

intensity as observed in expt no. 60 and 66 (light intensity 3.06×10^{-6} and 5.41×10^{-7} einstein $\text{min}^{-1} \text{cm}^{-2}$, respectively). The WGSR of the $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}^{\text{III}}(\text{bpy-4,4'-(COOH)}_2)\text{Cl}]^+$ system is surprisingly efficient given the many steps involved in the process (Scheme II) and the requirement that the metal complex functions as both CO oxidation and H_2O reduction catalyst as well as photosensitizer. Its efficiency compares well with the highly specific photoinduced reduction of CO_2 to CO mediated by fac- $\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3\text{Cl}$.^{63,64} In this case also the quantum yield for CO formation reaches values as high as 15% despite the multielectron nature of the process.

Summary

The results of the present study lead to several conclusions regarding the mechanism of the photochemical WGSR catalyzed by the $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}^{\text{III}}(\text{L})\text{Cl}]^+$ complexes. (1) The process is both specific and efficient for the photoinduced oxidation of CO and reduction of H_2O . Quantum yields reach 12.7% with 410-nm irradiation and may prove to be higher in the presence of even more electron withdrawing groups (like $-\text{SO}_2\text{CH}_3$ or $-\text{CF}_3$) on the 2,2'-bipyridine chelate. (2) The initial thermal step in the overall reaction sequence involves the coordination of carbon

monoxide by displacement of the chloride anion. (3) A two electron reduction of the Ir(III) metal center generates the neutral $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}^{\text{I}}(\text{L})]$ complex **8** which has been isolated and fully characterized. (4) Reactivity studies have proved that **8** is the key intermediate of the overall WGSR process. Oxidative addition of the proton on **8** gives the hydride complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}^{\text{III}}(\text{L})(\text{H})]^+$ which has also been characterized. (5) The photochemical step of the catalytic cycle is the protonation of this hydride to give H_2 and the starting complex. (6) Activation energies show that decarboxylation of intermediate **B** is the rate limiting step. Moreover, the presence of an electron withdrawing group on the bpy chelate halves the activation energy and thus favors the decarboxylation of **B**. Finally, this new family of iridium(III) complexes provides excellent catalysts for the photoassisted WGSR.

Acknowledgment. We thank Professor V. Balzani, Dr. D. Matt, and Dr. K. J. Watson for helpful and stimulating discussions, Dr. C. de Bellefon for measuring FT-IR spectra, E. Piedmont for assistance in the determination of the quantum yields, M. Y. Guibert for performing the GC/MS analyses, P. Malt e for determining 400 MHz NMR spectra, S. Lips for technical assistance with the carbon dioxide GC analysis, A. Geyer for the glass blowing of the thermostated Schlenk cell, and D. Blitz for help with the preparation of the manuscript. Financial support for this work was provided by the Centre National de la Recherche Scientifique.

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Metathetical Reactions of Re(VII) Alkylidene-Alkylidyne Complexes of the Type $\text{Re}(\text{CR}')(\text{CHR}')[\text{OCMe}(\text{CF}_3)_2]_2$ ($\text{R}' = \text{CMe}_3$ or CMe_2Ph) with Terminal and Internal Olefins

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Abstract: 1-Decene and methyl 9-decenoate react with *syn*- and *anti*- $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ to give *syn*- and *anti*- $\text{Re}(\text{C-}t\text{-Bu})[\text{CH}(\text{CH}_2)_7\text{Me}](\text{OR}_{\text{F}_6})_2$ and *syn*- and *anti*- $\text{Re}(\text{C-}t\text{-Bu})[\text{CH}(\text{CH}_2)_7\text{CO}_2\text{Me}](\text{OR}_{\text{F}_6})_2$, respectively ($\text{OR}_{\text{F}_6} = \text{OCMe}(\text{CF}_3)_2$). The new alkylidene complexes are unstable in the presence of excess terminal olefin and decompose upon attempted isolation. However, vinylferrocene reacts relatively smoothly and reversibly with *syn*- $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ in a noncoordinating solvent to yield *tert*-butylethylene and primarily *anti*- $\text{Re}(\text{C-}t\text{-Bu})(\text{CHFc})(\text{OR}_{\text{F}_6})_2$ (Fc = ferrocenyl). *anti*- $\text{Re}(\text{C-}t\text{-Bu})(\text{CHFc})(\text{OR}_{\text{F}_6})_2$ ($a = 9.769$ (2) Å, $b = 30.746$ (7) Å, $c = 10.140$ (2) Å, $\beta = 116.78$ (1)°, $V = 2719$ (2) Å³, space group = $P2_1/a$, $Z = 4$, $\text{FW} = 815.50$, $\rho(\text{calcd}) = 1.992$ g/cm³, $R = 0.052$, $R_w = 0.050$) was shown to be a pseudotetrahedral species with an unusually acute $\text{Re}=\text{C}_\alpha-\text{C}_\beta$ angle (114.8 (7)°) and short $\text{Re}=\text{C}$ bond (1.70 (1) Å). In the presence of THF or dimethoxyethane, complexes of the type *syn*- or *anti*- $\text{Re}(\text{C-}t\text{-Bu})(\text{CHR})(\text{OR}_{\text{F}_6})_2\text{S}_2$ ($\text{R} = \text{Me, Et, Ph; S} = \text{THF or 0.5DME}$) could be prepared in high yield from $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ and $\text{CH}_2=\text{CHR}$. Heteroatom-substituted (O, S, or N) terminal olefins react more rapidly than ordinary olefins with $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ in the presence of THF to yield complexes of the type *syn*- or *anti*- $\text{Re}(\text{C-}t\text{-Bu})(\text{CHX})(\text{OR}_{\text{F}_6})_2(\text{THF})_2$ ($\text{X} = \text{OR, SR, NR}_2$, or *p*-dimethylaminophenyl). The X-ray structure of *syn*- $\text{Re}(\text{C-}t\text{-Bu})(\text{CHOEt})(\text{OR}_{\text{F}_6})_2(\text{THF})_2$ ($a = 10.318$ (1) Å, $b = 18.303$ (2) Å, $c = 16.181$ (2) Å, $\beta = 96.98$ (2)°, $V = 3033$ (1) Å³, space group = $P2_1/c$, $Z = 4$, $\text{FW} = 819.74$, $\rho(\text{calcd}) = 1.795$ g/cm³, $R = 0.052$, $R_w = 0.050$) showed it to be a pseudooctahedral complex containing *cis* alkylidyne and alkylidene ligands and a THF ligand *trans* to each. The $\text{Re}-\text{O}$ bond to the THF *trans* to the neopentylidene ligand is significantly longer than that *trans* to the ethoxymethylene ligand; presumably it is the THF ligand *trans* to the neopentylidene ligand that exchanges more rapidly with free THF in solution. 2-Pentene or methyl oleate is metathesized in the presence of $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$, and intermediate alkylidene complexes can be observed in each case. Addition of 3-hexene to $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ followed by TMEDA yields $\text{Re}(\text{C-}t\text{-Bu})(\text{CHEt})(\text{OR}_{\text{F}_6})_2(\text{TMEDA})$. Internal olefins are metathesized only very slowly by $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ in the presence of several equivalents of THF or DME or especially in neat THF or DME.

Introduction

It is now well-established that many d^0 alkylidene complexes of Ti, Nb, Ta, Mo, or W will react with olefins¹⁻⁷ and that practical

olefin metathesis or ring-opening metathesis polymerization (ROMP) catalysts can be designed rationally by ligand variation.^{2,8}

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For example, a variety of functional groups in norbornenes and norbornadienes are tolerated by living ROMP initiators of the type $\text{Mo}(\text{CHR}')(\text{NAr})(\text{O}-t\text{-Bu})_2$ ($\text{R}' = t\text{-Bu}$ or CMe_2Ph , $\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2$).⁹⁻¹⁵ New types of ring-opening polymerizations^{7,16-22} and ring-closing reactions^{23,24} are possible with catalysts of this type, in some cases largely because they are active in the absence of Lewis acid cocatalysts.

In comparison, metathesis catalyzed by well-characterized rhenium complexes is in its infancy. In a previous paper²⁵ we described the synthesis of some new $\text{Re}(\text{VII})$ complexes of the type $\text{Re}(\text{CR}')(\text{CHR}')(\text{OR})_2$ ($\text{R}' = t\text{-Bu}$ or CMe_2Ph ; $\text{OR} =$ a bulky alkoxide) that are related to Mo and W metathesis catalysts of the type $\text{M}(\text{CHR}')(\text{NAr})(\text{OR})_2$ by virtue of the isoelectronic relationship between the $\text{M}=\text{N}$ - ($\text{M} = \text{Mo}$ or W) and $\text{Re}=\text{C}$ - fragments and have reported their activity for the metathesis of olefins in a preliminary fashion.²⁶ Potential advantages of homogeneous rhenium metathesis catalysts versus Mo or W catalysts, at least according to data accumulated using heterogeneous rhenium catalyst systems,²⁷⁻³⁰ are a greater tolerance of functionalities and a different and/or higher stereoselectivity in ROMP reactions. The possible trade-off for Re versus W or Mo catalysts is a decrease in reactivity and a greater tendency for rhenium to be reduced.

In this paper, we report reactions of rhenium complexes of the type $\text{Re}(\text{CR}')(\text{CHR}')[\text{OCMe}(\text{CF}_3)_2]_2$ with some internal and terminal olefins, including those that lead to heteroatom-substituted d^0 alkylidene complexes and productive metathesis of internal olefins. Reactions involving ethylene, norbornenes, and norbornadienes will be reported separately.

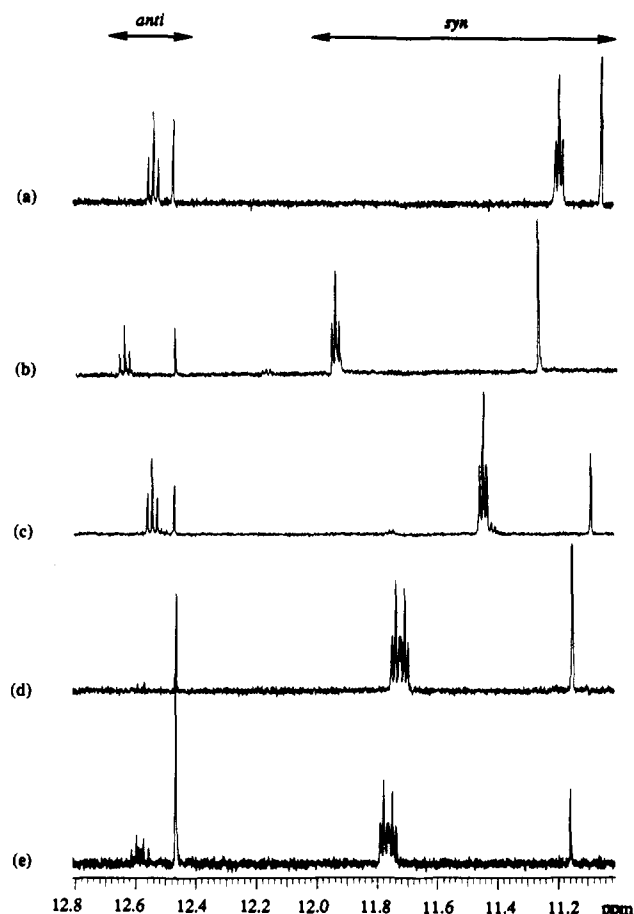


Figure 1. (a) $\text{Re}(\text{C}-t\text{-Bu})(\text{CH}-t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ (27 mM) in C_6D_6 plus 1 equiv of 1-decene. (b) Sample in part a plus 5 equiv of methyl acetate. (c) $\text{Re}(\text{C}-t\text{-Bu})(\text{CH}-t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ (34 mM) in C_6D_6 plus methyl 9-decenoate (0.7 equiv); spectrum recorded after 25 min. (d) $\text{Re}(\text{C}-t\text{-Bu})(\text{CH}-t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ (34 mM) in C_6D_6 plus (i) 1-decene (0.7 equiv) followed by (ii) methyl oleate (4.7 equiv); spectrum recorded after 15 min. (e) Sample in part d 14 h later; H_α intensities had decreased by 30%.

Results

Reactions Involving Terminal Olefins in the Absence of Coordinating Solvents and the X-ray Structure of *anti*- $\text{Re}(\text{C}-t\text{-Bu})(\text{CHf})(\text{OR}_{\text{F}_6})_2$ ($\text{Fc} = \text{Ferrocenyl}$). Reactions between ordinary terminal olefins and complexes of the type $\text{Re}(\text{CR}')(\text{CHR}')(\text{OR})_2$ ($\text{R}' = t\text{-Bu}$ or CMe_2Ph) in the absence of coordinating solvent (e.g., THF) are slow (hours) when $\text{OR} = \text{O}-t\text{-Bu}$ and fast (seconds) when $\text{OR} = \text{OCMe}(\text{CF}_3)_2$. For example, in Figure 1a is shown the reaction of 1 equiv of 1-decene with a mixture of *anti* (H_α at 12.48 ppm) and *syn* (H_α at 11.05 ppm) isomers of $\text{Re}(\text{C}-t\text{-Bu})(\text{CH}-t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ ²⁵ in benzene- d_6 ($\text{OR}_{\text{F}_6} = \text{OCMe}(\text{CF}_3)_2$). New resonances for *anti* (H_α at 12.54 ppm; $J_{\text{HH}} = 7$ Hz) and *syn* (H_α at 11.19 ppm; $J_{\text{HH}} = 5$ Hz) rotamers of $\text{Re}(\text{C}-t\text{-Bu})[\text{CH}(\text{CH}_2)_7\text{Me}](\text{OR}_{\text{F}_6})_2$ are clearly observable in equilibrium with those of *syn*- and *anti*- $\text{Re}(\text{C}-t\text{-Bu})(\text{CH}-t\text{-Bu})(\text{OR}_{\text{F}_6})_2$. (*syn* and *anti* assignments for $\text{Re}(\text{C}-t\text{-Bu})[\text{CH}(\text{CH}_2)_7\text{Me}](\text{OR}_{\text{F}_6})_2$ are based on the known upfield shift for H_α in *syn* rotamers vs H_α in *anti* rotamers for $\text{Re}(\text{C}-t\text{-Bu})(\text{CH}-t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ and other compounds of this type that are discussed later.²⁵) If several equivalents of 1-decene are added, the H_α resonances for *syn*- and *anti*- $\text{Re}(\text{C}-t\text{-Bu})[\text{CH}(\text{CH}_2)_7\text{Me}](\text{OR}_{\text{F}_6})_2$ lose intensity and all $\text{Re}(\text{C}-t\text{-Bu})(\text{CH}-t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ eventually is consumed, consistent with decomposition of *syn*- and *anti*- $\text{Re}(\text{C}-t\text{-Bu})[\text{CH}(\text{CH}_2)_7\text{Me}](\text{OR}_{\text{F}_6})_2$ in the presence of excess 1-decene. We show later that terminal alkylidene complexes of this type are relatively stable in dilute solution when they are prepared from an internal olefin. Therefore their instability in the presence of excess 1-decene can be ascribed either to some adverse reaction involving 1-decene or to one involving ethylene

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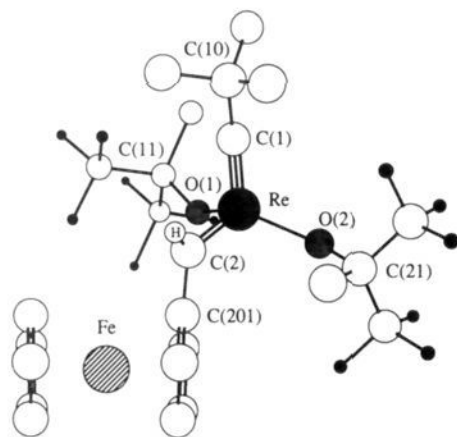


Figure 2. View of the molecular structure of *anti*- $\text{Re}(\text{C-}t\text{-Bu})(\text{CHFc})(\text{OR}_{\text{F}_6})_2$.

shown in eq 1 is reversible. In a typical reaction between $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ and vinylferrocene, the yield of $\text{Re}(\text{C-}t\text{-Bu})(\text{CHFc})(\text{OR}_{\text{F}_6})_2$ is greater in concentrated solutions, from which it crystallizes, or if *tert*-butylethylene is removed in vacuo. Some benzene-insoluble $\text{FcCH}=\text{CHFc}$ is formed, and yields of $\text{Re}(\text{C-}t\text{-Bu})(\text{CHFc})(\text{OR}_{\text{F}_6})_2$ are not high, consistent with some sample decomposition involving ethylene that is generated via productive metathesis. Thus far there does not appear to be any dramatic difference in reactivity of *syn* and *anti* forms of $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$, but quantitative proof must await more detailed studies in systems that are not reversible. Most likely such studies will be analogous to those reported recently between *syn*- and *anti*- $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{NAr})(\text{OR})_2$ and *norbornenes* and *norbornadienes*.³⁵

Crystals of pure *anti*- $\text{Re}(\text{C-}t\text{-Bu})(\text{CHFc})(\text{OR}_{\text{F}_6})_2$ were used in an X-ray study (Figure 2; Table II). The core structure of *anti*- $\text{Re}(\text{C-}t\text{-Bu})(\text{CHFc})(\text{OR}_{\text{F}_6})_2$ is a distorted tetrahedron. The bond angle of $95.9(4)^\circ$ between the alkydylidene and alkydylidene ligands is slightly smaller than that typically observed between mutually *cis* π -bonded ligands ($\sim 100^\circ$).²⁵ The $\text{O}(1)\text{-Re-O}(2)$ angle ($120.4(3)^\circ$) is greater than the corresponding angles in *syn*- $\text{W}(\text{NAr})(\text{CH-}t\text{-Bu})(\text{O-}t\text{-Bu})_2$ ($108.1(2)^\circ$ and $108.9(2)^\circ$) and *syn*- $\text{W}(\text{NAr})(\text{CHPh})(\text{OR}_{\text{F}_6})_2$ ($112.3(7)^\circ$). The O-Re-C angles (107° and 112°) are comparable ($\pm 3^\circ$) to the corresponding angles in the two tungsten imido alkydylidene complexes mentioned above.

The alkydylidene ligand is *anti*, as we expected on the basis of J_{CH} values; it is the only *pseudotetrahedral anti* complex (*Mo* or *W* imido complex or *Re* alkydylidene complex) to be crystallographically characterized. (An X-ray study of a five-coordinate adduct of an *anti* tungsten vinylalkylidene complex has been published.³³) The $\text{C}(1)\text{-Re-C}(2)\text{-C}(201)$ dihedral angle is $176.9(8)^\circ$, as one would expect given the π -bonding requirement of the alkydylidene ligand and the approximate right angle between the Re-C_α vectors of the alkydylidene and alkydylidene ligands. The $\text{Re}=\text{C}(2)$ bond distance ($1.88(1) \text{ \AA}$) is typical of an undistorted alkydylidene complex of a third row metal.^{1,2} The most striking feature of the alkydylidene ligand is the acute $\text{Re}=\text{C}_\alpha\text{-C}_\beta$ angle ($114.8(7)^\circ$). One might have expected a bond angle of $\sim 120^\circ$ or slightly larger if the steric bulk of the ferrocenyl substituent is taken into account. (The $\text{W}=\text{C}_\alpha\text{-C}_\beta$ angle in *anti*- $\text{W}(\text{trans-CHCH}=\text{CHMe})(\text{NAr})(\text{OR}_{\text{F}_6})_2$ (quinuclidine) is $126.3(5)^\circ$.³³) The reason for the relatively acute $\text{Re}=\text{C}_\alpha\text{-C}_\beta$ angle is unclear at this stage.

A peak was found in the electron difference map close to the position predicted for the alkydylidene α hydrogen atom. The length

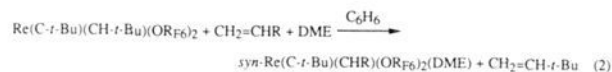
of the carbon-hydrogen bond ($\text{C}(2)\text{-H} = 1.136 \text{ \AA}$) and the size of the $\text{Re-C}(2)\text{-H}$ angle (126°) suggest that the α hydrogen atom does not interact with the alkydylidene ligand ($\text{C}(1)\text{-H}$ distance = 2.858 \AA) or with the metal to any significant extent. The $\text{C}(1)\text{-Re-C}(2)\text{-H}$ dihedral angle is 17° . The high J_{CH} value (173 Hz) is consistent with the $\text{C}_\alpha\text{-H}_\alpha$ bond having more *s* character. Therefore we suspect that higher values of J_{CH} in *anti* alkydylidene complexes in general can be ascribed to slightly smaller $\text{M-C}_\alpha\text{-C}_\beta$ bond angles and slightly larger $\text{M-C}_\alpha\text{-H}_\alpha$ angles than found in *syn* complexes.

The rhenium-carbon triple-bond length ($1.70(1) \text{ \AA}$) is among the shortest known for high-oxidation-state alkydylidene complexes.³⁸ It should be compared to the $\text{Re}=\text{C}$ bond lengths found in $[\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{Ar}'\text{NH}_2)_2\text{Cl}_2]_2$ ($\text{Ar}' = 2,6\text{-C}_6\text{H}_3\text{Me}_2$; $1.76(1) \text{ \AA}$),²⁵ $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2(\text{THF})$ ($1.75(1) \text{ \AA}$),²⁵ and $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{py})_2\text{I}_2$ ($1.742(9) \text{ \AA}$).³⁹ The $\text{Re-C}_\alpha\text{-C}_\beta$ bond angle in the alkydylidene ligand is close to linear ($\text{Re}=\text{C}(1)\text{-C}(11) = 174.0(8)^\circ$), and C_β is tipped slightly toward the alkydylidene ligand.

The alkoxyde Re-O-C bond angles ($140.3(6)^\circ$ and $141.8(6)^\circ$) are typical of an Re-O-C bond angle in an alkoxyde bound to a relatively electron-poor metal in a high oxidation state, although the magnitude of an M-O-C bond angle is not necessarily an accurate measure of the extent of π bonding between the metal and oxygen.^{37,40} The alkoxyde ligands are oriented differently, as shown by the $\text{C}(1)\text{-Re-O}(1)\text{-C}(11)$ and $\text{C}(1)\text{-Re-O}(2)\text{-C}(21)$ dihedral angles of $-1(1)^\circ$ and $70(1)^\circ$ and the $\text{C}(2)\text{-Re-O}(1)\text{-C}(11)$ and $\text{C}(2)\text{-Re-O}(2)\text{-C}(21)$ dihedral angles of $103(1)^\circ$ and $-34(1)^\circ$, respectively. In *syn*- $\text{W}(\text{NAr})(\text{CH-}t\text{-Bu})(\text{O-}t\text{-Bu})_2$ the *tert*-butoxyde ligands are related by a mirror plane, but in *anti*- $\text{Re}(\text{C-}t\text{-Bu})(\text{CHFc})(\text{OR}_{\text{F}_6})_2$ mirror symmetry is discouraged by the orientation of the ferrocenyl group toward one side of the $\text{Re}=\text{C}(2)$ bond.

The C_5 ring in the ferrocenyl substituent is rotated approximately 35° from a position in which it lies in the $\text{C}(1)\text{-Re-C}(2)$ plane. Therefore the cyclopentadienyl π system is not extensively conjugated with the $\text{Re}=\text{C}(2)$ π bond, although the relatively short $\text{C}(2)\text{-C}(201)$ bond ($1.45(1) \text{ \AA}$) is consistent with some multiple character. It may be noted in passing that the cyclopentadienyl rings of the ferrocenyl unit are eclipsed (dihedral angle $\text{C}(2)\text{-C}(201)\text{-Fe-C}(210) = -1(1)^\circ$), a feature usually seen only in ferrocene analogs where the rings are linked or are 1,1'-disubstituted.⁴¹

Reactions Involving Terminal Olefins in the Presence of Coordinating Solvents. Simple terminal olefins such as propylene, 1-butene, and 1-decene react much more slowly with *syn*- $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ in THF or 1,2-dimethoxyethane (DME) than in a noncoordinating solvent such as C_6D_6 , and the new alkydylidene complexes are formed in high yield. The reaction is faster if only a few equivalents of THF or DME are present in a noncoordinating solvent. For example, new alkydylidene complexes can be prepared conveniently by treating *syn*- $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ with a slight excess of the appropriate alkene in the presence of DME ($\sim 1\text{-}2$ equiv) in benzene (eq 2; $\text{R} = \text{Me}, \text{Et}$,



Ph). Addition of a stoichiometric amount of olefin limits productive metathesis to give ethylene, which reacts in a nonmetathetical manner ultimately to yield as yet unidentified products.³¹ The back-reaction between $\text{Re}(\text{C-}t\text{-Bu})(\text{CHR})(\text{OR}_{\text{F}_6})_2(\text{DME})$ complexes and *tert*-butylethylene appears to be relatively slow, possibly because DME is bound more strongly in the $\text{Re}=\text{CHR}$

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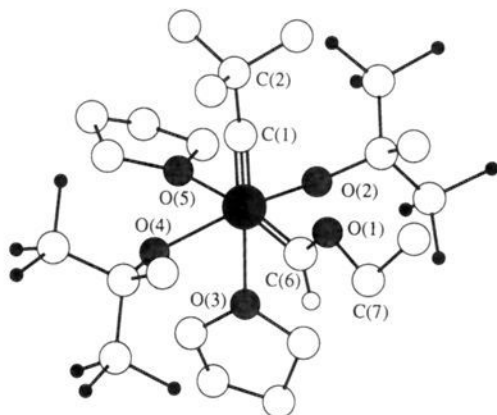


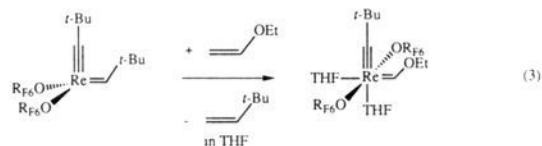
Figure 3. View of the molecular structure of *syn*-Re(C-*t*-Bu)(CHOEt)(OR_{F6})₂(THF)₂.

Table III. Intramolecular Distances (Å) and Angles (deg) for the Non-Hydrogen Atoms in *syn*-Re(C-*t*-Bu)(CHOEt)[OCMe(CF₃)₂]₂(THF)₂

Bond Distances			
Re-C(1)	1.713 (8)	O(1)-C(6)	1.35 (1)
Re-C(6)	1.883 (9)	O(1)-C(7)	1.44 (1)
Re-O(3)	2.374 (6)	Re-O(5)	2.297 (6)
Re-O(2)	2.036 (6)	Re-O(4)	2.026 (6)
Bond Angles			
C(1)-Re-O(2)	103.2 (3)	O(2)-Re-O(3)	77.3 (2)
C(1)-Re-O(5)	100.1 (3)	O(2)-Re-O(4)	149.0 (2)
C(1)-Re-O(4)	101.3 (3)	O(2)-Re-O(5)	78.7 (2)
C(1)-Re-C(6)	92.2 (4)	O(3)-Re-O(4)	77.4 (2)
C(1)-Re-O(3)	177.5 (3)	O(3)-Re-O(5)	77.6 (2)
C(6)-Re-O(2)	98.4 (3)	O(4)-Re-O(5)	78.5 (2)
C(6)-Re-O(3)	90.2 (3)	Re-C(1)-C(2)	177.7 (8)
C(6)-Re-O(4)	99.4 (3)	Re-O(2)-C(9)	135.9 (6)
C(6)-Re-O(5)	167.7 (3)	Re-O(4)-C(13)	136.9 (6)
Re-C(6)-O(1)	129.9 (6)	C(6)-O(1)-C(7)	118.5 (7)

complex than in the Re=CH-*t*-Bu complex for steric reasons. The DME adducts have the added advantage of being solids which can be recrystallized from pentane. Interestingly, the propylidene complex slowly gives rise to small amounts of the ethylidene complex, even in the solid state, by an as yet unknown mechanism.

syn-Re(C-*t*-Bu)(CH-*t*-Bu)(OR_{F6})₂ reacts cleanly with ethyl vinyl ether (1 to 5 equiv) in benzene or toluene in the presence of THF, or even in toluene at -80 ° or in neat THF at -10 °C, to produce orange, crystalline *syn*-Re(C-*t*-Bu)(CHOEt)(OR_{F6})₂(THF)₂ and neohexene quantitatively (eq 3). No productive metathesis is observed. This reaction is dramatically faster (at least an order of magnitude) than an analogous reaction involving an ordinary terminal olefin such as 1-butene (Table IV). Possible reasons for this difference are discussed later.



An X-ray study (Figure 3; Table III) revealed that *syn*-Re(C-*t*-Bu)(CHOEt)(OR_{F6})₂(THF)₂ is a distorted octahedron with Re-ligand bond distances and angles similar to those found in Re(C-*t*-Bu)(CH-*t*-Bu)(pyridine)₂I₂.³⁹ The alkylidene-Re-alkylidyne bond angle (C(1)-Re-C(6)) is close to 90°, while the three C(1)-Re-O(2,4,5) angles are approximately 10° larger. The Re-O(3) bond distance is approximately 0.07 Å longer than the Re-O(5) bond distance. Bond lengths and angles within the alkoxide ligands are not unusual.

The Re=C(1) bond length (1.713 (8) Å) is comparable to the Re≡C bond length found in *anti*-Re(C-*t*-Bu)(CHFc)(OR_{F6})₂ described above (1.70 (1) Å). It is somewhat surprising that the

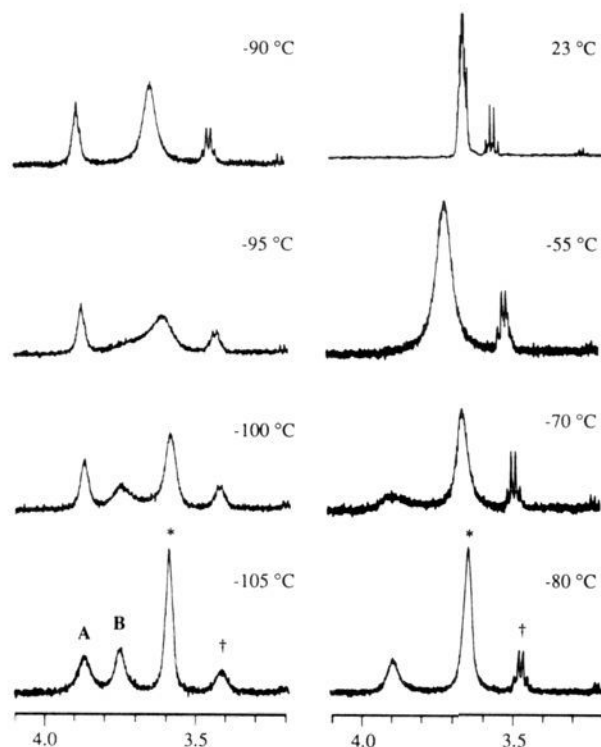


Figure 4. α proton resonances for THF in the variable-temperature ¹H NMR spectrum of *syn*-Re(C-*t*-Bu)(CHOEt)(OR_{F6})₂(THF)₂ in toluene-*d*₈ in the presence of ~2 equiv of free THF (* = free THF; † = OCH₂Me resonance in the OEt group).

Re≡C bond length is not measurably longer in the more coordinatively saturated six-coordinate species than in the ferrocenylmethylene derivative. Each Re≡C bond length is among the shortest known for high-oxidation-state alkylidyne complexes.³⁸

The alkylidene ligand is in the *syn* orientation, as proposed on the basis of the value for J_{CHa} (135 Hz). The Re=C(6) bond length (1.883 (9) Å) is similar to that found in other six-coordinate high-oxidation-state rhenium alkylidene complexes, [Re(C-*t*-Bu)(CH-*t*-Bu)(2,6-C₆H₃Me₂NH₂)Cl₂]₂ (1.89 (1) Å)²⁵ and Re(C-*t*-Bu)(CH-*t*-Bu)(py)₂I₂ (1.873 (9) Å).³⁹ The C(6)-O(1) bond (1.35 (1) Å) is approximately 0.09-Å shorter than the O(1)-C(7) bond, as one might expect, but it is slightly longer than that observed in a typical octahedral Fischer-carbene complex^{42,43} such as *cis*-[Mn(CO)₅](CO)₄Re[C(OMe)Me] (1.299 (8) Å).⁴⁴ This finding is consistent with little π bonding between C(6) and O(1), in contrast to some C-O π bonding found in a typical Fischer-type carbene complex. The Re-C(6)-O(1) angle (129.9 (6)°) is much smaller than the 140-150° typically observed in high-oxidation-state *syn* neopentylidene complexes, consistent with the reduced steric influence of the ethoxy substituent. The Re-C-O angle in *cis*-[Mn(CO)₅](CO)₄Re[C(OMe)Me]⁴⁴ is only 118.3 (5)°, consistent with yet a further decrease in steric influence of the methoxy group.

NMR studies of *syn*-Re(C-*t*-Bu)(CHOEt)(OR_{F6})₂(THF)₂ at -105° in toluene-*d*₈ show that the THF ligands (A and B) are inequivalent and not exchanging rapidly with free THF (*; Figure 4). As the temperature is raised, THF B begins to exchange with free THF significantly more rapidly than THF A. At -80 °C only THF B is exchanging rapidly on the NMR time scale with free THF, while both THF ligands exchange readily with free THF on the NMR time scale at -55 °C. We presume that THF

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Table IV. Approximate Half-Lives for the Reaction of $\text{syn-Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})[\text{OCMe}(\text{CF}_3)_2]_2$ (~ 0.1 M) with Olefins in THF- d_8

olefin	[olefin]/[Re]	T ($^\circ\text{C}$)	approx $t_{1/2}$
(EtO)CH=CH ₂	12	-10	5 min
(Me ₂ SiO)CH=CH ₂	15	10	5 min
(CH ₃ CH ₂)(MeO)CHCH=CH ₂	5	25	30 min
CH ₃ (CH ₂) ₃ CH=CH ₂	5	25	30 min
<i>cis</i> -CH ₃ CH ₂ CH=CHCH ₂ CH ₃	11	25	20 h

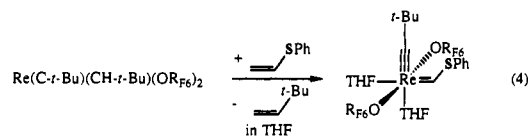
B, the one that exchanges most readily, is the one trans to the neopentylidene ligand, since that Re-O bond (Re-O(3)) is longer. We also presume at this stage that THF B exchanges dissociatively. THF A may exchange either dissociatively via $\text{syn-Re}(\text{C-}t\text{-Bu})(\text{CHOEt})(\text{OR}_{\text{F}_6})_2$ or associatively via $\text{syn-Re}(\text{C-}t\text{-Bu})(\text{CHOEt})(\text{OR}_{\text{F}_6})_2(\text{THF})_2$.

Photolysis of $\text{syn-Re}(\text{C-}t\text{-Bu})(\text{CHOEt})(\text{OR}_{\text{F}_6})_2(\text{THF})_2$ (C_6D_6 , Pyrex, medium-pressure Hg lamp) produces a mixture of *syn* and *anti* rotamers. Room temperature NMR data (C_6D_6) for the *syn* rotamer ($\delta\text{H}_\alpha = 11.56$, $\delta\text{C}_\alpha = 265.7$, $J_{\text{CH}\alpha} = 135$ Hz) differ from those of the *anti* rotamer ($\delta\text{H}_\alpha = 11.93$, $\delta\text{C}_\alpha = 266.7$, $J_{\text{CH}\alpha} = 163$ Hz) in a way that we have come to expect (Table I). Since one THF may be dissociated to a significant extent at room temperature, the spectra most likely are characteristic of $\text{syn-Re}(\text{C-}t\text{-Bu})(\text{CHOEt})(\text{OR}_{\text{F}_6})_2(\text{THF})$ and $\text{anti-Re}(\text{C-}t\text{-Bu})(\text{CHOEt})(\text{OR}_{\text{F}_6})_2(\text{THF})$, rather than the six-coordinate species. $\text{Re}(\text{C-}t\text{-Bu})(\text{CHOEt})(\text{OR}_{\text{F}_6})_2(\text{THF})_2$ (approximately 0.01 M) is stable in C_6D_6 over a period of several hours in the presence of several equivalents of ethyl vinyl ether. The relative stability of the $\text{Re}(\text{CHOEt})$ complex to excess ethyl vinyl ether might be ascribed to slow productive metathesis to give ethylene or to stabilization of the complex in the presence of an ether donor or to both.

When the reaction between $\text{syn-Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ and ethyl vinyl ether in C_6D_6 in the absence of any added THF is monitored by proton NMR, base-free, four-coordinate $\text{syn-Re}(\text{C-}t\text{-Bu})(\text{CHOEt})(\text{OR}_{\text{F}_6})_2$ can be observed. The reaction between $\text{syn-Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ and ethyl vinyl ether was rapid (seconds) at -80 $^\circ\text{C}$ in toluene- d_8 ; no intermediate metallacycle was observed, and neohexene formation was complete. It should be noted that the *syn*- H_α resonance in the THF adduct is found 0.53 ppm downfield of the H_α resonance in the base-free species. A downfield shift of up to ~ 1.5 ppm upon addition of a base is also observed commonly in Mo and W complexes of the type $\text{M}(\text{CH-}t\text{-Bu})(\text{NAr})(\text{OR})_2$.³³ Solutions of base-free $\text{Re}(\text{C-}t\text{-Bu})(\text{CHOEt})(\text{OR}_{\text{F}_6})_2$ decompose when concentrated to give $[\text{Re}(\text{C-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2]_2$ ⁴⁵ and $\text{EtOCH}=\text{CHOEt}$ as the only identifiable products.

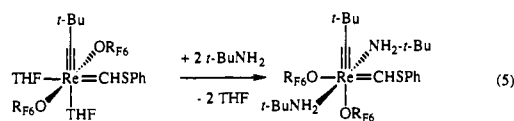
$\text{syn-Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ reacts rapidly (Table IV) with trimethylsilyl vinyl ether in tetrahydrofuran to afford $\text{syn-Re}(\text{C-}t\text{-Bu})(\text{CHOSiMe}_3)(\text{OR}_{\text{F}_6})_2(\text{THF})_2$ quantitatively. No productive metathesis products are observed in the presence of a 15-fold excess of olefin. Photolysis of $\text{syn-Re}(\text{C-}t\text{-Bu})(\text{CHOSiMe}_3)(\text{OR}_{\text{F}_6})_2(\text{THF})_2$ produces a mixture of *syn* and *anti* rotamers (Table I). $\text{Re}(\text{C-}t\text{-Bu})(\text{CHOSiMe}_3)(\text{OR}_{\text{F}_6})_2(\text{THF})_2$ readily loses tetrahydrofuran in vacuo and turns into an orange oil whose NMR spectrum shows that approximately one THF remains. Increased steric congestion at the metal is the most plausible explanation as to why one of the two THF ligands is lost more readily in the $\text{Re}=\text{CHOSiMe}_3$ complex than in the $\text{Re}=\text{CHOEt}$ complex.

Phenyl vinyl sulfide reacts with $\text{syn-Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ in tetrahydrofuran to afford $\text{syn-Re}(\text{C-}t\text{-Bu})(\text{CHSPh})(\text{OR}_{\text{F}_6})_2(\text{THF})_2$ quantitatively as an orange powder (eq 4). NMR data suggest that the structure is analogous to that of the $\text{Re}=\text{CHOEt}$ analog. Photolysis of $\text{syn-Re}(\text{C-}t\text{-Bu})(\text{CHSPh})(\text{OR}_{\text{F}_6})_2(\text{THF})_2$ (C_6D_6 , Pyrex, medium-pressure Hg lamp) yields a mixture of *syn* ($\delta\text{H}_\alpha = 12.31$, $\delta\text{C}_\alpha = 238.6$ in CD_2Cl_2 , $J_{\text{CH}\alpha} = 143$ Hz) and *anti* ($\delta\text{H}_\alpha = 12.50$, $\delta\text{C}_\alpha = 224.3$



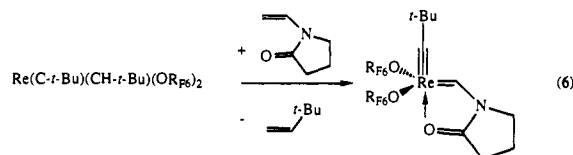
in CD_2Cl_2 , $J_{\text{CH}\alpha} = 184$ Hz) rotamers (Table I) in a 41:59 ratio. The 184-Hz CH coupling constant in the *anti* isomer is the largest yet observed in a d^0 alkylidene complex. $\text{Re}(\text{C-}t\text{-Bu})(\text{CHSPh})(\text{OR}_{\text{F}_6})_2(\text{THF})_2$ also is formed in seconds rapidly upon adding phenyl vinyl sulfide to $\text{Re}(\text{C-}t\text{-Bu})(\text{CHOEt})(\text{OR}_{\text{F}_6})_2(\text{THF})_2$ in C_6D_6 , a fact that suggests that degenerate metathesis (methylene exchange) is fast in such species. $\text{Re}(\text{C-}t\text{-Bu})(\text{CHSPh})(\text{OR}_{\text{F}_6})_2(\text{THF})_2$ is relatively stable in the absence of phenyl vinyl sulfide, but it decomposes to a large extent over a period of 1 h in the presence of excess phenyl vinyl sulfide, in contrast to the relative stability of $\text{Re}(\text{C-}t\text{-Bu})(\text{CHOEt})(\text{OR}_{\text{F}_6})_2(\text{THF})_2$ in the presence of ethyl vinyl ether.

Addition of *tert*-butylamine to a mixture of *syn*- and *anti*- $\text{Re}(\text{C-}t\text{-Bu})(\text{CHSPh})(\text{OR}_{\text{F}_6})_2(\text{THF})_2$ yields a mixture of two complexes that appear to have similar structures by NMR (inequivalent alkoxides and equivalent *tert*-butylamine ligands having diastereotopic NH_2 protons). The structure shown in eq 5 would



be consistent with the NMR data for each, although so far no crystallographically characterized six-coordinate d^0 complex has contained mutually trans donor ligands in an octahedral environment. If we assume that the two products are *syn* and *anti* rotamers of $\text{Re}(\text{C-}t\text{-Bu})(\text{CHSPh})(\text{OR}_{\text{F}_6})_2(t\text{-BuNH}_2)_2$ (42:58 ratio), then it is important to note that the $J_{\text{CH}\alpha}$ values in the two rotamers are approximately the same and that the H_α resonance and C_α resonance in one rotamer are not both found at higher field than those in the other, as is true in the other *syn/anti* combinations (Table I). Therefore there is an ambiguity as to which is the *syn* rotamer and which is the *anti* rotamer.

1-Vinyl-2-pyrrolidinone reacts with *syn*- or *anti*- $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ in methylene chloride or other noncoordinating solvents to give orange, crystalline *anti*- $\text{Re}(\text{C-}t\text{-Bu})[\text{CH}(\text{N}(\text{CH}_2)_3\text{CO})](\text{OR}_{\text{F}_6})_2$ (eq 6). The *anti* formulation is based

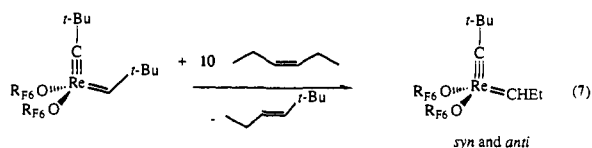


on the large value of $J_{\text{CH}\alpha}$ (173 Hz). This compound shows no evidence for isomerization to a *syn* rotamer, is stable in the solid state in the absence of coordinating solvent, and shows a decreased carbonyl stretching frequency (1614 cm^{-1} in Nujol) in its IR spectrum relative to that in 1-vinyl-2-pyrrolidinone (1723 cm^{-1}). All three facts are consistent with coordination of the carbonyl oxygen to the metal and therefore stabilization of the *anti* rotamer. The two alkoxide ligands are equivalent in this complex; the structure shown in eq 6 is one idealized possibility.

Although $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ reacts with ethyl vinyl ether in toluene- d_8 too rapidly to follow the reaction by routine NMR methods, the use of a coordinating solvent (THF- d_8) slows the rate to an observable level. At -10 $^\circ\text{C}$ in the presence of 12 equiv of olefin, the neopentylidene complex ($[\text{Re}] \sim 0.1$ M) is consumed at a rate that has a pseudo-first-order rate constant of ~ 0.1 min^{-1} ($t_{1/2} \approx 5$ min; Table IV). Trimethylsilyl vinyl ether does not react at the same rate until $+10$ $^\circ\text{C}$. The reaction rate for $\text{CH}_3\text{CH}_2\text{CH}(\text{OMe})\text{CH}=\text{CH}_2$ is about the same as that for a simple terminal olefin such as 1-hexene ($t_{1/2} = 30$ min at 25 $^\circ\text{C}$). *cis*-3-Hexene reacts very slowly under the same conditions ($t_{1/2} \sim 20$ h). The same disparity in metathesis rates between terminal and internal olefins was noted in the presence of DME;

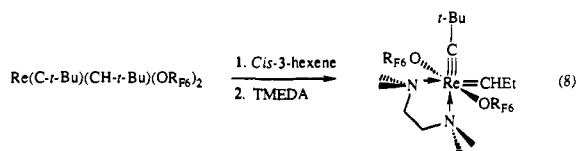
e.g., 30–50 mM solutions of $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ in benzene- d_6 in the presence of 1–4 equiv of DME required days to react completely with 1–2 equiv of *cis*-3-hexene and *cis*-2-butene, but 1-butene and propylene reacted to yield the new alkylidenes in under 30 min at room temperature. Interestingly, *p*-(dimethylamino)styrene reacted within 2 min with $\text{syn-Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ to yield $\text{Re}(\text{C-}t\text{-Bu})[\text{CH}(\text{p-C}_6\text{H}_4\text{NMe}_2)](\text{OR}_{\text{F}_6})_2(\text{DME})$, while pentafluorostyrene did not react within 1 h. For this reason we propose that olefins that contain O, N, or S directly bound to the olefinic carbon atom react more quickly than an ordinary olefin because they are more nucleophilic.

Reactions between $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ and Internal Olefins. $\text{syn-Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ (~ 0.01 M) reacts over a period of several hours in C_6D_6 with *cis*-2-pentene to form a mixture of *syn* and *anti* ethylidene and propylidene species along with the expected amounts of 4,4-dimethyl-2-pentene and 2,2-dimethyl-3-hexene, the primary metathesis products, all quantitatively according to NMR integration versus an internal standard. In the presence of 10 equiv of *cis*-3-hexene, $\text{syn-Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ is converted completely into *syn*- and *anti-Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2 in 6 h in C_6D_6 ($[\text{Re}] = 22$ mM, eq 7). The *syn* and *anti* propylidene complexes are stable at*



concentrations < 0.01 M for days in C_6D_6 or CD_2Cl_2 in the presence of *cis*-3-hexene, but $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ decomposes when solutions containing it (and *cis*-3-hexene and the initial metathesis products) are taken to dryness in vacuo. These findings suggest that the decomposition that results in reactions between $\text{syn-Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ and excess terminal olefins cannot be ascribed to an instability of the new terminal alkylidene complexes per se.

$\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ was prepared in situ in dichloromethane by adding *cis*-3-hexene to $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$. Addition of TMEDA to this sample yielded an isolable orange adduct quantitatively (eq 8). The proton NMR spectrum displays



only two broad resonances for the methyl and methylene protons of the TMEDA ligand at room temperature, consistent with rapid exchange of the TMEDA ligand in solution. The primary product is the *syn* rotamer on the basis of the chemical shift of the H_α resonance and the magnitude of J_{CH_α} .

Addition of 100 equiv of *cis*-2-pentene to $\text{syn-Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ in benzene yielded a 1:2:1 mixture of 2-butenes, 2-pentenenes, and 3-hexenes in 2.5 h at 25 °C. When an additional 100 equiv of *cis*-2-pentene was added to this mixture, equilibrium was restored in less than 30 min. Observation of an induction period and an increase in the rate of metathesis with time is consistent with a large increase in the rate of metathesis by complexes containing less bulky propylidene and ethylidene ligands (versus a neopentylidene ligand), a finding that qualitatively has been observed in several other circumstances involving well-characterized metathesis catalysts of the type $\text{M}(\text{CHR})(\text{NAr})(\text{OR}')_2$.^{36,46} This rhenium catalyst system is stable indefinitely at low concentrations (2 to 20 mM), and its absolute activity at room temperature is estimated to be approximately 250 equiv h^{-1} for metathesis of *cis*-2-pentene. It should be noted that

this rate qualitatively is significantly slower than that observed for $\text{W}(\text{CH-}t\text{-Bu})(\text{NAr})(\text{OR}_{\text{F}_6})_2$ ($\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2$).⁴⁷

$\text{syn-Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ reacts slowly with methyl oleate. After 12 h in C_6D_6 , 5 equiv of methyl oleate converted 40% of the initial $\text{syn-Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ (ca. 0.01 M) to two new alkylidene complexes with H_α resonances that we now know are characteristic of those for $\text{syn-Re}(\text{C-}t\text{-Bu})[\text{CH}(\text{CH}_2)_7\text{Me}](\text{OR}_{\text{F}_6})_2$ and $\text{syn-Re}(\text{C-}t\text{-Bu})[\text{CH}(\text{CH}_2)_7\text{CO}_2\text{Me}](\text{OR}_{\text{F}_6})_2$ (Figure 1). Methyl oleate reacts much more rapidly with *syn*- and *anti-Re}(\text{C-}t\text{-Bu})[\text{CH}(\text{CH}_2)_7\text{Me}](\text{OR}_{\text{F}_6})_2 than with *syn*- and *anti-Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2. Addition of 5 equiv of methyl oleate to a sample equivalent to that whose spectrum is shown in Figure 1a rapidly yields two new alkylidene H_α resonances at 11.74 and 11.71 ppm for $\text{syn-Re}(\text{C-}t\text{-Bu})[\text{CH}(\text{CH}_2)_7\text{Me}](\text{OR}_{\text{F}_6})_2$ and $\text{syn-Re}(\text{C-}t\text{-Bu})[\text{CH}(\text{CH}_2)_7\text{CO}_2\text{Me}](\text{OR}_{\text{F}_6})_2$, respectively (Figure 1d); no significant reaction between methyl oleate and *syn*- and *anti-Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2 is observed during that time period. After 24 h resonances for *anti-Re}(\text{C-}t\text{-Bu})[\text{CH}(\text{CH}_2)_7\text{Me}](\text{OR}_{\text{F}_6})_2 and *anti-Re}(\text{C-}t\text{-Bu})[\text{CH}(\text{CH}_2)_7\text{CO}_2\text{Me}](\text{OR}_{\text{F}_6})_2 appear at 12.60 and 12.57 ppm, respectively (Figure 1e), and ca. 30% of the sample had decomposed by this time. It is interesting to note that apparently both *anti*- and *syn-Re}(\text{C-}t\text{-Bu})[\text{CH}(\text{CH}_2)_7\text{Me}](\text{OR}_{\text{F}_6})_2 in the sample react with methyl oleate to yield $\text{syn-Re}(\text{C-}t\text{-Bu})[\text{CH}(\text{CH}_2)_7\text{Me}](\text{OR}_{\text{F}_6})_2$ and $\text{syn-Re}(\text{C-}t\text{-Bu})[\text{CH}(\text{CH}_2)_7\text{CO}_2\text{Me}](\text{OR}_{\text{F}_6})_2$ initially, and only with time (and concomitant decomposition) are the *anti* alkylidene complexes formed. More detailed studies will be required in order to determine whether this apparent selectivity (*syn* plus *cis* olefin yields *syn*; *anti* plus *cis* olefin yields *syn*) is real and, if so, to what extent it is general.******

Addition of 50 equiv of methyl oleate to $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ in dichloromethane produced a 1:2:1 mixture of $\text{Me}(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{Me}$, $\text{Me}(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{Me}$, and $\text{MeO}_2\text{C}(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{Me}$ in 12 h. After this mixture had stood for 24 h, another 50 equiv of methyl oleate could be brought to equilibrium in 7.5 h, again demonstrating an increase in the rate of metathesis as the neopentylidene initiator is consumed. As we now expect, the initial rate of metathesis can be increased by first forming a more reactive alkylidene complex. For example, treatment of $\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ with 10 equiv of *cis*-3-hexene for several hours followed by adding 50 equiv of methyl oleate lead to equilibrium between $\text{Me}(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{Me}$, $\text{Me}(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{Me}$, and $\text{MeO}_2\text{C}(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{Me}$ in 3 h. Addition of 100 equiv of additional methyl oleate to this remaining mixture led to an equilibrium mixture in 6 h. Therefore the absolute rate for methyl oleate metathesis by this catalyst system appears to be approximately 17 equiv h^{-1} at room temperature, approximately an order of magnitude slower than metathesis of *cis*-2-pentene.

Discussion

It is gratifying to find that complexes that contain rhenium in its highest possible oxidation state are those that are active for the metathesis of ordinary olefins. Prior to this work no example of a homogeneous rhenium metathesis catalyst has been reported, and there was no definitive evidence that suggested that $\text{Re}(\text{VII})$ is the active species in heterogeneous catalyst systems. There appears to be no reason to propose that the oxidation state of the metal in the active site in heterogeneous Re -based metathesis catalysts is different from that observed in these new homogeneous metathesis systems. Therefore it seems likely that the well-defined chemistry of the three metals that are the most active in classical metathesis systems (Mo, W, and Re^{27}) is similar in many respects; alkylidene ligands are formed in α hydrogen abstraction reactions,¹ four-coordinate species are the most active and the least stable toward bimolecular decomposition,² and the activity of the catalysts can be controlled by varying the nature of the alkoxide ligands,

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the most active catalysts being those that contain the most electron-withdrawing ligands. It is also clear that the presence of donor solvents such as THF or DME can dramatically alter the reactivity of rhenium catalysts, as one might expect on the basis of findings for phosphine adducts of Mo(VI)³³ and W(VI) alkylidene complexes^{7,32,33} and studies involving ring-opening of cyclooctatetraene by W(CH-*t*-Bu)(NAr)(OR_{F6})₂.¹⁶

It is important to note that the neopentylidene ligand is not altered in the metathetical reactions described here. For example, proton transfer from the alkylidene ligand to the neopentylidene ligand is not observed. Proton transfer from a neopentyl ligand in (Me₃CCH₂)₃W≡CSiMe₃ to the alkylidene α carbon atom has been observed,⁴⁸ but it is a relatively slow reaction. The neopentylidene ligand in the circumstances described so far appears to behave solely as an ancillary ligand. That is not the case in all circumstances, especially in reactions involving ethylene, as we will discuss elsewhere.³¹

Several important differences between Re and Mo or W have been revealed in this study. First, metathesis activity appears to be significantly lower for four-coordinate Re catalysts compared to Mo or W catalysts. Lower activity does not appear to be linked to significantly different rates of reactivity of syn versus anti rotamers, as is the case in certain circumstances for Mo(CH-*t*-Bu)(NAr)(OR)₂ catalysts.³⁵ Activity also appears to be attenuated more dramatically for rhenium complexes upon changing from hexafluoro-*tert*-butoxide to *tert*-butoxide ligands. For example, Re(C-*t*-Bu)(CH-*t*-Bu)(O-*t*-Bu)₂ does not react with norbornene⁴⁹ (while Re(C-*t*-Bu)(CH-*t*-Bu)(OR_{F6})₂ does) and M(CH-*t*-Bu)(NAr)(O-*t*-Bu)₂ complexes (M = Mo or W) do react rapidly with norbornene. At this stage it is not known whether fundamental differences between W(VI) and Re(VII) are the most plausible reason for the difference in reactivity or whether the presence of a M≡C bond instead of an M=N bond is at least as important a factor in determining reactivity. Some answers to such questions could be forthcoming if a type of rhenium alkylidene complex were available that is analogous to the 2,6-diisopropylimido ligand, i.e., the 2,6-diisopropylbenzylidene ligand. We now have evidence that this should be possible.⁵⁰

If we assume that four-coordinate Re(VII) alkylidene complexes are the most active catalysts in classical heterogeneous metathesis systems, an intriguing question is what other ligands are present? One possibility is the equivalent of Re(CHR)O₂X (X = some monoanionic ligand). But since we showed that Re(CH-*t*-Bu)(NR)₂X species would not react even with norbornene,⁵¹ we would not expect Re(CHR)O₂X complexes to react with ordinary olefins. A recent paper⁵² reported that Re(VII) alkylidene complexes can be prepared from lower oxidation-state species in the presence of acetylenes, even internal acetylenes. Therefore we have to consider the possibility that *alkylidene* ligands actually may be present in *classical* rhenium metathesis catalyst systems as supporting ligands, as well as in the well-characterized systems reported here.

An important question is why terminal olefins that contain O, S, or N directly bound to the olefinic carbon atom react so readily with Re(C-*t*-Bu)(CH-*t*-Bu)(OR_{F6})₂, even in THF, compared to the rate at which an ordinary terminal olefin reacts with Re(C-*t*-Bu)(CH-*t*-Bu)(OR_{F6})₂. Although a plausible answer is that the heteroatom assists formation of a metallacycle by coordinating to the metal first, as we have proposed in other circumstances,¹² the evidence obtained so far here suggests that it is simply the increased nucleophilicity of the heteroatom-substituted olefin that leads to its increased rate of reaction.

Ever since the discovery of "d⁰" alkylidene complexes,¹ we have been looking for complexes that contain a heteroatom directly bound to the alkylidene α carbon atom, a situation that appears

to be necessary to ensure the stability of many "low-oxidation-state" carbene complexes.^{1,42,43} We have now prepared several examples, but so far we can say that such species do not appear to have structural or reactivity features that clearly set them apart from their hydrocarbon analogs. It remains to be seen whether any chemistry of high-oxidation-state heteroatom alkylidene derivatives is significantly different from that of "ordinary" alkylidene complexes, whether heteroatom derivatives can be prepared for other metals (e.g., Mo), and, as mentioned above, whether the heteroatom significantly influences the reactivity of the alkylidene complex relative to the "ordinary" metal-carbon double bond. It is interesting to note that we have not yet found any clean interpretable reactions of complexes of the type Mo(CH-*t*-Bu)(NAr)(OR)₂ with vinyl ethers or vinyl sulfides, so perhaps rhenium complexes are inherently more tolerant of functional groups directly attached to the alkylidene α carbon atom, a proposal that would be consistent with the observed greater tolerance of classical heterogeneous Re catalysts toward functional groups.²⁷

Metathesis of methyl oleate (an example of an olefin with a "remote" functionality) and related natural products has been a high priority for more than two decades. The first successful metathesis of methyl oleate was reported in 1972.⁵³ Since that time, research activity in the area has been steady.^{29,54} Van Dam's original catalyst system, which consisted of WCl₆ activated by SnMe₄, is generally regarded to be homogeneous,²⁷ while variations of Mol's Re₂O₇/Al₂O₃/SnR₄ catalyst²⁹ remain the best heterogeneous catalysts for functionalized olefin metathesis. Well-defined homogeneous catalysts that contain an alkylidene ligand have also been reported to metathesize alkyl oleates. W(CH-*t*-Bu)(CH₂-*t*-Bu)Cl(2,6-diphenylphenoxide)₂(OR)₂ (R = Et, *i*-Pr) was reported to metathesize 100 equiv of ethyl oleate part of the way to equilibrium in 1 h at 85 °C,⁵⁵ while W(NAr)(CH-*t*-Bu)(OR_{F6})₂ was reported to metathesize 200–300 equiv of methyl oleate in 2–3 hrs at 25 °C.⁵⁶ Later it was found that Mo(NAr)(CH-*t*-Bu)(OR_{F6})₂ also would metathesize methyl oleate (60 equiv) to equilibrium in approximately 2 h at 25 °C (not optimized).⁵⁷ Recently Basset has reported an improved version of a catalyst that will metathesize 500 equiv of ethyl oleate in 60 min at 25 °C,⁵⁸ while some recent modifications of heterogeneous Re-based metathesis systems have shown improved activity (ca. 200 equiv of methyl oleate in 2 h at 20 °C).²⁹ ReMeO₃ on alumina also has been reported as an active catalyst for oleate metathesis.³⁰ However, in no case, to our knowledge, even in systems that contain well-defined Mo or W catalysts, has a metal-alkylidene complex derived from methyl oleate been observed.

The rhenium catalyst for oleate metathesis disclosed in this work appears to be relatively stable and long-lived, and for the first time the propagating alkylidene complexes that must be present in any oleate metathesis system have been observed. Unfortunately, the rate of metathesis appears to be limited by coordination of the ester carbonyl group to the metal in competition with olefinic double bonds. The benefit, as we also have observed in a qualitative sense, is that intermediate alkylidene complexes are more stable in the presence of a large excess of methyl oleate, perhaps because coordination of the ester to the metal also dramatically slows the rate of bimolecular decomposition of intermediate alkylidene complexes. Therefore a continued search for catalysts for oleate metathesis whose rates approach those for metathesis of ordinary olefins seems futile, since the rate of metathesis will be limited inherently by the ester functionality. On the other hand it now seems possible to design well-characterized catalysts that can be used in *relatively* high concentrations (relative to con-

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centrations of active species in classical systems) and that therefore will metathesize the olefin at a practical, if inherently limited, rate. Since the alkylidene moiety is unlikely ever to be indefinitely stable to the ester functionality, the challenge will be to design a catalyst system that will maximize the difference in reactivity of the internal olefin versus the ester. High turnovers in oleate metathesis ultimately will be limited by impurities (acids, hydroperoxides, etc.) that are much more likely than the ester group itself to destroy the alkylidene functionality in a catalyst.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques unless otherwise specified. Pentane was washed with sulfuric/nitric acid (95/5 v/v), sodium bicarbonate, and then water, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. Reagent grade diethyl ether, tetrahydrofuran, benzene, and 1,2-dimethoxyethane were distilled from sodium benzophenone ketyl under nitrogen. Toluene was distilled from molten sodium under nitrogen. Reagent grade methylene chloride was distilled from calcium hydride under nitrogen.

NMR data are listed in parts per million downfield from TMS. Coupling constants are quoted in Hertz. Obvious multiplicities and routine coupling constants often are not listed. Spectra were obtained at room temperature unless otherwise specified. Tetrahydrofuran- d_8 was freshly vacuum-distilled from sodium benzophenone ketyl. All other NMR solvents were deaerated by sparging with nitrogen, passed through a column of activated alumina, and then stored over activated molecular sieves (Linde, 3 Å) in the drybox.

cis-2-Pentene, *cis*-3-hexene, 1-decene, and ethyl vinyl ether (Aldrich) were degassed, vacuum-transferred, passed through a column of activated alumina, and stored in the drybox at -40°C . Trimethylsilyl vinyl ether was a gift from Dr. William Crowe. *tert*-Butylamine (Aldrich) was vacuum-transferred and then stored over molecular sieves in the drybox. Tetramethylethylenediamine (TMEDA, Aldrich) was distilled from BaO under nitrogen and then stored over molecular sieves in the drybox. Phenyl vinyl sulfide (Aldrich) and methyl oleate (99+%, Nu Chek Prep) were used as received. 1-Vinyl-2-pyrrolidinone (Aldrich) was passed through a column of activated alumina and stored in the drybox. Vinylferrocene (Strem) was recrystallized from pentane. $\text{Re}(\text{C}-t\text{-Bu})(\text{CH}-t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ ($\text{OR}_{\text{F}_6} = \text{OCMe}(\text{CF}_3)_2$) was prepared as described in the literature.²⁵ Methyl 9-decanoate was used as received in a sealed ampule courtesy of Catalytica Associates, Inc.

***syn*-Re(C-*t*-Bu)(CHMe)(OR_{F6})₂(DME).** A glass bomb was charged with 0.197 g (0.287 mmol) of *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)(OR_{F6})₂, 60 μL (0.577 mmol) of DME, and 8 mL of benzene. The mixture was cooled to -196°C and degassed, after which propylene (0.567 mmol) was condensed into the reaction vessel. After the reaction was thawed, the vessel was wrapped in foil and the solution was stirred for 2 h. DME (200 μL) was added to the brown solution, and the solvent was removed in vacuo to afford 0.200 g (94%) of a brown solid: ^1H NMR (C_6D_6 , 25°C) δ 12.49 (q, 1, $J_{\text{HH}} = 7$, CHMe), 3.83 (d, 3, $J_{\text{HH}} = 7$, CHMe), 3.19 (s, 6, OMe), 3.10 (s, 4, CH₂O), 1.25 (s, 6, OCMe(CF₃)₂), 1.15 (s, 9, CCMe₃); ^{13}C NMR (C_6D_6 , 25°C) δ 290.6 (s, CCMe₃), 254.0 (d, $J_{\text{CH}} = 129$, CHMe), 125.9 (q, $J_{\text{CF}} = 293$, CF₃), 80.6 (hept, $^2J_{\text{CF}} = 28$, OCMe(CF₃)₂), 71.4 (t, $J_{\text{CH}} = 145$, CH₂O), 60.6 (q, $J_{\text{CH}} = 144$, OMe), 53.5 (s, CCMe₃), 42.0 (q, $J_{\text{CH}} = 126$, CHMe), 30.0 (q, $J_{\text{CH}} = 124$, CCMe₃), 20.4 (q, $J_{\text{CH}} = 130$, OCMe(CF₃)₂). Anal. Calcd for $\text{C}_{19}\text{H}_{29}\text{F}_{12}\text{O}_4\text{Re}$: C, 31.02; H, 3.97. Found: C, 31.08; H, 4.10.

***syn*-Re(C-*t*-Bu)(CHEt)(OR_{F6})₂(DME).** A glass bomb was charged with 0.152 g (0.221 mmol) of *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)(OR_{F6})₂, 25 μL (0.241 mmol) of DME, and 6 mL of benzene. The solution was cooled to -196°C and degassed, and 1-butene (0.719 mmol) was condensed into the flask. After the solution was thawed, the vessel was wrapped in foil and the reaction was stirred for 2.5 h. DME (100 μL) was added, and the solvent was removed in vacuo to afford 0.160 g (96%) of a slightly gummy brown solid as the pure syn rotamer. After a solution of this product was stored for 6 days, 5% of the anti rotamer (δ 13.8) and 10% of *syn*-Re(C-*t*-Bu)(CHMe)(OR_{F6})₂(DME) were observed. Even samples stored at -40°C in the solid state showed detectable levels of the ethylidene complex after extended periods: ^1H NMR (C_6D_6 , 25°C) δ 12.30 (t, 1, $J_{\text{HH}} = 7$, CHEt), 4.28 (m, 2, $J_{\text{HH}} = 7$, 7, CHCH₂Me), 3.22 (s, 6, OMe), 3.14 (s, 4, CH₂O), 1.29 (br s, 6, OCMe(CF₃)₂), 1.15 (s, 9, CCMe₃), 0.96 (t, 3, $J_{\text{HH}} = 7$, CHCH₂Me); ^{13}C NMR (C_6D_6 , 25°C) δ 290.8 (s, CCMe₃), 261.2 (d, $J_{\text{CH}} = 128$, CHEt), 125.8 (q, $J_{\text{CF}} = 288$, CF₃), 80.4 (hept, $^2J_{\text{CF}} = 28$, OCMe(CF₃)₂), 71.5 (t, $J_{\text{CH}} = 145$, CH₂O), 60.7 (q, $J_{\text{CH}} = 145$, OMe), 53.5 (s, CCMe₃), 49.1 (t, $J_{\text{CH}} = 127$, CHCH₂Me), 30.0 (q, $J_{\text{CH}} = 128$, CCMe₃), 20.5 (q, $J_{\text{CH}} = 130$, OCMe(CF₃)₂), 16.6 (q, $J_{\text{CH}} = 126$, CHCH₂Me). Anal. Calcd for

$\text{C}_{20}\text{H}_{31}\text{F}_{12}\text{O}_4\text{Re}$: C, 32.04; H, 4.17. Found: C, 31.96; H, 4.11.

***syn*-Re(C-*t*-Bu)(CHPh)(OR_{F6})₂(DME).** A vial was loaded with 0.500 g (0.727 mmol) of *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)(OR_{F6})₂, 90 μL (0.866 mmol) of DME, 10 mL of benzene, and 84 μL of styrene (0.733 mmol). The vial was wrapped with foil, and the reaction was stirred for 4 h. DME (200 μL) was added to the brown solution, and the solvent was removed in vacuo to afford 0.554 g (96%) of a powdery brown solid which may be recrystallized from pentane: ^1H NMR (C_6D_6 , 25°C) δ 13.02 (s, 1, CHPh), 7.59 (d, 2, $J_{\text{HH}} = 7$, H_o), 7.26 (t, 2, $J_{\text{HH}} = 8$, H_m), 6.93 (t, 1, $J_{\text{HH}} = 7$, H_p), 3.28 (s, 6, OMe), 3.20 (s, 4, CH₂O), 1.26 (s, 9, CCMe₃), 1.16 (br s, 6, OCMe(CF₃)₂); ^{13}C NMR (C_6D_6 , 25°C) δ 291.2 (s, CCMe₃), 249.8 (d, $J_{\text{CH}} = 127$, CHPh), 149.2 (s, C_i), 129.5 (d, $J_{\text{CH}} = 157$, C_{aryl}), 129.0 (d, $J_{\text{CH}} = 160$, C_{aryl}), 128.2 (d, $J_{\text{CH}} = 158$, C_{aryl}), 125.9 (q, $J_{\text{CF}} = 289$, CF₃), 81.1 (hept, $^2J_{\text{CF}} = 28$, OCMe(CF₃)₂), 71.2 (t, $J_{\text{CH}} = 148$, CH₂O), 60.7 (q, $J_{\text{CH}} = 144$, OMe), 53.9 (s, CCMe₃), 29.8 (q, $J_{\text{CH}} = 127$, CCMe₃), 20.3 (q, $J_{\text{CH}} = 130$, OCMe(CF₃)₂). Anal. Calcd for $\text{C}_{24}\text{H}_{31}\text{F}_{12}\text{O}_4\text{Re}$: C, 36.14; H, 3.92. Found: C, 36.63; H, 4.07.

Re(C-*t*-Bu)[CH(*p*-C₆H₄NMe₂)](OR_{F6})₂(DME). The previous procedure was followed using 0.099 g (0.144 mmol) of *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)(OR_{F6})₂, 30 μL (0.289 mmol) of DME, and 0.022 g of *p*-(dimethylamino)styrene (0.149 mmol) in 2 mL of pentane. After 3.5 h a green precipitate of the desired product was isolated by filtration (0.025 g, 21%), and the brown supernatant was reduced to dryness yielding another 0.096 g (79%) of the product as a tacky brown solid: ^1H NMR (C_6D_6 , 25°C) δ 12.94 (s, 1, CHPh), 7.66 (d, 2, $J_{\text{HH}} = 9$, Ph), 6.62 (d, 2, $J_{\text{HH}} = 9$, Ph), 3.27 (s, 6, OMe), 3.23 (s, 4, CH₂O), 2.53 (s, 6, NMe₂), 1.39 (s, 9, CCMe₃), 1.29 (s, 6, OCMe(CF₃)₂). Anal. Calcd for $\text{C}_{26}\text{H}_{36}\text{F}_{12}\text{N}_2\text{O}_4\text{Re}$: C, 37.14; H, 4.32; N, 1.67. Found: C, 37.07; H, 4.52; N, 1.95.

Measurement of the Reaction Rates of Olefins with *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)(OR_{F6})₂ in THF-*d*₈. In a typical procedure, 0.033 g of *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)(OR_{F6})₂ was loaded into a resealable NMR tube along with 500 μL of THF-*d*₈ which had been freshly passed through a column of activated alumina. The sample was subjected to three freeze/pump/thaw cycles on a vacuum line, and 0.575 mmol of ethyl vinyl ether was condensed into the tube. The sample was sealed, thawed briefly at -78°C , and placed in an NMR probe that had been precooled to -80°C . The probe was warmed until the reaction began (ca. -10°C), and the reaction was monitored.

Measurement of the Reaction Rates of Olefins with *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)(OR_{F6})₂ in the Presence of DME. In a representative experiment, 400 μL (0.015 mmol) of a freshly prepared 0.038 M stock solution of *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)(OR_{F6})₂ in C_6D_6 was added to an NMR tube having a Teflon valve, followed by 2 μL of mesitylene (used as an internal standard), 3 μL of DME (0.029 mmol), and 100 μL of C_6D_6 . After three freeze/pump/thaw cycles, 0.043 mmol of propylene was vacuum-transferred onto the solution and the sample was sealed. The sample was brought to room temperature and the reaction observed by proton NMR to go to completion over a period of 23 min.

***syn*-Re(C-*t*-Bu)(CHOEt)(OR_{F6})₂(THF)₂.** Excess ethyl vinyl ether (0.60 mL, 6.3 mmol) was added to 0.87 g (1.26 mmol) of *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)(OR_{F6})₂ in 2 mL of tetrahydrofuran. The solution was stirred for 2 h at room temperature. The solvent was then removed in vacuo to afford a quantitative yield of orange crystals that were pure by ^1H NMR: ^1H NMR (C_6D_6) δ 11.56 (s, 1, CHOEt), 3.77 (m, 8, THF), 3.53 (q, 2, $J_{\text{HH}} = 7$, OCH₂Me), 1.42 (m, 8, THF), 1.33 (s, 6, OCMe(CF₃)₂), 1.25 (s, 9, CCMe₃), 0.95 (t, 3, $J_{\text{HH}} = 7$, OCH₂Me); ^{13}C NMR (C_6D_6) δ 295.9 (CCMe₃), 265.7 ($J_{\text{CH}} = 135$, CHOEt), 127.7 ($J_{\text{CF}} = 288$, OCMe(CF₃)₂), 81.5 (OCMe(CF₃)₂), 74.3 (t, $J_{\text{CH}} = 142$, OCH₂Me), 69.4 (THF), 54.9 (CCMe₃), 29.3 (CCMe₃), 25.5 (THF), 20.9 (OCMe(CF₃)₂), 15.4 (q, $J_{\text{CH}} = 128$, OCH₂Me). Anal. Calcd for $\text{C}_{24}\text{H}_{37}\text{F}_{12}\text{O}_5\text{Re}$: C, 35.17; H, 4.55. Found: C, 34.82; H, 4.42.

X-ray Structure of *syn*-Re(C-*t*-Bu)(CHOEt)(OR_{F6})₂(THF)₂. A yellow prismatic crystal of *syn*-Re(C-*t*-Bu)(CHOEt)(OR_{F6})₂(THF)₂ having approximate dimensions of $0.24 \times 0.32 \times 0.18$ mm was mounted on a glass fiber. Data were collected at -72°C on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo K α radiation. A total of 7559 reflections were collected in the range $3.0^\circ < 2\theta < 55.00^\circ$ with 7174 being unique. No crystal decay was evident during data collection. An empirical absorption correction was applied, using the program DI-FABS, which resulted in transmission factors ranging from 0.78 to 1.29. The structure was solved by Patterson methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions and refined isotropically. The final cycle of full-matrix least-squares refinement was based on 4623 reflections ($I > 3.00\sigma(I)$) and 379 variables and used the TEXSAN crystallographic software package from Molecular Structure Corporation. The final refinement converged with final $R = 0.052$ and $R_w = 0.050$. The maximum and minimum peaks on the final Fourier difference

map corresponded to 1.28 and $-2.36 e^{-}/\text{\AA}^3$, respectively. Crystal data are $a = 10.318$ (1) \AA , $b = 18.303$ (2) \AA , $c = 16.181$ (2) \AA , $\beta = 96.98$ (2) $^\circ$, $V = 3033$ (1) \AA^3 , space group = $P2_1/c$, $Z = 4$, $MW = 819.74$, $\rho(\text{calcd}) = 1.795$ g/cm^3 , $\mu = 41.62$ cm^{-1} .

syn/anti-Re(C-t-Bu)(CHOEt)(OR_{F6})₂(THF)₂. This mixture is obtained upon photolysis of Re(C-t-Bu)(CHOEt)(OR_{F6})₂(THF)₂ in pentane or benzene with a medium-pressure mercury lamp. anti rotamer: ¹H NMR (C₆D₆) δ 11.93 (s, 1, CHOEt), 3.96 (q, 2, $J_{\text{HH}} = 7$, OCH₂Me), 3.77 (m, 8, THF), 1.42 (m, 8, THF), 1.34 (s, 6, OMe(CF₃)₂), 1.21 (s, 9, CMe₃), 0.95 (t, 3, $J_{\text{HH}} = 7$, OCH₂Me); ¹³C NMR (C₆D₆) δ 301.3 (CCMe₃), 266.7 (CHOEt, $J_{\text{CH}} = 163$), 127.7 (OCMe(CF₃)₂, $J_{\text{CF}} = 288$), 81.5 (OCMe(CF₃)₂), 72.9 (OCH₂Me), 69.5 (THF), 56.2 (CCMe₃), 28.9 (OCMe₃), 25.5 (THF), 19.8 (OCMe(CF₃)₂), 15.4 (q, $J_{\text{CH}} = 125$, OCH₂Me).

Observation of syn- and anti-Re(C-t-Bu)(CHOEt)(OR_{F6})₂. A mixture of syn (90–95%) and anti (5–10%) rotamers was observed upon adding 1–5 equiv of ethyl vinyl ether to a solution of syn-Re(C-t-Bu)(CH-t-Bu)(OR_{F6})₂ (10–20 mg) in C₆D₆ (700 μL): ¹H NMR (syn rotamer; C₆D₆) δ 11.03 (s, 1, CHOEt), 3.35 (q, 2, $J_{\text{HH}} = 7$, OCH₂Me), 1.43 (s, 6, OMe(CF₃)₂), 1.25 (s, 9, CMe₃). The OCH₂Me resonance was obscured. Preparation of a sample concentrated enough for ¹³C NMR analysis resulted in decomposition to [Re(C-t-Bu)(OR_{F6})₂]₂.

syn-Re(C-t-Bu)(CHOSiMe₃)(OR_{F6})₂(THF)₂. Excess trimethylsilyl ether (0.60 mL, 6.3 mmol) was added to 0.87 g (1.26 mmol) of syn-Re(C-t-Bu)(CH-t-Bu)(OR_{F6})₂ in 2 mL of tetrahydrofuran. The solution was stirred for 2 h at room temperature, and the solvent was removed in vacuo to afford a quantitative yield of orange crystals that were pure by ¹H NMR: ¹H NMR (C₆D₆) δ 12.50 (s, 1, CHOSiMe₃), 3.78 (m, 8, THF), 1.42 (m, 8, THF), 1.33 (s, 6, OMe(CF₃)₂), 1.26 (s, 9, CMe₃), 0.04 (s, 9, SiMe₃); ¹³C NMR (C₆D₆) δ 295.6 (C-t-Bu), 259.5 ($J_{\text{CH}} = 135$, CHOEt), 127.5 (OCMe(CF₃)₂), 81.7 (OCMe(CF₃)₂), 69.7 (THF), 55.0 (CCMe₃), 29.6 (CCMe₃), 25.8 (THF), 21.2 (OCMe(CF₃)₂), -0.2 (OSiMe₃). Elemental analysis data could not be obtained due to the rapid loss of THF from the complex in vacuo.

anti-Re(C-t-Bu)(CHOSiMe₃)(OR_{F6})₂(THF)₂. A mixture of this compound and its syn rotamer can be prepared by photolyzing a C₆D₆ solution of the syn rotamer with a medium-pressure mercury lamp: ¹H NMR (C₆D₆) δ 12.82 (s, 1, CHOSiMe₃), 3.78 (m, 8, THF), 1.42 (m, 8, THF), 1.28 (s, 6, OMe(CF₃)₂), 1.22 (s, 9, CMe₃), 0.08 (s, 9, SiMe₃); ¹³C NMR (C₆D₆) δ 299.7 (C-t-Bu), 264.0 ($J_{\text{CH}} = 166$, CHOEt), 127.5 (OCMe(CF₃)₂), 81.7 (OCMe(CF₃)₂), 69.7 (THF), 55.9 (CCMe₃), 29.0 (CCMe₃), 25.8 (THF), 20.2 (OCMe(CF₃)₂), -0.1 (OSiMe₃).

syn-Re(C-t-Bu)(CHSPh)(OR_{F6})₂(THF)₂. Phenyl vinyl sulfide (76 μL , 0.58 mmol) was added to a solution of syn-Re(C-t-Bu)(CH-t-Bu)(OR_{F6})₂ (0.40 g, 0.58 mmol) in 3 mL of tetrahydrofuran. The orange solution was stirred for 1.5 h in a foil-wrapped vial, and the solvent was removed in vacuo. An analytically pure sample (0.40 g, 78%) was prepared by recrystallization from pentane: ¹H NMR (CD₂Cl₂) δ 12.31 (s, 1, CHSPh), 7.4–7.2 (m, 5, H_{aryl}), 3.88 (m, 8, THF), 1.89 (m, 8, THF), 1.46 (s, 9, CMe₃), 1.38 (s, 6, OMe(CF₃)₂); ¹³C NMR (CD₂Cl₂) δ 297.3 (CCMe₃), 238.6 (CHSPh, $J_{\text{CH}} = 143$), 142.4 (C₁), 129.5 and 128.2 (C_{o,m}), 127.7 (C_p), 125.1 ($J_{\text{CF}} = 291$, CF₃), 82.1 (OCMe(CF₃)₂), 69.9 (THF), 56.2 (CMe₃), 30.3 (CMe₃), 26.0 (THF), 20.7 (OCMe(CF₃)₂); ¹⁹F NMR (CD₂Cl₂) δ 26.69 (mult). Anal. Calcd for C₂₈H₃₇F₁₂O₄ReS: C, 38.05; H, 4.22. Found: C, 38.08; H, 4.49.

anti-Re(C-t-Bu)(CHSPh)(OR_{F6})₂(THF)₂. A mixture of syn and anti rotamers can be prepared by photolyzing a C₆D₆ solution of the syn rotamer with a medium-pressure mercury lamp. The solvent was removed in vacuo and the residue dissolved in CD₂Cl₂: ¹H NMR (CD₂Cl₂) δ 12.50 (s, 1, CHSPh), 7.4–7.2 (m, 5, H_{aryl}), 3.88 (m, 8, THF), 1.89 (m, 8, THF), 1.49 (s, 9, CMe₃), 1.37 (s, 6, OMe(CF₃)₂); ¹³C NMR (CD₂Cl₂) δ 300.8 (CCMe₃), 224.3 ($J_{\text{CH}} = 184$, CHSPh), 138.9 (C₁), 129.7 and 128.5 (C_{o,m}), 127.9 (C_p), 124.1 ($J_{\text{CF}} = 289$, CF₃), 81.1 (OCMe(CF₃)₂), 69.6 (THF), 55.4 (CMe₃), 29.7 (CMe₃), 26.0 (THF), 20.0 (OCMe(CF₃)₂); ¹⁹F NMR (CD₂Cl₂) δ 28.16 and 28.56.

anti-Re(C-t-Bu)[CHN(CH₂)₃C(O)](OR_{F6})₂. Vinyl pyrrolidinone (78 μL , 0.73 mmol) was added to a room temperature solution of syn-Re(C-t-Bu)(CH-t-Bu)(OR_{F6})₂ (0.500 g, 0.73 mmol) in 4 mL of CH₂Cl₂. After 20 min the solvent was removed in vacuo to afford orange crystals of product that was pure enough (by ¹H NMR) for further use. An analytical sample (0.28 g, 54%) was recrystallized from dichloromethane by adding pentane and cooling: ¹H NMR (C₆D₆) δ 10.92 (s, 1, CHR), 2.70 and 2.05 (t, 2 each, CH₂), 1.41 (s, 6, OMe(CF₃)₂), 1.27 (s, 9, CMe₃), 1.15 (s, 2, CH₂); ¹³C NMR (C₆D₆) δ 301.5 (CCMe₃), 213.3 ($J_{\text{CH}} = 173$, CHR), 124.4 ($J_{\text{CF}} = 285$, CF₃), 81.0 (OCMe(CF₃)₂), 52.3 (CMe₃), 47.7 ($J_{\text{CH}} = 146$, CH₂), 29.3 (CMe₃), 27.2 ($J_{\text{CH}} = 135$, CH₂), 21.1 ($J_{\text{CH}} = 135$, CH₂), 19.8 (OCMe(CF₃)₂); ¹⁹F NMR (C₆D₆) δ 28.85 and 28.33 (s, 6 each, OMe(CF₃)₂). Anal. Calcd for C₁₈H₂₂F₁₂N₂O₄Re: C, 30.26; H, 3.10; N, 1.96. Found: C, 30.53; H, 3.10; N, 1.90.

syn- and anti-Re(C-t-Bu)(CHSPh)(OR_{F6})₂(t-BuNH₂)₂. A solution of syn-Re(C-t-Bu)(CHSPh)(OR_{F6})₂(THF)₂ (85 mg, 0.096 mmol) in 600 μL of C₆D₆ was photolyzed in a thin-wall NMR tube with a medium-pressure mercury lamp (Pyrex filtered) for 1.8 h. A proton NMR showed that the mixture had been converted to a 41:59 mixture of syn and anti rotamers. The solution was then reduced to dryness in vacuo and dissolved in 2 mL of dichloromethane. Excess *tert*-butylamine (100 μL) was added, and the orange solution darkened slightly. After 5 min, the solution was reduced in vacuo to afford crystalline orange product as a 42:58 ratio of syn and anti rotamers: ¹H NMR (CD₂Cl₂, syn rotamer) δ 13.55 (s, 1, CHSPh), 7.4–7.2 (m, 5, H_{aryl}), 4.10 and 3.58 (br d, 2 each, NH₂), 1.63 and 1.45 (s, 3 each, OMe(CF₃)₂), 1.45 (s, 9, CMe₃), 1.19 (s, 18, H₂NCMe₃); ¹³C NMR (CD₂Cl₂) δ 286.8 (C-t-Bu), 262.15 ($J_{\text{CH}} = 151$, CHSPh), 145.5 (C₁), 129.3 and 127.2 (C_{o,m}), 127.1 (C_p), 126.4 ($J_{\text{CF}} = 290$, CF₃), 78.4 (OCMe(CF₃)₂), 30.9 (NH₂CMe₃), 29.3 (CMe₃), 21.2 and 18.0 (OCMe(CF₃)₂), the resonance for CMe₃ was obscured by the solvent resonance; ¹H NMR (CD₂Cl₂, anti rotamer) δ 13.76 (s, 1, CHSPh), 7.4–7.2 (m, 5, H_{aryl}), 4.06 and 3.58 (br d, 2 each, NH₂), 1.69 and 1.56 (s, 3 each, OMe(CF₃)₂), 1.47 (s, 9, CMe₃), 1.22 (s, 18, H₂NCMe₃); ¹³C NMR (CD₂Cl₂) δ 289.4 (C-t-Bu), 258.5 ($J_{\text{CH}} = 145$, CHSPh), 143.5 (C₁), 129.4 and 126.8 (C_{o,m}), 128.6 (C_p), 126.1 ($J_{\text{CF}} = 291$, CF₃), 79.3 (OCMe(CF₃)₂), 53.3 (CMe₃), 30.4 (NH₂CMe₃), 31.4 (CMe₃), 21.2 and 18.5 (OCMe(CF₃)₂). Anal. Calcd for C₂₈H₄₃F₁₂N₂O₄SRe: C, 37.96; H, 4.89; N, 3.16. Found: C, 38.05; H, 4.96; N, 2.88.

anti-Re(C-t-Bu)(CHFc)(OR_{F6})₂. A solution of vinylferrocene (0.31 g, 1.45 mmol) in 2 mL of dichloromethane was added to a -40 $^\circ\text{C}$ solution of syn-Re(C-t-Bu)(CH-t-Bu)(OR_{F6})₂ (1.00 g, 1.45 mmol) in 3 mL of dichloromethane dropwise over a period of 3 min while the reaction mixture was stirred vigorously. The orange solution darkened to red. After the reaction mixture was stirred at room temperature for 15 min, the solvent was removed in vacuo to afford a red oil that contained bright-orange crystals of *trans*-diferrocenylethylene. The oil was dissolved in pentane, the insoluble *trans*-diferrocenylethylene (50 mg) was removed by filtration, and the pentane was removed from the filtrate in vacuo. A proton NMR spectrum of the product showed it to be $\sim 95\%$ pure anti-Re(C-t-Bu)(CH-t-Bu)(OR_{F6})₂ containing $\sim 5\%$ of the syn rotamer. Crystallization from cold pentane afforded red microcrystalline product which was collected and washed with 3×2 mL of cold pentane (0.70 g, 59%). X-ray quality crystals were obtained from a saturated toluene solution at -40 $^\circ\text{C}$: ¹H NMR (C₆D₆) δ 13.15 (s, 1, CHFc), 4.21 and 4.16 (d, 2 each, $J_{\text{HH}} = 2$, Cp'), 4.07 (s, 5, Cp), 1.18 (s, 9, CMe₃), 1.14 (s, 6, OMe(CF₃)₂); ¹³C NMR (CD₂Cl₂, mixture of rotamers) δ 304.2 (CCMe₃), 232.3 ($J_{\text{CH}} = 173$, CHFc), 123.4 ($J_{\text{CF}} = 285$, CF₃), 81.4 (OCMe(CF₃)₂), 56.0 (CMe₃), 29.5 (CMe₃), 21.0 (OCMe(CF₃)₂); Cp resonances for the syn and anti isomers were not differentiated δ 98.8, 86.9, 70.8, 70.1, 69.6, 69.4, 69.2, and 67.1. ¹⁹F NMR (CD₂Cl₂) δ 28.42 and 27.73 (q). Anal. Calcd for C₂₄H₂₅F₁₂FeO₂Re: C, 35.35; H, 3.09. Found: C, 34.98; H, 2.92.

syn-Re(C-t-Bu)(CHFc)(OR_{F6})₂. This compound was observed in the reaction mixture upon photolyzing the anti isomer in dichloromethane or benzene: ¹H NMR (C₆D₆) δ 11.72 (s, 1, CHFc), 4.23 and 4.16 (d, 2 each, $J_{\text{HH}} = 2$, Cp'), 3.99 (s, 5, Cp), 1.19 (s, 9, CMe₃), 1.14 (s, 6, OMe(CF₃)₂); ¹³C NMR (CD₂Cl₂, mixture of rotamers) δ 298.5 (CCMe₃), 228.9 ($J_{\text{CH}} = 132$, CHFc), 123.4 ($J_{\text{CF}} = 285$ Hz, CF₃), 81.4 (OCMe(CF₃)₂), 55.6 (CMe₃), 30.0 (CMe₃), 21.5 (OCMe(CF₃)₂); Cp resonances are listed in the above example: ¹⁹F NMR (CD₂Cl₂) δ 28.65 and 28.12 (q).

X-ray Structure of anti-Re(C-t-Bu)(CHFc)(OR_{F6})₂. Data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo K α radiation. Of the 6950 reflections which were collected, 6366 were unique ($R_{\text{int}} = 0.144$); equivalent reflections were merged. The intensities of three representative reflections which were measured after every 60 min of X-ray exposure time remained constant throughout data collection time, indicating crystal and electronic stability (no decay correction was applied). The data were corrected for Lorentz and polarization effects. The structure was solved by a combination of the Patterson method and direct methods. The final cycle of full-matrix least-squares refinement (TEXRAY Structure Analysis Package, Molecular Structures Corporation (1985)) was based on 4201 observed reflections ($I > 3.00\sigma(I)$) and 361 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of $R = 0.050$ and $R_w = 0.052$. The non-hydrogen atoms were refined anisotropically. Crystal data are $a = 9.769$ (2) \AA , $b = 30.746$ (7) \AA , $c = 10.140$ (2) \AA , $\beta = 116.78$ (1) $^\circ$, $Z = 4$, $FW = 815.50$, $\rho = 1.992$ g/cm^3 , $\mu = 51.4$ cm^{-1} , space group = $P2_1/a$.

syn-Re(C-t-Bu)(CHEt)(OR_{F6})₂(TMEDA). *cis*-3-Hexene (0.94 mL, 7.6 mmol) was added to a solution of syn-Re(C-t-Bu)(CH-t-Bu)(OR_{F6})₂ (0.52 g, 0.76 mmol) in 3 mL of dichloromethane. The red color darkened upon stirring the reaction mixture at room temperature for 6 h. Tetra-

methyl ethylenediamine (0.14 mL, 0.91 mmol) was then added, and the reaction mixture was reduced to give orange microcrystals quantitatively. The analytical sample was prepared by cooling a saturated dichloromethane solution: $^1\text{H NMR}$ (C_6D_6) δ 12.20 (t, 1, $J_{\text{HH}} = 7$, CHEt), 4.57 (m, 2, CHCH_2Me), 2.27 (br s, 12, NMe_2), 2.01 (s, 4, $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$), 1.43 (s, 6, $\text{OCMe}(\text{CF}_3)_2$), 1.16 (s, 9, CMe_3), 1.02 (t, 3, $J_{\text{HH}} = 8$, CHCH_2Me); $^{13}\text{C NMR}$ (C_6D_6) δ 287.12 (CCMe_3), 273.29 ($J_{\text{CH}} = 125$, CHEt), 125.91 ($J_{\text{CF}} = 290$, CF_3), 81.04 ($\text{OCMe}(\text{CF}_3)_2$), 59.11 ($J_{\text{CH}} = 135$, $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$), 54.0 (CMe_3), 48.99 ($J_{\text{CH}} = 125$, CH_2Me), 30.81 (NMe_2), 28.62 (CH_2Me), 21.06 (CMe_3), 17.34 ($\text{OCMe}(\text{CF}_3)_2$). Anal. Calcd for $\text{C}_{24}\text{H}_{41}\text{F}_3\text{N}_2\text{O}_2\text{Re}$: C, 35.86; H, 5.14; N, 3.48. Found: C, 35.93; H, 5.04; N, 3.87.

Metathesis of *cis*-2-Pentene by $\text{Re}(\text{C}-t\text{-Bu})(\text{CH}-t\text{-Bu})(\text{OR}_{\text{F}_6})_2$. *cis*-2-Pentene (0.55 mL, 5 mmol) was added to a solution of *syn*- $\text{Re}(\text{C}-t\text{-Bu})(\text{CH}-t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ (0.05 mmol) in 5.0 mL of benzene in a septum-capped vial. Aliquots were periodically withdrawn with a syringe and quenched by passage through activated alumina, a procedure that a separate experiment showed to result in complete loss of metathesis activity. The concentrations of the 2-butenes, 2-pentenenes, and 3-hexenes were determined by gas chromatography. After 2.5 h at room temperature, equilibrium was achieved. Upon addition of another 100 equiv of *cis*-2-pentene to the remaining catalyst mixture, equilibrium was reestablished in 30 min.

Metathesis of Methyl Oleate by $\text{Re}(\text{C}-t\text{-Bu})(\text{CH}-t\text{-Bu})(\text{OR}_{\text{F}_6})_2$. To a solution of *syn*- $\text{Re}(\text{C}-t\text{-Bu})(\text{CH}-t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ (0.05 mmol) in 5.0 mL of methylene chloride was added an internal standard of mesitylene (35 μL , 0.25 mmol) and then 50 equiv of methyl oleate (0.85 mL, 2.52 mmol). The solution was stirred vigorously, and aliquots were periodically withdrawn and quenched by passage through activated alumina. The concentrations of the metathesis products were then determined by gas chromatography. Equilibrium was achieved within 12 h at room temperature. This catalyst solution was then allowed to remain undis-

turbed for an additional 24 h, and an additional 50 equiv of methyl oleate was added to the remaining catalyst mixture. Equilibrium was reestablished within 7.5 h at room temperature.

Increased Rate of Methyl Oleate Metathesis by Addition of *cis*-3-Hexene to $\text{Re}(\text{C}-t\text{-Bu})(\text{CH}-t\text{-Bu})(\text{OR}_{\text{F}_6})_2$. To a solution of *syn*- $\text{Re}(\text{C}-t\text{-Bu})(\text{CH}-t\text{-Bu})(\text{OR}_{\text{F}_6})_2$ (0.038 mmol) in 2.00 mL of methylene chloride was added 10 equiv of *cis*-3-hexene (47 μL , 0.38 mmol). The solution was then stirred for 7 h in order to prepare $\text{Re}(\text{C}-t\text{-Bu})(\text{CHEt})(\text{OR}_{\text{F}_6})_2$ in situ, and an additional 3.0 mL of methylene chloride and an internal standard of 1-phenyloctane (84 μL , 0.38 mmol) were then added. Methyl oleate (50 equiv) was then added. Equilibrium was achieved within 180 min at room temperature. After an additional 12.5 h at room temperature, an additional 100 equiv of methyl oleate was added to the catalyst mixture. Equilibrium was reestablished within 6 h.

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Supplementary Material Available: ORTEP drawing, fully labeled drawing, and tables of final positional parameters and final thermal parameters for *syn*- $\text{Re}(\text{C}-t\text{-Bu})(\text{CHOEt})(\text{OR}_{\text{F}_6})_2(\text{THF})_2$ and *anti*- $\text{Re}(\text{C}-t\text{-Bu})(\text{CHFc})(\text{OR}_{\text{F}_6})_2$ (12 pages); listings of final observed and calculated structure factors for *syn*- $\text{Re}(\text{C}-t\text{-Bu})(\text{CHOEt})(\text{OR}_{\text{F}_6})_2(\text{THF})_2$ and *anti*- $\text{Re}(\text{C}-t\text{-Bu})(\text{CHFc})(\text{OR}_{\text{F}_6})_2$ (74 pages). Ordering information is given on any current masthead page.

Exploiting Laser Based Methods for Low-Temperature Solid-State Synthesis: Growth of a Series of Metastable $(\text{Sr}_{1-x}\text{M}_x)_{1-\delta}\text{CuO}_2$ Materials

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Abstract: Pulsed laser deposition (PLD) has been used to prepare a series of $(\text{Sr}_{1-x}\text{Ca}_x)_{1-\delta}\text{CuO}_2$ thin film materials on (100) SrTiO_3 and (100) MgO at low temperatures. X-ray diffraction (XRD), electron diffraction (ED), and ion-channeling studies have shown that all of the $(\text{Sr}_{1-x}\text{Ca}_x)_{1-\delta}\text{CuO}_2$ materials ($x = 0-1$; $\delta = 0.1$) grown on (100) SrTiO_3 at 500 $^\circ\text{C}$ have a layered, tetragonal structure with the *c*-axis oriented perpendicular to the substrate surface. In contrast, the target materials prepared by conventional high-temperature techniques have an orthorhombic structure ($x = 0$, $\delta = 0$) or consist of multiple phases ($x = 0$, $\delta = 0.1$; $x > 0$, $\delta = 0, 0.1$). Rutherford backscattering studies have shown that the composition of the materials prepared by PLD are the same as the starting target stoichiometry, even when the targets contain multiple phases. The dependence of the product structure on growth temperature and substrate lattice constant were also determined. SrCuO_2 materials grown at 500, 600, and 700 $^\circ\text{C}$ exhibit a decreasing ratio of tetragonal/orthorhombic phase as the temperature increases. These results show that low-temperature growth traps the layered, tetragonal phase. Comparison of the SrCuO_2 structures obtained on (100) SrTiO_3 and (100) MgO substrates have also shown that product-substrate lattice matching is important in stabilizing the tetragonal phase and in orienting the crystallographic growth direction. In addition, the physical properties of these new materials have been characterized by electrical and magnetic measurements. The stoichiometric $(\text{Sr}_{1-x}\text{Ca}_x)_{1-\delta}\text{CuO}_2$ materials were found to be insulators. However, the nonstoichiometric $(\text{Sr}_{1-x}\text{Ca}_x)_{1-\delta}\text{CuO}_2$ materials exhibited systematic increases in conductivity with decreasing x . Furthermore, the $x = 0$ material, $\text{Sr}_{0.9}\text{CuO}_2$, showed a transition to a zero resistance state with an onset of ≈ 20 K. The implications of these studies to copper oxide superconductors are discussed.

Introduction

The synthesis of materials by conventional ceramic methods requires high reaction temperatures in order to facilitate diffusion and reaction in the solid state.¹⁻³ As a consequence, the products

derived from conventional solid-state methodologies are limited typically to the ones thermodynamically stable at high temperature. In the past most solid-state synthetic studies have focused on high-temperature reaction chemistry; however, there is now a considerable and rapidly growing interest in the development

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