Alkyl, Alkylidene, and Alkylidyne Complexes of Rhenium

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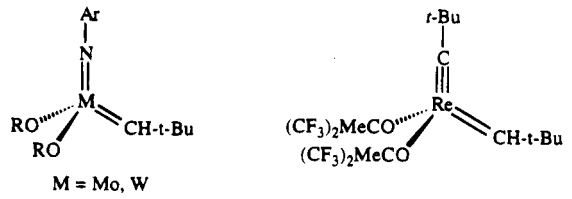
The reaction of Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)$_2$ with triflic acid, pentafluorophenol, HBF_4·OEt_2, or $[H(OEt_2)_2]^+[BAr^F_4]^-$ (Ar^F = 3,5-$C_6H_3(CF_3)_2$) yields complexes of the general formula Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$X (X = OTf, OC_6F_5, BF_4, BAr^F_4) in 60–80% yield. Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$X reacts with coordinating ligands L (L = py, CH_3CN, CD_3OD, THF) to form neopentane and Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(L)$_n$X (n = 1–3). The reaction of Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(py)$_2$(OTf) with NaC_5H_5, NaL_{OEt} (L_{OEt} = [CpCo($PO(OEt)_2$)$_3$], or $NaHBpz_3$ in THF yields Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(η^5-C_5H_5), Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(L_{OEt}), or Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)($HBpz_3$), respectively, while the reaction between Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(py)$_2$(OTf) and 1,4,7-trithiacyclononane produces colorless [Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(η^3-$S_3C_6H_{12}$)]$^+$[OTf]$^-$ in 96% yield. Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(L) (L = Cp, L_{OEt}) and [Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(η^3-$S_3C_6H_{12}$)]$^+$[OTf]$^-$ react with triflic acid to form Re(C-*t*-Bu)(CH-*t*-Bu)(L)(OTf) or [Re(C-*t*-Bu)(CH-*t*-Bu)(OTf)(η^3-$S_3C_6H_{12}$)]$^+$[OTf]$^-$, respectively. A similar reaction between Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(L_{OEt}) and $[H(OEt_2)_2]^+[BAr^F_4]^-$ in ether produces [Re(C-*t*-Bu)(CH-*t*-Bu)(OEt_2)(L_{OEt})]$^+$[BAr^F_4]$^-$. Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(py)$_2$(OTf) reacts with H_2C=CHR (R = OCH_2CH_3, C_6H_5) to yield neohexene and Re(C-*t*-Bu)(CHR)(CH_2-*t*-Bu)(py)$_2$(OTf) complexes. Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(py)$_2$(OTf) reacts with ethylene to form the unstable methylidene complex, Re(C-*t*-Bu)(CH_2)(CH_2-*t*-Bu)(py)$_2$(OTf), which can be trapped upon addition of bpy to yield red Re(C-*t*-Bu)(CH_2)(CH_2-*t*-Bu)(bpy)(OTf). Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(py)$_2$(OTf) reacts with excess ethylene to form colorless Re(C-*t*-Bu)[(CH_2)$_3$-*t*-Bu](C_2H_4)(py)$_2$(OTf) in 85% yield. Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(CH_3CN)(OTf) metathesizes 100 equiv of *cis*-2-pentene in less than 5 min, but the catalyst is not long-lived.

Introduction

Rhenium is one of three metals (along with molybdenum and tungsten) that are active in classical olefin metathesis systems.[1] In the early 1980s, evidence began to accumulate in favor of the proposition that the metal is in its highest possible oxidation state in classical olefin metathesis systems involving these metals (if the alkylidene ligand is viewed as a dianion).[2] A variety of four-coordinate d^0 alkylidene complexes of molybdenum,[3,4] tungsten,[5] and rhenium[6–8] were prepared and employed for the metathesis of acyclic and cyclic olefins. The most successful and best understood single-component olefin metathesis catalysts are the pseudotetrahedral species shown below.



The rates of metathesis of olefins by Re(C-*t*-Bu)(CH-*t*-Bu)[$OCMe(CF_3)_2$]$_2$ and its variations are estimated to be 2 orders of magnitude slower than the fastest Mo- or W-based systems.[8] In some cases alkylidene complexes will metathesize olefins rapidly only in the presence of Lewis acids such as $AlCl_3$.[9–12] In these mixtures, it is presumed that cationic species are the most active species for olefin metathesis and that they may be present only in low concentrations. Such a presumption is consistent with recent observations that well-defined cationic early-[13] and late-transition-metal[14] catalysts are especially active for the polymerization of olefins. Therefore we felt that a cationic alkylidene complex of rhenium might metathesize olefins at a rate comparable to that of the most active four-coordinate neutral molybdenum or tungsten catalysts. Very recently a variety of cationic tungsten alkylidene com-

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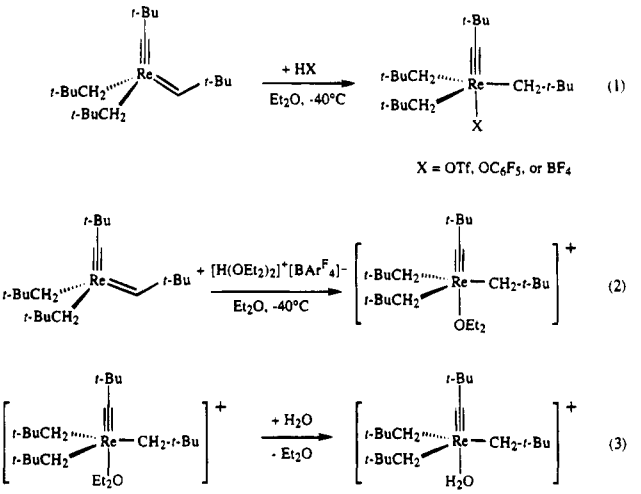
plexes were reported.[9,15,16] However, these coordinatively saturated complexes do not metathesize olefins in the absence of a cocatalyst. The challenge then is to prepare cationic alkylidene complexes that are not coordinatively or sterically saturated, that do not interact strongly with the anion, and that do not decompose to alkylidyne complexes[17] via loss of an α proton.

Although the primary goal of the research described here was to prepare cationic rhenium alkylidene complexes that were more active metathesis catalysts than Re(C-*t*-Bu)(CH-*t*-Bu)[OCMe(CF$_3$)$_2$]$_2$, another goal was to continue to search for rhenium alkylidene complexes that are stable to a range of functional groups, including alcohols and water. The alkylidene and alkylidyne ligands in the Re(C-*t*-Bu)(CH-*t*-Bu) core are stable to water under some circumstances. For example, [Re(C-*t*-Bu)(CH-*t*-Bu)Cl$_2$]$_x$ can be dissolved in water and be recovered unchanged by removing the water *in vacuo*.[7] Therefore we chose to focus on rhenium neopentylidene/neopentylidyne complexes that contain ligands that are not readily protonated, such as neopentyl, tris(pyrazolyl)borate (HBpz$_3$), 1,4,7-trithiacyclononane, η^5-C$_5$H$_5$, or [CpCo(PO(OEt)$_2$)$_3$]$^-$ ("L$_{OEt}$"),[18] and counterions X that are relatively poor ligands, i.e., triflate,[19] tetrafluoroborate, or B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$ ("BAr$^F_4$").[14]

Synthesis of Re(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$X. Our first goal was to prepare complexes of the type [Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)L$_n$]$^+$. The route we chose was to prepare complexes of the type Re(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$X in which X was either a noncoordinating or weakly coordinating anion (triflate, BAr$^F_4^-$, or BF$_4^-$) and in which α-hydrogen abstraction reactions would be facile. The reaction of Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)$_2$ with HX was investigated, since the reaction of Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)$_2$ with HCl had been previously found to yield Re(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$Cl.[20,21]

Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)$_2$ reacts with a variety of acids as shown in equations 1 and 2. The products are highly crystalline yellow solids that are obtained in yields that range from 60−80%. Wilkinson and coworkers reported the synthesis of Re(CSiMe$_3$)(CH$_2$SiMe$_3$)$_3$Cl and found in an X-ray study that it was a trigonal bipyramid with the trimethylsilylmethyl ligands occupying the equatorial sites.[22] When X = OC$_6$F$_5$ or OTf the structure is likely to be analogous to that of Re(CSiMe$_3$)(CH$_2$SiMe$_3$)$_3$Cl. Since BF$_4^-$ is known to coordinate through one of the fluorides in a variety of circumstances, we assume that it also coordinates to rhenium in this situation.

When the noncoordinating anion BAr$^F_4^-$ is employed, the resulting crystalline complex contains 1 equiv of ether, which we assume to be bound to the metal (eq 2). This ether is relatively labile and partially lost *in vacuo*. Therefore elemental analysis has not been correct or reproducible. A second problem is that if



traces of water are present in either [H(OEt$_2$)$_2$]$^+$[BAr$^F_4$]$^-$ or any solvent of recrystallization, highly crystalline [Re(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$(H$_2$O)]$^+$[BAr$^F_4$]$^-$(Et$_2$O) crystallizes as yellow blocks. A similar situation has been observed by Brookhart and co-workers in cationic Rh chemistry.[23] It should be noted that [Re(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$(H$_2$O)]$^+$[BAr$^F_4$]$^-$(Et$_2$O) is extremely crystalline and is isolated preferentially even if less than 1 equiv of water is present. The water is slowly lost *in vacuo*.

The water molecule in [Re(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$(H$_2$O)]$^+$[BAr$^F_4$]$^-$(Et$_2$O) can be observed by IR (ν_{O-H} = 3640, br) and ^{1}H NMR in CD$_2$Cl$_2$ (broad singlet at 7 ppm). In the ^{1}H NMR spectrum, resonances associated with the alkyl and alkylidyne groups are shifted from the resonances for [Re(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$(Et$_2$O)]$^+$[BAr$^F_4$]$^-$, so water is not merely present in the crystal lattice. Addition of D$_2$O leads to H/D exchange on the NMR time scale at 25 °C, while addition of ether to a sample of [Re(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$(H$_2$O)]$^+$[BAr$^F_4$]$^-$(Et$_2$O) results in only a single average ether resonance. We do not know whether the ether molecule is associated with the BAr$^F_4$ counterion, or whether it is weakly hydrogen bonded to the water ligand. Hydrogen bonding between pyridine and coordinated water has been observed by X-ray crystallography in [Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(py)$_2$(H$_2$O·py)]$^+$[BAr$^F_4$]$^-$ (see below).

Synthesis of Rhenium Neopentyl/Neopentylidene/Neopentylidyne Complexes. W(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$ is known to react with excess PMe$_3$ or dmpe under forcing conditions (100−110 °C) to form W(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(L)$_2$ (L = PMe$_3$, 1/2 dmpe).[24] We hoped that Re(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$X would react with coordinating ligands to form neopentane and Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(L)$_n$X. Such α-hydrogen abstraction reactions had not been observed for Re(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$Cl.[21] α-Hydrogen abstraction reactions generally are more facile in cationic systems or systems in which the metal is relatively electrophilic.[25] Thus it might be expected that Re(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$X (X = OTf, BF$_4$) and [Re(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$(H$_2$O)$_n$(Et$_2$O)]$^+$[BAr$^F_4$]$^-$ (n = 0, 1) would be more likely to undergo α-hydrogen abstraction reactions than Re(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$Cl.

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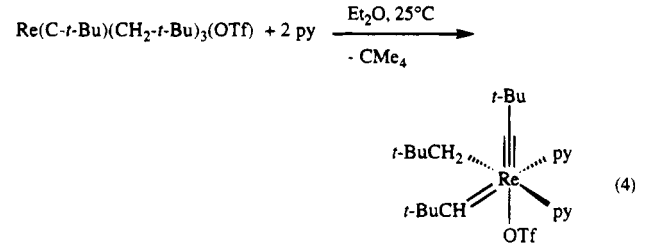
Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(OTf) reacts rapidly with 2–3 equiv of pyridine in ether to form neopentane and colorless Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(py)$_2$(OTf), which precipitates from the reaction mixture virtually quantitatively. The structure shown in eq 4 is based on NMR



(4)

data as well as by analogy with several structurally characterized six-coordinate rhenium neopentylidene/neopentylidyne complexes, all of which have several common features. The most important feature is that alkylidene and alkylidyne ligands are oriented *cis* to each other, and the remaining anionic ligands often are *cis* to the alkylidene and alkylidyne ligands.[7,8,20] Rapid exchange on the NMR time scale is observed when pyridine is added to a sample of Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(py)$_2$(OTf) at 25 °C in CD_2Cl_2. Only one rotamer is present, which we presume is the *syn* rotamer in which the *tert*-butyl group points toward the neopentylidyne ligand.

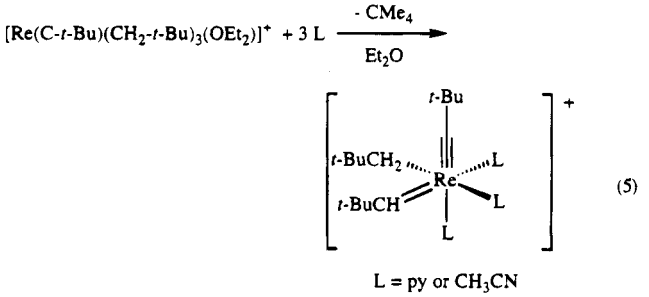
The reaction between Re($CCMe_2Ph$)(CH_2CMe_2Ph)$_3$(OTf) and excess pyridine in ether results in formation of pink Re($CCMe_2Ph$)($CHCMe_2Ph$)(CH_2CMe_2Ph)(py)$_2$(OTf), which is similar to Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(py)$_2$(OTf), according to NMR studies, but is much more soluble in ether and benzene.

The reaction between Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(OTf) and excess acetonitrile in ether results in formation of neopentane and Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(CH_3CN)(OTf) as a beige powder. Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(CH_3CN)$_n$(OTf) (n = 2 or 3, according to proton NMR spectra) is formed initially as crystals in the crude reaction mixture, but CH_3CN is readily lost upon isolation of the crystals to yield Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(CH_3CN)(OTf). When excess CH_3CN (6 equiv) is added to a C_6D_6 solution of Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(CH_3CN)(OTf), a spectrum analogous to that observed for "Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(CH_3CN)$_n$(OTf)" is obtained (as evidenced by shifts of all of the observed resonances), although only one CH_3CN resonance is found, consistent with rapid exchange of acetonitrile on the NMR time scale at 25 °C. The structure of Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(CH_3CN)(OTf) is not known, and attempts to grow crystals suitable for X-ray diffraction were unsuccessful. At this stage we assume that it is a neutral five-coordinate trigonal bipyramidal species.

Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(OTf) eliminates neopentane when it is dissolved in CD_3OD, and resonances consistent with formation of Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(CD_3OD)$_n$(OTf) (n = 1–3) are observed by proton NMR. Attempts to isolate Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(CD_3OD)$_n$(OTf) have not been successful, even though Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(CD_3OD)$_n$(OTf) appears to be stable for several hours in solution. Addition of pyridine to CD_3OD solutions of Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(CD_3OD)$_n$(OTf) yields Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(py)$_2$(OTf). Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(OTf) reacts slowly with neat THF-d_8 to form neopentane and Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(THF)$_n$(OTf), according to NMR studies, but again no crystalline product could be isolated.

Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(BF_4) reacts with excess acetonitrile to yield colorless crystals of Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(CH_3CN)$_2$(BF_4) in 70–80% yield. However, analogous complexes containing coordinating ligands other than CH_3CN could not be isolated, even though Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(L)$_n$(BF_4) (L = CD_3OD, THF-d_8) and neopentane are formed when Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(BF_4) is dissolved in CD_3OD or THF-d_8, according to NMR spectra. The reaction between Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(BF_4) and 3 equiv of pyridine in C_6D_6 proceeded cleanly to yield a compound whose ^{1}H NMR spectrum is consistent with the formulation Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(py)$_2$(X), but no product could be isolated, and it is not known whether X = BF_4 or F.

[Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(Et_2O)]$^+$[BAr^F_4]$^-$ reacts with pyridine or acetonitrile in ether to yield [Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(L)$_3$]$^+$[BAr^F_4]$^-$ (L = py, CH_3CN)



(5)

L = py or CH_3CN

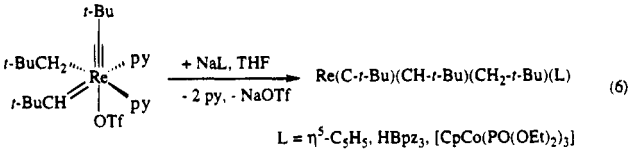
virtually quantitatively. Lower yields (70%) are obtained if [Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(Et_2O)]$^+$[BAr^F_4]$^-$ is generated *in situ* and pyridine or acetonitrile is added, although this procedure reduces the problem of contamination by water.

[Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(H_2O)(Et_2O)]$^+$[BAr^F_4]$^-$ reacts with 3 equiv of pyridine in ether to yield peach-colored cubes of [Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(py)$_2$(py·H_2O)]$^+$[BAr^F_4]$^-$. The water molecule could not be observed by IR or NMR spectroscopy. Crystals of [Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(py)$_3$(H_2O)]$^+$[BAr^F_4]$^-$ suitable for X-ray diffraction were grown from ether/pentane (3/1 v/v) solution at −40 °C, and the structure was determined by X-ray crystallography. Unfortunately, disorder in the CF_3 groups and the large number of atoms in the molecule prevented satisfactory refinement. Nonetheless, connectivity could be established in the cationic fragment. The water molecule was observed to be coordinated to rhenium *trans* to the neopentylidyne ligand, and a molecule of pyridine was located within hydrogen-bonding distance of the water molecule.

All of the rhenium neopentyl/neopentylidene/neopentylidyne complexes described in this section were stable in C_6D_6, CD_2Cl_2, pyridine-d_5, or THF-d_8 in the presence of water, but they were essentially insoluble in water itself.

Synthesis of Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(L) (L = Cp, $HBpz_3$, L_{OEt}). Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(py)$_2$(OTf) reacts with NaL (L = Cp, $HBpz_3$, [CpCo($PO(OEt)_2$)$_3$]("L_{OEt}") in THF to cleanly produce complexes of the type Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(L) in 80–95% yield (eq 6) and with 1,4,7-trithiacyclononane in dichloromethane to yield colorless crystals of [Re(C-

t-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)($S_3C_6H_{12}$)][OTf] quantitatively (eq 7). Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(L) and [Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)($S_3C_6H_{12}$)][OTf] are thermally stable, 18-electron compounds.



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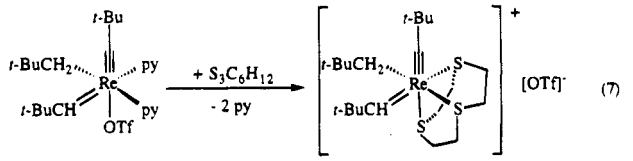

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Reaction of Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(L) and [Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(η^3-$S_3C_6H_{12}$)]$^+$[OTf]$^-$ with Acids. A possible route to complexes that contain the [Re(C-*t*-Bu)(CH-*t*-Bu)(L)]$^+$ core is shown in eqs 8 and 9. Complexes of the type Re(C-*t*-Bu)(CH-*t*-Bu)(L)Cl are readily synthesized from [Re(C-*t*-Bu)(CH-*t*-Bu)Cl_2]$_x$ and 1 equiv of NaL (L = Cp,[7] L_{OEt}). Unfortunately, however, all attempts to abstract chloride ion with silver or thallium salts were unsuccessful.

$$1/x[\text{Re(C-}t\text{-Bu)(CH-}t\text{-Bu)Cl}_2]_x + \text{NaL} \xrightarrow[-\text{NaCl}]{\text{THF, 25 °C}} \text{Re(C-}t\text{-Bu)(CH-}t\text{-Bu)(L)(Cl)} \quad (8)$$

$$\text{Re(C-}t\text{-Bu)(CH-}t\text{-Bu)(L)(Cl)} + \text{AgX} \xrightarrow[-\text{AgCl}]{} [\text{Re(C-}t\text{-Bu)(L)}]^+\text{X}^- \quad (9)$$

Therefore an indirect route to [Re(C-*t*-Bu)(CH-*t*-Bu)(L)]$^+$ complexes was developed that employs a combination of protonation and α-hydrogen abstraction reactions similar to that used to synthesize the Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)($L)_n$X species.

Reaction between Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(L) (L = Cp, [CpCo($PO(OEt)_2)_3$]) and triflic acid in ether yields Re(C-*t*-Bu)(CH-*t*-Bu)(L)(OTf) complexes in 50–80% yields (eq 10). We speculate that this reaction

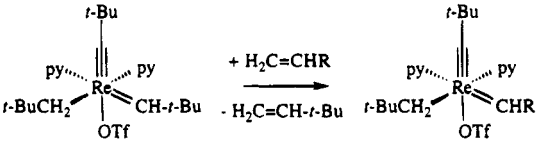
$$\text{Re(C-}t\text{-Bu)(CH-}t\text{-Bu)(CH}_2\text{-}t\text{-Bu)(L)} \xrightarrow[-\text{CMe}_4]{+\text{HX}} \text{Re(C-}t\text{-Bu)(CH-}t\text{-Bu)(L)(X)} \quad (10)$$

proceeds via initial protonation of C_α of the alkylidene ligand to form Re(C-*t*-Bu)(CH_2-*t*-Bu)$_2$(L)(OTf), followed by α-hydrogen abstraction to form neopentane and Re(C-*t*-Bu)(CH-*t*-Bu)(L)(OTf). It should be noted that, in the d^2 manifold, the neutral osmium complexes, Os(C-*t*-Bu)(CH_2-*t*-Bu)$_2$(L) (L = Cp, L_{OEt}, $HBpz_3$), show no evidence of α-hydrogen abstraction.[26,27] Re(C-*t*-Bu)(CH-*t*-Bu)(L_{OEt})(OTf) is thermally stable, but Re(C-*t*-Bu)(CH-*t*-Bu)Cp(OTf) decomposes slowly in the solid state at −40 °C to form an insoluble unidentified blue material. The C-H coupling constant in the alkylidene ligand in the cyclopentadienyl complex is only 90 Hz, a value that is 25–40 Hz lower than is typically observed for complexes containing the Re(C-*t*-Bu)(CH-*t*-Bu) core, including Re(C-*t*-Bu)(CH-*t*-Bu)(L_{OEt})(OTf) (121 Hz). Low $J_{CH\alpha}$ values have been attributed to an agostic interaction involving H_α in the alkylidene ligand.[25,28] If Re(C-*t*-Bu)(CH-*t*-Bu)(Cp)(OTf) is a neutral species, it is nominally a six-coordinate, 18-electron species in which an agostic interaction is not possible. On the other hand, an agostic interaction is possible if it exists as the cationic species, [Re(C-*t*-Bu)(CH-*t*-Bu)(Cp)]$^+$[OTf]$^-$. Re(C-*t*-Bu)(CH-*t*-Bu)(Cp)(OTf) reacts readily with pyridine to form stable [Re(C-*t*-Bu)(CH-*t*-Bu)(Cp)(py)]$^+$[OTf]$^-$, which can also be synthesized in a one-pot reaction from Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(Cp) and pyHOTf in CH_2Cl_2. As expected, $J_{CH\alpha}$ in [Re(C-*t*-Bu)(CH-*t*-Bu)(Cp)(py)]$^+$[OTf]$^-$ is 125 Hz, consistent with no agostic interaction being present. Therefore we suspect that Re(C-*t*-Bu)(CH-*t*-Bu)(Cp)(OTf) exists as the cationic complex [Re(C-*t*-Bu)(CH-*t*-Bu)(Cp)]$^+$[OTf]$^-$ in which there is an agostic Re=CH_α interaction.

The reaction between Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(L_{OEt}) and [$H(OEt_2)_2$]$^+$[BAr^F_4]$^-$ in ether at −40 °C proceeds cleanly to yield yellow, crystalline [Re(C-*t*-Bu)(CH-*t*-Bu)(L_{OEt})(Et_2O)]$^+$[BAr^F_4]$^-$. The presence of the tridentate ligand L_{OEt} requires that the neutral ether ligand be located *cis* to the neopentylidene and neopentylidyne ligands, although this is not normally the preferred site for a neutral donor ligand in six-coordinate alkylidene/alkylidyne complexes.

The reaction between [Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)($S_3C_6H_{12}$)]$^+$[OTf]$^-$ and triflic acid in dichloromethane proceeds cleanly to yield [Re(C-*t*-Bu)(CH-*t*-Bu)($S_3C_6H_{12}$)(OTf)]$^+$[OTf]$^-$. However, the reaction between Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(Cp) and [$H(OEt_2)_2$]$^+$[BAr^F_4]$^-$ or [pyH]$^+$[BAr^F_4]$^-$ in CH_2Cl_2 or ether failed to yield any isolable products. Likewise, reactions between Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)($HBpz_3$) and triflic acid or [$H(OEt_2)_2$]$^+$[BAr^F_4]$^-$ did not yield any characterizable products cleanly.

Reactions of the Neopentylidene/Neopentylidyne Complexes with Terminal Olefins. Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(py)$_2$(OTf) reacts with H_2C=CHR (R = OCH_2CH_3, C_6H_5) in benzene or dichloromethane to yield neohexene and the new alkylidene complexes, Re(C-*t*-Bu)(CHR)(CH_2-*t*-Bu)(py)$_2$(OTf) (eq 11). No evi-



(11)

dence for formation of the methylidene complex, Re(C-*t*-Bu)(CH_2)(CH_2-*t*-Bu)(py)$_2$(OTf), is seen. The ethoxymethylene complex is isolated as a thermally stable pink powder. It shows no evidence of bimolecular decomposition in solution at 25 °C. The two bound pyridine molecules are inequivalent on the NMR time scale at 25 °C in $CDCl_3$, and exchange with added pyridine does not occur on the NMR time scale under these conditions. Re(C-*t*-Bu)(CHC_6H_5)(CH_2-*t*-Bu)(py)$_2$(OTf) is isolated as beige crystals. The two bound pyridine ligands are inequivalent on the NMR time scale.

Hydrogen scrambling between the alkyl, alkylidene, and alkylidyne ligands in these complexes cannot be

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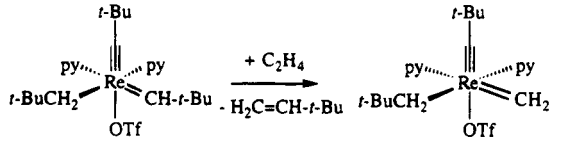
(27) LaPointe, A. M.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.*, in press.
(28) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 11831.

totally ruled out without a crystal structure determination. However, in d^0 systems, hydrogen scrambling among alkyl and alkylidene[29] or alkylidyne[30] ligands has been found to be a relatively high energy process. Re(C-*t*-Bu)(CHFc)[OCMe$(CF_3)_2$]$_2$ (Fc = (C_5H_4)FeCp) and Re(C-*t*-Bu)(CH-OEt)[OCMe$(CF_3)_2$]$_2$(THF)$_2$ were prepared by the reaction of Re(C-*t*-Bu)(CH-*t*-Bu)[OCMe$(CF_3)_2$]$_2$ with vinylferrocene or ethyl (vinyl) ether, respectively; X-ray structure determinations revealed that no scrambling of H_α had occurred between the carbene and neopentylidyne ligands.[8] Likewise, we found that Re(C-*t*-Bu)(CH-*t*-Bu)$(CD_2$-*t*-Bu$)_2$ shows no evidence for H/D scrambling among the neopentyl and neopentylidene ligands at 80 °C in toluene-d_8. On the basis of these results, we believe that scrambling of H_α does not occur in the alkyl/alkylidene/alkylidyne systems and that the complexes can be described by the formula Re(C-*t*-Bu)(CHR)$(CH_2$-*t*-Bu$)$(py)$_2$(OTf).

The reaction of Re(C-*t*-Bu)(CH-*t*-Bu)$(CH_2$-*t*-Bu$)$(py)$_2$(OTf) with 3–5 equiv of ethylene in C_6D_6 or CD_2Cl_2 initially yields neohexene and Re(C-*t*-Bu)$(CH_2)(CH_2$-*t*-Bu)(py)$_2$(OTf) (eq 12). However, the methylidene com-

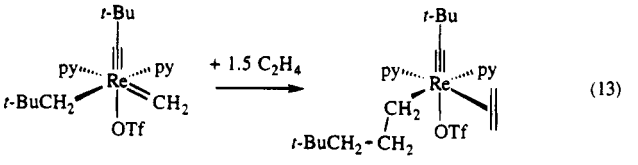


(12)

plex is unstable at 25 °C in C_6D_6, even in the presence of 2–5 equiv of pyridine. Upon isolation it decomposes to Re(C-*t*-Bu)[$(CH_2)_3$-*t*-Bu](C_2H_4)(py)$_2$(OTf) (see below) and unidentified products. However, addition of bipyridyl to solutions containing freshly prepared Re(C-*t*-Bu)$(CH_2)(CH_2$-*t*-Bu)(py)$_2$(OTf) yields red Re(C-*t*-Bu)$(CH_2)(CH_2$-*t*-Bu)(bpy)(OTf), which can be recrystallized from toluene/ether mixtures at −40 °C. Unfortunately, Re(C-*t*-Bu)$(CH_2)(CH_2$-*t*-Bu)(bpy)(OTf) is thermally unstable and for this reason has been characterized only by ^{1}H NMR and partially by ^{13}C NMR. In the proton NMR spectrum, two doublets (J_{HH} = 3 Hz) corresponding to H_α protons of the methylene ligand are observed at 14.05 (J_{CH} = 135 Hz) and 13.49 ppm (J_{CH} = 150 Hz).

The reaction between Re(C-*t*-Bu)(CH-*t*-Bu)$(CH_2$-*t*-Bu$)$(py)$_2$(OTf) and excess ethylene in benzene or dichloromethane yields a colorless microcrystalline solid whose proton NMR spectrum contained two inequivalent *tert*-butyl groups, two inequivalent bound pyridines, and a series of complex multiplets corresponding to five sets of inequivalent methylene groups. Because of the complexity of the spectrum and the fact that some of the resonances overlapped, it was impossible to assign the methylene portion of the spectrum. ^{19}F NMR confirmed the presence of the triflate anion, and elemental analysis confirmed the formulation $ReC_{25}H_{38}N_2F_3O_3S$. The reaction of Re(C-*t*-Bu)(CH-*t*-Bu)$(CH_2$-*t*-Bu$)$(py)$_2$(OTf) with $^{13}CH_2{}^{13}CH_2$ produced a product that contained three isotopically enriched peaks, a singlet at 20 ppm (J_{CH} = 123 Hz) with twice the intensity of the other two doublets (J_{CC} = 36 Hz) at 52 ppm (J_{CH} = 153 Hz) and 46 ppm (J_{CH} = 156 Hz). These results suggest that 1 equiv of ethylene was incorporated in a manner that rendered its two carbon atoms inequivalent and the other equivalent of ethylene was incorporated so that its two carbon atoms are equivalent. The reaction of Re(C-*t*-Bu)(CH-*t*-Bu)$(CH_2$-*t*-Bu$)$(py)$_2$(OTf) with excess C_2D_4 yields a complex with a greatly simplified ^{1}H NMR. Two peaks that had been complex multiplets in the unlabeled complex appeared as doublets in the labeled complex and therefore were assigned as the methylene protons in the original neopentyl ligand. These labeling experiments suggested that one of the molecules of ethylene had coordinated to the metal and the other had inserted into the metal–carbon single bond to yield Re(C-*t*-Bu)[$(CH_2)_3$-*t*-Bu](C_2H_4)(py)$_2$(OTf). No further reaction with ethylene is observed at 1 atm and 25 °C in C_6H_6.

In the reaction of Re(C-*t*-Bu)(CH-*t*-Bu)$(CH_2$-*t*-Bu$)$(py)$_2$(OTf) with an excess of ethylene, the only observed byproduct is neohexene (formed in the initial metathesis reaction) and the only observed intermediate is Re(C-*t*-Bu)$(CH_2)(CH_2$-*t*-Bu)(py)$_2$(OTf). There was no evidence for formation of any other organic product (such as propylene or cyclopropane). Therefore we speculate that Re(C-*t*-Bu)$(CH_2)(CH_2$-*t*-Bu)(py)$_2$(OTf) decomposes to "Re(C-*t*-Bu)$(CH_2$-*t*-Bu)(py)$_2$(OTf)" in a bimolecular process and that subsequent reaction of transient "Re(C-*t*-Bu)$(CH_2$-*t*-Bu)(py)$_2$(OTf)" with ethylene yields Re(C-*t*-Bu)[$(CH_2)_3$-*t*-Bu](C_2H_4)(py)$_2$(OTf) (eq 13).



(13)

Benzene solutions of Re(C-*t*-Bu)(CH-*t*-Bu)$(CH_2$-*t*-Bu$)(CH_3CN)_2(BF_4)$ become green when terminal olefins such as styrene or ethyl vinyl ether are added, and no evidence of productive metathesis is observed by NMR. The six-coordinate, cationic complexes [Re(C-*t*-Bu)(CH-*t*-Bu)$(CH_2$-*t*-Bu$)(L)_3]^+[BAr^F{}_4]^-$ (L = py, CH_3CN) do not react with styrene, ethyl vinyl ether, or ethylene in ether. Likewise, none of the neutral or cationic complexes containing a tridentate ligand reacts with terminal olefins such as styrene or ethylene. It is likely that at least one coordination site must be free for coordination of olefin to occur. Thus, under identical conditions (C_6D_6, 25 °C, 5–10 equiv olefin), Re(C-*t*-Bu)(CH-*t*-Bu)$(CH_2$-*t*-Bu$)$(py)$_2$(OTf) reacts rapidly with terminal olefins but Re(C-*t*-Bu)(CH-*t*-Bu)$(CH_2$-*t*-Bu$)$(bpy)(OTf) does not react.

Reaction of the Neopentylidene/Neopentylidyne Complexes with Unstrained Internal Olefins. Re(C-*t*-Bu)(CH-*t*-Bu)$(CH_2$-*t*-Bu$)(CH_3CN)$(OTf) reacts rapidly with 5–10 equiv of *cis*-3-hexene in C_6D_6 to yield a new propylidene complex that decomposes within 1 h at 25 °C. Similar results were obtained in reactions between Re(C-*t*-Bu)(CH-*t*-Bu)$(CH_2$-*t*-Bu$)(CH_3CN)$(OTf) and methyl oleate or oleic acid. When the reaction between Re(C-*t*-Bu)(CH-*t*-Bu)$(CH_2$-*t*-Bu$)(CH_3CN)_n$(OTf) and 5–10 equiv of *cis*-3-hexene in C_6D_6 is conducted in the presence of 5–10 equiv of CH_3CN, "Re(C-*t*-Bu)$(CHCH_2CH_3)(CH_2$-*t*-Bu$)(CH_3CN)_n$(OTf)" forms within 10 min, but still largely decomposes within 4 h in C_6D_6 at 25 °C. In neat CD_3CN, Re(C-*t*-Bu)(CH-*t*-Bu)$(CH_2$-*t*-Bu$)(CH_3CN)_n$(OTf) does not react with 5 equiv of *cis*-3-hexene at 25 °C. At

(29) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359.
(30) Caulton, K. G.; Chisholm, M. H.; Streib, W. E.; Xue, Z. *J. Am. Chem. Soc.* **1991**, *113*, 6082.

60 °C the reaction proceeds slowly (2/1 propylidene/neopentylidene after 1 h); in CD_3CN, Re(C-*t*-Bu)($CHCH_2CH_3$)(CH_2-*t*-Bu)(CH_3CN)$_n$(OTf) is stable for 24 h at 25 °C. Upon addition of excess 2,2,2-trimethyl-3-hexene to a CD_3CN solution of Re(C-*t*-Bu)($CHCH_2CH_3$)(CH_2-*t*-Bu)(CH_3CN)$_n$(OTf) at 25 °C, no metathesis was observed at room temperature in 24 h. Therefore, in acetonitrile, Re(C-*t*-Bu)($CHCH_2CH_3$)(CH_2-*t*-Bu)(CH_3CN)$_n$(OTf) is not much more reactive than the analogous neopentylidene complex.

Upon addition of 100 equiv of *cis*-2-pentene to Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(CH_3CN)$_n$(OTf) at 25 °C in benzene, an equilibrium mixture of butenes, pentenes, and hexenes was reached in ~5 min. However, no further metathesis occurred when another 100 equiv of *cis*-2-pentene was added 1 h later.

The reaction of Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(CD_3OD)$_n$(OTf) with 5−10 equiv of *cis*-3-hexene in CD_3OD occurs within 30 min at 25 °C. Re(C-*t*-Bu)($CHCH_2CH_3$)(CH_2-*t*-Bu)(CD_3OD)(OTf) is stable for several hours at 25 °C in CD_3OD. However, very little (<5%) metathesis was observed in the reaction of Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(CH_3OH)$_n$(OTf) with 100 equiv of *cis*-2-heptene in CH_3OH.

None of the other rhenium alkylidene complexes described here reacts with unstrained internal olefins. Low reactivity can be traced to the fact that the neutral donor ligands and/or multidentate ligands L (L = Cp, $HBpz_3$, L_{OEt}, $S_3C_6H_{12}$) are not sufficiently labile, so no coordination sites are available to bind the olefin.

Discussion

A wide variety of coordinating ligands was found to induce α-hydrogen abstraction reactions in Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(X) (X = OTf, BF_4, $BAr^F{}_4$) species. The finding that acetonitrile and methanol can induce α-hydrogen abstraction reactions is particularly interesting; these ligands are frequently incompatible with alkylidene complexes of tantalum, molybdenum, and tungsten. This result is a nice example of the greater tolerance of rhenium−carbon multiple bonds for a variety of organic functional groups. It should be noted that the coordinating ligands must be nucleophilic but not especially basic. For example, the reaction of Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(OTf) with quinuclidine or *tert*-butylamine results in deprotonation at C_α to form Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)$_2$. Similar results have been observed in the case of Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$Cl.[20,21]

Although quantitative experiments were not possible, α-hydrogen abstraction was significantly faster in the systems where cationic intermediates could form. Thus, for a given ligand, α-hydrogen abstraction reactions of Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(X) were much faster when X = OTf, $BAr^F{}_4$ than when X = Cl, OC_6F_5. For instance, the reaction of Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(OTf) with 3 equiv of pyridine in ether or pentane was complete within 10 min at 25 °C, while the reaction of Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$Cl with neat pyridine-d_5 required 24 h. These observations are consistent with earlier findings that demonstrated that α-hydrogen elimination reactions are faster in systems that are cationic or strongly polarized.[25]

The synthesis of a large number of complexes containing the rhenium neopentyl/neopentylidene/neopentylidyne core suggests that this system can support a wide range of ligand environments. Once formed, complexes containing the Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu) core are quite stable. All of the complexes described here that contain the Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu) core are thermally stable, in the solid state they are moderately stable to air and water, and in solution they are stable to water at 25 °C. For instance, a solid sample of Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)($HBpz_3$) showed no decomposition after a month of exposure to moist air. The tradeoff is that the complexes described here are not especially active for the metathesis of olefins, or, if they are, activity is short-lived as a consequence of (presumably) bimolecular decomposition reactions involving relatively small alkylidenes. An interesting result to note is the extremely low reactivity of the tetra(aryl)borate complexes. Since these systems are truly cationic, they might be expected to be more reactive than the triflate derivatives. However, the extreme electrophilicity of the metal center causes the coordinated pyridine, acetonitrile, or ether to be bound quite tightly to the metal, and no reactivity with olefins is observed. The most desirable anion would be one that is so weakly coordinated that it is readily displaced by an incoming olefin, but coordinated strongly enough to prevent decomposition of the "naked" cation.

In an attempt to surmount the problems of ligand dissociation and bimolecular decomposition, the complexes containing tridentate ligands such as Cp, $HBpz_3$, L_{OEt}, and 1,4,7-trithiacyclononane were synthesized and their reactivity with olefins was investigated. However, cationic "[Re(C-*t*-Bu)(CH-*t*-Bu)(L)]$^+$" is already a five-coordinate, 16-electron species, and dissociation of part of the tridentate ligand (to yield a more reactive intermediate) would be expected to be quite difficult. Furthermore, the Re(C-*t*-Bu)(CH-*t*-Bu)(L) fragment typically binds another ligand (triflate, pyridine, ether) to form exceedingly unreactive species. It should be noted that cationic tungsten alkylidene complexes containing a hydridotris(pyrazolyl)borate ligand do not react with olefins in the absence of a Lewis acid cocatalyst,[9,15,16] nor does five-coordinate Re(NAr)(CH-*t*-Bu)[$OCMe(CF_3)_2$]$_3$[11] or six-coordinate ReO($CHCHCPh_2$)[$OCMe(CF_3)_2$]$_3$(THF).[10] These results reaffirm the proposal that in a long-lived olefin metathesis catalyst, four coordination sites *must* be filled by nonlabile, ionic ligands which provide a large amount of steric protection. If additional neutral donor ligands are present, they must be quite labile. According to these general requirements, complexes such as [Re(NAr)(CHR)(OR′)$_2$]$^+$ and Re(N·BPh_3)(CHR)(OR′)$_2$ (if they could be synthesized) might be relatively reactive toward olefins, but relatively stable thermally.

A variety of reduction pathways for transition metal alkylidenes and alkylidynes have been discovered. These include bimolecular coupling to form an olefin and a reduced metal complex, intramolecular coupling with another metal−ligand multiple bond (e.g., in the reduction of Os(CH-*t*-Bu)$_2$(CH_2-*t*-Bu)$_2$ to Os(PMe_3)$_3$(*t*-Bu-C≡C-*t*-Bu)),[27] and a formally "3 + 2" addition of ethylene to a rhenium alkylidene/alkylidyne to form a metallacyclopentene complex.[31] In the "3 + 2" reaction, the "supporting" neopentylidyne ligand is involved; this illustrates one potential pitfall in the design of transi-

(31) Vaughan, G. A.; Toreki, R.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1993**, *115*, 2980.

tion metal catalysts. The reduction of Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(py)$_2$(OTf) to Re(C-*t*-Bu)((CH_2)$_3$-*t*-Bu)(py)$_2$(OTf) provides another example of involvement of the supporting ligands, in this case, insertion of ethylene into the metal–carbon single bond.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres HE-43 drybox or using standard Schlenk techniques unless otherwise specified. Pentane was washed with sulfuric/nitric acid (95/5 v/v), aqueous sodium bicarbonate solution, and then water, stored over $CaCl_2$, and then distilled from sodium benzophenone ketyl. Ether, tetrahydofuran, benzene, and 1,2-dimethoxyethane were distilled from sodium benzophenone ketyl under nitrogen or argon. Toluene was distilled from molten sodium under nitrogen or argon, and dichloromethane, acetonitrile, and pyridine were distilled from calcium hydride under nitrogen or argon. All deuterated NMR solvents were purchased from Cambridge Isotope Laboratories. Tetrahydofuran-d_8 was vacuum transferred from sodium benzophenone ketyl. C_6D_6, CD_2Cl_2, $CDCl_3$, CD_3CN, and pyridine-d_5 were stored over activated molecular sieves in the drybox. CD_3OD was used as received.

Neopentyl chloride was purchased from Strem and purified by literature methods.[32] *t*-BuCH_2MgCl was prepared by the published procedure.[32] Rhenium heptoxide (99.99%) was purchased from Aesar. [Re(C-*t*-Bu)(CH-*t*-Bu)Cl_2]$_x$[7] and [Re(C-*t*-Bu)(CH-*t*-Bu)(*t*-BuNH_2)Cl_2]$_2$[20] were prepared by literature methods, and Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)$_2$ was prepared by the published procedure[20] or from [Re(C-*t*-Bu)(CH-*t*-Bu)Cl_2]$_x$ and *t*-BuCH_2MgCl in THF at −40 °C. [H(OEt_2)$_2$]$^+$[BAr^F_4]$^-$ was prepared by literature methods.[14] Na[CpCo(PO(OEt)$_2$)$_3$][18] was a gift from Dr. Robert D. Simpson. Ethylene (polymer grade) was purchased from Matheson and used as received. $^{13}C_2H_4$ and C_2D_4 were purchased from Cambridge Isotope Laboratories. Pyridine and acetonitrile were distilled from calcium hydride. All other reagents were purchased from Aldrich and used as received.

NMR spectra were recorded on either a Bruker WM-250, Varian XL-300, or Varian UNITY-300 spectrometer. ^{1}H and ^{13}C data are listed in parts per million downfield from tetramethylsilane and were referenced by the residual solvent proton peak. ^{19}F data are listed in parts per million downfield from CF_2Cl_2 and were externally referenced. Coupling constants are listed in hertz. Obvious multiplicities and routine coupling constants are usually not listed. IR spectra were recorded in a Mattson spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer in our laboratories.

Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(OTf). Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)$_2$ (1.07 g, 2.28 mmol) was dissolved in 15 mL of ether, and the solution was cooled to −40 °C. Triflic acid (200 μL, 2.28 mmol) was added, and the solution was allowed to warm to room temperature and stir for 1 h. Ether was removed *in vacuo*, leaving a yellow-brown solid, which was extracted with pentane (50 mL). The solution was filtered through Celite, and the filtrate was concentrated to 10 mL and then cooled to −40 °C. Yellow, microcrystalline Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(OTf) was isolated, washed with cold pentane, and dried; yield 1.00 g (71%). The spectral data for the compound prepared in this manner matched those reported.[20,21]

[Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(Et_2O)]$^+$[BAr^F_4]$^-$. Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)$_2$ (230 mg, 0.49 mmol) was dissolved in 5 mL of ether, and solid [H(OEt_2)$_2$]$^+$[BAr^F_4]$^-$ (489 mg, 0.49 mmol) was added. After stirring the solution for 30 min at room temperature, the volume was reduced to 2 mL and the solution was stored at −40 °C overnight. Bright yellow crystals were collected and washed with cold ether; yield 506 mg (73%): ^{1}H NMR (CD_2Cl_2) δ 7.7 (s, 8, Ar), 7.6 (s, 4, Ar), 3.55 (q, 4, OCH_2-CH_3), 2.65 (s, 6, ReCH_2-*t*-Bu), 1.65 (s, 9, ReC-*t*-Bu), 1.20 (t, 6, OCH_2CH_3), 1.14 (s, 27, CH_2-*t*-Bu).

[Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(Et_2O)(H_2O)]$^+$[BAr^F_4]$^-$. [Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(Et_2O)(H_2O)]$^+$[BAr^F_4]$^-$ was prepared in a fashion identical to [Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(Et_2O)]$^+$[BAr^F_4]$^-$ except that 1 equiv of water was added by syringe prior to recrystallization from ether: ^{1}H NMR (CD_2Cl_2) δ 7.75 (s, 8, Ar), 7.6 (s, 4, Ar), 7.0 (s, 2, OH_2) 3.56 (q, 4, O(CH_2CH_3)$_2$), 2.56 (s, 6, CH_2-*t*-Bu), 1.65 (s, 9, C-*t*-Bu), 1.14 (s, 27, CH_2-*t*-Bu); ^{13}C NMR (CD_2Cl_2) δ 307.0 (Re*C*-*t*-Bu), 162.3 (q, CF_3, J_{CF} = 50 Hz), 135.3, 126.9, 123.3, 117.9 (C_{aryl}), 86.0 (CH_2-*t*-Bu), 66.2 (O(CH_2CH_3)$_2$), 55.6 (*C*CMe_3), 37.7 (CH_2CMe_3), 32.9 (CH_2CMe_3), 27.7 (C*C*Me_3), 15.4 (O(CH_2CH_3)$_2$); ^{19}F NMR (CD_2Cl_2) δ −62.3; IR (Nujol) cm^1 3640 (O–H). Anal. Calcd for $C_{56}H_{66}BF_{24}O_2$: C, 47.23; H, 4.67. Found: C, 47.53; H, 4.76.

[Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$]$^+$[BF_4]$^-$. Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)$_2$ (445 mg, 0.95 mmol) was dissolved in 8 mL of ether, and the solution was cooled to −40 °C. An 85% solution of HBF_4·Et_2O (190 mg, 1.0 mmol) was added, and a yellow precipitate formed immediately. The mixture was allowed to warm to room temperature and was stirred for 30 min. The precipitate was collected, washed with pentane, and determined to be >95% pure by ^{1}H NMR; yield 305 mg (58%): ^{1}H NMR (CD_2Cl_2) δ 2.75 (s, 6, CH_2-*t*-Bu), 1.62 (s, 9, C-*t*-Bu), 1.13 (s, 27, CH_2-*t*-Bu); ^{13}C NMR (CD_2Cl_2) δ 300.9 (*C*-*t*-Bu), 85.2 (*C*H_2-*t*-Bu), 54.8 (*C*CMe_3), 37.5 (CH_2CMe_3), 32.7 (CH_2CMe_3), 27.5 (C*C*Me_3); ^{19}F NMR (CD_2Cl_2) δ −141. Anal. Calcd for $ReC_{20}H_{42}BF_4$: C, 43.24; H, 7.62. Found: C, 43.37; H, 7.56.

Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(OC_6F_5). Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(OC_6F_5) was prepared in a manner similar to that employed to synthesize Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(OTf): ^{1}H NMR (C_6D_6) δ 2.75 (s, 6, ReCH_2-*t*-Bu), 1.29 (s, 9, ReC-*t*-Bu), 1.04 (s, 27, ReCH_2-*t*-Bu). Anal. Calcd for $ReC_{26}H_{42}F_5O$: C, 47.91; H, 6.49. Found: C, 47.84; H, 6.75.

Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(py)$_2$(O_3SCF_3). Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(O_3SCF_3) (106 mg, 0.172 mmol) was dissolved in 4 mL of ether. Pyridine (57 μL, 0.72 mmol) was added, and a white precipitate formed after several minutes. After 3 h the precipitate was collected, washed with pentane, and dried *in vacuo* to yield 108 mg (89%) of a white powder that was pure Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(py)$_2$(O_3SCF_3) by NMR and elemental analysis: ^{1}H NMR (CD_2Cl_2) δ 13.73 (s, 1, C*H*-*t*-Bu), 8.65, 8.6 (d, 2 each, py), 7.9, 7.8 (t, 1 each, py), 7.5, 7.3 (t, 2 each, py), 2.38 (d, 2, C$H_a$$H_b$-*t*-Bu, J_{HH} = 12), 1.84 (d, 2, C$H_a$$H_b$-*t*-Bu, J_{HH} = 12), 1.34, 1.22, 0.93 (s, 9 each, *t*-Bu); ^{13}C NMR (CD_2Cl_2) δ 289.1 (J_{CH} =128, *C*H-*t*-Bu), 287 (*C*-*t*-Bu) 155.3, 151.4 (py *ortho*), 139.1, 139.0 (py *meta*), 125.3, 125.0 (py *para*), 55.9, 48.3 (*C*Me_3, third resonance obscured by solvent peak), 34.1(*C*H_2-*t*-Bu), 33.9, 30.8, 29.1 (*C*Me_3); ^{19}F NMR (CD_2Cl_2) δ −78.3. Anal. Calcd for $ReC_{26}H_{40}F_3N_2O_3S$: C, 44.37; H, 5.73; N, 3.98. Found: C, 44.15; H, 5.70: N, 3.94.

Re(CCMe_2Ph)(CHCMe_2Ph)(CH_2CMe_2Ph)(py)$_2$(O_3SCF_3). Re(CCMe_2Ph)(CHCMe_2Ph)(CH_2CMe_2Ph)(py)$_2$(O_3SCF_3) was prepared in a manner analogous to that used to prepare Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(py)$_2$(O_3SCF_3) from crude Re(CCMe_2Ph)(CH_2CMe_2Ph)$_3$(O_3SCF_3) and excess pyridine in ether. A pink powder was obtained, which could be recrystallized from ether to yield analytically pure purplish-pink microcrystals: ^{1}H NMR (pyr-d_5) δ 14.0 (s, 1, C*H*CMe_2Ph), 7.66 (m, 3, H_{aryl}), 7.1 (m, 6, H_{aryl}), 3.15 (d, 1, J_{HH} = 12, C$H_a$$H_bCMe_2$Ph), 2.25 (br d, 1, C$H_a$$H_bCMe_2$Ph), 1.98, 1.88, 1.84, 1.67, 1.58, 1.57 (s, 3 each, CH_3). Anal. Calcd for $C_{41}H_{46}F_3N_2O_3SRe$: C, 55.33; H, 5.21; N, 3.15. Found: C, 55.23; H, 5.39; N, 3.15.

Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(CH_3CN)(O_3SCF_3). Re(C-*t*-Bu)(CH_2-*t*-Bu)$_3$(O_3SCF_3) (196 mg, 0.32 mmol) was dissolved in 3 mL of ether, and 1 mL of acetonitrile was added. The solution was stirred at room temperature for an hour, and then the solvent was removed *in vacuo*. The resulting beige solid was washed with pentane (180 mg, 96%): ^{1}H NMR

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(CD_3CN) δ 13.24 (s, 1, C*H*-*t*-Bu), 2.22 (d, 1, CH_aH_b-*t*-Bu, J_{HH} = 12), 1.34 (d, 1, CH$_a$*H*$_b$-*t*-Bu, J_{HH} = 12), 1.26, 1.14. 0.78 (s, 9 each, *t*-Bu); ^{13}C NMR (CD_3CN) δ 294.8 (*C*-*t*-Bu), 291.8 (*C*H-*t*-Bu, J_{CH} = 116), 53.5, 50.1, 48.1 (*C*Me$_3$), 33.5 (*C*H$_2$-*t*-Bu), 33.8, 30.4, 28.5 (C*Me*$_3$). Anal. Calcd for $ReC_{18}H_{33}F_3NO_3S$: C, 36.85; H, 5.67; N, 2.39. Found: C, 36.65; H, 5.63; N, 2.29.

[Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(py)$_3$]$^+$[BAr$^F_4$]$^-$. Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)$_2$ (160 mg, 0.34 mmol) was dissolved in 5 mL of ether, solid [H(OEt$_2$)]$^+$[BAr$^F_4$]$^-$ (344 mg, 0.34 mmol) was added, and the mixture was stirred for 45 min. Pyridine (110 μL, 1.39 mmol) was added, and the resulting red solution was allowed to stir for an additional 30 min. The volume of the solution was reduced to 3 mL and cooled to −40 °C overnight to yield orange-pink microcrystals (370 mg, 73%), which were washed with pentane and dried: ^{1}H NMR (pyr-d_5) δ 13.78 (s, 1, C*H*-*t*-Bu), 8.41 (s, 8, H$_{aryl}$), 7.81 (s, 4, H$_{aryl}$), 2.81 (d, 1, CH_aH_b-*t*-Bu, J_{HH} = 12), 1.82 (d, 1, CH$_a$*H*$_b$-*t*-Bu, J_{HH} = 12), 1.33, 1.24, 1.12 (9 each, *t*-Bu); ^{13}C NMR (py-d_5) δ 289.9 (*C*-*t*-Bu), 288.5 (*C*H-*t*-Bu, J_{CH} = 120), 163 (*C*F$_3$, J_{C-F} = 49), 155, 127.1, 120, 118.5 (*C*$_{aryl}$), 54.5, 53.4, 48.6 (*C*Me$_3$), 34.6 (*C*H$_2$-*t*-Bu), 34.2, 30.8, 28.9 (C*Me*$_3$). Anal. Calcd for $ReC_{62}H_{57}BF_{24}N_3$: C, 49.74; H, 3.83; N, 2.94. Found: C, 49.74; H, 4.13; N, 2.90.

[Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(py)$_2$(py·H$_2$O)]$^+$[BAr$^F_4$]$^-$. [Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(py)$_2$(py·H$_2$O)]$^+$[BAr$^F_4$]$^-$ was prepared from [Re(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$(OH$_2$)]$^+$[BAr$^F_4$]$^-$ and 3 equiv of pyridine in ether and was recrystallized from 2/1 ether/pentane at −40 °C. Orange cubes formed and were collected and dried. Spectral data matched those for [Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(py)$_3$]$^+$[BAr$^F_4$]$^-$ in pyridine-d_5. These complexes are insoluble in C_6D_6 and toluene-d_8 and decompose in CD_2Cl_2 and $CDCl_3$.

[Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(CH$_3$CN)$_3$][BAr$^F_4$]. Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)$_2$ (340 mg, 0.72 mmol) was dissolved in 5 mL of ether, solid [H(OEt$_2$)$_2$][BAr$^F_4$] (700 mg, 0.70 mmol) was added, and the mixture was stirred for 20 min. CH_3CN (1 mL) was added, and the solution was stirred for 45 min. The solvent was removed *in vacuo*, and the resulting beige powder was washed with pentane until the washings were colorless. An analytical sample was recrystallized from ether/pentane: ^{1}H NMR (C_6D_6) δ 13.38 (s, 1, Re*CH*-*t*-Bu), 8.25 (s, 8, H$_{aryl}$), 7.53 (s, 4, H$_{aryl}$), 2.47 (d, 1, Re*CH*$_a$H$_b$-*t*-Bu, J_{HH} = 12), 1.56 (d, 1, ReCH$_a$*H*$_b$-*t*-Bu, J_{HH} = 12), 1.21, 1.15, 1.07 (s, 9 each, *t*-Bu), 0.78 (br s, 9, C*H*$_3$CN); ^{13}C NMR (CD_3CN) δ 298 (*C*-*t*-Bu), 292.1 (*C*H-*t*-Bu), 163 (q,*C*F$_3$, J_{C-F} = 48), 130.9, 127.6, 124.0, 120.4 (C$_{aryl}$), 54.0, 49.2, 33.8 (*C*Me$_3$), 48.5 (*C*H$_2$-*t*-Bu), 34.0, 30.6, 28.7 (C*Me*$_3$). Anal. Calcd for $C_{53}H_{51}BF_{24}N_3Re$: C, 46.03; H, 3.72; N, 3.04. Found: C, 45.70; H, 3.99; N, 2.79.

Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(CH$_3$CN)$_2$(BF$_4$). Re(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$(BF$_4$) (43 mg, 0.078 mmol) was dissolved in 1 mL of ether, and 1 mL of CH_3CN was added. The solution immediately became colorless and was stirred for 1 h at room temperature. The solvents were removed *in vacuo*, and the resulting solid was washed with pentane to yield 35 mg (74%) of pale yellow Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(CH$_3$CN)$_2$(BF$_4$): ^{1}H NMR (C_6D_6) δ 13.59 (s, 1, C*H*-*t*-Bu), 2.68 (d, 1, J_{HH} = 12, CH_aH_b-*t*-Bu), 1.95 (d, 1, J_{HH} = 12, CH$_a$*H*$_b$-*t*-Bu), 1.80 (br s, 3, C*H*$_3$CN), 1.51 (br s, 6, C*H*$_3$CN), 1.32, 1.28, 1.19 (s, 9 each, *t*-Bu); ^{13}C NMR (CD_3CN) δ 296.1 (Re*C*CMe$_3$), 291.5 (Re*C*H-*t*-Bu, J_{CH} = 122), 53.6, 48.7, 48.1 (*C*Me$_3$), 33.6, 30.2, 28.3 (C*Me*$_3$), 33.4 (CH$_2$-*t*-Bu); ^{19}F NMR (C_6D_6) δ −151.3. Anal. Calcd for $ReC_{19}H_{36}N_2BF_4$: C, 40.35; H, 6.42; N, 4.95. Found: C, 40.30; H, 6.45; N, 4.82.

Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(CD$_3$OD)$_n$(O$_3$SCF$_3$). Re(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$(O$_3$SCF$_3$) (15 mg) was transferred to an NMR tube which was capped with a septum cap and brought out of the drybox. CD_3OD (1 mL) was added by syringe to yield a yellow solution of Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(CD$_3$OD)$_n$(O$_3$SCF$_3$). Experiments employing an internal standard showed that Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(CD$_3$OD)$_n$(O$_3$SCF$_3$) is formed in >90% yield: ^{1}H NMR (CD_3OD) δ 13.00 (s, 1, C*H*-*t*-Bu), 2.82 (d, 1, CH_aH_b-*t*-Bu, J_{HH} = 12), 2.39 (d, 1, CH$_a$*H*$_b$-*t*-Bu, J_{HH} = 12), 1.36, 1.26, 1.15 (s, 9 each, *t*-Bu).

Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(THF-*d*$_8$)$_n$(O$_3$SCF$_3$). Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(THF-d_8)$_n$(O$_3$SCF$_3$) was prepared in the same manner as Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(CD$_3$OD)$_n$(O$_3$SCF$_3$) in THF-d_8, although it took 2 h for Re(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$(O$_3$SCF$_3$) to react completely: ^{1}H NMR (THF-d_8) δ 13.08 (s, 1, C*H*-*t*-Bu), 2.50 (d, 1, CH_aH_b-*t*-Bu, J_{HH} = 12), 1.48 (d, 1, CH$_a$*H*$_b$-*t*-Bu, J_{HH} = 12), 1.36, 1.27, 0.94 (s, 9 each, *t*-Bu).

ReCl(L$_{OEt}$)(C-*t*-Bu)(CH-*t*-Bu). Solid [Re(C-*t*-Bu)(CH-*t*-Bu)Cl$_2$]$_k$ (44 mg, 0.11 mmol) and NaL$_{OEt}$ (55 mg, 0.10 mmol) were combined, and 3 mL of THF was added. The orange-red mixture was stirred for 1.5 h, and the THF was then removed *in vacuo* to yield an orange-pink solid, which was extracted with ether. Ether was then removed *in vacuo* to yield a pink film (85 mg, 95%). An analytical sample was recrystallized from ether/pentane at −40 °C: ^{1}H NMR (C_6D_6) δ 13.95 (s, 1, Re*CH*-*t*-Bu), 4.89 (s, 5, Cp), 3.8−4.6 (m, 12 total, POC*H*$_2$CH$_3$), 1.62, 1.54 (s, 9 each, *t*-Bu), 1.0−1.4 (m, 18 total, POCH$_2$C*H*$_3$). Anal. Calcd for $ReCoC_{27}H_{54}ClO_9P_3$: C, 36.18; H, 6.07. Found: C, 35.94; H, 5.92.

Re(η^5-C$_5$H$_5$)(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu). Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(py)$_2$(O$_3$SCF$_3$) (100 mg, 0.14 mmol) was dissolved in 5 mL THF, and a THF solution of NaCp (0.15 mmol) was added. The resulting orange mixture was stirred for 1 h, and the volatile components were removed *in vacuo*. The resulting beige solid was extracted with pentane (10 mL), and solvent was removed *in vacuo* to yield a beige oil (62 mg, 96%) that was pure by ^{1}H NMR: ^{1}H NMR (C_6D_6) δ 12.67 (s, 1, Re*CH*-*t*-Bu), 5.32 (s, 5, η^5-C$_5$*H*$_5$), 2.52 (d, 1, J_{HH} = 12, Re*CH*$_a$H$_b$-*t*-Bu), 2.36 (d, 1, J_{HH} =12, ReCH$_a$*H*$_b$-*t*-Bu), 1.34, 1.12, 1.11 (s, 9 each, *t*-Bu); ^{13}C NMR (C_6D_6) δ 285.7 (Re*C*-*t*-Bu), 265.6 (Re*C*H-*t*-Bu, J_{CH} =116), 97.6 (*C*$_5$H$_5$), 52.9, 47.6, 33.0 (*C*Me$_3$), 34.2, 31.9, 29.4 (C*Me*$_3$), 17.4 (Re*C*H$_2$-*t*-Bu). Anal. Calcd for $ReC_{20}H_{35}$: C, 52.03; H, 7.64. Found: C, 52.54; H, 7.75.

Re(L$_{OEt}$)(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu). Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(py)$_2$(O$_3$SCF$_3$) (78 mg, 1.10 mmol) was dissolved in 5 mL of THF, and solid NaL$_{OEt}$ was added. The mixture was stirred for 1.5 h, and then the THF was removed *in vacuo* to yield a yellow solid. The solid was extracted with 2 mL of ether, and the ether was removed *in vacuo* to yield pure Re(L$_{OEt}$)(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu) as a pale yellow solid (97 mg, 94%): ^{1}H NMR (C_6D_6) δ 13.02 (s, 1, Re*CH*-*t*-Bu), 4.90 (s, 5, η^5-C$_5$H$_5$), 3.8−4.4 (m, 12 total, POC*H*$_2$CH$_3$), 2.73 (d, 2, J_{HH} = 12, Re*CH*$_a$H$_b$-*t*-Bu), 1.79 (d, 2, J_{HH} = 12, ReCH$_a$*H*$_b$-*t*-Bu), 1.59, 1.52, 1.39 (s, 9 each, *t*-Bu), 1.0−1.3 (m, 18 total, POCH$_2$C*H*$_3$); ^{13}C NMR (C_6D_6) δ 281.6 (Re*C*-*t*-Bu), 275.7 (Re*C*H-*t*-Bu, J_{CH} = 125), 89.5 (η^5-*C*$_5$H$_5$), 61.1 (POCH$_2$CH$_3$), 54.8 (Re*C*H$_2$-*t*-Bu), 51.7, 46.3, 34.2 (*C*Me$_3$), 34.7, 32.5, 29.7 (C*Me*$_3$), 17.3 (POCH$_2$*C*H$_3$). Anal. Calcd for $CoOsC_{32}H_{65}O_9P_3$: C, 41.24; H, 7.03. Found: C, 40.93; H, 6.86.

Re(HBpz$_3$)(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu). Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(py)$_2$(O$_3$SCF$_3$) (90 mg, 0.128 mmol) was dissolved in 3 mL of THF, and solid NaHBpz$_3$ (30 mg, 0.127 mmol) was added. The resulting solution was allowed to stir for 1 h, and then the THF was removed *in vacuo*. The residue was extracted with ether, the resulting solution was filtered through Celite, and the ether was removed *in vacuo* to yield a white solid; yield 67 mg (0.110 mmol, 86%): ^{1}H NMR (C_6D_6) δ 13.22 (s, 1, Re*CH*-*t*-Bu), 8.34, 8.09, 7.79 (s, 1 each, pz), 7.34, 7.32, 7.28 (s, 1 each, pz), 5.97, 5.88, 5.80 (s, 1 each, pz), 2.74 (d, 2, J_{HH} = 12, Re*CH*$_a$H$_b$-*t*-Bu), 1.74 (d, 2, J_{HH} = 12, ReCH$_a$*H*$_b$-*t*-Bu), 1.40, 1.35, 1.24 (s, 9 each, *t*-Bu); ^{13}C NMR (C_6D_6) δ 289.3 (Re*C*-*t*-Bu), 282.7 (Re*C*H-*t*-Bu), 148.1, 144.3, 141.7, 135.0, 134.5, 134.0, 105.9, 105.4, 105.2 (pz), 53.0 (Re*C*H$_2$-*t*-Bu), 52.3, 47.7, 34.3 (*C*Me$_3$), 34.7, 31.3, 29.1 (C*Me*$_3$). Anal. Calcd for $ReC_{24}H_{40}N_6B$: C, 47.28; H, 6.61; N, 13.79. Found: C, 47.53; H, 6.18; N, 13.85.

Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(C$_6$H$_{12}$S$_3$)(O$_3$SCF$_3$). Re(C-*t*-Bu)(CH-*t*-Bu)(CH$_2$-*t*-Bu)(py)$_2$(O$_3$SCF$_3$) (183 mg, 0.26 mmol) was dissolved in 5 mL of dichloromethane, and solid $S_3C_6H_{12}$ (70 mg, 0.39 mmol) was added. The solution was stirred for 2

h, and then the dichloromethane was removed *in vacuo* to yield a colorless solid, which was recrystallized from dichloromethane/pentane at −40 °C; yield 180 mg (95%): ^{1}H NMR (CD_2Cl_2) δ 12.91 (s, 1, ReC-*t*-Bu), 2.95−3.9 (m, 12 total, $S_3C_6H_{12}$), 2.59 (d, 1, $ReCH_aH_b$-*t*-Bu, J_{HH} = 12), 1.54 (d, 1, $ReCH_aH_b$-*t*-Bu, J_{HH} = 12), 1.27, 1.17, 0.92 (s, 9 each, *t*-Bu); ^{13}C NMR (CD_2Cl_2) δ 294.9 (ReC-*t*-Bu), 283.5 (ReCH-*t*-Bu), 53.6 ($ReCH_2$-*t*-Bu), 49.5, 40.3, 40.2, 38.7, 36.6, 36.3 ($S_3C_6H_{12}$), 35.2, 33.2, 32.1 (CMe_3), 33.6, 29.6, 28.2 (CMe_3). Anal. Calcd for $ReC_{22}H_{42}O_3S_4F_3$: C, 36.39; H, 5.83. Found: C, 36.17; H, 5.40.

Re(η^5-C_5H_5)(C-*t*-Bu)(CH-*t*-Bu)(O_3SCF_3). Re(η^5-C_5H_5)(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu) (110 mg, 0.23 mmol) was dissolved in 5 mL of ether, and the mixture was cooled to −40 °C. Triflic acid (20 μL, 0.22 mmol) was added, and the mixture was warmed to room temperature and stirred for 10 min. Ether was then removed *in vacuo*, and the solid was extracted with pentane (10 mL). Pentane was removed *in vacuo* from the filtrate, and a microcrystalline colorless solid was collected; yield 104 mg (84%): ^{1}H NMR (C_6D_6) δ 13.72 (s, 1, ReC*H*-*t*-Bu), 5.27 (s, 5, η^5-C_5H_5), 1.29, 1.14 (s, 9 each, *t-Bu*); ^{13}C NMR (C_6D_6) δ 306.5 (ReC-*t*-Bu), 298.6 (ReCH-*t*-Bu, J_{CH} = 90), 98.5 (C_5H_5), 54.4, 48.8 (CMe_3), 31.7, 29.4 (CMe_3); ^{19}F NMR (C_6D_6) δ −75.5. Re(η^5-C_5H_5)(C-*t*-Bu)(CH-*t*-Bu)(O_3SCF_3) is too unstable in the solid state for elemental analysis.

[Re(η^5-C_5H_5)(C-*t*-Bu)(CH-*t*-Bu)(py)]$^+$[OTf]$^-$. Re(Cp)(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu) (65 mg, 0.141 mmol) was dissolved in 5 mL of CH_2Cl_2, and the solution was cooled to −40 °C. Solid pyHOTf (31 mg, 0.135 mmol) was added, and the solution became yellow. The mixture was allowed to warm to room temperature and was stirred for 1 h. Dichloromethane was removed *in vacuo*, and a pale yellow solid was isolated, washed with pentane, and crystallized from a CH_2Cl_2/ether mixture at −40 °C; yield 50 mg (60%): ^{1}H NMR (C_6D_6) δ 14.33 (s, 1, ReC*H*-*t*-Bu), 8.60 (d, 2, py), 7.13 (t, 1, py), 7.00 (t, 2, py), 5.76 (s, 5, C_5H_5), 1.08, 1.00 (s, 9 each, *t-Bu*); ^{13}C NMR ($CDCl_3$) δ 311.4 (ReC-*t*-Bu), 295.8 (ReCH-*t*-Bu, J_{CH} = 125), 161.5, 140.4, 127.3 (py), 99.3 (Cp), 55.1, 50.4 (CMe_3), 30.6, 28.8 (CMe_3). Anal. Calcd for $ReC_{21}H_{29}NF_3O_3S$: C, 40.77; H, 4.72; N, 2.26. Found. C, 41.02; H, 4.67; N, 2.20.

Re(L_{OEt})(C-*t*-Bu)(CH-*t*-Bu)(O_3SCF_3). Re(L_{OEt})(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu) (100 mg, 0.11 mmol) was dissolved in 5 mL of ether, and the solution was cooled to −40 °C. Triflic acid (10 μL, 0.11 mmol) was added, and the yellow mixture was warmed to room temperature and stirred for 45 min. Ether was then removed *in vacuo*, and the sticky yellow solid was recrystallized from ether/pentane at −40 °C to yield yellow prisms; yield 63 mg (59%): ^{1}H NMR (CD_2Cl_2) δ 13.77 (s, 1, ReC*H*-*t*-Bu), 5.13 (s, 5, η^5-C_5H_5), 3.4−4.2 (br m, 12 total, $POCH_2CH_3$), 1.34, 1.33 (s, 9 each, *t-Bu*), 1.16 (br m, 18, $POCH_2CH_3$); ^{13}C NMR (CD_2Cl_2) δ 300.8 (ReCH-*t*-Bu, J_{CH} = 121), 298.0 (ReC-*t*-Bu), 90.1 (C_5H_5), 61.9 (br, $POCH_2CH_3$), 46.9 (CMe_3, other CMe_3 peak obscured by the solvent peak), 32.9, 29.5 (CMe_3), 16.7 ($POCH_2CH_3$); ^{19}F NMR (CD_2Cl_2) δ −78.1. Anal. Calcd for $CoReC_{28}H_{54}F_3O_{12}P_3S$: C, 33.30; H, 5.39. Found: C, 32.92; H, 5.10.

[Re(L_{OEt})(C-*t*-Bu)(CH-*t*-Bu)(Et_2O)]$^+$[BAr^F_4]$^-$. Re(L_{OEt})(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu) (140 mg, 0.15 mmol) was dissolved in 5 mL of ether, and the solution was cooled to −40 °C. Solid [H(OEt_2)$_2$][BAr^F_4] (149 mg, 0.15 mmol) was added and the yellow solution was allowed to warm to room temperature and stirred for 1.5 h. Ether was removed *in vacuo* and the yellow-tan solid was recrystallized from ether/pentane at −40 °C overnight; yield 140 mg (50%): ^{1}H NMR (CD_2Cl_2) δ 13.78 (s, 1, ReC*H*-*t*-Bu), 7.72 (s, 8, Ar^F), 7.56 (s, 4, Ar^F), 5.32 (s, 5, Cp), 3.8−5.2 (m, 12, OCH_2CH_3), 3.40 (br q, 4, OCH_2CH_3), 1.33, 1.31 (s, 9 each, *t*-Bu), 1.0−1.3, (m, 24 total, OCH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 302.9 (ReCH-*t*-Bu, J_{CH} = 124), 299.0 (ReC-*t*-Bu), 163.0 (q, CF_3, J_{C-F} = 48), 135.0, 130.0, 126.6, 123.0 (C_{aryl}), 90.1 (Cp), 61.8 (OCH_2CH_3), 61.5 (OCH_2CH_3), 32.7, 29.3 (CMe_3), 53.0, 46.9 (CMe_3), 16.5 (OCH_2CH_3), 12.6 (OCH_2CH_3). Anal. Calcd for $ReCoC_{63}H_{76}BF_{24}O_{10}P_3$: C, 42.08; H, 4.26. Found: C, 42.39; H, 4.23.

[Re($S_3C_6H_{12}$)(C-*t*-Bu)(CH-*t*-Bu)(O_3SCF_3)]$^+$[O_3SCF_3]$^-$. [Re($S_3C_6H_{12}$)(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)]$^+$[O_3SCF_3]$^-$ (60 mg, 0.083 mmol) was dissolved in 5 mL of CH_2Cl_2, and the solution was cooled to −40 °C. Triflic acid (8 μL, 0.09 mmol) was added, and the resulting pale pink mixture was warmed to room temperature and stirred for 45 min. CH_2Cl_2 was then removed *in vacuo*, and the resulting microcrystalline pale pink solid was washed with pentane and dried; yield 40 mg (60%): ^{1}H NMR (CD_2Cl_2) δ 14.56 (s, 1, ReC*H*-*t*-Bu), 3.1−4.2 (overlapping multiplets, 12 total, $S_3C_6H_{12}$), 1.43, 1.32 (s, 9 each, *t-Bu*); ^{13}C NMR (CD_2Cl_2) δ 306.4 (ReCH-*t*-Bu, J_{CH} = 116), 304.6 (ReC-*t*-Bu), 55.2, 51.6 (CMe_3), 43.7, 41.9, 36.5, 34.0, 32.9, 30.1 ($S_3C_6H_{12}$), 29.7, 28.5 (CMe_3); ^{19}F NMR (CD_2Cl_2) δ −75.6, −78.6. Anal. Calcd for $ReC_{18}H_{31}F_6O_6S_5$: C, 26.89; H, 3.89. Found: C, 26.96; H, 3.74.

Re(C-*t*-Bu)(CHC_6H_5)(CH_2-*t*-Bu)(py)$_2$(OTf). Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(py)$_2$(OTf) (49 mg, 0.26 mmol) was dissolved in 3 mL of CH_2Cl_2. Styrene (36 μL, 0.315 mmol) was added, and the resulting orange solution was allowed to stir at room temperature for 1.5 h. The volatiles were removed *in vacuo* to yield a beige powder, which was washed with pentane (10 mL) and recrystallized from CH_2Cl_2/ether to yield beige microcrystals: ^{1}H NMR (CD_2Cl_2) δ 14.35 (s, 1, ReC*H*C_6H_5), 8.76, 8.46 (d, 2 each, py *ortho*), 8.00, 7.80 (br t, 1 each, py *meta*), 7.76 (d, 2, J_{HH} = 9, phenyl *ortho*), 7.55, 7.38 (t, 2 each, py *meta*), 7.25 (m, 3, phenyl *meta* and *para*), 2.52 (d, 2, J_{HH} = 12, $ReCH_aH_bCMe_3$), 2.07 (d, 2, J_{HH} = 12, $ReCH_aH_bCMe_3$), 1.33, 0.86 (s, 9 each, *t*-Bu); ^{13}C NMR (CD_2Cl_2) δ 290.4 (ReC-*t*-Bu), 270.3 (ReCHC$_6$H$_5$, J_{CH} = 128 Hz), 155.2, 153.2, 152.2, 139.6, 139.4, 129.7, 128.7, 128.4, 125.6 (py and phenyl), 57.6 ($ReCH_2C_6H_5$), 36.1 (CMe_3), 34.0, 28.5 (CMe_3). Anal. Calcd for $C_{28}H_{36}N_2F_3O_3SRe$: C, 46.46; H, 5.01; N, 3.87. Found: C, 46.16; H, 5.04; N, 3.63.

Re(C-*t*-Bu)(CHOEt)(CH_2-*t*-Bu)(py)$_2$(OTf). Re(C-*t*-Bu)(CHOEt)(CH_2-*t*-Bu)(py)$_2$(OTf) was prepared from Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(py)$_2$(OTf) and ethyl vinyl ether in a manner similar to that used in the preparation of Re(C-*t*-Bu)(CHC_6H_5)(CH_2-*t*-Bu)(py)$_2$(OTf). A pink solid was obtained after dichloromethane was removed *in vacuo*; this was washed with ether and dried; yield 60%: ^{1}H NMR ($CDCl_3$) δ 12.89 (ReC*H*-*t*-Bu), 8.76, 8.45 (d, 2 each, py), 7.83, 7.70 (t, 1 each, py), 7.40, 7.20 (d, 2 each, py), 4.07 (q, 2, OCH_2CH_3), 2.03 (d, 1, $ReCH_aH_b$-*t*-Bu), 1.38 (d, 1, $ReCH_aH_b$-*t*-Bu), 1.31 (t, 3, OCH_2CH_3), 1.20, 0.94 (s, 9 each, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ 288.1 (ReCHOEt), 280.3 (ReC-*t*-Bu), 154.6, 153.1, 138.6, 138.2, 125.4, 124.8 (py), 75.4 (OCH_2CH_3), 50.6, 35.0 (CMe_3), 33.8, 27.9 (CMe_3), 16.1 (OCH_2CH_3).

Re(C-*t*-Bu)(CH_2)(CH_2-*t*-Bu)(bpy)(OTf). ^{1}H NMR (C_6D_6) δ 14.03, (d, 1, $ReCH_aH_b$, J_{HH} = 3, J_{CH} = 135), 13.50 (d, 1, $ReCH_aH_b$, J_{HH} = 3, J_{CH} = 150), 6.4−9 (m, 8 total, bpy), 2.79 (d, 1, $ReCH_aH_b$-*t*-Bu), 1.86 (d, 1, $ReCH_aH_b$-*t*-Bu), 1.39, 0.86 (s, 9 each, *t*-Bu); ^{13}C (partial) δ 258 ($ReCH_2$). Due to the instability of Re(C-*t*-Bu)(CH_2)(CH_2-*t*-Bu)(bpy)(OTf) at −40 °C, a pure sample could not be prepared, and neither elemental analysis nor a complete set of ^{13}C NMR data could be obtained. The ^{13}C data were obtained by preparing a sample of Re(C-*t*-Bu)($^{13}CH_2$)(CH_2-*t*-Bu)(bpy)(OTf).

Re(C-*t*-Bu)[$(CH_2)_3$-*t*-Bu](C_2H_4)(py)$_2$(O_3SCF_3). Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(py)$_2$(O_3SCF_3) (176 mg, 0.25 mmol) was dissolved in 10 mL of benzene and stirred under an atmosphere of ethylene for 45 min. The brown-orange solution was then reduced in volume to 2 mL, and 5 mL of pentane was added to precipitate a beige powder, which was then washed with 15 mL of pentane and dried to yield a beige solid; yield 135 mg (78%). An analytical sample was recrystallized from ether at −40 °C: ^{1}H NMR (C_6D_6) δ 8.9, 8.7 (d, 2 each, py *ortho*), 6.65 (br m, 2, py *meta*), 6.45 (br m, 4, py *para*), 3.5 (br m, 4, C_2H_4), 3.15 (m, 1, $ReCH_2$−), 2.51 (m, 1, $ReCH_2$−), 2.42 (overlapping multiplets, 2 total, $ReCH_2CH_aH_b$ and $Re(CH_2)_2CH_aH_b$, partial assignment by C_2D_4 labeling experiment), 2.04 (m, 1, $ReCH_2CH_aH_b$), 1.80 (m, 1, $Re(CH_2)_2CH_aH_b$), 1.16, 0.80 (s, 9 each, *t*-Bu); ^{13}C NMR (C_6D_6) δ 248.2 (ReC-*t*-

Bu), 153.9, 153.7 (py *ortho*), 138.4, 137.6 (py *meta*), 125.4, 125.1 (py *para*), 53.9 ($ReCH_2CH_2-$, $J_{CH} = 153$, $J_{C-C} = 36$), 53.0, 50.6 (CMe_3), 51.2 ($Re(CH_2)_2CH_2-$), 46.6 ($ReCH_2CH_2-$, $J_{CH} = 156$, $J_{C-C} = 36$), 29.9, 25.8 (CMe_3), 20.7 (C_2H_4, $J_{CH} = 123$); ^{19}F NMR (C_6D_6) δ −78.7. Anal. Calcd for $ReC_{25}H_{38}N_2F_3O_3SRe$: C, 43.53; H, 5.55; N, 4.02. Found: C, 43.71; H, 5.76; N, 4.02.

Observation of Re(C-*t*-Bu)(CHEt)(CH_2-*t*-Bu)(CD_3CN)$_n$(OTf). A 2:1 mixture of Re(C-*t*-Bu)(CHEt)(CH_2-*t*-Bu)(CD_3CN)$_n$(OTf) and Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(CD_3CN)$_n$(OTf) was generated by heating a CD_3CN solution of Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)(CD_3CN)(OTf) (12 mg, 0.02 mmol) and *cis*-3-hexene (10 μL, 0.08 mmol) at 60 °C for 1 h. Partial ^1H NMR (CD_3CN) δ 13.53 (t, 1, ReC*H*Et), 3.5 (d of m, 2 total, ReCHCH_2-CH_3), 2.2 (d, 1, ReCH_aH_b-*t*-Bu), 1.25, 0.9 (s, 9 each, *t*-Bu). The remaining resonances could not be assigned due to overlap with the resonances associated with *cis*-3-hexene.

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