICHD), 1.89 (d, J_{HH} = 4.6 Hz, ICHDC*H*D), 0.91 (s, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (ppm, C_6D_6): 49.2 (t, J_{CD} = 19.9 Hz, CHD), 33.4 (s, $C(CH_3)_3$), 28.9 (s, $C(CH_3)_3$), 1.8 (t, J_{CD} = 22.8 Hz, ICHD).

Preparation of *erythro*-BrCHDCHDC$(CH_3)_3$ (*erythro*-8-d_2). A Schlenk flask was charged with *erythro*-**13**-d_2 (1.55 g, 4.51 mmol; from the preparation of *erythro*-**2**-d_2), *N*-bromosuccinimide (0.81 g, 4.45 mmol), and a stir bar and was cooled to 0 °C. Then cold benzene (20 mL) was added. The mixture was stirred for 30 min at 0–10 °C and then for 30 min at room temperature. The benzene was removed by distillation through a 25-cm Vigreux column. The residue was distilled under reduced pressure (46–47 °C, 25 Torr, Kugelrohr) to give *erythro*-**8**-d_2 as a colorless liquid (0.51 g, 3.06 mmol, 82%). $^1H\{^2H\}$ NMR (δ, CD_2Cl_2; Figure 3): 3.40 (d, J_{HH} = 12.1 Hz, BrCHD), 1.81 (d, J_{HH} = 12.1 Hz, BrCHDC*H*D), 0.93 (s, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (ppm, CD_2Cl_2): 47.5 (t, J_{CD} = 19.6 Hz, CHD), 32.0 (s, $C(CH_3)_3$), 30.0 (t, J_{CD} = 23.0 Hz, BrCHD), 29.1 (s, $C(CH_3)_3$).

Preparation of *threo*-BrCHDCHDC$(CH_3)_3$ (*threo*-8-d_2). Complex *threo*-**13**-d_2 (1.82 g, 5.29 mmol; from the preparation of *threo*-**2**-d_2), *N*-bromosuccinimide (0.95 g, 5.32 mmol), and benzene (20 mL) were reacted in a procedure analogous to that given for *erythro*-**8**-d_2. An identical workup gave *threo*-**8**-d_2 as a colorless liquid (0.70 g, 4.18 mmol, 79%). $^1H\{^2H\}$ NMR (δ, CD_2Cl_2; Figure 3): 3.40 (d, J_{HH} = 5.0 Hz, BrCHD), 1.81 (d, J_{HH} = 5.0 Hz, BrCHDC*H*D), 0.93 (s, $C(CH_3)_3$).

Preparation of *erythro*-[$(\eta^5$-$C_5H_5)$Re(NO)(PPh_3)-(ICHDCHDC$(CH_3)_3$)]$^+BF_4^-$ (*erythro*-3**-d_2).** Complex **1** (0.278 g, 0.497 mmol), *erythro*-**2**-d_2 (0.429 g, 0.320 mL, 1.491 mmol), and HBF_4·OEt_2 (0.050 mL, 0.497 mmol) were reacted in a procedure analogous to that given for **3**. An identical workup gave *erythro*-**3**-d_2 (0.336 g, 0.398 mmol, 81%) as a tan powder, mp 145–150 °C dec. IR (cm^{-1}, CH_2Cl_2): ν_{NO} 1709 vs. $^1H\{^2H\}$ NMR (δ, CD_2Cl_2; Figure 4): 7.53–7.26 (m, 3 C_6H_5), 5.67 (s, C_5H_5), 3.64/3.29 (d, J_{HH} = 13.3 Hz, IC*H*D), 1.74/1.72 (d, J_{HH} = 13.3 Hz, ICHDC*H*D), 0.91 (s, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (ppm, CD_2Cl_2, −40 °C): 135.2 (d, J_{CP} = 13.1 Hz, *o*-Ph), 133.5 (d, J_{CP} = 57.6 Hz, *i*-Ph), 131.8 (d, J_{CP} = 2.4 Hz, *p*-Ph), 129.2 (d, J_{CP} = 11.0 Hz, *m*-Ph), 91.7 (s, C_5H_5), 45.7 (t, J_{CD} = 19.3 Hz, ICHDCHD), 32.9 (s, $C(CH_3)_3$), 28.5 (s, $C(CH_3)_3$), 25.4 (td, J_{CD} = 20.5 Hz, J_{CP} = 2.1 Hz, ICHD). $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2, −40 °C): 12.05 (s). Mass spectrum ((+)-FAB (7 kV, Ar, 3-nitrobenzyl alcohol/CH_2Cl_2), *m/z* (relative intensity), ^{187}Re): 758 (3^+-d_2, 18%), 671 (3^+-d_2 − $C_6H_{11}D_2$, 24%), 544 (3^+-d_2 − $IC_6H_{11}D_2$, 100%).

Preparation of *threo*-[$(\eta^5$-$C_5H_5)$Re(NO)(PPh_3)-(ICHDCHDC$(CH_3)_3$)]$^+BF_4^-$ (*threo*-3**-d_2).** Complex **1** (0.297 g, 0.532 mmol), *threo*-**2**-d_2 (0.340 g, 0.254 mL, 1.60 mmol), and HBF_4·OEt_2 (0.053 mL, 0.532 mmol) were reacted in a procedure analogous to that given for **3**. An identical workup gave *threo*-**3**-d_2 (0.359 g, 0.425 mmol, 80%) as a tan powder, mp 145–150 °C. $^1H\{^2H\}$ NMR (δ, CD_2Cl_2; Figure 4): 7.53–7.26 (m, 3 C_6H_5), 5.67 (s, C_5H_5), 3.64/3.29 (d, J_{HH} = 4.9 Hz, IC*H*D), 1.74/1.72 (d, J_{HH} = 4.9 Hz, ICHDC*H*D), 0.91 (s, $C(CH_3)_3$). Other spectroscopic data were identical with those of *erythro*-**3**-d_2.

Reactions of *erythro*-3-d_2 and *threo*-3-d_2 with PPN^+Br^-. The following procedure is representative. A 5-mm NMR tube was charged with *threo*-**3**-d_2 (0.0284 g, 0.0336 mmol), PPN^+Br^- (0.0417 g, 0.0674 mmol), and Ph_3SiCH_3 (0.0115 g, 0.042 mmol) and was capped with a septum. The tube was immersed in liquid N_2, and CD_2Cl_2 was slowly added. The tube was then kept at −40 °C for 12 h. Subsequent analysis by ^1H and ^{31}P NMR spectroscopy (room temperature) showed the formation of **6** (0.0333 mmol, 99%) and *erythro*-**8**-d_2 (0.0326 mmol, 97%). $^1H\{^2H\}$ NMR: see Figure 5.

Reactions of *erythro*-3-d_2 and *threo*-3-d_2 with PPh_3. The following procedure is representative. A 5-mm NMR tube was charged with *threo*-**3**-d_2 (0.0367 g, 0.0435 mmol), PPh_3 (0.0227 g, 0.0865 mmol), and Ph_3SiCH_3 (0.0121 g, 0.0441 mmol) and was capped with a septum. The tube was immersed in liquid N_2, and CD_2Cl_2 was slowly added. The tube was then kept at −40 °C for 12 h. Subsequent analysis by ^1H and ^{31}P NMR spectroscopy (room temperature) showed the formation of **6** (0.0431 mmol, 99%) and *erythro*-**7**-d_2 (0.0431 mmol, 99%). $^1H\{^2H\}$ NMR (δ, CD_2Cl_2; Figure 6): 7.90–7.64 (m, 3 C_6H_5), 3.05 (pseudo t, J_{HH}, J_{HP} = 13.4 Hz, PCHD), 1.53 (dd, J_{HH} = 13.4 Hz, J_{HP} = 7.9 Hz, CCHDC), 0.99 (s, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (ppm, CD_2Cl_2): 135.8 (d, J_{CP} = 2.9 Hz, *p*-Ph), 133.8 (d, J_{CP} = 10.1 Hz, *m*-Ph), 131.0 (d, J_{CP} = 12.6 Hz, *o*-Ph), 118.1 (d, J_{CP} = 86.7 Hz, *i*-Ph), 35.4 (dt, J_{CP} = 5.2 Hz, J_{CD} = 19.4 Hz, PCHD), 31.4 (d, J_{CP} = 14.1 Hz, $C(CH_3)_3$), 28.6 (s, $C(CH_3)_3$), 18.9 (dt, J_{CP} = 52.3 Hz, J_{CD} = 20.3 Hz, CCHDC). Compound *threo*-**7**-d_2 exhibited very similar NMR spectra, except for the CHD ^1H NMR resonances ($^3J_{HH}$ = 4.3 Hz).

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