ALKYL, ALKYLIDENE, AND ALKYLIDYNE COMPLEXES OF RHENIUM AND OSMIUM

by

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Submitted to the Department of Chemistry in Partial Fulfillment of the Requirements for the Degree of

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MAR 01 1995
This doctoral thesis has been examined by a Committee of the Department of Chemistry as follows:

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To my parents,
for their love and support throughout the years.
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ABSTRACT

Chapter 1

The reaction of Re(C-t-Bu)(CH-t-Bu)(CH2-t-Bu)2 with triflic acid, pentafluorophenol, HBF4·OEt2, or [H(OEt2)2]+[BARF4]− (ArF = 3,5-C6H3(CF3)2) yields complexes of the general formula Re(C-t-Bu)(CH2-t-Bu)3X (X = OTf, OC6F5, BF4, BARF4). Re(C-t-Bu)(CH2-t-Bu)3X reacts with coordinating ligands L (L = py, CH3CN, CD3OD, THF) to form neopentane and Re(C-t-Bu)(CH2-t-Bu)(CH2-t-Bu)(L)nX (n = 1-3). The complexes Re(C-t-Bu)(CH2-t-Bu)(CH2-t-Bu)(L)nX are stable to water. The reaction of Re(C-t-Bu)(CH2-t-Bu)(CH2-t-Bu)(py)2(OTf) with NaC5H5, NaOEt (L(OEt = [CpCo(PO(OEt)2)3]), or NaHBPz3 in THF yields Re(C-t-Bu)(CH2-t-Bu)(CH2-t-Bu)(L(n3-C5H5), Re(C-t-Bu)(CH2-t-Bu)(CH2-t-Bu)(L(1,4,7-trithiacyclononane yields colorless [Re(C-t-Bu)(CH2-t-Bu)(CH2-t-Bu)(n3-C5H12)(OTf)]. Re(C-t-Bu)(CH2-t-Bu)(CH2-t-Bu)(L) (L = Cp, L(OEt)) and [Re(C-t-Bu)(CH2-t-Bu)(CH2-t-Bu)(n3-S3C6H12)(OTf)] react with triflic acid to form Re(C-t-Bu)(CH2-t-Bu)(L)(OTf) or [Re(C-t-Bu)(CH2-t-Bu)(OTf)(n3-S3C6H12)]+[OTf], respectively. A similar reaction between Re(C-t-Bu)(CH2-t-Bu)(CH2-t-Bu)(L)(OEt) and [H(OEt2)2]+[BARF4]− in ether produces [Re(C-t-Bu)(CH2-t-Bu)(OEt2)(L(OEt))]+[BARF4]−. The reaction of the neopentylidyne, neopentyldiyne complexes with a variety of olefins was investigated. Re(C-t-Bu)(CH2-t-Bu)(CH2-t-Bu)(py)2(OTf) reacts with H2C=CHR (R = H, OCH2CH3, C6H5) to yield neohexene and Re(C-t-Bu)(CHR)(CH2-t-Bu)(py)2(OTf). Re(C-t-Bu)(CH2-t-Bu)(CH2-t-Bu)(CH3CN(OTf) metathesizes 100 equivalents of cis-2-pentene in less than 5 minutes, but the catalyst is not long-lived. Re(C-t-Bu)(CH-t-Bu)(CH2-t-Bu)(py)2(OTf) polymerizes strained cyclic olefins such as norbornene or...
MTD (MTD = methyltricyclocodecene) in a “living” manner, yielding polymers with M_w/M_n < 1.3. Features governing the rate of α-hydrogen abstraction and the reactivity with olefins and some aspects of catalyst design are discussed.

Chapter 2

Addition of dienopentylzinc, dienophylyne, or dimethylethylene to [PPh_4][OsCl_4O_2] in dichloromethane gave OsO_2R_2 complexes (R = neopentyl, neophyl, or mesityl). An analogous reaction between Zn(CH_2SiMe_3)_2 and [PPh_4][OsCl_4O_2] in dichloromethane gave [OsO_2(CH_2SiMe_3)_2]_n. OsO_2(CH_2-t-Bu)_2 reacts with 2 equivalents of trimethylaluminum in pentane to yield orange crystals of [Os(CH_3)(CH_2-t-Bu)_2]_2, while addition of Al(CH_2-t-Bu)_3(THF) to OsO_2(CH_2-t-Bu)_2 in THF gave red [OsO(CH_2-t-Bu)_2]_n. The reaction between OsO_2(CH_2-t-Bu)_2 and 2 equivalents of Ta(CH-t-Bu)(CH_2-t-Bu)_3 in pentane yielded insoluble [TaO(CH_2-t-Bu)_2]_n and syn,anti-Os(CH-t-Bu)_2(CH_2-t-Bu)_2. A mixture of syn,anti-Os(CH-t-Bu)_2(CH_2-t-Bu)_2 and anti,anti-Os(CH-t-Bu)_2(CH_2-t-Bu)_2 is formed when solutions of syn,anti-Os(CH-t-Bu)_2(CH_2-t-Bu)_2 in toluene-δ are photolyzed at -85°C with a medium pressure mercury lamp. [OsO_2(CH_2SiMe_3)_2]_n reacts with two equivalents of Ta(CH-t-Bu)(CH_2-t-Bu)_3 in pentane to yield a 1:1 mixture of syn,anti-Os(CH-t-Bu)_2(CH_2SiMe_3)_2 and anti,anti-Os(CH-t-Bu)_2(CH_2SiMe_3)_2. Isolated anti,anti-Os(CH-t-Bu)_2(CH_2SiMe_3)_2 is a thermally stable orange crystalline solid. An X-ray study of anti,anti-Os(CH-t-Bu)_2(CH_2SiMe_3)_2 showed the core of the molecule to be a distorted tetrahedron in which the two neopentylidene ligands lie in the same plane and Os=C = 1.836 (7) Å. Extended Hückel calculations performed on Os(CH_2)_2(CH_2)_2 suggest that the HOMO is an orbital of primarily d_2 character that lies between and in the plane of the two methylene ligands, the LUMO is the π* system of the bis(methylidene), and the HOMO-1 and HOMO-2 are bonding combinations of the π system. The relative reactivities and stabilities of the syn, anti and anti, anti rotamers of Os(CH-t-Bu)(CH_2R)_2 are discussed. When Os(CH-t-Bu)_2(CH_2-t-Bu)_2 is dissolved in neat trimethylphosphine, orange-red, pentanesoluble, air- and water-sensitive Os(PMe_3)_3(η^2-t-BuC=CH-t-Bu) can be isolated in 30-40% isolated yield after one hour. An X-ray study of Os(PMe_3)_3(η^2-t-BuC=CH-t-Bu) showed it to be a pseudo-tetrahedral species in which C=C = 1.30 (1) Å. Os(PMe_3)_3(η^2-t-BuC=CH-t-Bu) reacts with carbon monoxide to form colorless Os(PMe_3)_2(CO)(η^2-t-BuC=CH-t-Bu), with dihydrogen in the presence of excess trimethylphosphine to give cis-Os(H)(PMMe_3)_4 and di-t-butylethylene, and with [H(OEt)_2]_2*[BArF_4]^- to give yellow, crystalline [Os(H)(PMMe_3)_3(η^2-t-BuC=CH-t-Bu)]*[BArF_4]^- . Addition of excess PMe_3 to [Os(H)(PMMe_3)_3(η^2-t-BuC=CH-t-Bu)]*[BArF_4]^- yields [Os(H)(PMMe_3)_5]^[BArF_4]^-.

Chapter 3

Syn, anti-Os(CH-t-Bu)_2(CH_2-t-Bu)_2 reacts with pyridinium triflate in the presence of more than 2 equivalents of pyridine to yield neopentane and orange, air-stable Os(C-t-Bu)(CH_2-t-Bu)_2(py)_2(OTf). OsO_2(CH_2-t-Bu)_2 reacts with one equivalent of Ta(CH-t-Bu)(py)_2X_3 (X = Cl, Br) in mixtures of dichloromethane and pyridine to form neopentane and orange Os(C-t-Bu)(CH_2-t-Bu)(py)_2X_2. The general requirement that Os(VI) complexes require at least two metal-ligand π-bonds appears to drive the α-hydrogen elimination reaction, and the proposed mono(neopentylidene) intermediates could not be observed. Os(C-t-Bu)(CH_2-t-Bu)_2(py)_2(OTf) reacts with
LiO-t-Bu or LiN(SiMe₃)₂ in THF to yield the four-coordinate complexes, Os(C-t-Bu)(CH₂-t-Bu)L₂ (L = O-t-Bu or LiN(SiMe₃)₂), or with NaC₅H₅ in THF to yield yellow Os(C-t-Bu)(CH₂-t-Bu)L₂(η⁵-C₅H₅). Analogous reactions between Os(C-t-Bu)(CH₂-t-Bu)L₂(py)₂(OTf) and Na[CpCo(P(O)(OEt)₂)₃] (NaLOE₁) or sodium trispyrazolylborate (NaHBpz₃) in THF yield Os(C-t-Bu)(CH₂-t-Bu)L₂(LOE₁) or Os(C-t-Bu)(CH₂-t-Bu)(HBPz₃), respectively. An X-ray study of Os(C-t-Bu)(CH₂-t-Bu)L₂(HBPz₃) showed it to be a pseudoctahedral molecule in which Os = 1.73 (2) Å. Os(C-t-Bu)(CH₂-t-Bu)L₂(py)₂(OTf) reacts with tert-butylacetylene in CD₂Cl₂ to yield neopentane and the η¹-acetylide complex, Os(C-t-Bu)(CH₂-t-Bu)(C≡C-t-Bu)(py)₂(OTf). Addition of 1 equivalent of bipyridine to Os(C-t-Bu)(CH₂-t-Bu)(C≡C-t-Bu)(py)₂(OTf) yields red, crystalline Os(C-t-Bu)(CH₂-t-Bu)(C≡C-t-Bu)(bipy)(OTf). Aspects of the α-hydrogen reaction in the Os(VI) complexes and the reactivity of osmium-carbon multiple bonds are discussed.

Chapter 4

OsO₂R₂ (R = CH₂-t-Bu, CH₂CMe₂Ph) reacts with one equivalent of Ta(NAr)(O-t-Bu)₃ in THF or two equivalents of Ta(NAr)(O-t-Bu)₃ in pentane or toluene to form OsO(NAr)(R)₂ or Os(NAr)₂(R)₂, respectively, in 50-80% yield. TaO(O-t-Bu)₃ is readily removed by filtering the reaction mixture through silica gel. OsO(NAr)(CH₂-t-Bu)₂ reacts with two equivalents of HCl or Me₃SiI in CH₂Cl₂ or DME to form Os(NAr)(CH₂-t-Bu)Cl₂ or Os(NAr)(CH₂-t-Bu)Cl₂, respectively, in 60-80% yield. OsO(NAr)(CH₂-t-Bu)₂ reacts with SiMe₃X in CH₂Cl₂ to form green, crystalline Os(NAr)(CH₂-t-Bu)₂(OSiMe₃)(X) (X = Cl, OTf) in 60-80% yield. The reaction of OsO(NAr)(CH₂-t-Bu)₂ with two equivalents of trimethylaluminum yields red trans-Os(NAr)(CH₂-t-Bu)₂(CH₃)₂. The reaction of OsO(NAr)(CH₂-t-Bu)₂ with Ta(CH-t-Bu)(CH₂-t-Bu)₃ in pentane yields [Os(NAr)(t-BuCHCH-t-Bu)](μ-O)₂[Os(NAr)(CH₂-t-Bu)₂]. None of the Os(VI) di(neopentyl) complexes shows any evidence for controlled α-hydrogen abstraction reactions. Aspects of the imido/oxo exchange reactions are discussed.

Thesis Supervisor: Professor Richard R. Schrock

Title: Frederick G. Keyes Professor of Chemistry
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>Ar</td>
<td>2,6-C(_6)H(_3)-(i-Pr)(_2)</td>
</tr>
<tr>
<td>Ar'</td>
<td>2,6-C(_6)H(_3)Me(_2)</td>
</tr>
<tr>
<td>Ar(_F)</td>
<td>3,5-C(_6)H(_3)(CF(_3))(_2)</td>
</tr>
<tr>
<td>bpy</td>
<td>2,2'-bipyridyl</td>
</tr>
<tr>
<td>t-Bu</td>
<td><em>tert</em>-butyl</td>
</tr>
<tr>
<td>br</td>
<td>broad</td>
</tr>
<tr>
<td>C(_\alpha)</td>
<td>alpha carbon; carbon bound to the metal</td>
</tr>
<tr>
<td>C(_\beta)</td>
<td>carbon bound to C(_\alpha)</td>
</tr>
<tr>
<td>C(_{isp})</td>
<td>carbon in an aromatic ring bound to an atom bound to the metal</td>
</tr>
<tr>
<td>C(_{meta})</td>
<td>carbon in the meta position of an aromatic ring</td>
</tr>
<tr>
<td>C(_{para})</td>
<td>Carbon in the para position of an aromatic ring</td>
</tr>
<tr>
<td>cm(^{-1})</td>
<td>reciprocal centimeters</td>
</tr>
<tr>
<td>C(_p)</td>
<td>cyclopentadienyl</td>
</tr>
<tr>
<td>C(_p^\prime)</td>
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</tr>
<tr>
<td>d</td>
<td>doublet</td>
</tr>
<tr>
<td>dme</td>
<td>dimethoxymethane</td>
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</tr>
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</tr>
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<tr>
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<td>H(_\alpha)</td>
<td>hydrogen bound to C(_\alpha)</td>
</tr>
<tr>
<td>H(_\beta)</td>
<td>hydrogen bound to C(_\beta)</td>
</tr>
<tr>
<td>HBPz(_3)</td>
<td>tris(pyrazolyl)borate</td>
</tr>
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</table>
$H_{\text{meta}}$  hydrogen in the meta position of an aromatic ring
$H_{\text{ortho}}$  hydrogen in the ortho position of an aromatic ring
$H_{\text{para}}$  hydrogen in the para position of an aromatic ring
$Hz$  Hertz
$IR$  infrared (spectroscopy)
$J$  coupling constant, in Hertz
$LOEt$  $[\text{CpCo(PO(OEt)2)}_3]^-$
$Me$  methyl
$min$  minutes
$mult$  multiplet
$NMR$  nuclear magnetic resonance (spectroscopy)
$OTf$  triflate ($O_3SCF_3^-$)
$Ph$  phenyl
$i$-$Pr$  isopropyl
$py$  pyridine
$q$  quartet
$s$  singlet
$sept$  septet
$TMSCl$  trimethylsilyl chloride
$TMSI$  trimethylsilyl iodide
$TMSOTf$  trimethylsilyl triflate
$t$  triplet
$THF$  tetrahydrofuran
$v$-$br$  very broad
$\delta$  chemical shift in ppm downfield from a standard reference (usually tetramethylsilane, $\text{CCl}_3\text{F}$ for $^{19}\text{F}$ spectra)
CHAPTER 1: ALKYL, ALKYLIDENE, AND ALKYLIDYNE COMPLEXES OF RHENIUM(VII)
Introduction

In the classical olefin metathesis systems, rhenium is one of three metals that are active catalyst precursors.\(^1\) Although the rhenium-based systems are less active, they are more tolerant of functional groups present in the olefins (such as esters) than the molydenum- or tungsten-based systems. For this reason, there has been considerable interest in the development of well-defined rhenium metathesis catalysts.

In the early 1980’s, evidence began to accumulate in favor of the proposition that the metal center is in its highest possible oxidation state in the classical systems (if the alkylidene ligand is viewed as a dianion.) This led to the development of a variety of four-coordinate d\(^0\) alkylidene complexes of molybdenum,\(^2,3\) tungsten, and rhenium.\(^4-6\) Some of these complexes are well-defined single-component olefin metathesis catalysts and are shown below. It should be noted that these complexes contain an imido (M = Mo, W) or alkylidyne (M = Re) ligand to maintain the metal in its highest oxidation state.

\[
\begin{array}{c}
\text{Me(CF}_3\text{)}_2\text{CO} \quad \text{t-Bu} \\
\text{Me(CF}_3\text{)}_2\text{CO} \\
\end{array} \\
\begin{array}{c}
\text{Re} \quad \text{t-Bu} \\
\text{RO} \\
\end{array} \\
\begin{array}{c}
\text{NAr} \\
\text{RO} \\
\end{array} \\
\begin{array}{c}
\text{M = Mo, W} \\
\text{Ar = 2,6-(i-Pr)}_2\text{C}_6\text{H}_3 \\
\end{array}
\]

Re(C-t-Bu)(CH-t-Bu)[OC(CF\text{)}_3\text{Me}]_2 and its derivatives were the only single-component rhenium complexes that would metathesize olefins; however, these catalysts were not very active metathesis catalysts. A maximum rate of 250 turnovers/hour is
obtained for the metathesis of cis-2-pentene, and an initiation period is required. This is orders of magnitude slower than the Mo- and W-based systems. Olefin metathesis has been observed in mixtures of rhenium alkylidene complexes such as Re(NAr)(CH-t-Bu)[OC(CF3)2Me]37 or ReO(CHCHCPh2)[OC(CF3)2Me]3(THF)8 and Lewis acids, but many common Lewis acids such as AlCl3 and BAr3 can react with some functional groups. Thus, the main advantage of having a rhenium catalyst is lost. Additionally, these two-component systems are not well-defined and the active species is not known. It is thought that the Lewis acid abstracts an alkoxide to form a reactive cationic rhenium alkylidene complex or coordinates to the oxo group to form a more electrophilic species.

Enhanced reactivity has been observed in a variety of cationic early-9 and late-transition metal10 polymerization catalysts. However, at the time that this research was begun, cationic alkylidene complexes had not been studied as potentially active metathesis catalysts. Indeed, few cationic alkylidene complexes were known. While this work was in progress, a variety of cationic tungsten alkylidene complexes were reported.11,12 These complexes do not metathesize olefins in the absence of a cocatalyst.

One goal of the research described in this chapter was to prepare cationic or otherwise electrophilic rhenium alkylidene complexes that were more active metathesis catalysts than neutral Re(C-t-Bu)(CH-t-Bu)[OC(CF3)2Me]2. The other goal was to exploit the lower oxophilicity of rhenium and develop rhenium alkylidene complexes that are truly stable to a wide range of functional groups, including alcohols and water. The alkylidene and alkylidyne ligands of the Re(C-t-Bu)(CH-t-Bu) core are fairly stable to weak acids such as alcohols or water. For instance, [Re(C-t-Bu)(CH-t-Bu)Cl2]x can be dissolved in water and later recovered unchanged.5 Complexes of the general formula Re(C-t-Bu)(CH-t-Bu)(OR)2 are susceptible to protonolysis of the alkoxide or
aryloxide ligands, and thus these ligands should be avoided in the design of new catalysts. If the alkylidene, alkylidyne core is to be maintained, the counterion ("X"), the remaining mono(anionic) ligand and/or neutral donor ligands ("L") can, in theory, be selected to suit various purposes. In the work described in this chapter, we chose to focus on rhenium neopentylidene, neopentylidyne complexes containing either a neopentyl group or a tridentate donor ligand such as tris(pyrazolyl)borate (Hbpz3), 1,4,7-trithiacyclononane, η⁵-C₃H₅ or [CpCo(PO(OEt)₂)₃]⁻ ("LOEt".).¹³ These supporting ligands were chosen based on steric and stability of the resulting rhenium complexes to water. The counterions X were chosen based on their tendency to form cationic complexes and was limited to triflate,¹⁴ B(3,5-(CF₃)₂C₆H₃)₄ ("BArF₄"),¹⁰ and tetrafluoroborate.

**Synthesis of Re(C-t-Bu)(CH₂-t-Bu)₃X**

It was necessary to develop a synthetic route to Re(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(L)nX. Attempted mono(alkylations) of [Re(C-t-Bu)(CH-t-Bu)Cl₂]ₓ are unsuccessful, yielding mixtures of Re(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu)₂ and [Re(C-t-Bu)(CH-t-Bu)Cl₄]ₓ. Direct protonolysis of a rhenium-carbon single bond in Re(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu)₂ is not possible; the reaction of Re(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu)₂ with HCl instead results in protonation of Cₐ of the alkylidene ligand, forming Re(C-t-Bu)(CH₂-t-Bu)₃Cl.¹⁵ Since α-hydrogen abstraction reactions might be possible for the complexes Re(C-t-Bu)(CH₂-t-Bu)₃X, the scope of this protonation reaction was reinvestigated to provide a greater variety of counterion X. In particular, non-coordinating or labile ligands such as triflate, BArF₄⁻ or BF₄⁻ were of interest, for reasons detailed above.
Scheme 1.1: Reaction of Re(C-t-Bu)(CH-γ-Bu)(CH-γ-Bu)2 with Acids.
The reaction of Re(C-\textit{t}-Bu)(CH-\textit{t}-Bu)(CH_{2-\textit{t}-Bu})_2 with a variety of acids was investigated and the results are shown in Scheme 1.1. The reaction is very general and a variety of acids can be used. Yields range from 60-80% and the resulting products are highly crystalline yellow solids. Wilkinson and coworkers have reported the synthesis and structure of Re(CSiMe_3)(CH_2SiMe_3)_3Cl; it has a trigonal bipyramidal structure with the trimechylsilylimethyl ligands occupying the equatorial sites.\textsuperscript{16} When \(X = OC_6F_5\), OTf, or Cl, it is likely that Re(C-\textit{t}-Bu)(CH_2-\textit{t}-Bu)_3(X) is structurally similar to Re(CSiMe_3)(CH_2SiMe_3)_3Cl.

When \(X = BF_4^-\) or BArF_4\textsuperscript{2-}, it is somewhat more difficult to assign a structure. The complexes continue to exhibit C\(_3\) symmetry, and it is possible that they adopt a pseudo-tetrahedral structure. However, this seems unlikely in view of their extreme electrophilicity. The BF\(_4^-\) anion may coordinate through one of the fluoride atoms, resulting in a trigonal bipyramidal structure. When the truly non-coordinating anion BArF\(_4^-\) is present, the complex maintains one equivalent of ether, although ether is partially lost in vacuo, rendering elemental analysis difficult. If traces of water are present either in [H(OEt\(_2\))\textsubscript{2}]\textsuperscript{+}[BArF_4\textsuperscript{2-}] or in the recrystallization solvent, yellow blocks of Re(C-\textit{t}-Bu)(CH_2-\textit{t}-Bu)_3(H_2O)]\textsuperscript{+}[BArF_4\textsuperscript{2-}]\textsuperscript{2-}(Et_2O) are isolated. Contamination of [H(OEt\(_2\))\textsubscript{2}]\textsuperscript{+}[BArF_4\textsuperscript{2-}] with water and coordination of water by cationic Rh complexes containing the BArF\(_4^-\) anion has been observed by Brookhart and coworkers and is a problem no matter how carefully anhydrous conditions are maintained.\textsuperscript{17} It should be noted that the water adduct is extremely crystalline and is isolated preferentially if less than 1 equivalent of water is present. Water is slowly lost in vacuo.

The water molecule can be observed by IR (\(\nu_{\text{O-H}} = 3640\), br) and \(\text{^1H NMR}\) in CD\(_2 Cl_2\) (br s, 7 ppm). In the \(\text{^1H NMR}\) spectrum, the resonances associated with the alkyl and alkylidyne groups are shifted from the resonances observed for [Re(C-\textit{t}-Bu)(CH\(_2\)-\textit{t}-Bu)_3(Et\(_2\))\textsuperscript{+}[BArF_4\textsuperscript{2-}], so water is not merely present in the crystal lattice.
Exchange with added D$_2$O is observed on the NMR time scale at 25°C; exchange with added ether also occurs at 25°C on the NMR time scale. The ether molecule may be associated with the BArF$_4$ counterion, or it may be weakly hydrogen bonded with the bound water molecule. A similar mode of binding for pyridine has been observed by X-ray crystallography in [Re(C-t-Bu)(CH$_2$-t-Bu)(CH$_2$-t-Bu)(py)$_2$(py-H$_2$O)]$^+${BArF$_4$}$^-$ (see below.)

When water is added to ether or dichloromethane solutions of [Re(C-t-Bu)(CH$_2$-t-Bu)$_3$(Et$_2$O)(H$_2$O)]$^+${BArF$_4$}$^-$ or Re(C-t-Bu)(CH$_2$-t-Bu)$_3$X, a two-phase system is formed, and no evidence for an α-hydrogen abstraction reaction is observed. However, it should be noted only low concentrations of water can be introduced in this manner. Other solvents (THF, CH$_3$CN, CH$_3$OH) in which Re(C-t-Bu)(CH$_2$-t-Bu)$_3$X are soluble themselves induce an α-hydrogen abstraction reaction, so extensive studies of the reactivity of Re(C-t-Bu)(CH$_2$-t-Bu)$_3$X with water were not possible.

**Synthesis of Rhenium Neopentyl, Neopentylidene, Neopentylidyne Complexes**

The reaction of W(C-t-Bu)(CH$_2$-t-Bu)$_3$ with excess PMe$_3$ or dmpe under forcing conditions (100 - 110°C) had previously been found to form W(C-t-Bu)(CH-t-Bu)(CH$_2$-t-Bu)(L)$_2$ (L = PMe$_3$, 1/2 dmpe).$^{18}$ It was 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. Edwards had not observed any evidence for α-hydrogen abstraction reactions in Re(C-t-Bu)(CH$_2$-t-Bu)$_3$Cl,$^{19}$ but α-hydrogen abstraction reactions are generally more facile in systems that are cationic or otherwise electrophilic.$^{20}$ 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)]$^+${BArF$_4$}$^-$ (n = 0,1) would be more likely to undergo α-hydrogen abstraction reactions than either the neutral rhenium...
complex Re(C-t-Bu)(CH$_2$-t-Bu)$_3$Cl or W(C-t-Bu)(CH$_2$-t-Bu)$_3$. This was found to be true for these systems and the results are described below.

Re(C-t-Bu)(CH$_2$-t-Bu)$_3$(OTf) reacts rapidly with 2-3 equivalents 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 and is isolated in virtually quantitative yield.

\[
\text{Re(C-t-Bu)(CH$_2$-t-Bu)$_3$(OTf)} + 2 \text{py} \xrightarrow{\text{Et$_2$O, 25ºC}} \text{ReCH$_2$-t-Bu} + \text{CMe$_4$} - \text{py}
\]

The structure shown above is proposed based on the $^1$H NMR spectrum as well as several structurally characterized six-coordinate rhenium neopentyldiene, neopentyldyne complexes, which exhibit several common features. First, the alkylidene and alkylidyne ligands are oriented cis to each other, and the remaining anionic ligands are cis to the alkylidene and alkylidyne ligands.$^{5,6,15}$ If these features are present in Re(C-t-Bu)(CH-t-Bu)(CH$_2$-t-Bu)(py)$_2$(OTf), the orientation of the alkyl, alkylidene, and alkylidyne ligands is fac, as shown. The triflate ligand, being only a weak $\sigma$-bonding ligand, might be either cis or trans to the alkylidyne; however, the multiple-bonding requirements of the alkylidyne ligand strongly labilize any bonds trans to it, and thus it seems more likely that the only weakly coordinating triflate ligand might occupy this site. Exchange is with added pyridine is observed on the NMR time scale at 25ºC in CD$_2$Cl$_2$. 
Neophyl complexes can be synthesized in identical fashion. Thus, the reaction of crude Re(CCMe₂Ph)(CH₂CMe₂Ph)₃(OTf) with excess pyridine in ether results in formation of pink Re(CCMe₂Ph)(CHCMe₂Ph)(CH₂CMe₂Ph)(py)₂(OTf). This complex is similar to Re(Č-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(py)₂(OTf) but is much more soluble in ether and benzene.

The reaction of Re(Č-t-Bu)(CH₂-t-Bu)₃(OTf) with excess acetonitrile in ether results in formation of neopentane and isolation of beige Re(Č-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(CH₃CN)(OTf). Crystals of what is presumed to be Re(Č-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(CH₃CN)ₙ(OTf) (n = 2 or 3) are formed initially in the reaction mixture, but CH₃CN is readily lost in vacuo, yielding Re(Č-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(CH₃CN)(OTf). When excess CH₃CN (6 equivalents) is added to a C₆D₆ solution of Re(Č-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(CH₃CN)(OTf), Re(Č-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(CH₃CN)ₙ(OTf) is formed (as evidenced by shifts of all of the observed resonances), and exchange of CH₃CN occurs at 25°C. The structure of Re(Č-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(CH₃CN)(OTf) is not known, and attempts to grow crystals suitable for X-ray diffraction were unsuccessful.

Re(Č-t-Bu)(CH₂-t-Bu)₃(OTf) eliminates neopentane when it is dissolved in CD₃OD and Re(Č-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(CD₃OD)ₙ(OTf) is observed by ¹H NMR. Attempts to isolate Re(Č-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(MeOD)ₙ(OTf) were unsuccessful, since CD₃OD is readily lost in vacuo. However, it is stable for several hours in solution. Addition of pyridine to CD₃OD solutions of Re(Č-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(MeOD)ₙ(OTf) results in formation of Re(Č-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(py)₂(OTf). Re(Č-t-Bu)(CH₂-t-Bu)₃(OTf) reacts slowly with neat THF-d₈ to form neopentane and Re(Č-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(THF)ₙ(OTf). THF is readily lost in vacuo, however, and Re(Č-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(THF)ₙ(OTf) could not be isolated.
The reaction of Re(C-t-Bu)(CH₂-t-Bu)₃(BF₄) with excess acetonitrile yields colorless crystals of Re(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(CH₃CN)₂(BF₄) in 70 - 80% yield. However, tetrafluoroborate complexes containing coordinating ligands other than CH₃CN could not be isolated. The reaction of Re(C-t-Bu)(CH₂-t-Bu)₃(BF₄) with CD₃OD and THF-d₈ is similar to that of the triflate complexes. Re(C-t-Bu)(CH₃-t-Bu)(CH₂-t-Bu)(L)ₙ(BF₄) (L = CD₃OD, THF-d₈) and neopentane are formed when Re(C-t-Bu)(CH₂-t-Bu)₃(BF₄) is dissolved in CD₃OD or THF-d₈; these complexes could not be isolated. The reaction of Re(C-t-Bu)(CH₂-t-Bu)₃(BF₄) with 3 equivalents of pyridine in C₆D₆ was observed to proceed cleanly by ¹H NMR to yield Re(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(py)₂(X) (X = F or BF₄) but no clean product could be isolated no matter how carefully the reaction conditions are controlled. It is possible that fluoride abstraction from the BF₄ anion is occurring.

The reaction of [Re(C-t-Bu)(CH₂-t-Bu)₃(Et₂O)]⁺[BARF₄]⁻ with pyridine or acetonitrile in ether yields [Re(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(L)₃⁺[BARF₄]⁻ (L = py, CH₃CN) virtually quantitatively. Lower yields (70%) are obtained if [Re(C-t-Bu)(CH₂-t-Bu)₃(Et₂O)]⁺[BARF₄]⁻ is generated in situ and pyridine or acetonitrile is added - however, this reduces the problem of contamination by water.
The reaction of \([\text{Re(C-t-Bu)CH}_2\text{-t-Bu)}_3(\text{H}_2\text{O})(\text{Et}_2\text{O})]^+ [\text{BARF}_4]^-\) with 3 equivalents of pyridine in ether yields peach-colored cubes of \([\text{Re(C-t-Bu)CH-t-Bu)CH}_2\text{-t-Bu)}(\text{py})_2(\text{py-H}_2\text{O})]^+ [\text{BARF}_4]^-\). The water molecule could not be observed by IR or NMR spectroscopy. However, crystals of \([\text{Re(C-t-Bu)CH-t-Bu)CH}_2\text{-t-Bu)}(\text{py})_2(\text{py-H}_2\text{O})]^+ [\text{BARF}_4]^-\) suitable for X-ray diffraction were grown from \(\text{Et}_2\text{O/pentane } (3/1 \text{ v/v})\) at \(-40^\circ\text{C}\) and the structure was determined by X-ray crystallography. Dr. W. M. Davis collected the data set and Dr. W. M. Davis and Prof. C. C. Cummins solved the structure. Unfortunately, due to disorder in the \(\text{CF}_3\) groups and the large number of atoms in the molecule, the structure could not be refined satisfactorily. Nonetheless, the connectivity in the cationic fragment could be established. The water molecule was observed to be coordinated to rhenium \textit{trans} to neopentylidyne ligand, and a molecule of pyridine was located within hydrogen-bonding distance to the water molecule.

All of the rhenium neopentyl, neopentylidene, neopentylidyne complexes described in this section were stable to water in \(\text{C}_6\text{D}_6\), \(\text{CD}_2\text{Cl}_2\), pyridine-d5, or THF-d8. Unfortunately, they were not water soluble so their reactivity in water could not be investigated. Methanol was substituted when a protic solvent was required.

**Synthesis of \(\text{Re(C-t-Bu)CH-t-Bu)CH}_2\text{-t-Bu)(L)} (L = \text{Cp, HBPz}_3, \text{LOEt}_3\)**

The \([\text{Re(C-t-Bu)CH}_3\text{-t-Bu)}_2\text{(C}_2\text{-t-Bu)^+}\) core can be modified by addition of neutral or mono(anionic) six-electron ligands. The reaction of \(\text{Re(C-t-Bu)CH-t-Bu)(CH}_2\text{-t-Bu)(py)}_2(\text{OTf})\) with \(\text{NaL (L = Cp, HBPz}_3, [\text{CpCo(PO(\text{OEt})_2)_3}] ("\text{LOEt}_3")\) in THF cleanly produces \(\text{Re(C-t-Bu)(CH-t-Bu)CH}_2\text{-t-Bu)}(L)\) in 80-95% yield. (Scheme 1.2)
Scheme 1.2: Synthesis 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)(L)(H)$_3$-S$_3$C$_6$H$_{12}$(OTf).
A cationic complex that is similar to Re(C-\text{-}Bu)(CH-t-Bu)(CH_2-t-Bu)(L) can also be synthesized. Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)(py)_2(OTf) reacts with 1,4,7-trithia-\text{cyclon}onane in dichloromethane to form colorless crystals of [Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)](S_3C_6H_{12})][OTf] in virtually quantitative yield.

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. The synthesis of these complexes demonstrates the ability of the [Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)]^+ core to support a wide range of ligand environments. It should be noted that although the synthesis of Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)(L) proceeds very cleanly when the stable [Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)]^+ core is already present, the reaction of Re(C-t-Bu)(CH-t-Bu)(L)(Cl) with neopentyl lithium or t-BuCH_2MgCl does not yield Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)(L). Reduction to unknown products occurs instead.

**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)(\eta^3-S_3C_6H_{12})]^+[OTf]^- with Acids**

As mentioned in the introduction, cationic complexes of the general formula [Re(C-t-Bu)(CH-t-Bu)(L)]^+ (L = Cp, L_{OEt}, HBpz_3) were of interest as potential olefin metathesis catalysts. Initially, the most direct synthetic route to these complexes was investigated, and is shown below.

\[
\begin{align*}
1/x \ [\text{Re(C-t-Bu)(CH-t-Bu)Cl}_2]_x + \text{NaI} & \xrightarrow{\text{THF}, 25^\circ C} \ \text{Re(C-t-Bu)(CH-t-Bu)(L)(Cl)} \\
\text{- NaCl} & \\
\text{Re(C-t-Bu)(CH-t-Bu)(L)(Cl) + AgX} & \xrightarrow{\text{}} \ [\text{Re(C-t-Bu)(CH-t-Bu)(L)]^+[X]}^- \\
\text{- AgCl} &
\end{align*}
\]

**Scheme 1.3: Proposed Synthesis of [Re(C-t-Bu)(CH-t-Bu)(L)]^+[X]^-.**
The complexes Re(\(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{L})(\text{Cl})\) are readily synthesized from \([\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})\text{Cl}_2]_x\) and one equivalent of \(\text{NaL (L = Cp, LOE}_{t\text{Bu}}\) in THF. \(\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{Cp})(\text{Cl})\) has been previously reported.\(^5\) Unfortunately, all attempts to abstract the chloride ion with silver or thallium salts were unsuccessful, and thus a more indirect route to complexes containing the \([\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{L})]^+\) core was developed using a combination of protonation and \(\alpha\)-hydrogen abstraction reactions similar to that used in the synthesis of \(\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{CH}_2\text{-}t\text{-Bu})(\text{L})_n\text{X}\).

The reaction of \(\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{CH}_2\text{-}t\text{-Bu})(\text{L})\) (\(\text{L = Cp, CpCo(PO(OE}_{t\text{Bu}}\text{)}_2\text{)}_3\)) with triflic acid in ether yields \(\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{L})(\text{OTf})\) in moderate (50 - 80\%) yield. We believe that the reaction proceeds via initial protonation of \(C_\alpha\) of the alkylidene ligand to form \(\text{Re}(\text{C-}t\text{-Bu})(\text{CH}_2\text{-}t\text{-Bu})_2(\text{L})(\text{OTf})\), followed by \(\alpha\)-hydrogen abstraction to form neopentane and \(\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{L})(\text{OTf})\), although in this system, there is no direct evidence for this mechanism. It should be noted that although \(d^0\), cationic "\([\text{Re}(\text{C-}t\text{-Bu})(\text{CH}_2\text{-}t\text{-Bu})_2(\text{L})]^+\)" is unstable and undergoes an \(\alpha\)-hydrogen abstraction, the neutral \(d^2\) osmium complexes \(\text{Os}(\text{C-}t\text{-Bu})(\text{CH}_2\text{-}t\text{-Bu})_2(\text{L})\) described in Chapter 3 show no evidence of \(\alpha\)-hydrogen abstraction. This result nicely illustrates the lowered tendency for \(\alpha\)-hydrogen abstraction to occur in \(d^2\) complexes of osmium. Further comparisons between \(d^0\) complexes of Mo, W, and Re and \(d^2\) complexes of osmium will be made in Chapters 2-4.

\[
\text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{CH}_2\text{-}t\text{-Bu})(\text{L}) + \text{HX} \rightarrow \text{Re}(\text{C-}t\text{-Bu})(\text{CH}_2\text{-}t\text{-Bu})_2(\text{L})(\text{X})
\]

\[
\text{Re}(\text{C-}t\text{-Bu})(\text{CH}_2\text{-}t\text{-Bu})_2(\text{L})(\text{X}) + \text{CMe}_4 \rightarrow \text{Re}(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{L})(\text{X})
\]

\textit{Scheme 1.4: Proposed Mechanism of Formation of Re(\text{C-}t\text{-Bu})(\text{CH-}t\text{-Bu})(\text{L})(\text{X}).}
Re(C-t-Bu)(CH-t-Bu)(L_{OE})_2(OTf) is a thermally stable complex. Because of its stability we believe it is a neutral six coordinate complex rather than a cationic complex. Re(C-t-Bu)(CH-t-Bu)(Cp)(OTf) can be isolated as a colorless microcrystalline solid in 84% yield; however, it is thermally unstable, especially in the solid state, decomposing to form an insoluble blue material. If Re(C-t-Bu)(CH-t-Bu)(Cp)(OTf) is a neutral species, it is nominally a 6-coordinate, 18-electron species. If it exists as the cationic species, [Re(C-t-Bu)(CH-t-Bu)(Cp)]^+[OTf]^ - (or if the triflate ligand is labile) an α-agostic interaction is possible. 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 of Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)(Cp) and pyHOTf in CH_2Cl_2.

The reaction of Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)(L_{OE})_2 with [H(OEt)_2]^+[BARF_4]^ - in ether at -40°C proceeds cleanly to yield yellow, crystalline [Re(C-t-Bu)(CH-t-Bu)(L_{OE})(Et_2O)]^+[BARF_4]^ -. The presence of the tridentate ligand L_{OE} requires that the neutral ether ligand be located cis to the neopentylidyne and neopentylidyne ligands, although this is not normally the preferred site for a neutral donor ligand in six-coordinate alkylidene, alkylidyne complexes.

The reaction of [Re(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)(S_3C_6H_{12})]^+[OTf]^ - with triflic acid in CH_2Cl_2 proceeds cleanly to yield [Re(C-t-Bu)(CH-t-Bu)(S_3C_6H_{12})(OTf)]^+[OTf]^ -. The two triflate ligands are inequivalent by ^19F NMR in CD_2Cl_2 and THF-d_8, suggesting a mono(cationic) structure. It should be noted that although bis(triflate) complexes of the M(NR)(CHR') core (M = Mo, W) are very common,^221 [Re(C-t-Bu)(CH-t-Bu)(S_3C_6H_{12})(OTf)]^+[OTf]^ - is the first bis(triflate) complex containing the Re(C-t-Bu)(CH-t-Bu) core, despite extensive synthetic efforts in this group towards such complexes. It is possible that the tridentate ligands such as
1,4,7-trithiacyclononane are necessary to stabilize the highly electrophilic [Re(C-r-Bu)(CH-r-Bu)(OTf)$_2$] core.

The reaction of Re(C-r-Bu)(CH-r-Bu)(CH$_2$-r-Bu)(Cp) with [H(OEt)$_2$]$_2$+[BarF$_4$] or pyHBarF$_4$ in CH$_2$Cl$_2$ or ether failed to yield any isolable products. It is unclear why the cyclopentadienyl complexes are more unstable than the complexes containing oxygen or sulfur ligands. Slippage of the cyclopentadienyl ring may be one possible cause of the instability of these complexes. The reaction of Re(C-r-Bu)(CH-r-Bu)(CH$_2$-r-Bu)(HBpz$_3$) with triflic acid or [H(OEt)$_2$]$_2$+[BarF$_4$] does not yield any clean products. In this case, acid may attack the tris(pyrazolyl)borate ligand and cause decomposition.

Reactions of the Neopentylidene, Neopentylidyne Complexes with Terminal Olefins

The reaction of terminal olefins with the rhenium neopentylidene, neopentylidyne complexes was investigated. The catalytic metathesis of terminal olefins is interest because ethylene can be selectively removed from the product mixture, allowing the isolation of the desired coupled alkenes. Similarly, acyclic terminal dienes can be polymerized by acyclic diene metathesis polymerization (ADMET).

Alkyldiene complexes that cleanly metathesize terminal olefins are required to initiate both ADMET and the metathetical coupling of terminal olefins. Additionally, the intermediate methylidene and substituted alkyldiene complexes must be relatively stable towards bimolecular decomposition. H. Fox had found that the use of coordinating solvents such as DME stabilizes the intermediate alkyldiene complexes and permits effective metathesis of terminal olefins and dienes. Since many of the rhenium neopentylidene, neopentylidyne complexes described in this chapter are
already five- or six-coordinate, they were excellent possible candidates for the
metathesis of terminal olefins.

The reaction of Re(C-t-Bu)(CH-t-Bu)(CH$_2$-t-Bu)(py)$_2$(OTf) with H$_2$C=CHR (R = OC$_2$H$_2$CH$_3$, C$_6$H$_5$) in benzene or dichloromethane results in formation of neohexene
and isolation of the substituted alkylidene complex, Re(C-t-Bu)(CHR)(CH$_2$-t-
Bu)(py)$_2$(OTf). No evidence for formation of the methyldiene complex, Re(C-t-
Bu)(CH$_2$)(CH$_2$-t-Bu)(py)$_2$(OTf), is seen.

\[\text{Re(C-t-Bu)(CH-t-Bu)(CH$_2$-t-Bu)(py)$_2$(OTf)} + H_2C=CHR \rightarrow \text{Re(C-t-Bu)(CHR)(CH$_2$-t-Bu)(py)$_2$(OTf)} \]

\[R = C$_6$H$_5\]
OEt

Hydrogen scrambling between the alkyl, alkylidene, and alkylidyne ligands in
these complexes cannot be totally ruled out without a crystal structure determination.
However, in d$^0$ systems, hydrogen scrambling among alkyl and alkylidene$^{23}$ or
alkylidyne$^{24}$ ligands has been found to be a relatively high energy process. Re(C-t-
Bu)(CHFc)[OC(CF$_3$)$_2$Me]$_2$ (Fc = (C$_5$H$_4$)FeCp) and Re(C-t-Bu)(CH-
OEt)[OC(CF$_3$)$_2$Me]$_2$(THF)$_2$ were prepared by the reaction of Re(C-t-Bu)(CH-t-
Bu)[OC(CF$_3$)$_2$Me]$_2$ with vinyl ferrocene or ethyl(vinyl)ether, respectively; X-ray
structure determinations revealed that no scrambling of H$_2$ had occurred between the
carbene and neopentylidyne ligands.$^{6}$ Likewise, Re(C-t-Bu)(CH-t-Bu)(CD$_2$-t-Bu)$_2$
showed no evidence for H/D scrambling among the neopentyl and neopentylidyne
ligands at 80°C in toluene-d8. Based on these experiments, we believe that scrambling of Hα does not occur in the alkyl, alkyldiene, alkyldyne systems and the complexes can be described by the formula Re(C-t-Bu)(CHR)(CH2-t-Bu)(py)2(OTf).

The ethoxymethylidene complex, Re(C-t-Bu)(CHOEt)(CH2-t-Bu)(py)2(OTf) is isolated as a pink powder. It shows no evidence of bimolecular decomposition; this result is consistent with earlier studies in which Re(C-t-Bu)(CH-t-Bu)(OR)2 reacts with ethyl vinyl ether to form transient Re(C-t-Bu)(CHOEt)(OR)2, which can be trapped as the six-coordinate base adduct, Re(C-t-Bu)(CHOEt)(OR)2(THF)2 or, in the absence of coordinating ligands, decomposes to [Re(C-t-Bu)(OR)2]2. The two bound pyridine molecules are inequivalent on the NMR time scale at 25°C in CDCl3, and exchange with added pyridine does not occur on the NMR time scale under these conditions.

Re(C-t-Bu)(CHC6H5)(CH2-t-Bu)(py)2(OTf) is isolated as beige crystals. As is the case with Re(C-t-Bu)(CHOEt)(CH2-t-Bu)(py)2(OTf), the two bound pyridine ligands are inequivalent on the NMR time scale in CDCl3 at 25°C. It is likely that in these less crowded complexes, pyridine is bound more tightly than in Re(C-t-Bu)(CH-t-Bu)(CH2-t-Bu)(py)2(OTf).

The reaction of Re(C-t-Bu)(CH-t-Bu)(CH2-t-Bu)(py)2(OTf) with ethylene in C6D6 or CD2Cl2 is more complex and is summarized in Scheme 1.5. Initially, neohexene is formed and the methylidene complex, Re(C-t-Bu)(CH2)(CH2-t-Bu)(py)2(OTf), is observed. No evidence for metallacycle formation is seen. The methylidene complex is fairly unstable in C6D6, even in the presence of 2-5 equivalents of pyridine. Upon isolation it decomposes to Re(C-t-Bu)((CH2)3-t-Bu)((C2H4)(py)2(OTf) (see below) and unidentified decomposition products. Addition of bpy to solutions of Re(C-t-Bu)(CH2)(CH2-t-Bu)(py)2(OTf) results in formation of red Re(C-t-Bu)(CH2)(CH2-t-Bu)(bpy)(OTf) which can be recrystallized with difficulty from toluene/ether mixtures at -40°C.
Scheme 1.5: Reaction of $\text{Re(\text{-}C\text{-}t\text{-}Bu)(\text{CH-t-Bu})(\text{CH}_2\text{-}t\text{-}Bu)(\text{py})_2(OTf)}$ with Ethylene.
Re(C-\text{-}t\text{-}Bu)(\text{CH}_2)(\text{CH}_2\text{-}t\text{-}Bu)(\text{bpy})(\text{OTf}) is somewhat unstable and for this reason it has only been characterized by $^1\text{H}$ NMR and partially by $^{13}\text{C}$ NMR. Two doublets ($J_{\text{H-H}} = 3 \text{ Hz}$) corresponding to $\text{H}_\alpha$ of the methylene ligand are observed at 14.03 ($J_{\text{C-H}} = 135 \text{ Hz}$) and 13.50 ppm ($J_{\text{C-H}} = 150 \text{ Hz}$).

The reaction of Re(\text{C-}t\text{-}Bu)(CH-t-Bu)(\text{CH}_2-t-Bu)(\text{py})_2(\text{OTf}) with excess ethylene in benzene or dichloromethane yields a colorless microcrystalline solid whose $^1\text{H}$ NMR spectrum was observed to contain 2 inequivalent tert-butyl groups, 2 inequivalent bound pyridines, and a series of complex multiplets corresponding to 5 sets of inequivalent methylene groups. Because of the complexity of the spectrum and the fact that some of the peaks overlapped, it was impossible to assign this portion of the spectrum. $^{19}\text{F}$ NMR confirmed the presence of the triflate anion, and elemental analysis confirmed the formulation ReC$_{25}$H$_{38}$N$_2$F$_3$O$_3$S. In a related system, the reaction of Mo(NAr)(CH-t-Bu)(OR)$_2$ with excess ethylene was found to yield an unstable species whose $^1\text{H}$ NMR were consistent with a molybdenum metallacyclopentane.$^{26}$ Thus, the product of the reaction of Re(\text{C-}t\text{-}Bu)(\text{CH}-t\text{-}Bu)(\text{CH}_2-t-Bu)(\text{py})_2(\text{OTf}) with excess ethylene was initially thought to be a metallacyclopentane complex, Re(\text{C-}t\text{-}Bu)(\text{CH}_2-t-Bu)((\text{CH}_2)_4)(\text{py})_2(\text{OTf})$.

However, experiments employing $^{13}\text{CH}_2^{13}\text{CH}_2$ and CD$_2$CD$_2$ proved that the product obtained is not a metallacyclopentane complex. First, the reaction of Re(\text{C-t-Bu})(\text{CH-t-Bu})(\text{CH}_2-t-Bu)(\text{py})_2(\text{OTf}) with $^{13}\text{CH}_2^{13}\text{CH}_2$ revealed that rather than observing 2 or 4 isotopically enhanced peaks in the $^{13}\text{C}$ spectrum, as would be expected for a symmetric or asymmetric metallacyclopentane complex, respectively, three isotopically enriched peaks were observed. The proposed structure and a partial atom labeling scheme are shown in Figure 1.1.
Figure 1.1: Proposed structure and partial atom labeling scheme for Re(C-t-Bu)(CH-t-Bu)(CH\textsubscript{2}-t-Bu)(py)\textsubscript{2}(OTf).

A singlet at 20 ppm (C(4) and C(4')); \( J_{\text{CH}} = 123 \) Hz was observed in the isotopically enriched \( ^{13}\text{C} \) NMR spectrum. This singlet corresponds to a molecule of ethylene bound \( \eta^2 \) to the metal center, as shown in Figure 1.1. Two doublets (\( J_{\text{CC}} = 36 \) Hz) were observed at 52 (\( J_{\text{CH}} = 153 \) Hz) and 46 ppm (\( J_{\text{CH}} = 156 \) Hz) suggesting that one equivalent of ethylene was incorporated in a manner that rendered the two carbon atoms magnetically inequivalent. The proposed connectivity of these carbon atoms (C(1) and C(2)) is shown in Figure 1.1. We believe that an insertion of one equivalent of ethylene into the metal carbon single bond had occurred. Data from the reaction of Re(C-t-Bu)(CH-t-Bu)(CH\textsubscript{2}-t-Bu)(py)\textsubscript{2}(OTf) with excess C\textsubscript{2}D\textsubscript{4} support this proposal. The reaction of Re(C-t-Bu)(CH-t-Bu)(CH\textsubscript{2}-t-Bu)(py)\textsubscript{2}(OTf) with excess C\textsubscript{2}D\textsubscript{4} yields a complex with a greatly simplified \( ^1\text{H} \) NMR. Two peaks which had been complex multiplets in the unlabeled complex appeared as doublets in the labeled complex and were assigned as the methylene protons on C(3), which were present in the original neopentyl ligand. The labeling experiments suggest that one of the molecules of ethylene had coordinated to the metal and the other had inserted into the metal-carbon
single bond, yielding \( \text{Re}(C-t\text{-Bu})[(CH_2)_3-t\text{-Bu}](C_2H_4)(py)_2(OTf) \). In this rather unusual series of reactions, an olefin metathesis catalyst begins to behave like a Ziegler-Natta catalyst upon decomposition. However, no further insertion of ethylene is observed at 25°C and 1 atm C_2H_4.

In the reaction of \( \text{Re}(C-t\text{-Bu})(CH-t\text{-Bu})(CH_2-t\text{-Bu})(py)_2(OTf) \) with an excess of ethylene, the only observed by-product is neoheptene (formed in the initial metathesis reaction) and the only observed intermediate is \( \text{Re}(C-t\text{-Bu})(CH_2)(CH_2-t\text{-Bu})(py)_2(OTf) \). No evidence of propylene or cyclopropane formation is observed by \(^1\)H NMR. The observed decomposition of \( \text{Re}(C-t\text{-Bu})(CH_2)(CH_2-t\text{-Bu})(py)_2(OTf) \) to \( \text{Re}(C-t\text{-Bu})[(CH_2)_3-t\text{-Bu}](C_2H_4)(py)_2(OTf) \) and unidentified decomposition products in the absence of ethylene suggests that \( \text{Re}(C-t\text{-Bu})(CH_2)(CH_2-t\text{-Bu})(py)_2(OTf) \) decomposes with loss of ethylene, probably through a bimolecular process. Such intermolecular coupling reactions are a common reduction pathway for methylidyne complexes. A possible mechanism of formation of \( \text{Re}(C-t\text{-Bu})[(CH_2)_3-t\text{-Bu}](C_2H_4)(py)_2(OTf) \) is shown in Scheme 1.5.

A variety of reduction pathways for transition metal alkylidenes and alkylidyenes 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-CC-t-Bu)), and a formally "3+2" addition of ethylene to a rhenium alkylidene-alkylidyne to form a metallacyclopentene complex.\(^{27} \) In the "3 + 2" reaction, the "supporting" neopentylidyne ligand is involved; this illustrates one potential pitfall in the design of transition metal catalysts. The reduction of \( \text{Re}(C-t\text{-Bu})(CH-t\text{-Bu})(CH_2-t\text{-Bu})(py)_2(OTf) \) to \( \text{Re}(C-t\text{-Bu})[(CH_2)_3-t\text{-Bu}](py)_2(OTf) \) provides another example of involvement of the supporting ligands, in this case the neopentyl group.
The facile reduction of Re(C-t-Bu)(CH₂)(CH₂-t-Bu)(py)₂(OTf) in the presence of excess ethylene suggests that these complexes are not suitable ADMET catalysts. H. Fox had found that the use of a coordinating solvent slowed the rate of bimolecular decomposition. However, even in the presence of 5-10 equivalents of pyridine, Re(C-t-Bu)(CH₂)(CH₂-t-Bu)(py)₂(OTf) is readily reduced.

Benzene solutions of Re(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(CH₃CN)₂(BF₄) 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)(CH₂-t-Bu)(L)₃]+[BARF₄]⁻ (py, CH₃CN) do not react with styrene, ethyl vinyl ether or ethylene in ether. Likewise, all of the neutral or cationic complexes containing a tridentate ligand (Re(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(L), Re(C-t-Bu)(CH-t-Bu)(L)(OTf), [Re(C-t-Bu)(CH-t-Bu)(L)(OEt₂)]⁺, [Re(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(S₃C₆H₁₂)]⁺OTf⁻, or [Re(C-t-Bu)(CH-t-Bu)(S₃C₆H₁₂)(OTf)]⁺[OTf⁻] do not react 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 (C₆D₆, 25°C, 5-10 equiv. olefin) Re(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(py)₂(OTf) reacts rapidly with terminal olefins, but Re(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(bpy)(OTf) does not react.

Reaction of the Neopentylidene, Neopentylidyne Complexes with Unstrained Internal Olefins

The metathesis of asymmetric, unstrained internal olefins is an important industrial process, allowing the conversion of inexpensive olefins into more valuable products. For instance, metathesis of methyl oleate (Me(CH₂)₇CH=CH(CH₂)₇CO₂Me) yields a 1:2:1 mixture of Me(CH₂)₇CH=CH(CH₂)₇Me, Me(CH₂)₇CH=CH(CH₂)₇CO₂Me, and MeO₂C(CH₂)₇CH=CH(CH₂)₇CO₂Me; the
diester thus obtained can be converted in good yield to civetone, a fairly expensive chemical used extensively in the perfume industry. However, the metathesis of unstrained internal olefins requires a more active catalyst than is needed for the metathesis of terminal or strained cyclic olefins. Re(C-t-Bu)(CH-t-Bu)[OC(CF3)2Me]2 was found to have a maximum turnover rate of 250 h⁻¹ for cis-2-pentene and 17 h⁻¹ for methyl oleate, and an initiation period was required.⁴,⁶ The reactivity of the rhenium neopentyldiene, neopentylidyne complexes described above with unstrained internal olefins was investigated.

Re(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(CH₃CN)(OTf) reacts rapidly with 5-10 equivalents of cis-3-hexene in C₆D₆ to yield a new propylidene complex. In the absence of coordinating solvents, "Re(C-t-Bu)(CHCH₂CH₃)(CH₂-t-Bu)(CH₃CN)(OTf)" decomposes within 1 hour at 25°C. It is likely that this complex is unstable to bimolecular decomposition. Similar results were obtained in the reaction of Re(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(CH₃CN)(OTf) with methyl oleate and oleic acid. When the reaction of Re(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(CH₃CN)ₙ(OTf) with 5-10 equivalents of cis-3-hexene in C₆D₆ is conducted in the presence of 5-10 equivalents of CH₃CN, Re(C-t-Bu)(CHCH₂CH₃)(CH₂-t-Bu)(CH₃CN)ₙ(OTf) forms within 10 minutes; this propylidene complex is slightly more stable, but decomposes within 4 hours in C₆D₆. The presence of a few equivalents of acetonitrile does not shut down the reaction with internal olefins, but it does stabilize the propylidene complex somewhat. However, in neat CD₃CN, Re(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(CH₃CN)ₙ(OTf) does not react with 4 equivalents of cis-2-hexene at 25°C. At 60°C metathesis occurs slowly (2:1 propylidene/neopentylidyne after 1 hour). Re(C-t-Bu)(CHCH₂CH₃)(CH₂-t-Bu)(CH₃CN)ₙ(OTf) is stable for 24 hours at 25°C.

Toreki had observed that an initiation period was required for the bulky rhenium neopentylidyne complexes, so it was thought that Re(C-t-Bu)(CHCH₂CH₃)(CH₂-t-
Bu)(CH₃CN)ₙ(OTf) might be a suitable metathesis catalyst in CD₃CN. To test this hypothesis, excess 2,2,2-trimethyl-3-hexene was added to a CD₃CN solution of Re(C-t-Bu)(CHCH₂CH₃)(CH₂-t-Bu)(CH₃CN)ₙ(OTf) at 25°C. If metathesis of internal olefins by Re(C-t-Bu)(CHCH₂CH₃)(CH₂-t-Bu)(CH₃CN)ₙ(OTf) occurred at 25°C, the reaction with 2,2,2-trimethyl-3-hexene would yield a mixture of the propylidene and neopentylidene species. Since it was already established that the neopentylidene species does not react with internal olefins at 25°C, the reaction might be expected to lead to a net conversion back to the neopentylidene complex (and a mixture of olefins). However, no metathesis was observed at room temperature, suggesting that Re(C-t-Bu)(CHCH₂CH₃)(CH₂-t-Bu)(CH₃CN)ₙ(OTf) is not much more reactive than its neopentylidene precursor.

When the reaction of 100 equivalents of cis-2-pentene with Re(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(CH₃CN)(OTf) at 25°C in benzene is monitored by gas chromatography, a 1:2:1 (equilibrium) mixture of butenes: pentenes: hexenes is reached in less than 5 minutes. However, no further metathesis is observed when an additional 100 equivalents of cis-2-pentene is added one hour later. Since the NMR experiments conducted in the presence of acetonitrile did not seem to offer many advantages over those done in benzene, analogous reactions were not monitored by gas chromatography.

The reaction of Re(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(CD₃OD)ₙ(OTf) with 5-10 equivalents of cis-3-hexene in CD₃OD occurs within 30 minutes at 25°C. Re(C-t-Bu)(CHCH₂CH₃)(CH₂-t-Bu)(CD₃OD)(OTf) is stable for several hours at 25°C in CD₃OD. However, very little (<5%) metathesis was observed in the reaction of Re(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(CH₃OH)ₙ(OTf) with 100 equivalents of cis-2-heptene in CH₃OH.
None of the other rhenium alkylidene complexes described in this chapter reacts with unstrained internal olefins. It is likely that the low reactivity can be traced to the fact that the neutral donor ligands and/or the multidentate ligands \( L \) (\( L = \text{Cp}, \text{HBpz}_3, \text{L}_{\text{OE1}}, \text{S}_3\text{C}_6\text{H}_{12} \)) are not particularly labile.

Reactions of the Rhenium Neopentylidene, Neopentylidyne Complexes with Strained Cyclic Olefins

The ring opening metathesis polymerization (ROMP) of strained cyclic olefins by the rhenium neopentylidene complexes was investigated. NMR studies showed \( \text{Re(C-t-Bu)(CH}_4\text{t-Bu)(CH}_2\text{t-Bu)(py)}_2(\text{OTf}) \) to be potentially a good catalyst, with \( k_p/k_i < 2 \) in \( \text{C}_6\text{D}_6 \). \( \text{Re(C-t-Bu)(CH}_2\text{t-Bu)(CH}_2\text{t-Bu)(py)}_2(\text{OTf}) \) reacts with 100 equivalents of norbornene in benzene to form poly(norbornene). The polymer was capped with benzaldehyde, precipitated with methanol, and analyzed by GPC. A bimodal distribution was seen, suggesting that there were either capping problems or oxygen contamination prior to quenching. The polydispersity \( (M_w/M_n = 1.23) \) was rather high but still indicative of a living polymerization. The polydispersities of the individual peaks was 1.06.

Due to the fairly low yields (50-70%) obtained, the capping problems, and the bimodal distributions observed in the polymers, it appeared that \( \text{Re(C-t-Bu)(CH}_2\text{t-Bu)(CH}_2\text{t-Bu)(py)}_2(\text{OTf}) \) is not an ideal ROMP catalyst, and the polymerization chemistry was not explored further. However, \( \text{Re(C-t-Bu)(CH}_2\text{t-Bu)(CH}_2\text{t-Bu)(py)}_2(\text{OTf}) \) may prove to be a reasonable ROMP catalysts for monomers that cannot be polymerized by other means, such as monomers containing hydroxyl groups.
Discussion and Conclusions.

The synthesis of the rhenium neopentyl, neopentylidene, neopentyldiyne complexes proved to be straightforward. A wide variety of coordinating ligands were found to induce \( \alpha \)-hydrogen abstraction reactions in Re(C-t-Bu)(CH\(_2\)-t-Bu)\(_3\)(X) (X = OTf, BAr\(^F\)\(_4\)). Particularly interesting is the finding that acetonitrile and methanol can induce \( \alpha \)-hydrogen abstraction reactions; these ligands are frequently incompatible with alkylidene complexes of tantalum, molybdenum and tungsten, and this result is a nice example of the greater tolerance of rhenium-carbon multiple bonds for a variety of organic functional groups. Another interesting feature is that for these systems, the coordinating ligands must be fairly nucleophilic but not particularly basic. The reaction of Re(C-t-Bu)(CH\(_2\)-t-Bu)\(_3\)(OTf) with quinuclidine or tert-butylamine results in deprotonation at C\(_\alpha\) to form Re(C-t-Bu)(CH-t-Bu)(CH\(_2\)-t-Bu)\(_2\). Edwards had observed similar results with Re(C-t-Bu)(CH\(_2\)-t-Bu)\(_3\)Cl.

Although quantitative experiments were not possible, the \( \alpha \)-hydrogen abstraction was significantly faster in the systems complexes which could possibly form cationic intermediates. Thus, for a given ligand, \( \alpha \)-hydrogen abstraction reactions of Re(C-t-Bu)(CH\(_2\)-t-Bu)\(_3\)(X) (X = OTf, BAr\(^F\)\(_4\)) were much faster than for Re(C-t-Bu)(CH\(_2\)-t-Bu)\(_3\)(X) (X = Cl, OC\(_6\)F\(_5\)). For instance, the reaction of Re(C-t-Bu)(CH\(_2\)-t-Bu)\(_3\)(OTf) with three equivalents of pyridine in ether or pentane was complete within 10 minutes at 25°C, while the reaction of Re(C-t-Bu)(CH\(_2\)-t-Bu)\(_3\)Cl with neat pyridine-\( d_5 \) required 24 hours. These observations are consistent with earlier findings that demonstrated that \( \alpha \)-hydrogen abstraction reactions are faster in systems that are cationic or strongly polarized.\(^{20}\)

The synthesis of a large number of complexes containing the rhenium neopentyl, neopentylidene, neopentyldiyne core suggests that this system can support a
wide range of ligand environments. Once formed, the rhenium neopentyl, neopentyldiene, neopentyldyne core is quite stable. All of the complexes described which contain the rhenium neopentyl, neopentyldiene, neopentyldyne core are thermally stable and in the solid state are moderately stable to air and water, and are stable to water in solution. 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 reactivity of the rhenium neopentyldiene, neopentyldyne complexes with a variety of olefins was investigated. As anticipated, some control over the reactivity is possible by varying the counterion and type of neutral ligands present. For instance, Re(C-t-Bu)(CH-t-Bu)(CH_{2-t-Bu})(py)_2(OTf) reacts cleanly with terminal olefins and strained cyclic olefins at 25°C, but does not react with unstrained internal olefins under these conditions. Thus, it is a potential catalyst for ROMP, ADMET, and the coupling of terminal olefins. By replacing pyridine with acetonitrile in the coordination sphere, a much more reactive system is generated, and Re(C-t-Bu)(CH-t-Bu)(CH_{2-t-Bu})(CH_3CN)_n(OTf) reacts rapidly with unstrained internal olefins.

The reactivity of the complexes described here is linked to lability of the donor ligands. For instance, under identical conditions, Re(C-t-Bu)(CH-t-Bu)(CH_{2-t-Bu})(py)_2(OTf) reacts with terminal olefins but Re(C-t-Bu)(CH-t-Bu)(CH_{2-t-Bu})(bpy)(OTf) does not. 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 in the coordinated pyridine, acetonitrile, or ether to be bound quite tightly to the metal, and no reactivity with olefins is observed. In these systems, the use of a "partially coordinating" ligand such as triflate results in complexes that are better catalysts.
Unfortunately, the lability of the neutral donor ligands which allows the complexes to react with olefins also makes the complexes susceptible to bimolecular decomposition. This is observed in the reduction of \( \text{Re}(C-t\text{-Bu})(\text{CH}_2)(\text{CH}_2-t\text{-Bu})(\text{py})_2(\text{OTf}) \) to \( \text{Re}(C-t\text{-Bu})((\text{CH}_2)_3-t\text{-Bu})(\text{C}_2\text{H}_4)(\text{py})_2(\text{OTf}) \) and the instability of \( \text{Re}(C-t\text{-Bu})(\text{CHCH}_2\text{CH}_3)(\text{CH}_2-t\text{-Bu})(\text{CH}_3\text{CN})_n(\text{OTf}) \). The alkyl, alkylidene, alkylidyne core is bulky enough when there is a tert-butyl substituent on the alkylidene, but when the alkylidene has a smaller substituent these complexes decompose readily, even in the presence of excess pyridine or acetonitrile.

In an attempt to surmount the problem of ligand dissociation, the complexes containing tridentate ligands such as \( \text{Cp}, \text{HBpz}_3, \text{L}_{\text{OE}} \text{t} \) and 1, 4, 7-trithiacyclononane were synthesized and their reactivity with olefins was investigated. However, cationic \( [\text{Re}(C-t\text{-Bu})(\text{CH}-t\text{-Bu})(L)]^+ \) 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 \( \text{Re}(C-t\text{-Bu})(\text{CH}-t\text{-Bu})(L) \) fragment typically binds another ligand (triflate, pyridine, ether), forming 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,\(^{11,12} \) nor does 5-coordinate \( \text{Re}(\text{NAr})(\text{CH}-t\text{-Bu})[\text{OC}(\text{CF}_3)_2\text{Me}]_3 \) or six-coordinate \( \text{Re}(\text{O})(\text{CHCHCPh}_2)(\text{THF})[\text{OC}(\text{CF}_3)_2\text{Me}]_3. \)\(^8 \) These results reaffirm the proposal that in a successful, long-lived olefin metathesis catalyst, four coordination sites must be filled by non-labile, 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 \( \text{[Re(NAr)(CHR)(OR')_2]^+} \) and \( \text{[Re(N·BPPh_3)(CHR)(OR')_2} \) (if they could be synthesized) would be potentially useful as metathesis catalysts which might surpass the alkylidene-alkylidyne systems.
The synthesis and study of the rhenium neopentyl, neopentylidene, neopentyldyne complexes described here was an informative exercise in catalyst design and synthetic organometallic chemistry, even though no truly useful metathesis catalysts were developed. Many of the d⁰ rhenium complexes here are similar to the d⁲ osmium complexes described in Chapters 2-4, allowing comparisons to be made and providing new insight into the nature of the metal-carbon single, double, and triple bonds for the middle transition metals.
Experimental

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 CaCl₂, and then distilled from sodium benzophenone ketyl. Ether, tetrahydrofuran, 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. Tetrahydrofuran-d₈ was vacuum transferred from sodium benzophenone ketyl. C₆D₆, CD₂Cl₂, CDCl₃, CD₃CN, and pyridine-d₅ were stored over activated molecular sieves in the drybox. CD₃OD was used as received.

Neopentyl chloride was purchased from Strem and purified by literature methods.²⁸ NpMgCl²⁸ and Np₂Zn²³ were prepared by the published procedure. Rhenium heptaoxide (99.99%) was purchased from Aesar. [Re(C-t-Bu)(CH-t-Bu)Cl₂]₅ and [Re(C-t-Bu)(CH-t-Bu)(t-BuNH₂)Cl₂]₁₅ were prepared by literature methods, and Re(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu)₂ was prepared by the published procedure¹⁵ or from [Re(C-t-Bu)(CH-t-Bu)Cl₂]ₓ and t-BuCH₂MgCl in THF at -40°C. [H(OEt₂)₂]⁺[BaR₄]⁻ was prepared by literature methods.¹⁰ Na[CpCo(PO(OEt)₂)₃]¹³ was a generous gift from Dr. Robert D. Simpson. Ethylene (polymer grade) was purchased from Matheson and used as received. ¹³C₂H₄ and C₂D₄ were purchased from Cambridge Isotope Laboratories. 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$_2$Cl$_2$ 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.

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\text{Re(C-t-Bu)(CH}_2\text{-t-Bu)}_2(\text{OTf})_3. \text{Re(C-t-Bu)(CH}_2\text{-t-Bu)}_2(\text{CH}_2\text{-t-Bu)}_2 \text{(1.07 g, 2.28 mmol) was dissolved in 15 mL Et}_2\text{O 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 hour. Ether was removed in vacuo, leaving a yellow-brown solid which was extracted with pentane (50 mL) and the solution was filtered through celite. The filtrate was concentrated to 10 mL and then cooled to -40°C. Yellow, microcrystalline Re(C-t-Bu)(CH}_2\text{-t-Bu)}_3(\text{OTf}) \text{was isolated, washed with cold pentane, and dried. (1.00 g, 71%). The spectral data for the compound prepared in this manner matched those reported.}^{15,19}
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[\text{Re(C-t-Bu)(CH}_2\text{-t-Bu)}_3(\text{Et}_2\text{O})]+[\text{BarF}_4]^- \text{. Re(C-t-Bu)(CH}_2\text{-t-Bu)}_2(\text{CH}_2\text{-t-Bu)}_2 (230 mg., 0.49 mmol.) was dissolved in 5 mL of Et}_2\text{O and solid } [\text{H(OEt}_2)_2]+[\text{BarF}_4]^- \text{ (489 mg, 0.49 mmol) was added. After stirring the solution for 30 minutes 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 Et}_2\text{O. (506 mg, 73%): } \text{^1H NMR (CD}_2\text{Cl}_2) \delta 7.7 (s, 8, Ar), 7.6 (s, 4, Ar), 3.55 (q, 4, OCH}_2\text{CH}_3), 2.65 (s, 6, ReCH}_2\text{-t-Bu), 1.65 (s, 9, ReC-t-Bu), 1.20 (t, 6, OCH}_2\text{CH}_3), 1.14 (s, 27, CH}_2\text{-t-Bu).}
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[Re(C-t-Bu)(CH2-t-Bu)3(Et2O)(H2O)]+[BARF4]- was prepared in a fashion identical to [Re(C-t-Bu)(CH2-t-Bu)3(Et2O)]+[BARF4]- except one equivalent of water was added by syringe prior to recrystallization from ether. 1H NMR (CD2Cl2) δ 7.75 (s, 8, Ar), 7.6 (s, 4, Ar), 7.0 (s, 2, OH2) 3.56 (q, 4, O(CH2CH3)2), 2.56 (s, 6, CH2-t-Bu), 1.65 (s, 9, C-t-Bu), 1.14 (s, 27, CH2-t-Bu); 13C NMR (CD2Cl2) δ 307.0 (ReC-t-Bu), 162.3 (q, CF3, JCF = 50 Hz), 135.3, 126.9, 123.3, 117.9 (Caryl), 86.0 (CH2-t-Bu), 66.2 (O(CH2CH3)2), 55.6 (CCMe3), 37.7 (CH2CMe3), 32.9 (CH2CMe3), 27.7 (CCMe3), 15.4 (O(CH2CH3)2). 19F NMR (CD2Cl2) δ -62.3. IR (Nujol) cm-1 3640 (O-H). Anal. Calcd for C56H66BF24O2: C, 47.23; H, 4.67. Obs. C, 47.53; H, 4.76.

[Re(C-t-Bu)(CH2-t-Bu)3]2+[BF4]-. Re(C-t-Bu)(CH-t-Bu)(CH2-t-Bu)2 (445 mg, 0.95 mmol.) was dissolved in 8 mL of Et2O and the solution was cooled to -40° C. 85% HBF4-Et2O (190 mg, 1.0 mmol.) was added and a yellow precipitate formed immediately. The mixture was allowed to warm to room temperature and stirred 30 minutes. The precipitate was collected and washed with pentane and determined to be >95% pure by 1H NMR. (305 mg = 58%): 1H NMR (CD2Cl2) δ 2.75 (s, 6, CH2-t-Bu), 1.62 (s, 9, C-t-Bu), 1.13 (s, 27, CH2-t-Bu); 13C NMR (CD2Cl2) δ 300.9 (C-t-Bu), 85.2 (CH2-t-Bu), 54.8 (CCMe3), 37.5 (CH2CMe3), 32.7 (CH2CMe3), 27.5 (CCMe3); 19F NMR (CD2Cl2) δ -141. Anal. Calcd for ReC20H42BF4: C, 43.24; H, 7.62. Found C, 43.37; H, 7.56.

Re(C-t-Bu)(CH2-t-Bu)3(OC6F5). Re (C-t-Bu)(CH2-t-Bu)3(OC6F5) was prepared in a manner similar to that used for Re(C-t-Bu)(CH2-t-Bu)3(OTf). 1H NMR (C6D6) δ 2.75 (s, 6, ReCH2-t-Bu), 1.29 (s, 9, ReC-t-Bu), 1.04 (s, 27, ReCH2-t-Bu). Anal. Calcd for ReC26H42F5O: C, 47.91; H, 6.49. Found: C, 47.84; H, 6.75.
Re(C-t-Bu)(CH-t-Bu)(CH2-t-Bu)(py)2(O3SCF3). Re(C-t-Bu)(CH2-t-Bu)3(O3SCF3) (106 mg, 0.172 mmol) was dissolved in 4 mL of Et2O. Pyridine (57 µL, 0.72 mmol) was added and a white precipitate formed after several minutes. After three hours the precipitate was collected and 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)(CH2-t-Bu)(py)2(O3SCF3) by NMR and elemental analysis: 1H NMR (CD2Cl2) δ 13.73 (s, 1, CH-t-Bu), 2.38 (d, 2, CHaHb-t-Bu, JHH = 12 Hz), 1.84 (d, 2, CHaHb-t-Bu, JHH = 12 Hz), 1.34, 1.22, 0.93 (s, 9 each, t-Bu); 13C NMR (CD2Cl2) δ 289.1 (JCH =128 Hz CH-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 (CMe3, third resonance obscured by solvent peak), 34.1(CH2-t-Bu), 33.9, 30.8, 29.1 (CMe3); 19F NMR δ (CD2Cl2) -78.3. Anal. Calcd for ReC26H46F3N2O3S: C, 44.37; H, 5.73; N, 3.98. Found: C, 44.15; H, 5.70; N, 3.94.

Re(CCMMe2Ph)(CHCMMe2Ph)(CH2CMe2Ph)(py)2(O3SCF3). Re(CCMMe2Ph)(CHCMMe2Ph)(CH2CMe2Ph)(py)2(O3SCF3) was prepared analogously to Re(C-t-Bu)(CH-t-Bu)(CH2-t-Bu)(py)2(O3SCF3) from crude Re(CCMMe2Ph)(CH2CMe2Ph)3(O3SCF3) and excess pyridine in ether. A pink powder was obtained which could be recrystallized from ether to yield analytically pure purplish-pink microcrystals: 1H NMR (pyr-d5) δ 14.0 (s, 1, CHCMMe2Ph), 7.66 (m, 3, Haryl), 7.1 (m, 6, Haryl), 3.15 (d, 1, JHH=12Hz, CHaHbCMMe2Ph), 2.25 (br.d, 1, CHaHbCMMe2Ph), 1.98, 1.88, 1.84, 1.67, 1.58, 1.57 (s, 3 each, CH3). Anal. Calcd for C41H46F3N2O3SRe: 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)(CH2-t-Bu)(py)3]+[BARF4]− Re(C-t-Bu)(CH-t-Bu)(CH2-t-Bu)2 (160 mg, 0.34 mmol) was dissolved in 5 mL of Et2O and solid [H(OEt2)]+[BARF4]− (344 mg., 0.34 mmol) was added and the mixture was allowed to stir for 45 minutes. Pyridine (110 µL, 1.39 mmol) was added and the resulting red
solution was allowed to stir for an additional 30 minutes. 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-$d_5$) $\delta$ 13.78 (s, 1, CH$_7$-Bu), 8.41 (s, 8, H$_{aryl}$), 7.81 (s, 4, H$_{aryl}$), 2.81 (d, 1, CH$_3$H$_7$r-Bu, J$_{HH}$ = 12 Hz), 1.82 (d, 1, CH$_8$H$_{t}$ Bu, J$_{HH}$ = 12 Hz), 1.33, 1.24, 1.12 (9 each, t-Bu); $^{13}$C NMR (pyr-$d_5$) $\delta$ 289.9 (C-$t$-Bu), 288.5 (CH-$t$-Bu, J$_{CH}$= 120 Hz), 163 (CF$_3$, J$_{CF}$ = 49 Hz), 155, 127.1, 120, 118.5 (C$_{aryl}$), 54.5, 53.4, 48.6 (CMe$_3$), 34.6 (CH$_2$-$t$-Bu), 34.2, 30.8, 28.9 (CMe$_3$). Anal. Calcd for ReC$_{62}$H$_{77}$BF$_{24}$N$_3$: C, 49.74; H, 3.83; N, 2.94. Found: C, 49.74; H, 4.13; N, 2.90.

$\text{[Re(C-}t\text{-Bu})(CH-t-Bu)(CH}_2$-$t$-Bu)(py)$_2$(py-H$_2$O)$]^+$$[\text{BARF}_4^-$. $\text{[Re(C-}t\text{-Bu})(CH-t-Bu)(CH}_2$-$t$-Bu)(py)$_2$(py-H$_2$O)$]^+$$[\text{BARF}_4^-$. is prepared from $[\text{Re(C-}t\text{-Bu})(CH}_2$-$t$-Bu)$_3$(OH$_2$)$]^+$$[\text{BARF}_4^-$. and 3 equiv. pyridine in ether and is recrystallized from 2/1 Et$_2$O/pentane at -40°C. Orange cubes formed and were collected and dried. Due to the difficulty of removing traces of water from pyridine-$d_5$, spectral data matched those for $[\text{Re(C-}t\text{-Bu})(CH-t-Bu)(CH}_2$-$t$-Bu)(py)$_2$]$^[\text{BARF}_4^-$. in pyridine-$d_5$. These complexes are insoluble in C$_6$D$_6$ and CD$_3$CN and decompose in CD$_2$Cl$_2$ and CDC$_3$.

Re(C-$t$-Bu)(CH-$t$-Bu)(CH$_2$-$t$-Bu)(CH$_3$CN)(O$_3$SCF$_3$). Re(C-$t$-Bu)(CH$_2$-$t$-Bu)$_3$(O$_3$SCF$_3$) (196 mg, 0.32 mmol) was dissolved in 3 mL of Et$_2$O 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 (CD$_3$CN) $\delta$ 13.24 (s, 1, CH-$t$-Bu), 2.22 (d, 1, CH$_8$H$_{t}$-Bu, J$_{HH}$ = 12 Hz), 1.34 (d, 1, CH$_8$H$_{t}$-Bu, J$_{HH}$ = 12 Hz), 1.26, 1.14, 0.78 (s, 9 each, t-Bu); $^{13}$C NMR (CD$_3$CN) $\delta$ 294.8 (C-$t$-Bu), 291.8 (CH-$t$-Bu, J$_{CH}$ = 116 Hz), 53.5, 50.1, 48.1 (CMe$_3$), 33.5 (CH$_2$-$t$-Bu), 33.8, 30.4, 28.5 (CMe$_3$). Anal. Calcd for ReC$_{18}$H$_{33}$F$_3$NO$_3$S: 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)(CH2-t-Bu)(CH3CN)3][BARF4]: Re(C-t-Bu)(CH-t-Bu)(CH2-t-Bu)2 (340 mg, 0.72 mmol) was dissolved in 5 mL of Et2O and solid [H(OEt2)2][BARF4] (700 mg, 0.70 mmol) was added and the mixture was allowed to stir for 20 minutes. CH3CN (1 mL) was added and the solution was stirred for 45 minutes. The solvent was removed in vacuo and the resulting beige powder was washed with pentane until the washings were clear. An analytical sample was recrystallized from Et2O/pentane: 1H NMR (C6D6) δ 13.38 (s, 1, ReCH-t-Bu), 8.25 (s, 8, Haryl), 7.53 (s, 4, Haryl), 2.47 (d, 1, ReCHaHb-t-Bu, JHH = 12 Hz), 1.56 (d, 1, ReCHaHb-t-Bu, JHH = 12 Hz), 1.21, 1.15, 1.07 (s, 9 each, t-Bu), 0.78 (br. s, 9, CH3CN); 13C NMR (CD3CN) δ 298 (C-t-Bu), 292.1 (CH-t-Bu), 163 (q, CF3, JCF = 48 Hz.), 130.9, 127.6, 124.0, 120.4 (Caryl), 54.0, 49.2, 33.8 (CMe3), 48.5 (CH2-t-Bu), 34.0, 30.6, 28.7 (CMe3). Anal. Calcd for C53H51BF24N3Re: 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)(CH2-t-Bu)(CH3CN)2(BF4). Re(C-t-Bu)(CH2-t-Bu)3(BF4) (43 mg, 0.078 mmol) was dissolved in 1 mL of Et2O and 1 mL of CH3CN was added. The solution immediately became colorless and was stirred for 1 hour 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)(CH2-t-Bu)(CH3CN)2(BF4): 1H NMR (C6D6) δ 13.59 (s, 1, CH-t-Bu), 2.68 (d, 1, JHH = 12Hz, CHaHb-t-Bu), 1.95 (d, 1, JHH = 12Hz, CHaHb-t-Bu), 1.80 (br s., 3, CH3CN), 1.51 (br s, 6, CH3CN), 1.32, 1.28, 1.19 (s, 9 each, t-Bu); 13C NMR (CD3CN) δ 296.1 (ReCCMe3), 291.5 (ReCH-t-Bu, JCH = 122 Hz), 53.6, 48.7, 48.1 (CMe3), 33.6, 30.2, 28.3 (CMe3), 33.4 (CH2-t-Bu); 19F NMR (C6D6) δ -151.3. Anal. Calcd for ReC19H36N2BF4: C, 40.35; H, 6.42; N, 4.95. Found: C, 40.30; H, 6.45; N, 4.82.
Re(C-\text{-}t\text{-}Bu)(\text{CH}\text{-}t\text{-}Bu)(\text{CH}2\text{-}t\text{-}Bu)(\text{CD}3\text{OD})\text{n}(\text{O}3\text{SCF}3). \quad \text{Re(C-\text{-}t\text{-}Bu)(CH}2\text{-}t\text{-}Bu)\text{)}(\text{O}3\text{SCF}3) (15 \text{ mg}) \text{ was transferred to a NMR tube which was capped with a septum cap and brought out of the drybox. CD}3\text{OD (1 mL) was added to yield a yellow solution of Re(C-\text{-}t\text{-}Bu)(CH-t-Bu)(CH2-t-Bu)(CD3OD)\text{n}(O3SCF3). Experiments employing an internal standard showed that Re(C-t-Bu)(CH-t-Bu)(CH2-t-Bu)(CD3OD)\text{n}(O3SCF3) is formed in >90% yield: } 1\text{H NMR (CD3OD)} \delta 13.00 (s, 1, CH-t-Bu), 2.82 (d, 1, CH8H3-t-Bu, JHH = 12 Hz), 2.39 (d, 1, CH8H3-t-Bu, JHH = 12 Hz), 1.36, 1.26, 1.15 (s, 9 each, t-Bu).

Re(C-t-Bu)(CH-t-Bu)(CH2-t-Bu)(THF-d8)\text{n}(O3SCF3) \quad \text{Re (C-t-Bu)(CH-t-Bu)(CH2-t-Bu)(THF-d8)}\text{n}(O3SCF2) \text{ was prepared in the same manner as Re(C-t-Bu)(CH-t-Bu)(CH2-t-Bu)(CD3OD)\text{n}(O3SCF3) using THF-d8, although it took two hours for Re(C-t-Bu)(CH2-t-Bu)\text{)}(O3SCF3) \text{ to react completely: } 1\text{H NMR (THF-d8)} \delta 13.08 (s, 1, CH-t-Bu), 2.50 (d, 1, CH8H3-t-Bu, JHH = 12 Hz), 1.48 (d, 1, CH8H3-t-Bu, JHH = 12 Hz), 1.36, 1.27, 0.94 (s, 9 each, t-Bu).

ReCl(LOEt)(C-t-Bu)(CH-t-Bu) \text{ Solid [ReCl2(C-t-Bu)(CH-t-Bu)]x} (44 \text{ mg, 0.11 mmol}) \text{ and NaLOEt} (55 \text{ mg, 0.10 mmol}) \text{ were combined and 3 mL of THF was added. The orange-red mixture was stirred for 1.5 hours and the THF was then removed in vacuo to yield an orange-pink solid, which was extracted with Et2O. Ether was then removed in vacuo to yield a pink film (85 \text{ mg, 95%}). An analytical sample was recrystallized from Et2O/pentane at -40°C: } 1\text{H NMR (C6D6)} \delta 13.95 (s, 1, ReCH-t-Bu), 4.89 (s, 5, Cp), 3.8 - 4.6 (m, 12 total, P(OCH2CH3), 1.62, 1.54 (s, 9 each, t-Bu), 1.0 - 1.4 (m, 18 total, POCH2CH3). \text{ Anal. Calcd for ReCoC27H54ClO9P3: } C, 36.18; H, 6.07. \text{ Found: } C, 35.94; H, 5.92.
Re(η⁵-C₅H₅)(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu). Re(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(py)₂(O₃SCF₃) (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 hour and the volatiles 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 ¹H NMR: ¹H NMR (C₆D₆) δ 12.67 (s, 1, ReCH₃-C₇-Bu), 5.32 (s, 5, η⁵-C₅H₅), 2.52 (d, 1, JHH=12 Hz, ReCH₃C₇-Bu), 2.36 (d, 1, JHH=12 Hz, ReCH₃C₇-Bu), 1.34, 1.12, 1.11 (s, 9 each, t-Bu); ¹³C NMR (C₆D₆) δ 285.7 (ReC-t-Bu), 265.6 (ReCH₃-C₇-Bu, JCH=116 Hz), 97.6 (C₅H₅), 52.9, 47.6, 33.0 (CMes), 34.2, 31.9, 29.4 (CMes), 17.4 (ReCH₂-t-Bu). Anal. Calcd for ReC₂₀H₃₅: C, 52.03; H, 7.64. Found: C, 52.54; H, 7.75.

Re(LΟEt)(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu). Re(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu)(py)₂(O₃SCF₃) (78 mg, 1.10 mmol) was dissolved in 5 mL of THF and solid NaLΟEt 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 Et₂O and the ether was removed in vacuo to yield pure Re(LΟEt)(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu) as a pale yellow solid (97 mg, 94%): ¹H NMR (C₆D₆) δ 13.02 (s, 1, ReCH₃-C₇-Bu), 4.90 (s, 5, η⁵-C₅H₅), 3.8-4.4 (m, 12 total, POCH₂CH₃), 2.73 (d, 2, JHH = 12 Hz, ReCH₃C₇-Bu), 1.79 (d, 2, JHH = 12 Hz, ReCH₃C₇-Bu), 1.59, 1.52, 1.39 (s, 9 each, t-Bu), 1.0-1.3 (m, 18 total, POCH₂CH₃); ¹³C NMR (C₆D₆) δ 281.6 (ReC-t-Bu), 275.7 (ReCH₃-C₇-Bu, JCH = 125 Hz), 89.5 (η⁵-C₅H₅), 61.1 (POCH₂CH₃), 54.8 (ReCH₂-t-Bu), 51.7, 46.3, 34.2 (CMes), 34.7, 32.5, 29.7 (CMes), 17.3 (POCH₂CH₃). Anal. Calcd for CoOsC₃₂H₆₅O₉P₃: C, 41.24; H, 7.03. Found: C, 40.93; H, 6.86.
Re(HBpz3)(C-t-Bu)(CH-t-Bu)(CH2-t-Bu)(py)2(O3SCF3) (90 mg, 0.128 mmol) was dissolved in 3 mL of THF and solid NaHBPz3 (30 mg, 0.127 mmol) was added. The resulting solution was allowed to stir for one hour and then the THF was removed in vacuo. The residue was extracted with pentane and 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%): 1H NMR (CD62D) δ 13.22 (s, 1, ReCH-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, JHH = 12 Hz, ReCH4H6-t-Bu), 1.74 (d, 2, JHH = 12 Hz, ReCH4H6-t-Bu), 1.40, 1.35, 1.24 (s, 9 each, t-Bu): 13C NMR (CD62D) δ 289.3 (ReC-t-Bu), 282.7 (ReCH-t-Bu), 148.1, 144.3, 141.7, 135.0, 134.5, 134.0, 105.9, 105.4, 105.2 (pz), 53.0 (ReCH2-t-Bu), 52.3, 47.7, 34.3 (CMe3), 34.7, 31.3, 29.1 (CMe3). Anal. Calcd for ReC24H40N6B: 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)(CH2-t-Bu)(C6H12S3)(O3SCF3). Re(C-t-Bu)(CH-t-Bu)(CH2-t-Bu)(py)2(O3SCF3) (183 mg, 0.26 mmol) was dissolved in 5 mL of dichloromethane and solid S3C6H12 (70 mg, 0.39 mmol) was added. The solution was stirred for 2 hours 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%): 1H NMR (CD2Cl2) δ 12.91 (s, 1, ReCC-t-Bu), 2.95 - 3.9 (m, 12 total, S3C6H12), 2.59 (d, 1, ReCH4H6-t-Bu, JHH=12 Hz), 1.54 (d, 1, ReCH4H6-t-Bu, JHH=12 Hz), 1.27, 1.17, 0.92 (s, 9 each, t-Bu); 13C NMR (CD2Cl2) δ 294.9 (ReC-t-Bu), 283.5 (ReCH-t-Bu), 53.6 (ReCH2-t-Bu), 49.5, 40.3, 40.2, 38.7, 36.6, 36.3 (S3C6H12), 35.2, 33.2, 32.1 (CMe3), 33.6, 29.6, 28.2 (CMe3). Anal. Calcd for ReC22H42O3S4F3: C, 36.39; H, 5.83. Found: C, 36.17; H, 5.40.
Re(η⁵-C₅H₅)(C-t-Bu)(CH-t-Bu)(O₂SCF₃).

Re(η⁵-C₅H₅)(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu) (110 mg, 0.23 mmol) was dissolved in 5 mL of Et₂O 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 minutes. 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. (104 mg, 84%) ¹H NMR (C₆D₆) δ 13.72 (s, 1, ReCH-t-Bu), 5.27 (s, 5, η⁵-C₅H₅), 1.29, 1.14 (s, 9 each, t-Bu); ¹³C NMR (C₆D₆) δ 306.5 (ReC-t-Bu), 298.6 (ReCH-t-Bu, J_C-H = 90), 98.5 (C₅H₅), 54.4, 48.8 (CMe₃), 31.7, 29.4 (CMe₃); ¹⁹F NMR (C₆D₆) δ -75.5. Re(η⁵-C₅H₅)(C-t-Bu)(CH-t-Bu)(O₂SCF₃) is too unstable in the solid state for elemental analysis.

[Re(η⁵-C₅H₅)(C-t-Bu)(CH-t-Bu)(py)]⁺[OTf]⁻.

Re(Cp)(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu) (65 mg, 0.141 mmol) was dissolved in 5 mL of CH₂Cl₂ and the solution was cooled to -40°C. Solid pyHOTf (3 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 hour. Dichloromethane was removed in vacuo, and a pale yellow solid was isolated, washed with pentane, and crystallized from a CH₂Cl₂/Et₂O mixture at -40°C. (50 mg, 60%). ¹H NMR (C₆D₆) δ 14.33 (s, 1, OsCH-t-Bu), 8.60 (d, 2, py), 7.13 (t, 1, py), 7.00 (t, 2, py), 5.76 (s, 5, C₅H₅), 1.08, 1.00 (s, 9 each, t-Bu). Anal. Calcd for ReC₂₁H₂₉NF₃O₃S: C, 40.77; H, 4.72; N, 2.26. Found. C, 41.02; H, 4.67; N, 2.20.

Re(LOEt)(C-t-Bu)(CH-t-Bu)(O₂SCF₃).

Re(LOEt)(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu) (100 mg, 0.11 mmol) was dissolved in 5 mL of Et₂O 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 minutes. Ether was then removed in vacuo and
the sticky yellow solid was recrystallized from Et₂O/pentane at -40°C to yield yellow prisms. (63 mg, 59%): ¹H NMR (CD₂Cl₂) δ 13.77 (s, 1, ReCH-t-Bu), 5.13 (s, 5, η⁵-C₅H₅), 3.4-4.2 (br m, 12 total, POCH₂CH₃), 1.34, 1.33 (s, 9 each, t-Bu), 1.16 (br m, 18, POCH₂CH₃); ¹³C NMR (CD₂Cl₂) δ 300.8 (ReCH-t-Bu), 298.0 (ReC-t-Bu), 90.1 (C₅H₅), 61.9 (br, POCH₂CH₃), 46.9 (CMe₃, other CMe₃ peak obscured by the solvent peak), 32.9, 29.5 (CMe₃), 16.7 (POCH₂CH₃); ¹⁹F NMR (CD₂Cl₂) δ -78.1. Anal. Calcd for CoReC₂₈H₅₄F₃O₁₂P₃S: C, 33.30; H, 5.39. Found: C, 32.92; H, 5.10.

[Re(OEt₂)(C-t-Bu)(CH₅-t-Bu)(Et₂O)][BARF₄]+. Re(OEt₂)(C-t-Bu)(CH₅-t-Bu) (140 mg, 0.15 mmol) was dissolved in 5 mL of Et₂O and the solution was cooled to -40°C. Solid [H(OEt₂)]₂[BARF₄] (149 mg, 0.15 mmol) was added and the yellow solution was allowed to warm to room temperature and stirred for 1.5 hours. Ether was removed in vacuo and the yellow-tan solid was recrystallized from ether/pentane at -40°C overnight (140 mg, 50%): ¹H NMR (CD₂Cl₂) δ 13.78 (s, 1, ReCH-t-Bu), 7.72 (s, 8, ArF), 7.56 (s, 4, ArF), 5.32 (s, 5, Cp), 3.8 - 5.2 (m, 12, POCH₂CH₃), 3.40 (br. q., 4, O(CH₂CH₃)₂), 1.33, 1.31 (s, 9 each, t-Bu), 1.0 - 1.3, (m, 24 total, PO(OCC₂CH₃)₂ and O(CH₂CH₃)₂); ¹³C NMR (CDCl₃) δ 302.9 (ReCH-t-Bu, J₇-H = 124), 299.0 (ReC-t-Bu), 163.0 (q,CF₃, J_CF = 48 Hz), 135.0, 130.0, 126.6, 123.0 (Caryl), 90.1 (Cp), 61.8 (POCH₂CH₃), 61.5 (O(CH₂CH₃), 32.7, 29.3 (CMe₃), 53.0, 46.9 (CMe₃), 16.5 (O(CH₂CH₃), 12.6 (P(OCH₂CH₃)₂). Anal. Calcd for ReCoC₆₃H₇₆BF₂₄O₁₀P₃: C, 42.08; H, 4.26. Found: C, 42.39; H, 4.23.

[Re(S₃C₆H₁₂)(C-t-Bu)(CH₅-t-Bu)(O₃SCF₃)]+[O₃SCF₃]+. [Re(S₃C₆H₁₂)(C-t-Bu)(CH₅-t-Bu)CH₂-t-Bu][O₃SCF₃]+ (60 mg, 0.083 mmol) was dissolved in 5 mL of CH₂Cl₂ and the solution was cooled to -40°C. Triflic acid (8μL, 0.09 mmol) was added and the resulting pale pink mixture was warmed to room temperature and stirred for 45 minutes. CH₂Cl₂ was then removed in vacuo and the resulting microcrystalline
pale pink solid was washed with pentane and dried. (40 mg, 60%): $^1$H NMR (CD$_2$Cl$_2$) δ 14.56 (s, 1, ReCH-t-Bu), 3.1-4.2 (overlapping multiplets, 12 total, S$_3$C$_6$H$_{12}$), 1.43, 1.32 (s, 9 each, t-Bu); $^{13}$C NMR (CD$_2$Cl$_2$) δ 306.4 (ReCH-t-Bu, J$_{C-H} = 116$ Hz), 304.6 (ReC-t-Bu), 55.2, 51.6 (CMe$_3$), 43.7, 41.9, 36.5, 34.0, 32.9, 30.1 (S$_3$C$_6$H$_{12}$), 29.7, 28.5 (CMe$_3$); $^{19}$F NMR (CD$_2$Cl$_2$) δ $-$75.6, $-$78.6. Anal. Calcd for ReC$_{18}$H$_{31}$F$_6$O$_6$S$_5$: C, 26.89; H, 3.89. Found: C, 26.96; H, 3.74.

Re(C-t-Bu)(CHC$_6$H$_5$)(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$_2$Cl$_2$. Styrene (36 µL, 0.315 mmol) was added and the resulting orange solution was allowed to stir at room temperature for 1.5 hours. The volatiles were removed in vacuo to yield a beige powder which was washed with pentane (10 mL) and recrystallized from CH$_2$Cl$_2$/ether to yield beige microcrystals: $^1$H NMR (CD$_2$Cl$_2$) δ 14.35 (s, 1, ReCHC$_6$H$_5$), 8.76, 8.46 (d, 2 each, py ortho), 8.00, 7.80 (br t, 1 each, py meta), 7.76 (d, 2, J$_{H-H}$=9 Hz, phenyl ortho ), 7.55, 7.38 (t, 2 each, py meta), 7.25 (m 3, phenyl meta,para), 2.52 (d, 2, J$_{HH}=$12 Hz, ReCH$_3$H$_5$CMe$_3$), 2.07 (d, 2, J$_{HH}=$12 Hz, ReCH$_3$H$_5$CMe$_3$), 1.33, 0.86 (s, 9 each, t-Bu); $^{13}$C NMR (CD$_2$Cl$_2$) δ 290.4 (ReCMe$_3$), 270.3 (ReCHC$_6$H$_5$, J$_{C-H} = 128$ 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$_2$C$_6$H$_5$), 36.1 (CMe$_3$), 34.0, 28.5 (CMe$_3$). Anal. Calcd for C$_{28}$H$_{36}$N$_2$F$_3$O$_3$SRe: 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$_6$H$_5$)(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$_3$) $\delta$ 12.89 (ReCH-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$_2$CH$_3$), 2.03 (d, 1, ReCH$_a$H$_b$-t-Bu), 1.38 (d, 1, ReCH$_a$H$_b$-t-Bu), 1.31 (t, 3, OCH$_2$CH$_3$), 1.20, 0.94 (s, 9 each, t-Bu); $^{13}$C NMR (CDCl$_3$) $\delta$ 288.1 (ReCHOEt), 280.3 (ReC-t-Bu), 154.6, 153.1, 138.6, 138.2, 125.4, 124.8 (py), 75.4 (OCH$_2$CH$_3$), 50.6, 35.0 (CMe$_3$), 33.8, 27.9 (CMe$_3$), 16.1 (OCH$_2$CH$_3$).

Re(C-t-Bu)(CH$_2$)(CH$_2$-t-Bu)(bpy)(OTf). $^1$H NMR (C$_6$D$_6$) $\delta$ 14.03, (d, 1, ReCH$_a$H$_b$, $J_{HH} = 3, J_{CH} = 135$), 13.50 (d, 1, ReCH$_a$H$_b$, $J_{HH} = 3, J_{CH} = 150$)), 6.4 - 9 (m, 8 total, bpy), 2.79 (d, 1, ReCH$_a$H$_b$-t-Bu), 1.86 (d, 1, ReCH$_a$H$_b$-t-Bu), 1.39, 0.86 (s, 9 each, t-Bu). $^{13}$C (partial) 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 elemental analysis and a complete set of $^{13}$C NMR data could not be obtained. The partial set of $^{13}$C data was 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$_2$H$_4$)(py)$_2$(O$_3$SCF$_3$). Re(C-t-Bu)(CH-t-Bu)(CH$_2$-t-Bu)(py)$_2$(O$_3$SCF$_3$) (176 mg, 0.25 mmol.) was dissolved in 10 mL of benzene and stirred under an atmosphere of ethylene for 45 minutes. 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. (135 mg, 78%) An analytical sample was recrystallized from ether at -40°C: $^1$H NMR (C$_6$D$_6$) $\delta$ 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$_2$H$_4$), 3.15 (m, 1, ReCH$_2$-), 2.51 (m, 1, ReCH$_2$-), 2.42 (overlapping multiplets, 2 total, ReCH$_2$CH$_a$H$_b$ and Re(CH$_2$)$_2$H$_a$H$_b$, partial assignment by C$_2$D$_4$ labeling experiment.), 2.04 (m, 1, ReCH$_2$CH$_a$H$_b$ ), 1.80 (m, 1, Re(CH$_2$)$_2$H$_a$H$_b$), 1.16, 0.80 (s, 9 each, t-Bu); $^{13}$C NMR (C$_6$D$_6$) $\delta$ 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
(ReCH₂CH₂, JCH = 153 Hz, JCC = 36 Hz), 53.0, 50.6 (CMeq), 51.2, (Re(CH₂)₂CH₂),
46.6 (ReCH₂CH₂, JCH = 156 Hz, JCC = 36 Hz), 29.9, 25.8 (CMeq), 20.7 (C₂H₄, JCH =
123 Hz); ¹⁹F NMR (C₆D₆) δ. Anal. Calcd for ReC₂₅H₃₉N₂F₃O₃SRe: C, 43.53; H,
5.55; N, 4.02. Found: C, 43.71; H, 5.76; N, 4.02.

Observation of Re(C₉-Bu)(CH₃)(CH₂-t-Bu)(CD₃CN)₅(OTf). A 2:1
mixture of Re(C₉-Bu)(CH₃)(CH₂-t-Bu)(CD₃CN)₅(OTf) and Re(C₉-Bu)(CH₃-t-
Bu)(CH₂-t-Bu)(CD₃CN)₅(OTf) was generated by heating a CD₃CN solution of Re(C₉-
Bu)(CH₃-t-Bu)(CH₂-t-Bu)(CD₃CN)(OTf) (12 mg, 0.02 mmol) and cis-3-hexene (10 μL,
0.08 mmol) at 60°C for 1 hour. Partial ¹H NMR (CD₃CN) δ 13.53 (t, 1, ReCH₂Et), 3.5
(d of p, 2 total, ReCHCH₂CH₃), 2.2 (d, 1, ReCH₃), 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.

Polymerization of Norbornene. Norbornene (153 mg, 1.59 mmol) was
dissolved in 5.0 mL of benzene. A solution of Re(C₉-Bu)(CH₃-t-Bu)(CH₂-t-
Bu)(py)₂(OTf) (11 mg, 0.016 mmol) in benzene (0.50 mL) was added dropwise with
vigorously stirring. The solution was allowed to stir for 2 hours at 25°C, and excess
benzaldehyde (100 μL) was added. The mixture was stirred for 45 minutes to cap the
polymer, and then the polymer was precipitated by adding the reaction mixture
dropwise to methanol. Colorless poly(norbornene) was collected and dried (yield = 98
mg, 64%). M_w/M_n = 1.23.
References for Chapter 1


CHAPTER 2: ALKYL AND ALKYLIDENE COMPLEXES OF OSMIUM(VI)
Introduction

In this chapter, a variety of alkyl and alkyldene complexes of osmium(VI) are described. Alkyldene and alkyldyne complexes that contain a metal in its highest possible formal oxidation state are now relatively well-known for Mo, W, and Re.\textsuperscript{1} Os(VIII) is extremely prone to reduction, however, and no organometallic complexes of Os(VIII) have been reported. A variety of Os(VI) alkyl complexes have been reported.\textsuperscript{2-5} These complexes also contain at least two metal-ligand \(\pi\) bonds to stabilize the metal in the relatively high oxidation state. However, at the time that this research was begun, there were no osmium carbene complexes and only a few osmium carbyne complexes that could be described as Os(VI). A large number of Os(VI) oxo, imido, and nitrido complexes have been prepared, however, and that led us to believe that Os(VI) alkylidenes and alkyldynes could be prepared. It should be noted that all of the known Os(VI) complexes contain at least two metal-ligand \(\pi\)-bonds, if the oxo or imido ligand is viewed as a triply bonded ligand. For the purpose of consistency with the formalisms used in early transition metal chemistry, an alkyldene ligand is viewed as a dianionic ligand and an alkyldyne ligand is viewed as a trianionic ligand. Although these conventions are formalisms and should be viewed with a certain amount of skepticism, they do provide a standard for comparing a range of carbene and carbyne complexes.

We were interested in preparing neopentyldene and neopentylidyne complexes of Os(VI) in order to compare the details of their preparation to that of the d\textsuperscript{0} alkylidenes and alkylidyynes. However, "standard" methods of preparing d\textsuperscript{0} alkylidenes and alkylidyynes\textsuperscript{1} failed for Os(VI). This failure may be attributed to several factors. First, alkylations of known Os(VI) starting materials often result in reduction. Second, d\textsuperscript{2} complexes are less prone to \(\alpha\)-hydrogen abstraction reactions than their d\textsuperscript{0} analogs.
This can be attributed to the fact that the d² complexes are more electron-rich than the d⁰ analogs. Lastly, prior to this work the only known Os(VI) neopentyl complexes were Os(NAr)₂(CH₂-t-Bu)₂ and [OsN(CH₂-t-Bu)₄]⁺[n-Bu₄N]⁺.⁵ Any attempted alkylidene syntheses ought to focus on neopentyl ligands, which are most likely to undergo 𝛼-hydrogen abstraction reactions. If neopentylidene and neopentylidyne complexes of Os(VI) could be prepared, we were interested in comparing their reactivity with that of d⁰ alkylidene and alkylidyne complexes. This chapter describes the synthesis and study of some neopentyl and neopentylidene complexes of osmium and introduces alkylidene/oxo exchange reactions as a means of synthesizing otherwise inaccessible alkylidene complexes.

Alkylidene complexes of ruthenium and osmium are also of interest due to their possible intermediacy in heterogeneous olefin metathesis reactions. During the course of the research, Grubbs reported the synthesis of a variety of ruthenium and osmium carbenes of the general formula MCl₂(PR₃)₂(CHCHCPh₂).⁶⁻⁸ The ruthenium complexes are catalysts for the metathesis of a variety of olefins, although the osmium complexes are inactive. While these complexes are useful catalysts for metathesis reactions and help prove the intermediacy of metal carbenes in the ruthenium- and osmium-based heterogeneous systems, in terms of structure and bonding they are similar to a variety of ruthenium and osmium carbene complexes which have been prepared by Roper and others. In all of these complexes, the metal can be described as being in the +4 oxidation state if the carbene ligand is viewed as a dianion.

**Synthesis of OsO₂R₂**

The reaction of [OsCl₄O₂][PP₄]₂ with dialkyl or diarylzinc reagents in dichloromethane yields OsO₂R₂ (R = CH₂-t-Bu, CH₂CMe₂Ph, mesityl) in 50-80% yield. If excess ZnR₂ is added, further alkylation of OsO₂R₂ does not occur. The
reaction is very clean and the crude product obtained by pentane or toluene extraction can be used without further purification. OsO₂(mesityl)₂ was originally prepared in 29% yield from OsO₄ by Wilkinson and coworkers.⁹ An X-ray structural analysis of OsO₂(mesityl)₂ revealed that it has a distorted tetrahedral structure, and it is likely that OsO₂(CH₂-t-Bu)₂ and OsO₂(CH₂CMe₂Ph)₂ have similar structures.

\[
\begin{align*}
[\text{OsO}_2\text{Cl}_4][\text{PPh}_4]_2 & \quad + \quad \text{ZnR}_2 & \quad \xrightarrow{\text{CH}_2\text{Cl}_2} & \quad \text{OsO}_2\text{R}_2 \\
R & = \text{CH}_2\text{t-Bu} & \text{CH}_2\text{CMe}_2\text{Ph} & \text{mesityl}
\end{align*}
\]

When [OsCl₄O₂][PPh₄]₂ is allowed to react with bis(trimethylsilylmethyl)zinc in dichloromethane, [OsO₂(CH₂SiMe₃)₂]ₙ is formed. In solution, [OsO₂(CH₂SiMe₃)₂]ₙ has low symmetry, with the two trimethylsilyl groups non-equivalent. All four methylene hydrogens are non-equivalent as well. This data suggests that [OsO₂(CH₂SiMe₃)₂]ₙ is not monomeric. It can be converted to monomeric trans-OsO₂(CH₂SiMe₃)₂(py)₂ by addition of pyridine. It is generally accepted that although a trimethylsilylmethyl group is larger than a neopentyl group, the bulk is further away from the metal center, allowing the complex to oligomerize.

**Alkylation and Reduction Reactions of OsO₂(CH₂-t-Bu)₂**

The reaction of OsO₂(CH₂-t-Bu)₂ with a variety of alkylating agents was investigated as a possible route to alkylidene and alkylidyne complexes. OsO₂(CH₂-t-Bu)₂ reacts with 2 equivalents of trimethylaluminum in pentane to yield diamagnetic orange crystals of a complex with the formulation [Os(CH₃)(CH₂-t-Bu)₂]ₙ, according to NMR data and elemental analysis. The product is readily purified by
passing a pentane solution through silica gel and is isolated in 43% yield. The neopentyl groups are equivalent on the NMR time scale, and the α protons are also equivalent, suggesting that $[\text{Os(CH}_3\text{)}(\text{CH}_2\text{-}t\text{-Bu})_2]_n$ has a highly symmetric structure. For this reason, $[\text{Os(CH}_3\text{)}(\text{CH}_2\text{-}t\text{-Bu})_2]_n$ is proposed to be a dimeric species similar to the triply bonded dimers, $[\text{Ru(CH}_3\text{)}(\text{CH}_2\text{-}t\text{-Bu})_2]_2$, $[\text{Ru(CH}_2\text{-}t\text{-Bu})_3]_2$, and $[\text{Os(η}^3\text{-C}_3\text{H}_5)(\text{CH}_2\text{-}t\text{-Bu})_2]_2$.\(^{11}\)

The reaction of $\text{OsO}_2(\text{CH}_2\text{-}t\text{-Bu})_2$ with $\text{Al(CH}_2\text{-}t\text{-Bu})_3(\text{THF})$ in THF results in formation of a red diamagnetic solid with the formulation $[\text{OsO(CH}_2\text{-}t\text{-Bu})_2]_n$, according to NMR and IR data and elemental analysis. The two neopentyl groups are non-equivalent on the NMR time scale, and all four α protons are non-equivalent as well, suggesting that this complex has little symmetry. The reaction of stronger alkylating reagents ($t\text{-BuCH}_2\text{Li}$, $\text{Mg(CH}_2\text{-}t\text{-Bu})_2$(dioxane), $t\text{-BuCH}_2\text{MgCl}$), with $\text{OsO}_2(\text{CH}_2\text{-}t\text{-Bu})_2$ was unsuccessful, yielding mixtures of $[\text{OsO(\text{CH}_2\text{-}t\text{-Bu})}_2]_n$, $\text{Os(CH}_2\text{-}t\text{-Bu})_2(\text{CH}_2\text{-}t\text{-Bu})_2$ (see below) and unidentified products. A similar mixture of products was obtained in the reaction of $(\text{OsO}_2\text{Cl}_4)(\text{PPh}_4)_2$ with $\text{NpMgCl}$ in $\text{CH}_2\text{Cl}_2$. Due to the difficulties associated with synthesizing Os(VI) alkylidenes and alkylidene precursors from $\text{OsO}_2\text{R}_2$, it was necessary to develop a new synthetic route to alkylidene complexes.

**Exchange Reactions of Metal Oxo Complexes**

The reaction of a metal oxo complex with a phosphorane or early transition metal alkylidene complex might be expected to yield a new alkylidene and a phosphine oxide or early transition metal oxo complex, respectively. This sort of exchange reaction is similar to the Wittig reaction of phosphoranes with ketones or the "Wittig-like" reaction of transition metal alkylidenes with aldehydes or ketones. However,
despite the similarities and the fact that such alkylidene/oxo exchange reactions were first attempted more than ten years ago,\textsuperscript{12} no successful alkylidene/oxo exchange reactions had been reported prior to this work.

A variety of exchange reactions have been reported for $d^0$ metal complexes and are shown in Scheme 2.1. No exchange reactions involving $d^2$ oxo complexes had been reported prior to this work. During the course of this research, additional exchange reactions of $d^0$ metal complexes were reported by Gibson; however, these reactions were merely monitored by NMR and no attempts were made to adapt these reactions for preparative chemistry.\textsuperscript{13} The known exchange reactions include imido/oxo exchange reactions of $\text{OsO}_4$ with phosphinimines or molybdenum imido complexes.\textsuperscript{14,15} $\text{Os(NR)}_n\text{OsO}_{4-n}$ ($n = 2-3$) have been prepared in this manner. Alkoxide/alkylidene exchange reactions between tantalum and tungsten have been reported, but it should be noted that in this reaction, the only ligand not exchanged between tungsten and tantalum is the oxo group.\textsuperscript{12} This reaction emphasizes a key point in the selection of potential exchange reactions; the "supporting" ligands may themselves be exchanged between metals, sometimes more readily that the multiply bonded ligands.
$\text{OsO}_4 + \text{Mo(NAr)_2(O-t-Bu)_2} \xrightarrow{\text{THF}} \text{Os(NAr)_2O}_2 + \text{MoO}_2(\text{O-t-Bu})_2$

$\text{OsO}_4 + 1.5 \text{Mo(NAr)_2(O-t-Bu)_2} \xrightarrow{\text{THF}} \text{Os(NAr)_3O}_2 + 1.5 \text{MoO}_2(\text{O-t-Bu})_2$

$\text{OsO}_4 + 3 \text{R}_3\text{P=N-t-Bu} \xrightarrow{\text{CH}_2\text{Cl}_2} \text{OsO(N-t-Bu)_3} + 3 \text{R}_3\text{P=O}$

$\text{WO(O-t-Bu)}_4 + \text{Ta(CH-t-Bu)Cl}_3(\text{PR}_3)_2 \xrightarrow{\text{Et}_2\text{O/pentane}} \text{WO(CH-t-Bu)Cl}_2(\text{PR}_3)_2 + \text{Ta(O-t-Bu)}_4\text{Cl}$

**Scheme 2.1.** Exchange reactions of d⁰ oxo complexes.
Bis(alkylidene) Complexes of Os(VI)

Tantalum neopentylidene complexes proved to be efficient alkylidene transfer reagents for OsO₂R₂. The reaction of OsO₂(CH₂-t-Bu)₂ with 2 equivalents of Ta(CH₂-t-Bu)(CH₂-t-Bu)₃¹⁶ in pentane resulted in precipitation of insoluble [TaO(CH₂-t-Bu)₃]ₙ. The reaction mixture is purified by passage through silica gel and orange-red \( \text{syn, anti-Os(CH-t-Bu)₂(CH₂-t-Bu)₂} \) is isolated in 70% yield.

The two neopentyl groups are related by a mirror plane, suggesting a pseudo-tetrahedral structure, as shown above. In the \(^1\text{H}\) and \(^{13}\text{C}\) NMR, the two alkylidene ligands are non-equivalent (δHα = 16.33, 11.55 ppm; δCα = 224.2, 210.5 ppm) and the \( J_{\text{CHα}} \) are significantly different (\( J_{\text{CH}} = 150, 130 \text{ Hz} \)). The data are consistent with one of the neopentylidene ligands having its tert-butyl group oriented towards the other neopentylidene ligand (syn orientation) and the other neopentylidene has its tert-butyl group pointed away from the first neopentylidene (anti orientation). Syn and anti alkylidenes have been observed in a variety of four, five, and six coordinate \( d^0 \) Mo, W, and Re alkylidene complexes and typically exhibit characteristic \( J_{\text{CHα}}, \delta\text{Hα, and } \delta\text{Cα} \) values. In the four coordinate species, syn alkylidenes exhibit lower C-H coupling constants and upfield chemical shifts in both the \(^1\text{H}\) and \(^{13}\text{C}\) NMR.¹⁷ These features have been ascribed to an α-agostic interaction. The syn and anti alkylidenes will be discussed in greater detail in the next section. \( \text{syn, anti-Os(CH-t-Bu)₂(CH₂-t-Bu)₂} \) is a
thermally unstable oil; nonetheless, it can be isolated > 90% pure. The only other product typically observed is the rotational isomer, \textit{anti, anti}-\text{Os(CH}-t\text{-Bu)}_2(\text{CH}_2-t\text{-Bu})_2. \textit{anti, anti}

The reaction between OsO$_2$(CD$_2$-t-Bu)$_2$ and 2 equivalents of Ta(CH-t-Bu)(CH$_2$-t-Bu)$_3$ in toluene-$d_8$ at -78°C yields Os(CH-t-Bu)$_2$(CD$_2$-t-Bu)$_2$ initially, but when the solution is allowed to warm to 0°C H and D scramble among the $\alpha$-carbon atoms of the neopentyl and neopentylidene ligands. Since steric hindrance will prevent rapid intermolecular reactions, $H_\alpha/D_\alpha$ scrambling is more likely to be intramolecular. There are two possibilities. One is a degenerate H (or D) transfer from $C_\alpha$ of a neopentyl group to $C_\alpha$ of a neopentylidene group. The other is H (or D) transfer from one neopentylidene ligand to the other to give Os(C-t-Bu)(CH$_2$-t-Bu)$_3$, the $d^2$ analog of W(C-t-Bu)(CH$_2$-t-Bu)$_3$,\textsuperscript{18} as an intermediate. We prefer the

![Diagram of molecular structures]

latter explanation for two reasons. First, $\alpha$-hydrogen abstraction is known to occur more readily from an alkylidene ligand than an alkyl ligand.\textsuperscript{1} Also, the reaction between Os(C-t-Bu)(CH$_2$-t-Bu)$_2$(py)$_2$(O$_3$SCF$_3$) or Os(C-t-Bu)(CH$_2$-t-Bu)(py)$_2$Cl$_2$ (see later) and 1 or 2 equivalents neopentyl lithium, respectively, yields Os(CH-t-Bu)$_2$(CH$_2$-t-Bu)$_2$. It is interesting to note that in the $d^0$ manifold, W(CSiMe$_3$)(CH$_2$CMMe$_3$)$_3$ is converted into W(CCMMe$_3$)(CH$_2$CMMe$_3$)$_2$(CH$_2$SiMe$_3$) only relatively slowly. Kinetic data support the intermediacy of a bis(alkylidene) species in this transformation.\textsuperscript{19}
The reaction of \([\text{OsO}_2(\text{CH}_2\text{SiMe}_3)]_n\) with two equivalents of \(\text{Ta(CH-\text{-}t-Bu})(\text{CH}_2\text{-}t\text{-}Bu)_3\) in pentane yields a 1:1 mixture of \textit{syn}, \textit{anti}-\text{Os(CH-\text{-}t-Bu)}_2(\text{CH}_2\text{SiMe}_3)_2\) and \textit{anti}, \textit{anti}-\text{Os(CH-\text{-}t-Bu)}_2(\text{CH}_2\text{SiMe}_3)_2\). No evidence for alkyl group exchange between tantalum and osmium is observed. Pure \textit{anti}, \textit{anti}-\text{Os(CH-\text{-}t-Bu)}_2(\text{CH}_2\text{SiMe}_3)_2\) can be isolated by passing the reaction mixture through silica gel, since the \textit{syn}, \textit{anti} rotamer is unstable to acidic conditions. The NMR data for \textit{anti}, \textit{anti}-\text{Os(CH-\text{-}t-Bu)}_2(\text{CH}_2\text{SiMe}_3)_2\) are consistent with it having a \(\text{C}_2\text{v}\) structure with the two neopentyldienes oriented \textit{anti} to each other. (\(\delta H_\alpha = 15.15; \delta C_\alpha = 225.1; J_{\text{CH}} = 146\text{ Hz}\)) \textit{anti}, \textit{anti}-\text{Os(CH-\text{-}t-Bu)}_2(\text{CH}_2\text{SiMe}_3)_2\) is a thermally stable orange solid which can be crystallized from \(\text{Et}_2\text{O}/\text{CH}_3\text{CN}\) mixtures or with difficulty from pentane at \(-40^\circ\text{C}\).

**X-ray Crystal Structure of \textit{anti}, \textit{anti}-\text{Os(CH-\text{-}t-Bu)}_2(\text{CH}_2\text{SiMe}_3)_2**

Crystals of \textit{anti}, \textit{anti}-\text{Os(CH-\text{-}t-Bu)}_2(\text{CH}_2\text{SiMe}_3)_2\) suitable for X-ray diffraction were grown over a month from pentane at \(-40^\circ\text{C}\) and the structure was determined by Dr. W. M. Davis. A drawing of the molecular structure of \textit{anti}, \textit{anti}-\text{Os(CH-\text{-}t-Bu)}_2(\text{CH}_2\text{SiMe}_3)_2\) is shown in Figure 2.1.

Several features in the structure of \textit{anti}, \textit{anti}-\text{Os(CH-\text{-}t-Bu)}_2(\text{CH}_2\text{SiMe}_3)_2\) should be noted. The structure is a distorted tetrahedron. The angle between the two neopentyldiene groups is 94.9 (4)° and the angle between the two trimethylsilyl groups is 122.7 (4). Such distortions are common in four coordinate complexes containing two metal-ligand multiple bonds.\textsuperscript{20} The Os=C bond distance is 1.836 (7) Å, which is 0.05 - 0.10 Å shorter than most Os=C bond lengths in low-valent osmium carbene complexes, which suggests that there is greater metal-carbon double bond character in \textit{anti}, \textit{anti}-\text{Os(CH-\text{-}t-Bu)}_2(\text{CH}_2\text{SiMe}_3)_2.\textsuperscript{20} Alternately, the shorter Os=C bond distance can be
ascribed to the fact that this complex is four coordinate rather than six coordinate. (No other four coordinate osmium carbene complexes have been reported.) However, the Os=C bond distance is comparable to that observed in several osmium alkylidene complexes. The Os=C bond length is slightly shorter than that of the six-coordinate osmium methylidene complex, Os(CH₂)(Cl)(η²-C(O)C₆H₄CH₃)(PPh₃)₂ (1.86 (1)Å)²¹ and is somewhat longer than the Os=C bond length observed in six-coordinate trans-Os(TTP)(CHSiMe₃)(THF) (1.79 (2)Å) (TPP = tetra(phenyl)porphyrin).²² Thus, it seems more likely that the short M=C bond length is due to the lack of π-donor ligands on Cα rather than the coordination geometry or formal oxidation state of the metal.

The distance between the two alkylidene α carbons is 2.71 Å, which is much too long for there to be any sort of bonding between these carbons. Additionally, the orientation of the alkyl substituents is perpendicular to that which would be expected in an olefin adduct. anti, anti-Os(CH-t-Bu)₂(CH₂SiMe₃)₂ is unambiguously a bis(alkylidene) complex rather than a di-t-butylethylene complex.

M=C-C bond angles in alkylidenes range from 115-170°. The larger angles might arise as a consequence of an α-agostic interaction in the more electrophilic complexes.²³ Although a variety of anti alkylidene complexes have been studied, very few have been structurally characterized, and these complexes have M=C-C bond angles much closer to 120°. However, the majority of these complexes are five or six coordinate and/or have some sort of feature (steric, electronic, or a pendant group that coordinates to the metal center) that enforces the preference for the anti configuration of the alkylidene ligands and possibly influences the bond angle. For instance, the only structurally characterized four coordinate anti alkylidene complex is Re(C-t-Bu)(CHFc)[OC(CF₃)₂CH₃]₂ (Fc = Fe(Cp)(C₅H₄)).²⁴ In the synthesis of this complex, the steric bulk of the ferrocenyl group presumably causes the anti rotamer to be formed almost exclusively, and the Re=C-C bond angle is only 114.8 (7) Å.
Figure 2.1: A drawing of anti, anti-Os(CHt-Bu)₂(CH₂SiMe₃)₂ generated using atomic coordinates obtained by X-ray crystallography.
**Table 2.1:** Intramolecular Distances (Å) for the Non-Hydrogen Atoms of \textit{anti, anti-} Os(CH-t-Bu)$_2$(CH$_2$SiMe$_3$)$_2$.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance</th>
<th>Bond</th>
<th>Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os - C(1)</td>
<td>2.070 (6)</td>
<td>Si(1) - C(4)</td>
<td>1.88 (1)</td>
</tr>
<tr>
<td>Os - C(1')</td>
<td>2.070 (6)</td>
<td>Si(1) - C(5)</td>
<td>1.861 (8)</td>
</tr>
<tr>
<td>Os - C(2)</td>
<td>1.836 (7)</td>
<td>C(2) - C(5)</td>
<td>1.502 (9)</td>
</tr>
<tr>
<td>Os - C(2')</td>
<td>1.836 (7)</td>
<td>C(6) - C(7)</td>
<td>1.50 (1)</td>
</tr>
<tr>
<td>Si(1) - C(1)</td>
<td>1.881 (7)</td>
<td>C(6) - C(8)</td>
<td>1.54 (1)</td>
</tr>
<tr>
<td>Si(1) - C(3)</td>
<td>1.892 (9)</td>
<td>C(6) - C(9)</td>
<td>1.51 (1)</td>
</tr>
</tbody>
</table>

**Table 2.2:** Intramolecular Bond Angles (deg.) for the Non-Hydrogen Atoms of \textit{anti, anti-} Os(CH-t-Bu)$_2$(CH$_2$SiMe$_3$)$_2$.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Angle</th>
<th>Atoms</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1) - Os - C(1')</td>
<td>122.7 (4)</td>
<td>C(3) - Si(1) - C(5)</td>
<td>108.3 (4)</td>
</tr>
<tr>
<td>C(1) - Os - C(2)</td>
<td>109.2 (3)</td>
<td>C(4) - Si(1) - C(5)</td>
<td>108.5 (4)</td>
</tr>
<tr>
<td>C(1) - Os - C(2')</td>
<td>108.6 (3)</td>
<td>Os - C(1) - Si(1)</td>
<td>125.6 (4)</td>
</tr>
<tr>
<td>C(1') - Os - C(2)</td>
<td>108.6 (3)</td>
<td>Os - C(2) - C(6)</td>
<td>130.9 (6)</td>
</tr>
<tr>
<td>C(1') - Os - C(2')</td>
<td>109.2 (3)</td>
<td>C(2) - C(6) - C(7)</td>
<td>112.1 (6)</td>
</tr>
<tr>
<td>C(2) - Os - C(2')</td>
<td>94.9 (4)</td>
<td>C(2) - C(6) - C(8)</td>
<td>107.6 (6)</td>
</tr>
<tr>
<td>C(1) - Si(1) - C(3)</td>
<td>106.4 (4)</td>
<td>C(2) - C(6) - C(9)</td>
<td>109.0 (6)</td>
</tr>
<tr>
<td>C(1) - Si(1) - C(4)</td>
<td>114.7 (3)</td>
<td>C(7) - C(6) - C(8)</td>
<td>108.5 (7)</td>
</tr>
<tr>
<td>C(1) - Si(1) - C(5)</td>
<td>110.1 (4)</td>
<td>C(7) - C(6) - C(9)</td>
<td>109.7 (7)</td>
</tr>
<tr>
<td>C(3) - Si(1) - C(4)</td>
<td>108.6 (5)</td>
<td>C(8) - C(6) - C(9)</td>
<td>110.0 (7)</td>
</tr>
</tbody>
</table>
Table 2.3: Positional Parameters and B(eq.) for the Non-Hydrogen Atoms of \textit{anti}, \textit{anti-Os(CH-t-Ru)2(CH2SiMe3)2}.

<table>
<thead>
<tr>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>B(eq.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os</td>
<td>0</td>
<td>0.20780 (7)</td>
<td>0.25</td>
<td>2.21 (2)</td>
</tr>
<tr>
<td>Si(1)</td>
<td>0.1246 (1)</td>
<td>0.1789 (4)</td>
<td>0.2111 (1)</td>
<td>3.05 (8)</td>
</tr>
<tr>
<td>C(1)</td>
<td>0.0623 (4)</td>
<td>0.046 (1)</td>
<td>0.2264 (4)</td>
<td>2.9 (3)</td>
</tr>
<tr>
<td>C(2)</td>
<td>0.0517 (3)</td>
<td>0.410 (1)</td>
<td>0.3314 (4)</td>
<td>2.8 (3)</td>
</tr>
<tr>
<td>C(3)</td>
<td>0.2139 (5)</td>
<td>0.099 (2)</td>
<td>0.3026 (6)</td>
<td>5.5 (4)</td>
</tr>
<tr>
<td>C(4)</td>
<td>0.1195 (5)</td>
<td>0.484 (1)</td>
<td>0.2044 (6)</td>
<td>5.1 (4)</td>
</tr>
<tr>
<td>C(5)</td>
<td>0.1118 (6)</td>
<td>0.071 (2)</td>
<td>0.1165 (6)</td>
<td>5.7 (5)</td>
</tr>
<tr>
<td>C(6)</td>
<td>0.1093 (4)</td>
<td>0.382 (1)</td>
<td>0.4210 (4)</td>
<td>3.2 (3)</td>
</tr>
<tr>
<td>C(7)</td>
<td>0.1301 (5)</td>
<td>0.147 (1)</td>
<td>0.4432 (5)</td>
<td>4.3 (4)</td>
</tr>
<tr>
<td>C(8)</td>
<td>0.0835 (5)</td>
<td>0.466 (2)</td>
<td>0.4708 (5)</td>
<td>5.0 (5)</td>
</tr>
<tr>
<td>C(9)</td>
<td>0.1706 (4)</td>
<td>0.514 (2)</td>
<td>0.4414 (5)</td>
<td>4.7 (4)</td>
</tr>
<tr>
<td>Table 2.4: Crystal Data for Os(CH-r-Bu)₂(CH₂SiMe₃)₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------------------------------------</td>
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<tr>
<td><strong>Empirical Formula</strong></td>
<td>C₁₈H₄₀Si₂Os</td>
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<tr>
<td><strong>Formula Weight</strong></td>
<td>502.89</td>
<td></td>
<td></td>
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<tr>
<td><strong>Crystal Color, Habit</strong></td>
<td>orange, prismatic</td>
<td></td>
<td></td>
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<tr>
<td><strong>Crystal Dimensions (mm)</strong></td>
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<td></td>
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<tr>
<td><strong>Crystal System</strong></td>
<td>monoclinic</td>
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<tr>
<td><strong>No. Reflections Used for Unit Cell</strong></td>
<td>25 (14.0 - 27.0)</td>
<td></td>
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<tr>
<td><strong>Determination (2θ range)</strong></td>
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</tr>
<tr>
<td>a</td>
<td>24.007 (3) Å</td>
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<tr>
<td>b</td>
<td>6.146 (1) Å</td>
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<tr>
<td>c</td>
<td>20.110 (3) Å</td>
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<tr>
<td>β</td>
<td>126.02 (2)°</td>
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<tr>
<td>V</td>
<td>2399 (2) Å³</td>
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<tr>
<td><strong>Space Group</strong></td>
<td>C2/c</td>
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</tr>
<tr>
<td>Z</td>
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<td></td>
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</tr>
<tr>
<td>Dcalc</td>
<td>1.392g/cm³</td>
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<td></td>
</tr>
<tr>
<td>F₀₀₀</td>
<td>1008</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>μ(MoKα)</td>
<td>54.14 cm⁻¹</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>0.045</td>
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<td></td>
</tr>
<tr>
<td>Rw</td>
<td>0.041</td>
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</tbody>
</table>
The extremely acute Re=C-C angle has been attributed to the electronic effect of the ferrocene substituent. In \textit{anti, anti-}Os(CH-t-Bu)\textsubscript{2}(CH\textsubscript{2}SiMe\textsubscript{3})\textsubscript{2}, the Os=C-C bond angle is 130.9(6)°, which is slightly greater than the W=C-C bond angle observed in \textit{anti-}W(NAr')(CHCHCHCH\textsubscript{3})\textsubscript{2}[OC(CF\textsubscript{3})\textsubscript{2}CH\textsubscript{3}]\textsubscript{2} (quinuclidine) (126.3 (5)°).\textsuperscript{25}

\textbf{Extended Hückel Calculations on Os(CH\textsubscript{2})\textsubscript{2}(CH\textsubscript{3})\textsubscript{2}}

Extended Hückel calculations were performed on Os(CH\textsubscript{2})\textsubscript{2}(CH\textsubscript{3})\textsubscript{2} using the CaCHe system. Atomic coordinates for osmium and the methyl and methyldiene carbons were taken from the X-ray structure determination of \textit{anti, anti-}Os(CH-t-Bu)(CH\textsubscript{2}SiMe\textsubscript{3})\textsubscript{2}. The hydrogen atoms on the methylene ligands were located in the plane formed by the metal center and the two methyldiene carbons. This orientation is in agreement with the solid-state structure of \textit{anti, anti-}Os(CH-t-Bu)\textsubscript{2}(CH\textsubscript{2}SiMe\textsubscript{3})\textsubscript{2} as well as crystal structures of alkylidene-imido and alkylidene-alkylidyne complexes. For the purposes of the calculations, the atomic coordinates were chosen so that the metal center and the two methyldiene ligands were located on the xz plane, bisected by the z axis. The results of the calculations are shown in Figure 2.2.

Several features should be noted. The HOMO is an orbital of primarily d\textsubscript{xy} symmetry, bisecting the methyldiene ligands. Calculations on a variety of Os imido complexes had previously shown that the HOMO is primarily metal-based in these systems.\textsuperscript{2} The LUMO is the \pi\textsuperscript{*} system of the bis(methyldiene). The HOMO-1 and HOMO-2 are various bonding combinations of the \pi system.
Figure 2.2: Bonding in Os(CH₂)₂(CH₃)₂
(according to Extended Huckel calculations.)

* These MO's are viewed looking down the z axis.
It should be noted that there are sizable contributions from both the metal d orbitals and the carbon p orbitals, suggesting that the metal carbon double bond has a highly covalent nature. This is in agreement with the reactivity of anti, anti-Os(CH-t-Bu)₂(CH₂SiMe₃)₂. Thus, the bonding in Os(CH₂)₂(CH₃)₂ can be described by neither the Fischer nor Schrock extremes. The metal-centered HOMO is characteristic of Fischer carbenes, yet the highly covalent nature of the M=C bonds is more in agreement with Schrock carbenes.

The model is perhaps useful for describing the bonding in anti, anti-1b, but the syn, anti rotamers might be expected to have a more linear M-C-C bond angle for the syn alkylidene and possibly an agostic interaction with the metal center. This would change the bonding situation considerably, and possibly alter the order of the MO’s. Experimentally, this may explain the extreme differences in stability and reactivity towards acids between syn, anti and anti, anti rotamers, which will be discussed in the next section.

Photochemical Rotamerization of Os(CH-t-Bu)₂(R)₂

When solutions of syn, anti-Os(CH-t-Bu)(CH₂-t-Bu)₂ in toluene-d₈ are photolyzed at -85°C, isomerization of one of the neopentyldiene ligands occurs to form anti, anti-Os(CH-t-Bu)₂(CH₂-t-Bu)₂. Likewise, anti, anti-Os(CH-t-Bu)₂(CH₂SiMe₃)₂ isomerizes to syn, anti-Os(CH-t-Bu)₂(CH₂SiMe₃)₂ under the same conditions. Typically, 1:1 mixtures of the two rotameric forms can be obtained in this manner. NMR data for the four species are summarized in Scheme 2.2.

A number of qualitative observations were made and provide insight into the nature of the bis(alkylidene) complexes. First, the syn, anti rotamers were more thermally unstable than the anti, anti rotamers. Second, scrambling of H₂ occurs only in the syn, anti rotamers. A third observation is that the syn, anti rotamers react
quickly with acids, but the _anti, anti_ rotamers are inert to acids. This result would appear to be somewhat counterintuitive, since if there is an $\alpha$-agostic interaction the _syn, anti_ rotamer can be viewed as a sixteen electron complex and might be thought to be less reactive. However, if the agostic interaction of the _syn_ alkylidene is viewed as an equilibrium between a $d^2$ alkylidene and a $d^0$ alkylidyne hydride complex, the metal center can be viewed as being more oxidized, thus rendering the remaining neopentylidene ligand more nucleophilic at $C_\alpha$. 
Scheme 2.2: Photochemical Rotamerization of Os(CH-t-Bu)_2R_2.
Reactions of OsO$_2$(CH$_2$-t-Bu)$_2$ with Titanium and Molybdenum Alkyldiene Complexes.

No reaction was observed between OsO$_2$(CH$_2$-t-Bu)$_2$ and Mo(NAr)(CH-t-Bu)(O-t-Bu)$_2$. The reaction of OsO$_2$(CH$_2$-t-Bu)$_2$ with Tebbe’s reagent, Cp$_2$Ti(µ-CH$_2$)(µ-Cl)Al(CH$_3$)$_2$ in the presence of DMAP resulted in formation of insoluble precipitate, as would be expected if [Cp$_2$TiO]$_n$ were formed; however, no tractable products could be obtained. Cp$_2$Ti(CH(t-Bu)CH$_2$CH$_2$)$_2$ does not react with OsO$_2$(CH$_2$-t-Bu)$_2$ at room temperature in C$_6$D$_6$, although the reaction of Cp$_2$Ti(CH(t-Bu)CH$_2$CH$_2$) with OsO$_2$(CH$_2$-t-Bu)$_2$ in neat neohexene results in immediate precipitation of [Cp$_2$TiO]$_n$. [OsO(CH$_2$-t-Bu)$_2$]$_n$ is the only product isolated from the reaction mixture.

Reduction of syn, anti-Os(CH-t-Bu)$_2$(CH$_2$-t-Bu)$_2$

Although Os(CH-t-Bu)$_2$(CH$_2$-t-Bu)$_2$ does not bind ligands such as pyridine, acetonitrile, or triphenylphosphine oxide, it is readily reduced by phosphines such as trimethylphosphine, dimethylphenylphosphine, dmpe, or methylidiphenylphosphine. This is hardly surprising, since only a few Os(VI) organometallic complexes are stable to phosphines, and all of these complexes contain strongly stabilizing nitrido$^4$ or arylimido groups.$^2$ Evidence for neopentane formation is seen when the reaction of Os(CH-t-Bu)$_2$(CH$_2$-t-Bu)$_2$ with phosphines is monitored by $^1$H NMR, but products such as Os(C-t-Bu)(CH-t-Bu)(CH$_2$-t-Bu)(PR$_3$)$_2$ could not be isolated.

When Os(CH-t-Bu)$_2$(CH$_2$-t-Bu)$_2$ is dissolved in neat trimethylphosphine and allowed to react for an hour at 25°C, orange-red, pentane-soluble Os(PMe$_3$)$_3$(η$^2$-t-BuCC-t-Bu) can be isolated in 30-40% yield, recrystallized. Os(PMe$_3$)$_3$(η$^2$-t-BuCC-t-
Bu) can also be sublimed at 60°C (0.01 torr). The isolated yield is low due to the extreme solubility of these complexes and relatively small scale of the reaction.

\[ \text{t-BuCH}_2\text{Os=Os=t-Bu} \quad \text{PMe}_3 \quad \text{Me}_2\text{P} \quad \text{PMe}_3 \quad \text{orange crystals} \]

\(^{13}\text{C NMR revealed a resonance at 192 ppm, which is significantly upfield from typical terminal alkylidyne C\text{\textalpha} chemical shifts of 250-300 ppm,}^{20} \text{yet is almost 100 ppm downfield from the values observed in Os(CO)\textsubscript{4}(RCCR).}^{28,29} \text{The} ^{13}\text{C NMR data for C\text{\textalpha} is similar to that observed in the bis(carbyne) complexes, trans-[M(CNHR)\textsubscript{2}(dmpe)\textsubscript{2}]^{2+} (M = Mo, W) (190 - 205 ppm).}^{30} \text{IR failed to reveal the presence of an \eta^2-acetylene.} \]

\textbf{X-ray Structure Determination of Os(PMe}_3\textsubscript{3}(\eta^2-t\text{-BuCC-t-Bu})

Because of the ambiguity, the structure of Os(PMe}_3\textsubscript{3}(\eta^2-t\text{-BuCC-t-Bu}) was determined by X-ray crystallography and the \eta^2-alkyne structure was confirmed. Crystals of Os(PMe}_3\textsubscript{3}(\eta^2-t\text{-BuCC-t-Bu}) suitable for X-ray diffraction were grown by slow evaporation of Et\textsubscript{2}O from Et\textsubscript{2}O/CH\textsubscript{3}CN mixtures at 25°C over several days. Dr. W. M. Davis collected the data set and solved the structure. A drawing of the X-ray structure of Os(PMe}_3\textsubscript{3}(\eta^2-t\text{-BuCC-t-Bu}) is shown in Figure 2.3.
Figure 2.3: A drawing of Os(PMe₃)₃(η²-t-BuCC-t-Bu) based on atomic coordinates obtained by X-ray crystallography.
**Table 2.5: Intramolecular Distances (Å) for the Non-Hydrogen Atoms of Os(η²-t-BuCC-t-Bu)(PMe₃)₃.**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance</th>
<th>Bond</th>
<th>Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os - P(1)</td>
<td>2.219 (3)</td>
<td>P(3) - C(5)</td>
<td>1.83 (1)</td>
</tr>
<tr>
<td>Os - P(2)</td>
<td>2.291 (3)</td>
<td>P(3) - C(6)</td>
<td>1.83 (1)</td>
</tr>
<tr>
<td>Os - P(3)</td>
<td>2.295 (3)</td>
<td>C(7) - C(8)</td>
<td>1.30 (1)</td>
</tr>
<tr>
<td>Os - C(7)</td>
<td>2.02 (1)</td>
<td>C(7) - C(9)</td>
<td>1.51 (2)</td>
</tr>
<tr>
<td>Os - C(8)</td>
<td>2.01 (1)</td>
<td>C(8) - C(10)</td>
<td>1.54 (2)</td>
</tr>
<tr>
<td>P(1) - C(1)</td>
<td>1.83 (1)</td>
<td>C(9) - C(11)</td>
<td>1.48 (2)</td>
</tr>
<tr>
<td>P(1) - C(2)</td>
<td>1.83 (1)</td>
<td>C(9) - C(12)</td>
<td>1.56 (2)</td>
</tr>
<tr>
<td>P(1) - C(19)</td>
<td>1.84 (1)</td>
<td>C(9) - C(13)</td>
<td>1.51 (2)</td>
</tr>
<tr>
<td>P(2) - C(3)</td>
<td>1.84 (1)</td>
<td>C(10) - C(14)</td>
<td>1.52 (2)</td>
</tr>
<tr>
<td>P(2) - C(17)</td>
<td>1.84 (1)</td>
<td>C(10) - C(15)</td>
<td>1.51 (2)</td>
</tr>
<tr>
<td>P(2) - C(18)</td>
<td>1.84 (1)</td>
<td>C(10) - C(16)</td>
<td>1.54 (2)</td>
</tr>
<tr>
<td>P(3) - C(4)</td>
<td>1.83 (1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 2.6: Selected Intramolecular Bond Angles (deg.) Involving the Non-Hydrogen Atoms of Os(η²-t-BuCC-t-Bu)(PMe₃)₃.**

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Angle</th>
<th>Atoms</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(1) - Os - P(2)</td>
<td>93.5 (1)</td>
<td>Os - C(7) - C(8)</td>
<td>70.5 (7)</td>
</tr>
<tr>
<td>P(1) - Os - P(3)</td>
<td>94.0 (1)</td>
<td>Os - C(7) - C(9)</td>
<td>145.4 (9)</td>
</tr>
<tr>
<td>P(1) - Os - C(7)</td>
<td>116.0 (3)</td>
<td>Os - C(8) - C(7)</td>
<td>71.9 (7)</td>
</tr>
<tr>
<td>P(1) - Os - C(8)</td>
<td>115.3 (3)</td>
<td>Os - C(8) - C(10)</td>
<td>148.2 (9)</td>
</tr>
<tr>
<td>P(2) - Os - P(3)</td>
<td>96.5 (1)</td>
<td>C(7) - C(8) - C(10)</td>
<td>140 (1)</td>
</tr>
<tr>
<td>P(2) - Os - C(7)</td>
<td>139.8 (3)</td>
<td>C(7) - Os - C(8)</td>
<td>37.6 (4)</td>
</tr>
<tr>
<td>P(2) - Os - C(8)</td>
<td>106.4 (4)</td>
<td>C(8) - C(7) - C(9)</td>
<td>144 (1)</td>
</tr>
<tr>
<td>P(3) - Os - C(7)</td>
<td>107.2 (2)</td>
<td>P(3) - Os - C(8)</td>
<td>140.8 (3)</td>
</tr>
</tbody>
</table>
Table 2.7: Positional Parameters and B(eq) for the Non-Hydrogen Atoms of Os(η<sup>2</sup>-t-BuCC-t-Bu)(PMe<sub>3</sub>)<sub>3</sub>.

<table>
<thead>
<tr>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>B(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os</td>
<td>0.08798 (4)</td>
<td>0.24816 (3)</td>
<td>0.09928 (2)</td>
<td>1.53 (2)</td>
</tr>
<tr>
<td>P(1)</td>
<td>-0.0268 (3)</td>
<td>0.2660 (2)</td>
<td>-0.0257 (2)</td>
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</tr>
<tr>
<td>P(2)</td>
<td>-0.0518 (3)</td>
<td>0.3339 (2)</td>
<td>0.1719 (2)</td>
<td>2.4 (2)</td>
</tr>
<tr>
<td>P(3)</td>
<td>0.2659 (3)</td>
<td>0.3337 (2)</td>
<td>0.0676 (2)</td>
<td>2.4 (2)</td>
</tr>
<tr>
<td>C(1)</td>
<td>0.073 (1)</td>
<td>0.2396 (8)</td>
<td>-0.1215 (8)</td>
<td>5.5 (8)</td>
</tr>
<tr>
<td>C(2)</td>
<td>-0.179 (2)</td>
<td>0.2011 (8)</td>
<td>-0.037 (1)</td>
<td>5.7 (9)</td>
</tr>
<tr>
<td>C(3)</td>
<td>-0.017 (1)</td>
<td>0.3301 (7)</td>
<td>0.2893 (7)</td>
<td>3.6 (7)</td>
</tr>
<tr>
<td>C(4)</td>
<td>0.239 (1)</td>
<td>0.4265 (7)</td>
<td>0.013 (1)</td>
<td>4.8 (8)</td>
</tr>
<tr>
<td>C(5)</td>
<td>0.360 (1)</td>
<td>0.3649 (7)</td>
<td>0.1657 (8)</td>
<td>3.8 (7)</td>
</tr>
<tr>
<td>C(6)</td>
<td>0.420 (1)</td>
<td>0.3052 (7)</td>
<td>0.0045 (8)</td>
<td>4.1 (7)</td>
</tr>
<tr>
<td>C(7)</td>
<td>0.180 (1)</td>
<td>0.1435 (6)</td>
<td>0.1165 (7)</td>
<td>1.9 (6)</td>
</tr>
<tr>
<td>C(8)</td>
<td>0.058 (1)</td>
<td>0.1449 (6)</td>
<td>0.1548 (7)</td>
<td>2.1 (6)</td>
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<tr>
<td>C(9)</td>
<td>0.308 (1)</td>
<td>0.0945 (7)</td>
<td>0.0991 (8)</td>
<td>3.2 (7)</td>
</tr>
<tr>
<td>C(10)</td>
<td>-0.035 (1)</td>
<td>0.0929 (7)</td>
<td>0.2107 (8)</td>
<td>3.1 (7)</td>
</tr>
<tr>
<td>C(11)</td>
<td>0.347 (2)</td>
<td>0.0986 (7)</td>
<td>0.007 (1)</td>
<td>5.1 (8)</td>
</tr>
<tr>
<td>C(12)</td>
<td>0.288 (2)</td>
<td>0.0079 (8)</td>
<td>0.123 (1)</td>
<td>7 (1)</td>
</tr>
<tr>
<td>C(13)</td>
<td>0.429 (2)</td>
<td>0.1245 (9)</td>
<td>0.155 (1)</td>
<td>6 (1)</td>
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<tr>
<td>C(14)</td>
<td>0.044 (1)</td>
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<tr>
<td>C(15)</td>
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<td>C(16)</td>
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<td>C(17)</td>
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<td>C(18)</td>
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<td>0.4392 (7)</td>
<td>0.1606 (8)</td>
<td>3.9 (7)</td>
</tr>
<tr>
<td>C(19)</td>
<td>-0.109 (2)</td>
<td>0.3566 (8)</td>
<td>-0.064 (1)</td>
<td>5.8 (9)</td>
</tr>
<tr>
<td>Property</td>
<td>Value</td>
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<tr>
<td>----------------------------------------------</td>
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</tr>
<tr>
<td><strong>Empirical Formula</strong></td>
<td>C_{19}H_{45}P_{3}Os</td>
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</tr>
<tr>
<td><strong>Formula Weight</strong></td>
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<tr>
<td><strong>Crystal Color, Habit</strong></td>
<td>orange, parallelepiped</td>
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</tr>
<tr>
<td><strong>Crystal Dimensions (mm)</strong></td>
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<tr>
<td><strong>Crystal System</strong></td>
<td>monoclinic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>No. Reflections Used for Unit Cell</strong></td>
<td>25 (15.0 - 28.0)</td>
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<tr>
<td><strong>Determination (2θ range)</strong></td>
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</tr>
<tr>
<td>a</td>
<td>9.4148 (8) Å</td>
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</tr>
<tr>
<td>b</td>
<td>17.317 (1) Å</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>c</td>
<td>15.467 (1) Å</td>
<td></td>
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</tr>
<tr>
<td>β</td>
<td>90.98 (2°)</td>
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<tr>
<td>V</td>
<td>2521.2 (5) Å³</td>
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<tr>
<td><strong>Space Group</strong></td>
<td>P21/n</td>
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<tr>
<td><strong>Z</strong></td>
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<tr>
<td><strong>D_{calc}</strong></td>
<td>1.466 g/cm³</td>
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<tr>
<td><strong>F_{000}</strong></td>
<td>1120</td>
<td></td>
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<td></td>
</tr>
<tr>
<td><strong>μ(MoKα)</strong></td>
<td>52.50 cm(^{-1})</td>
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<tr>
<td><strong>R</strong></td>
<td>0.032</td>
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<tr>
<td><strong>R_w</strong></td>
<td>0.037</td>
<td></td>
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</tr>
</tbody>
</table>
In the solid state structure of Os(PMe₃)₃(η²-t-Bu-CC-t-Bu), several features should be noted. The C-C bond length of the coordinated alkyne is 1.30 (1) Å, which is a bit longer than that observed in Os(CO)₄(Me₃SiCCSiMe₃) (1.273 (8) Å)²⁹ and is well within the range of normal C-C bond lengths in electron-rich alkyne complexes.³¹ The strength of the metal-alkyne interaction can more readily be assessed by the metal-C(alkyne) bond distance and the back-bending angle of the substituents on the alkyne ligand. The Os-C(7) and Os-C(8) bond lengths are 2.02 (1) Å and 2.01 (1) Å, respectively. This is significantly shorter than the bond lengths observed in Os(CO)₄(Me₃SiCCSiMe₃) (2.267 (6) Å and 2.244 (6) Å).²⁹ Likewise, the bend-back angles at C(7) (34.6 (9)°) and C(8) (31.8 (9)°) are larger than those observed in Os(CO)₄(Me₃SiCCSiMe₃) (20.9 (6)° and 26.3 (6)°).²⁹ The structural data suggest that the metal-alkyne interaction is significantly stronger in Os(PMe₃)₃(η²-t-BuCC-t-Bu) than it is in Os(CO)₄(Me₃SiCCSiMe₃). This conclusion is consistent with the ¹³C data, electron-counting and coordination arguments, and the fact that the carbonyl ligands are better π-acceptors than PMe₃ and should compete more effectively with the alkyne for π-backbonding.

Possible Mechanisms of Formation of Os(PMe₃)₃(η²-t-BuCC-t-Bu)

It is not possible to study the mechanism of formation of Os(PMe₃)₃(η²-t-BuCC-t-Bu) by standard methods, since the reaction is quite fast and only yields clean product when neat trimethylphosphine is used as the solvent. However, the production of neopentane when Os(CH-t-Bu)₂(CH₂-t-Bu)₂ is allowed to react with 2-10 equivalents of trimethylphosphine in C₆D₆ suggests that α-hydrogen abstraction reactions are occurring. Two plausible mechanisms are shown in Scheme 2.3. In both proposed mechanisms phosphine-induced α-hydrogen abstraction forms Os(C-t-
Bu)(CH-t-Bu)(CH_2-t-Bu)(PMe_3)_2. In the “bis(alkylidyne)” mechanism, an additional α-hydrogen abstraction occurs to form transient Os(C-t-Bu)_2((PMe_3)_2. Coordination of a third phosphine would then induce coupling of the two neopentyldiyne ligands to form Os(PMe_3)_3(t-BuCCt-Bu). Alternately, the alkylidene and alkylidyne fragments could couple to yield a “η^2-vinyl” intermediate, which then eliminates neopentane to form Os(PMe_3)_3(t-BuCCt-Bu). At low phosphine concentrations, other modes of decomposition predominate, but in neat trimethylphosphine the reduction to Os(PMe_3)_3(t-BuCC-t-Bu) is the predominant process occurring. An alternate mechanism, consisting of phosphine-induced formation of Os(η^2-t-BuCHCH-t-Bu)(CH_2-t-Bu)_2(PMe_3)_n (n = 2, 3) followed by dehydrogenation of bound di-t-butylethylene to form Os(PMe_3)_3(t-BuCCt-Bu) and 2 equivalents of neopentane, cannot be excluded, but we prefer the carbene-carbyne mechanisms based on precedent with d^0 systems and the fact that the proposed carbene-carbyne mechanisms are similar to that proposed for reductive coupling of carbon monoxide and isocyanides by anionic group 5 and 6 metal complexes. A similar coupling reaction of a methylidyne ligand with carbon monoxide in the presence of Lewis acids has been reported.\textsuperscript{32} In these systems, mechanistic studies support the intermediacy of a carbene-carbyne intermediate, but no studies have been able to determine the intimate details of the conversion of the carbene-carbyne to acetylene adduct.\textsuperscript{33} In a related d^0 system, W(C-t-Bu)(CH-t-Bu)(CH_2-t-Bu)(dmpe) reacts with added dmpe to form W(C-t-Bu)(H)(dmpe)_2 and di-t-butylethylene.\textsuperscript{18,34} In the tungsten system, formation of the alkylidyne-hydride complex is preferred over formation of W(PMe_3)_3(t-BuCC-t-Bu).
Scheme 2.3: Proposed Mechanisms of Formation of Os(PMe₃)₃(η²-t-BuCC-t-Bu)
Reactivity of Os(PMe₃)₃(η²-t-BuCC-t-Bu)

Most organooosmium complexes can be described as Os(II) or Os(IV). Mononuclear complexes of Os(0) are extremely rare, and the majority contain several π-acid ligands, usually carbonyls, olefins, or acetylenes. The air- and water-stable complexes Os(CO)₄(RCCR) (R = H, SiMe₃, CF₃) have been prepared by Takats and coworkers in the photochemical reaction of Os₃(CO)₁₂ with alkynes. However, the reactivity of these complexes with small molecules has not been extensively studied. Similarly, Os(PMe₃)₅ is the only Os(0) phosphine complex that has been reported, and no further reports of its reactivity have been published. Interestingly, we found that Os(PMe₃)₅ does not react with bis(trimethylsilyl)acetylene or 2-butyne to form Os(PMe₃)₃(RCCR). Os(PMe₃)₅ undergoes reversible phosphine dissociation to form transient Os(PMe₃)₄; possible intermediates such as “Os(PMe₃)₄(RCCR)” or “Os(PMe₃)₃” must be sterically disfavored or relatively high energy species. If “Os(PMe₃)₄(RCCR)” can form, it may simply lose alkyne rather than phosphine.

Os(PMe₃)₃(η²-t-BuCC-t-Bu) does not readily lose di-t-butylacetylene. Os(PMe₃)₃(η²-t-BuCC-t-Bu) fails to react with neat 2-butyne or bis(trimethylsilyl)acetylene at room temperature. Likewise, no exchange is observed with added PMe₃ in C₆D₆, and Os(PMe₃)₃(η²-t-BuCC-t-Bu) does not react with excess acetonitrile, ethylene, 3 equivalents of tricyclohexyl phosphine or two equivalents of bipyridyl or TMEDA.

Os(PMe₃)₃(η²-t-BuCC-t-Bu) reacts with carbon monoxide in benzene or pentane to form colorless Os(PMe₃)₂(CO)₂(η²-t-BuCC-t-Bu). No further loss of phosphines occurs in the presence of a large excess of CO, and di-t-butylacetylene is not displaced. In Os(PMe₃)₂(CO)₂(η²-t-BuCC-t-Bu), the acetylene ligand is formally a two-electron donor, and this is manifested in the chemical shift of the acetylenic carbon
(106.8 ppm), which is almost 100 ppm upfield from the chemical shifts of the complexes where di-tert-butylacetylene is a four-electron donor.

Os(PMe₃)₃(η²-t-BuCC-t-Bu) is extremely air- and water-sensitive. Os(PMe₃)₃(η²-t-BuCC-t-Bu) reacts rapidly with acids and pyridinium salts, but a clean product can only be isolated when [H(OEt₂)]⁺[BARF₄]⁻ is the proton source. Yellow, crystalline [Os(H)(PMe₃)₃(η²-t-BuCC-t-Bu)]⁺[BARF₄]⁻ is isolated in 70% yield. The hydride resonance is found at -6.16 ppm. Its quartet structure suggests that it is equally coupled to the three phosphine ligands on the NMR time scale (J_HP = 12 Hz).

\[
\begin{align*}
\text{Me}_3\text{P} & \quad \text{Os} & \quad \text{Me}_3\text{P} \\
\text{Me}_3\text{P} & \quad \text{PMe}_3
\end{align*}
\]

In the presence of 5 equivalents of PMe₃ in CH₂Cl₂ [Os(H)(t-BuCC-t-Bu)(PMe₃)₃⁺[BARF₄]⁻ loses di-t-butylacetylene to form colorless cubes of [Os(H)(PMe₃)₅⁺[BARF₄]⁻ in virtually quantitative yield. This complex is an analog of [Os(H)(PMe₃)₅⁺[OTf]⁻ and has similar spectral data. It is interesting to note that in the presence of trimethylphosphine, di-t-butylacetylene is readily lost from the more electrophilic Os(II) species but not from the neutral Os(0) species, although di-t-butylacetylene may be regarded as a four-electron donor in both cases. This is an example of the greater affinity of Os(II) for σ-donor ligands such as PMe₃ compared to the π-acceptor ligand, di-t-butylacetylene; the opposite is observed in the Os(0) complex, Os(t-Bu⁺C≡C-t-Bu)(PMe₃)₃.

The reaction of Os(PMe₃)₃(η²-t-BuCC-t-Bu) with dihydrogen was investigated. Os(PMe₃)₃(η²-t-BuC≡C-t-Bu) reacts with dihydrogen in the presence of excess trimethylphosphine to give cis-OsH₂(PMe₃)₄ and di-t-butylethylene. In the absence
of excess phosphine, Os(PMe₃)₃(η²-t-BuC≡C-t-Bu) in C₆D₆ reacts with dihydrogen (1 atm) to form di-t-butylethylene, but the fate of the metal could not be determined. No further hydrogenation of di-t-butylethylene was observed in the presence or absence of PMe₃, and no hydrogenation of added 4-octyne was observed.

Discussion and Conclusions

Alkylidene/oxo exchange reactions were found to be an efficient route to the Os(VI) bis(alkylidenes). This represents a new synthetic route to alkylidene complexes as well as a new non-reductive means of functionalizing oxo groups. Although the scope of these experiments was limited to Os(VI) dioxo complexes, the alkylidene/oxo exchange reaction may ultimately prove useful for other metals or for functionalizing metal oxide surfaces. syn,anti-Os(CH-t-Bu)₂(CH₂-t-Bu)₂ may be regarded as another member of the series Ta(CH-t-Bu)(CH₂-t-Bu)₃, W(C-t-Bu)(CH₂-t-Bu)₃, and Re(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu)₂. Like these complexes, syn,anti-Os(CH-t-Bu)₂(CH₂-t-Bu)₂ is formed in low yield from the reaction of a metal halide (TaCl₅, WCl₆) or oxide (Re₂O₇) with neopentylmagnesium chloride, or in higher yield from a multi-step route. Unlike these complexes, this complex is d², not d⁰, however.

Os(CH-t-Bu)₂R₂ can adopt either the syn, anti or anti, anti configuration. As is the case with d⁰ complexes of molybdenum, tungsten, and rhenium, the two rotameric forms exhibit markedly different reactivity. In the d² osmium complexes, the likely
presence of an agostic interaction of the syn neopentylidene has a large influence on the reactivity and stability of these complexes. Unfortunately, quantitative investigations were not possible.

There are several features of the Os(CH-t-Bu)₂(R)₂ complexes that are puzzling. One is that the two rotameric forms of Os(CH-t-Bu)₂(R)₂ exhibit markedly different reactivity. For example, for a given alkyl group, the syn,anti isomer is much less thermally stable than the anti,anti rotamer and decomposes with loss of neopentane or tetramethyldisilane over several hours at 25°C in C₆D₆ or toluene-d₈. Also, the syn,anti isomers react with acids, while the anti,anti isomers are stable under identical conditions. Another difference is that α protons appear to scramble in the syn,anti rotamer more readily. Lastly, it is puzzling why Os(C-t-Bu)(CH₂-t-Bu)₃ is not the lower energy form of Os(CH-t-Bu)₂(CH₂-t-Bu)₂, while Os(C-t-Bu)(CH₂-t-Bu)₂(O-t-Bu) (see Chapter 3) is preferred over hypothetical Os(CH-t-Bu)₂(CH₂-t-Bu)(O-t-Bu). It is interesting to note that in C₃ᵥ symmetric Os(C-t-Bu)(CH₂-t-Bu)₃ the dₓᵧ and dₓ²₋ᵧ² orbitals (if the z axis passes through the Os≡C bond) would be degenerate and d² Os(C-t-Bu)(CH₂-t-Bu)₃ therefore could be paramagnetic. That degeneracy is broken in the Os(VI) neopentylidyne complexes reported in Chapter 3 as a consequence of π bonding.

The reduction of Os(CH-t-Bu)₂(CH₂-t-Bu)₂ in the presence of neat trimethylphosphine to form Os(PMe₃)₃(t-BuCC-t-Bu) may be thought to proceed through an alkylidene-alkylidyne intermediate. Such reductive coupling to form alkynes is the subject of much current interest. Examples of reductive coupling have been observed in for M = Nb, Ta, Cr, Mo, and W, but to our knowledge this is the first possible example of a later transition metal participating in such a reaction. Earlier efforts to extend this chemistry to Tc and Re were unsuccessful.
The osmium bis(neopentyldiene) complexes are rare examples of bis(alkylidene) complexes and are the first four-coordinate osmium carbenes reported. The first goal of the project, the synthesis of stable Os(VI) alkylidene complexes, was achieved. In the next chapter, the synthesis and reactivity of osmium(VI) neopentyldiyne complexes is described.
Experimental

General Details. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres HE-43 dry box 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 CaCl₂, 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 Isotopes. Tetrahydofuran-d₈ was vacuum transferred from sodium benzophenone ketyl. C₆D₆, CD₂Cl₂, CDCI₃, CD₃CN, and pyridine-d₅ were stored over activated molecular sieves in the dry box. CD₃OD was used as received.

OsO₄ was purchased from Strem Chemicals and converted to K₂[OsO₂(OH)₄] by the literature procedure, or reclaimed from osmium-containing wastes by hypochlorite oxidation and distillation into KOH solution. Ethanol was added to the resulting solution to precipitate K₂[OsO₂(OH)₄]. (PPh₄)₂[OsO₂Cl₄], Zn(CH₃-t-Bu)₂, Mg(CH₂-t-Bu)₂(dioxane), LiCH₂-t-Bu, Cp₂Ti(μ-CH₂)(μ-Cl)AlMe₂, Ta(CH₂-t-Bu)(CH₂-t-Bu)₃, Os(PMe₃)₅, and [H(OEt₂)₂]⁺[BAR₄]⁻ were prepared by literature methods. Al(CH₂-t-Bu)₃(THF) was prepared from AlCl₃ and t-BuCH₂MgCl in THF and then sublimed. Trimethylphosphine was purchased from Strem or Aldrich. Silica gel was typically 70-230 mesh (Aldrich) or 230-400 mesh (Bodman).
NMR spectra were recorded on either a Bruker WM-250, Varian XL-300, Varian UNITY-300 or Varian VXR-500 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$_2$Cl$_2$ 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.

**OsO$_2$(CH$_2$t-Bu)$_2$.** Dineopentylzinc (0.853 g, 4.12 mmol) was added to a slurry of [P(C$_6$H$_5$)$_4$]$_2$[OsO$_2$(Cl)$_4$] (2.00 g, 1.92 mmol) in 50 mL of CH$_2$Cl$_2$. The solution immediately became purple-brown. The solution was stirred for 30 minutes and then filtered through silica gel. The solvent was removed in vacuo to yield a brown-purple solid, which was then extracted with pentane, filtered, and the volume of the filtrate was reduced to 5 mL. Upon cooling the resulting solution to -40°C, purple-brown needles formed and were collected and dried; yield 460 mg (66%): $^1$H NMR (C$_6$D$_6$) $\delta$ 4.21 (s, 4, CH$_2$t-Bu), 0.97 (s, 18, t-Bu); $^{13}$C NMR (C$_6$D$_6$) $\delta$ 34.9 (CMe$_3$), 34.0 (CH$_2$CMe$_3$, J$_{CH}$ = 133), 31.1 (CMe$_3$, J$_{CH}$ = 126); IR (Nujol) cm$^{-1}$ 937, 981 (s, OsO$_2$). Anal. Calcd for OsC$_{10}$H$_{22}$O$_2$: C, 32.95; H, 6.08. Found: C, 33.33; H, 6.00.

**OsO$_2$(CH$_2$CMe$_2$Ph)$_2$.** [P(C$_6$H$_5$)$_4$]$_2$[Os(O)$_2$(Cl)$_4$] (0.99 g, 0.95 mmol) was slurried in 10 mL of CH$_2$Cl$_2$ and the mixture was cooled to -40°C. Zn(CH$_2$CMe$_2$Ph)$_2$ (0.330 mg, 1.00 mmol) was added and the mixture immediately darkened. The solution was allowed to warm to room temperature and stirred for 2 hours. The solvent was removed in vacuo to yield a brown-purple solid, which was then extracted with toluene. The toluene was then removed in vacuo to yield a brown oil which was pure OsO$_2$(CH$_2$CMe$_2$Ph)$_2$ by $^1$H NMR (260 mg, 56%): $^1$H NMR (C$_6$D$_6$) $\delta$ 7.0-7.2 (m, 5,
Ph), 4.44 (s, 4, OsCH$_2$CM$_2$Ph), 1.29 (s, 12, OsCH$_2$CM$_2$Ph); $^{13}$C NMR (C$_6$D$_6$) $\delta$ 148.4, 127.3, 126.2, 125.8 (Ph), 41.6 (OsCH$_2$CM$_2$Ph), 34.1 (OsCH$_2$CM$_2$Ph) 29.5 (OsCH$_2$CM$_2$Ph); IR (Nujol) cm$^{-1}$ 979, 936 (Os=O).

[Os(O)$_2$(CH$_2$SiMe$_3$)$_2$)$_n$. [P(C$_6$H$_5$)$_4$][Os(O)$_2$(Cl)$_4$] (0.998 g, 0.96 mmol) was slurred in 10 mL of CH$_2$Cl$_2$ and the mixture was cooled to -40°C. Zn(CH$_2$SiMe$_3$)$_2$ (0.45 g, 1.88 mmol) was added and the mixture immediately darkened. The solution was allowed to warm to room temperature and stirred for 30 minutes and then passed through silica gel. The solvent was removed in vacuo to yield a brown-purple solid, which was then extracted with pentane. After removal of the pentane in vacuo, a purple-brown microcrystalline solid was obtained (204 mg, 52%): $^1$H NMR (C$_6$D$_6$) $\delta$ 5.07, 4.20, 4.16, 3.51 (d, 1 each, OsCH$_2$SiMe$_3$, $J_{HH} = 9$ Hz), 0.36, 0.17 (s, 9 each, SiMe$_3$); $^{13}$C NMR (C$_6$D$_6$) $\delta$ 41.4, 30.6 (OsCH$_2$SiMe$_3$), 1.4, 0.8 (SiMe$_3$); IR (Nujol) cm$^{-1}$ 860 (bridging Os=O).

[(tBuCH$_2$)$_2$OsO]$_n$. OsO$_2$(CH$_2$-t-Bu)$_2$ (179 mg, 0.41 mmol) was dissolved in 5 mL of THF and solid Al(CH$_2$-t-Bu)$_3$(THF) (125 mg, 0.40 mmol) was added. The resulting red solution was stirred for 1.5 hours at room temperature and the volatiles removed in vacuo to yield a red solid which was dissolved in pentane and passed through silica gel to remove the aluminum-containing byproducts. The volatiles were removed from the resulting red solution and a red film was obtained which was pure [OsO(CH$_2$-t-Bu)$_2$]$_n$ by NMR (108 mg, 75%). A crystalline sample for elemental analysis could be obtained by recrystallization from ether/acetonitrile mixtures at -40°C: $^1$H NMR (C$_6$D$_6$) $\delta$ 5.83 (d, 1, CH$_a$H$_b$-t-Bu, $J_{HH} = 10$ Hz), 4.99 (d, 1, CH$_a$H$_b$-t-Bu, $J_{HH} = 10$ Hz), 5.20 (d, 1, CH$_a$H$_b$-t-Bu, $J_{HH} = 12$ Hz), 4.40 (d, 1, CH$_a$H$_b$-t-Bu, $J_{HH} = 12$ Hz), 1.40, 1.33 (s, 9H each, t-Bu); $^{13}$C NMR (C$_6$D$_6$) $\delta$ 53.5, 42.5 (CH$_2$-t-Bu),
37.5, 36.5 (CH₂CMe₃), 32.6 (CH₂CMe₃, the two †Bu peaks were coincident in C₆D₆); IR (Nujol) cm⁻¹ 980 (vs, Os=0). Anal. Calcd for OsC₁₀H₂₂O: C, 34.47; H, 6.36. Found: C, 34.38; H, 6.14.

[Os(CH₃)(CH₂-t-Bu)]₂. OsO₂(CH₂-t-Bu)₂ (225 mg, 0.60 mmol) was dissolved in 10 mL of pentane and the solution was cooled to -40°C. Trimethylaluminum (0.96 mmol, as a 2.0 M solution in hexanes) was added and the mixture was allowed to warm to room temperature. The mixture became dark and a precipitate occurred. After 20 minutes, the solution was filtered through celite to yield a bright orange solution, and the volatiles were removed in vacuo, leaving an orange crystalline solid which was > 95% pure by ¹H NMR. (93 mg, 43%) An analytical sample was recrystallized from ether/ acetonitrile at -40°C: ¹H NMR (C₆D₆) δ 3.46 (s, 6, OsCH₂), 3.03 (s, 8, CH₂CMe₃), 1.23 (s, 36, CMe₃); ¹³C NMR (C₆D₆) δ 66.7 (CH₂-t-Bu), 37.9 (CMe₃), 32.7 (CMe₃), 31.4 (OsCH₃). Anal. Calcd for Os₂C₂₂H₅₀: C, 38.02; H, 7.25. Found: C, 38.15; H, 7.79.

**syn, anti-Os(CH-t-Bu)₂(CH₂-t-Bu)₂.** OsO₂(CH₂-t-Bu)₂ (100 mg, 0.27 mmol) was dissolved in 10 mL of pentane and the solution was chilled to -40°C. Ta(CH-t-Bu)(CH₂-t-Bu)₃ (304 mg, 0.65 mmol) was dissolved in 3 mL of pentane. The solution was cooled to -40°C and then added dropwise to the stirring solution of OsO₂(CH₂-t-Bu)₂. [Ta(O)(CH₂-t-Bu)₃]₃n precipitated immediately. The mixture was allowed to warm to room temperature and was stirred for 30 minutes. The resulting orange-brown mixture was vacuum filtered quickly through silica gel and solvents were removed from the filtrate in vacuo to yield an orange-red oil (83 mg, 65%) which was >90% pure by ¹H NMR. (The main impurity is the rotational isomer, **anti, anti-Os(CH-t-Bu)₈(CH₂-t-Bu)₂**.) Occasionally, some pentane-insoluble colorless material remained after the first
filtration and the crude oil was redissolved in 2-5 mL of pentane and filtered through a pipette full of silica gel: $^1$H NMR (C$_6$D$_6$) $\delta$ 16.33 (s, 1, CH-t-Bu, $J_{CH} = 150$), 11.54 (s, 1, CH-t-Bu, $J_{CH} = 130$), 2.65 (AB quartet, 4, CH$_2$-t-Bu), 1.33 (s, 9, CH-t-Bu), 1.17 (s, 9, CH-t-Bu), 0.99 (s, 18, CH$_2$-t-Bu); $^{13}$C NMR (toluene-$d_8$) $\delta$ 224.2 (CH-t-Bu), 210.5 (CH-t-Bu), 50.1 (CH$_2$-t-Bu), 48.2, 43.9, 32.7 (CMe$_3$), 33.6 (CH$_2$CMe$_3$), 31.0, 27.8 (CHCMe$_3$). syn, anti-Os(CH-t-Bu)$_2$(CH$_2$-t-Bu)$_2$ is too unstable to be analyzed.

**anti, anti-Os(CH-t-Bu)(CH$_2$-t-Bu)$_2$.** $^1$H NMR (tol-$d_8$) $\delta$ 14.90 (s, 2, OsCH-t-Bu), 2.28 (s, 4, OsCH$_2$-t-Bu), 1.26, 0.88 (s, 18 each, t-Bu); $^{13}$C (tol-$d_8$) $\delta$ 226.9 (OsCH-t-Bu, $J_{C-H} = 142$ Hz), 61.0 (OsCH$_2$-t-Bu), 45.6, 35.1 (CMe$_3$), 34.9, 31.9 (CMe$_3$).

**anti, anti-Os(CH-t-Bu)$_2$(CH$_2$SiMe$_3$)$_2$.** In the dark, [OsO$_2$(CH$_2$SiMe$_3$)$_2$]$_n$ (244 mg, 0.62 mmol/n) was dissolved in 10 mL of pentane and the solution was chilled to $-40^\circ$C. Ta(CH-t-Bu)(CH$_2$-t-Bu)$_3$ (603 mg, 1.29 mmol) was dissolved in 3 mL of pentane and chilled to $-40^\circ$C and then added to the cold solution of [OsO$_2$(CH$_2$SiMe$_3$)$_2$]$_n$ with stirring. TaO(CH$_2$-t-Bu)$_3$ precipitated as the mixture warmed to room temperature. The brown reaction mixture was stirred for 45 minutes and then vacuum-filtered quickly through silica gel. Pentane was removed from the filtrate in vacuo to yield an orange brown solid. (120 mg, 38%). anti, anti-Os(CH-t-Bu)$_2$(CH$_2$SiMe$_3$)$_2$ can be easily recrystallized from Et$_2$O/CH$_3$CN mixtures at $-40^\circ$C, or with difficulty, form pentane or hexamethyldisiloxane at $-40^\circ$C: $^1$H NMR (C$_6$D$_6$) $\delta$ 15.15 (s, 2, OsCH-t-Bu), 1.18 (s, 18, OsCH-t-Bu), 0.83 (s, 4, OsCH$_2$SiMe$_3$), 0.00 (s, 18, SiMe$_3$); $^{13}$C NMR (C$_6$D$_6$) $\delta$ 225.1 (OsCH-t-Bu, $J_{CH} = 146$), 47.4 (OsCMe$_3$), 28.6 (CMe$_3$), 22.6 (OsCH$_2$SiMe$_3$), 3.04 (SiMe$_3$).
syn, anti-\(\text{Os(CH-t-Bu)}_2(\text{CH}_2\text{SiMe}_3)_2\). \(^1\text{H}\) NMR (\(\text{C}_6\text{D}_6\)) \(\delta\) 16.70 (s, 1, anti-\(\text{OsCH-t-Bu}\)), 12.27 (s, 1, syn -\(\text{OsCH-t-Bu}\)), 1.32, 1.17 (s, 9 each, t-Bu), 0.11 (s, 18, \(\text{SiMe}_3\)). (the diastereotopic \(\text{CH}_2\)'s could not be located.) \(^{13}\text{C}\) (tol-\(\text{d}_8\); partial data) \(\delta\) 221 (anti-\(\text{OsCH-t-Bu}\), \(J_{\text{CH}} = 148\) Hz), 210 (syn-\(\text{OsCH-t-Bu}\), \(J_{\text{CH}} = 130\) Hz).

**X-Ray Structure Determination of \(\text{Os(CH-t-Bu)}_2(\text{CH}_2\text{SiMe}_3)_2\).** An orange prismatic crystal of \(\text{C}_{18}\text{H}_{40}\text{Si}_2\text{Os}\) having approximate dimensions of 0.180 x 0.210 x 0.280 mm was mounted on a glass fiber. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite chromated Mo K\(\alpha\) radiation. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range 14.00 < \(2\theta\) < 27.00 corresponded to a monoclinic cell with dimensions: \(a = 24.007(3)\) Å, \(b = 6.146(1)\) Å, \(c = 20.110(3)\) Å, \(\beta = 126.06(2)^\circ\), \(V = 2399\) (2) Å\(^3\). For \(Z = 4\) and F. W. = 502.89, the calculated density is 1.392 g/cm\(^3\). Based on the systematic absences of \(hkl: h + k \neq 2n\) and \(h0l: l \neq 2n\), packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be: \(c2/c\) (#15).

The data were collected at a temperature of \(-72 \pm (1)^\circ\)C using the \(\omega-2\theta\) scan technique to a maximum \(2\theta\) value of 54.9\(^\circ\). Omega scans of several intense reflections, made prior to data collections, had an average width at half-height of 0.22\(^\circ\) with a take-off angle of 2.8\(^\circ\). Scans of \((0.80 + 0.35\ \tan\theta)\) were made at speeds 1.9 to 16.5/min (in omega). Moving-crystal moving counter background measurements were made by scanning an additional 25% above and below the scan range. The counter aperture consisted of a variable horizontal slit with a width ranging from 2.0 to 2.5 mm and a vertical slit set to 2.0 mm. The diameter of the incident beam collimator was 0.7 mm
and the crystal to detector distance was 21 cm. For intense reflections an attenuator was automatically inserted in front of the detector.

Of the 5140 reflections which were collected, 5044 were unique \( R_{int} = 0.096 \); equivalent reflections were merged. The intensities of three representative reflections which were measured after every 60 minutes of X-ray exposure time remained constant throughout data collections indicating crystal and electronic stability (no decay corrections were applied). The linear absorption coefficient for Mo K\( \alpha \) is 54.1 cm\(^{-1} \). An empirical absorption correction, using the program DIFABS, was applied which resulted in transmissions factors ranging from 0.75 to 1.44. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 0.38151 x 10\(^{-7} \)).

The structure was solved by a combination of the Patterson method and direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 2297 observed reflections (I > 3.00σ(I)) and 97 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of: \( R = 0.045; R_w = 0.041 \).

The standard deviation of an observation of unit weight was 1.34. The weighting scheme was based on counting statistics and included a factor \( p = 0.02 \) to downweight the intense reflections. Plots of \( \Sigma w(|F_o| - |F_c|)^2 \) versus |F\( o \)|, reflection order in data collection, sin\( \theta \)/\( \lambda \) and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.57 and -1.57e\(^{-7} \)Å\(^3 \), respectively.

Neutral atom scattering factors were taken from Cromer and Waber. Anomalous dispersion effects were included in F\( \text{calc} \); the values for \( \Delta f' \) and \( \Delta f'' \) were
those of Cromer. All calculations were performed using the TEXSAN crystallographic
data package of Molecular Software Corporation.

Os(PMe$_3$)$_3$(t-BuCC-t-Bu). Os(CH-t-Bu)$_2$(CH$_2$-t-Bu)$_2$ (175 mg, 0.37 mmol) was dissolved in 2 mL of trimethylphosphine. The red solution was stirred for 1 hour at room temperature, and then PMe$_3$ was removed in vacuo and the resulting dark red solid was extracted with 5 mL of pentane and filtered. Pentane was removed in vacuo, and an orange solid was isolated. Recrystallization from Et$_2$O/CH$_3$CN yielded 65 mg (32%) of orange flakes: $^1$H NMR (C$_6$D$_6$) $\delta$ 1.55 (s, 18, t-Bu), 1.48 (d, 27, PMe$_3$, $^2$J$_{PH}$ = 6 Hz); $^{13}$C NMR (C$_6$D$_6$) $\delta$ 192.3 (br d, t-BuCC-t-Bu, $^2$J$_{CP}$ = 10 Hz), 37.9 (CMe$_3$), 33.6 (CMe$_3$), 29.4 (d, PMe$_3$, $^1$J$_{CP}$ = 30 Hz); $^{31}$P NMR (C$_6$D$_6$) $\delta$ -39.5. Anal. Calcd for OsC$_{19}$H$_{45}$P$_3$: C; 40.99. H; 8.15. Found: C; 41.32. H; 8.36.

Crystal Structure of Os(η$^2$-t-BuCC-t-Bu)(PMe$_3$)$_3$. Crystals of Os(η$^2$-t-BuCC-t-Bu)(PMe$_3$)$_3$ suitable for X-ray diffraction were grown by slow evaporation of Et$_2$O from Et$_2$O/CH$_3$CN solutions of Os(η$^2$-t-BuCC-t-Bu)(PMe$_3$)$_3$ at 25°C over several days. An orange parallelepiped crystal of C$_{19}$H$_{45}$P$_3$Os having approximate dimensions of 0.120 x 0.120 x 0.280 mm was mounted on a glass fiber. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo K$_\alpha$ radiation. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully chromated reflections in the range 15.00 < 2θ < 28.00 corresponded to a monoclinic unit cell with dimensions a = 9.4148(8) Å, b = 17.317(1) Å, c = 15.467(1) Å, and $\beta$ = . For Z = 4 and F. W. = 556.69, the calculated density is 1.466 g/cm$^3$. Based on the systematic absences of h01: h + 1≠ 2n and 0k0: k ≠ 2n, the space group was determined to be P21/n (#14). The data were collected at -78°C using the $\omega$-2θ scan technique to a maximum 2θ value of 88.3°. Omega scans of several intense
reflections, made prior to data collection, had an average width at half-height of 0.23° with a take-off angle of 2.8°. Scans of \((0.80 + 0.35\tan\theta)\) were made at speeds ranging from 1.5° to 16.5°/min (in omega). Moving-crystal moving counter background measurements were made by scanning an additional 25% above and below the scan range. The counter aperture consisted of a variable horizontal slit with a width ranging from 2.0 to 2.5 mm and a vertical slit set to 2.0 mm. The diameter of the incident beam collimator was 0.7 mm and the crystal to detector distance was 21 cm. For intense reflections an attenuator was automatically inserted in front of the detector.

Of the 10883 reflections which were collected, 10484 were unique \((R_{int} = 0.058)\); equivalent reflections were merged. The intensities of three representative reflections which were measured after every 60 minutes of X-ray exposure time remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied). The linear absorption coefficient for Mo Kα is 52.5 cm⁻¹. An empirical absorption correction, using the program DIFABS3, was applied which resulted in transmission factors ranging from 0.80 to 1.40. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1738 observed reflections \((I > 3.00\sigma(I))\) and 208 variable parameters and converged (largest parameter shift was 0.55 times its esd) with unweighted and weighted agreement factors of \(R = 0.032\) and \(R_w = 0.037\).

The standard deviation of an observation of unit weight was 1.62. The weighting scheme was based on counting statistics and included a factor \((p = 0.03)\) to downweight the intense reflections. Plots of \(\Sigma_w(|F_0| - |F_c|)^2\) versus \(|F_0|\), reflection order in data collection, \(\sin\theta/\lambda\) and various classes of indices showed no unusual trends. The
maximum and minimum peaks on the final difference Fourier map corresponded to 0.62 and -0.91e^-/\text{A}^3, respectively. Neutral atom scattering factors were taken from Cromer and Waber. Anomalous dispersion effects were included in F_{calc}; the values of $\Delta f'$ and $\Delta f''$ were those of Cromer. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation.

Os(PMe$_3$)$_2$(CO)$_2$(t-BuC≡C-t-Bu). Os(PMe$_3$)$_3$(t-BuC≡C-tBu) (30 mg, 0.057 mmol) was dissolved in 5 mL of pentane and the solution was placed under 0.8 atm. CO. The mixture immediately became pale beige and was stirred at 25°C for 1 hour. Pentane and PMe$_3$ were removed in vacuo, yielding a colorless crystalline solid which was pure Os(PMe$_3$)$_2$(CO)$_2$(t-BuC≡C-t-Bu) by NMR (yield: 25 mg, 83%). Os(PMe$_3$)$_2$(CO)$_2$(t-BuC≡C-t-Bu) is quite volatile and can be further purified by sublimation at 50°C under a static vacuum of 0.01 torr. $^1$H NMR (CD$_6$D$_6$) $\delta$ 1.35 (s, 18, t-Bu), 1.15 (t, 18, PMe$_3$); $^{13}$C NMR (CD$_6$D$_6$) $\delta$ 195.6 (CO), 106.8 (C≡C), 34.0 (CMe$_3$), 31.2 (CMe$_3$), 19.4 (PMe$_3$); $^{31}$P NMR (CD$_6$D$_6$) $\delta$ -53.3. IR (Nujol, cm$^{-1}$) 1948, 1885 (vs, CO), 1772 (w, C≡C). Anal. Calcd for OsC$_{18}$H$_{36}$O$_2$P$_2$: C, 40.29; H, 6.76. Found: C, 40.37; H, 6.68.

[Os(H)(PMe$_3$)$_3$(t-BuCC-t-Bu)]$^+$(BAR$_4^-$). Os(PMe$_3$)$_3$(t-BuCC-t-Bu) (40 mg, 0.072 mmol) was dissolved in 5 mL of Et$_2$O and the solution was cooled to -40°C. Solid HBAR$_4$(Et$_2$O)$_2$ was added and the orange-yellow solution was warmed to room temperature and stirred for 1.5 hours. Ether was removed in vacuo and the resulting yellow solid was washed with 5 mL of pentane and recrystallized at room temperature by slow diffusion of pentane into an ether solution of the crude product. Yellow plates were collected, washed with pentane and dried. (71 mg, 70%): $^1$H NMR (CD$_2$Cl$_2$) $\delta$ 7.73 (br s, 8, Arortho), 7.57 (br s, 4, Arpara), 1.77 (br s, 27, PMe$_3$), 1.45 (s, 18, t-Bu), -6.16 (q, OsH, $^1$J$_{PH}$ = 12 Hz); $^{13}$C NMR (CD$_2$Cl$_2$) $\delta$ 172.1 (m, t-BuCC-t-Bu), 160.6 (q,
Ar Cipso, J_Cb = 20 Hz), 133.6 (Ar C^ortho), 127.7 (q, Ar C^meta, J_CF = 31 Hz), 123.5 (q, CF_3, J_CF = 271 Hz), 37.4 (CMe_3), 31.6 (CMe_3), 24.1 (br d, PMe_3, J_CP = 40 Hz); ^{31}P NMR (CD_2Cl_2) δ -41.5. Anal. Calcd for OsC_51H_58F_24BP_3: C; 43.11. H; 4.11. Found: C; 43.13. H; 3.95.

[Os(H)(PMe_3)_3]+[BArF_4]^-. [Os(H)(PMe_3)_3(t-BuCC-t-Bu)]+[BArF_4]^-. (20 mg, 0.014 mmol) was dissolved in 3 mL of dichloromethane. Excess PMe_3 (15 μL, 0.14 mmol) was added. The solution immediately became colorless. After 1 hour, dichloromethane and excess PMe_3 were removed in vacuo, leaving a colorless solid that was crystallized from an Et_2O/pentane mixture at -40°C. Colorless cubes were collected and dried. (18 mg, 90%). ^1H NMR (CD_2Cl_2) δ 7.73 (s, 8, Ar^ortho), 7.56 (s, 4, Ar^para), 1.68 (s, 36, PMe_3), 1.49 (d, 9, PMe_3, J_PH = 7 Hz), -12.25 (dp, 1, OsH). ^{31}P NMR (CD_2Cl_2) δ -53.4, -58.4 (PMe_3). ^13C NMR (CD_2Cl_2) δ 162.1 (q, Ar Cipso, J_CB = 50 Hz), 135.2 (Ar C^ortho), 129.2 (q, Ar C^meta, J_CF = 30 Hz), 125.0 (q, CF_3, J_CF = 271 Hz), 27.2 (overlapping m, PMe_3). Anal. Calcd for OsC_47H_58BF_24P_5: C; 43.43. H; 4.07. Found: C; 43.70. H; 4.17.
CHAPTER 3: ALKYLIDYNE COMPLEXES OF OSMIUM(VI)
Introduction

A variety of carbyne complexes of ruthenium and osmium have been reported. As mentioned in Chapter 2, the majority of these complexes can be described as Os(IV) if the carbyne ligand is viewed as being a trianionic ligand. To our knowledge, the only other "Os(VI)" carbynes known are OsCl₂(NCS)(C₅H₄NMe₂)(PPh₃)₂,⁴⁵ [Os(CR)(NH₃)₅]³⁺ (R = C₆H₅, ⁴⁶(CH₂)₃CHO⁴⁷) and OsCl₂(CCH₂R)(H)(P(i-Pr)₃)₂.⁴⁸ These six-coordinate complexes are all prepared from lower oxidation state osmium precursors. There had been no examples of osmium alkylidyne preparation by α-hydrogen abstraction reactions, and very few investigations of the reactivity of the metal-carbon triple bonds in the Os(VI) carbynes. The synthesis and reactivity of a variety of four, five, and six-coordinate osmium neopentylidyne complexes is described in this chapter.

Synthesis of Os(C-t-Bu)(CH₂-t-Bu)₂(py)₂(OTf)

The reaction of syn, anti-Os(CH-t-Bu)₂(CH₂-t-Bu)₂ with pyridinium triflate in the presence of excess pyridine results in the formation of neopentane and orange, air-stable Os(C-t-Bu)(CH₂-t-Bu)₂(py)₂(OTf). If pyDOTf is used, deuterium is found in a statistical distribution the α-carbon atoms of the neopentyl ligands in Os(C-t-Bu)(CH₂-t-Bu)₂(py)₂(OTf). This result is consistent with a mechanism involving protonation of one of the neopentylidene ligands in Os(CH-t-Bu)₂(CH₂-t-Bu)₂ followed by α-hydrogen abstraction in intermediate "Os(CH-t-Bu)(CH₂-t-Bu)₃(py)ₙ" to form Os(C-t-Bu)(CH₂-t-Bu)₂(py)₂(OTf). This mechanism is consistent with observations that α-hydrogen abstraction is generally more facile in complexes that are cationic or otherwise electrophilic.¹ It should be noted that in a closely related d⁰ system described in Chapter 1, Re(C-t-Bu)(CH-t-Bu)(CH₂-t-Bu)₂ reacts with triflic acid in non-
coordinating solvents to yield the stable complex, Re(C-t-Bu)(CH₂-t-Bu)₃(OTf), which then reacts with added pyridine to form neopentane and Re(C-t-Bu)(CH₂-t-Bu)(CH₂-t-Bu)(py)₂(OTf).

"Os(CH-t-Bu)(CH₂-t-Bu)₃(py)₃(OTf)"

In the ¹H NMR, the two neopentyl groups are related by a mirror plane and the two bound pyridines are equivalent. Exchange with added pyridine occurs on the NMR time scale at 25°C in CD₂Cl₂. IR reveals a triflate stretch at 1303 cm⁻¹, suggesting that the triflate ion is bound to the metal.⁴⁹ All data are consistent with the structure shown above. However, attempts to grow crystals of Os(C-t-Bu)(CH₂-t-Bu)₂(py)₂(OTf) suitable for X-ray diffraction were unsuccessful.

In the absence of coordinating ligands, the reaction of Os(CH-t-Bu)₂(CH₂-t-Bu)₂ with acids failed to yield any clean products. Although the proposed product, "Os(CH-t-Bu)(CH₂-t-Bu)₃(X)" would appear to be quite similar to the stable d⁰ rhenium complexes, Re(C-t-Bu)(CH₂-t-Bu)₃(X), it should be emphasized that in the chemistry of both Re(VII) and Os(VI), at least two metal-ligand π bonds are required to stabilize the metal in the high oxidation state. Re(C-t-Bu)(CH₂-t-Bu)₃(X) fulfills this criterion since it has a metal-carbon triple bond, as do Os(VI) complexes such as
OsOR₄,⁴⁴ [OsNR₄]⁻³ and Os(NAr)(CH₂-t-Bu)₂(CH₃)₂ (see Chapter 4), where the imido and oxo ligands can be viewed as triply-bonded ligands. In the absence of coordinating ligands "Os(CH-t-Bu)(CH₂-t-Bu)₃(X)" decomposes.

**Synthesis of Os(C-t-Bu)(CH₂-t-Bu)(py)₂X₂**

OsO₂(CH₂-t-Bu)₂ reacts with one equivalent of Ta(CH-t-Bu)(py)₂X₃ (X = Cl, Br) in dichloromethane/pyridine mixtures to form neopentane and orange Os(C-t-Bu)(CH₂-t-Bu)(py)₂X₂. In the absence of excess pyridine, yields are lower.

\[
\text{OsO}_2(\text{CH}_2-\text{t-Bu})_2 + \text{Ta(CH}^{-}\text{t-Bu})(\text{py})_2\text{X}_3 \xrightarrow{-1/\text{x} \ [\text{TaO}_2\text{X(py)}_n]} \text{CH}_2\text{Cl}_2/\text{py} \xrightarrow{-\text{CMe}_4} \text{X} \rightarrow \text{t-BuCH}_2 \xrightarrow{-\text{CMe}_4} 70-90\% \quad X = \text{Cl, Br}
\]

"Os(CH-t-Bu)(CH₂-t-Bu)₂(py)X₂"

This unusual reaction is a combination of an alkylidene/oxo exchange reaction, a halide/oxo exchange reaction, and an α-hydrogen abstraction reaction. Intermediate "Os(CH-t-Bu)(CH₂-t-Bu)₂X₂(py)ₙ" contains only one metal-ligand π-bond and is not observed. This "one-pot" synthesis is mechanismically more complex than the two-step synthesis of Os(C-t-Bu)(CH₂-t-Bu)₂(py)₂(OTf). When OsO₂(CD₂-t-Bu)₂ is reacted with Ta(CH-t-Bu)(py)₂Cl₃, Os(C-t-Bu)(CD₂-t-Bu)(py)₂Cl₂ is formed exclusively, suggesting that the neopentylidene ligand transferred from tantalum to osmium is converted into the neopentylidyne. Any possible degenerate exchange of Hα/Dα among the alkyl and alkylidene ligands in intermediate "Os(CH-t-Bu)(CD₂-t-Bu)₂Cl₂"
must be slower (if it exists at all) than the non-degenerate $\alpha$-hydrogen abstraction reaction.

Os(\textit{C-t-Bu})(\textit{CH-t-Bu})(\textit{py})_2X_2$ are air- and water-stable. No conversion to "Os(\textit{C-t-Bu})(\textit{CH$_2$-t-Bu})(O)(\textit{py})_n" ($n = 1, 2$) is observed in the presence of water. The pyridine ligands do not undergo exchange with added pyridine on the NMR time scale at $25^\circ$C in CD$_2$Cl$_2$.

The reaction of OsO$_2$(\textit{CH$_2$-t-Bu})$_2$ with Ta(\textit{CH-t-Bu})(L)$_2$Cl$_3$ ($L = $ THF, 1/2 bpy, PMe$_3$) in CD$_2$Cl$_2$ yields Os(\textit{C-t-Bu})(\textit{CH$_2$-t-Bu})(L)$_2$Cl$_2$; these products are unstable and cannot be isolated. We believe such species to be present in solution since the addition of pyridine to solutions of Os(\textit{C-t-Bu})(\textit{CH$_2$-t-Bu})(\textit{THF})$_2$Cl$_2$ results in formation of Os(\textit{C-t-Bu})(\textit{CH$_2$-t-Bu})(\textit{py})$_2$Cl$_2$. The reaction of OsO$_2($ \textit{CH$_2$-t-Bu}$)$_2$ with Ta(CHPh)(PMe$_3$)$_2$Cl$_3$ does not yield any identifiable products. Likewise, the reaction of [OsO$_2$(\textit{CH$_2$SiMe$_3$})$_2$]$_n$ with Ta(\textit{CH-t-Bu})(\textit{py})$_2$Cl$_3$ yields no clean products. The failure of these reactions may be interpreted in terms of the greater tendency of neopentyl and neopentylidene ligands to undergo $\alpha$-hydrogen abstraction reactions. Other modes of decomposition of intermediate "Os(CHR)(\textit{CH$_2$R'})$_2$Cl$_2$" can compete with $\alpha$-hydrogen abstraction except when $R = R' =$ tert-butyl. Once again, Os(VI) requires more than one metal-ligand $\pi$ bond. Such results suggest that mono(alkylidene) complexes of osmium(VI) will be stable only in the presence of another metal ligand multiple bond.

**Reactivity of the Os(VI) Neopentyldyne Complexes with Nucleophiles**

It was hoped that Os(\textit{C-t-Bu})(\textit{CH$_2$-t-Bu})$_2$(\textit{py})$_2$(OTf) could be deprotonated to form Os(\textit{C-t-Bu})(\textit{CH-t-Bu})(\textit{CH$_2$-t-Bu})(\textit{py})$_2$. Such a complex would be a d$^2$ analog to W(\textit{C-t-Bu})(\textit{CH-t-Bu})(\textit{CH$_2$-t-Bu})(L)$_2$ ($L = $ PMe$_3$, dmpe)$^{18}$ and [Re(\textit{C-t-Bu})(\textit{CH-t-}
Bu)(CH$_2$-t-Bu)(L)$_3$]$^+$(see Chapter 1). However, due the lability of the pyridine and triflate ligands, nucleophilic attack at osmium instead occurred, resulting in the formation of new 4- and 6-coordinate osmium neopentyldide complexes. It should be noted that deprotonation of C$_\alpha$ is rarely a facile reaction, even in d$^0$ alkyl complexes.

Os(C-t-Bu)(CH$_2$-t-Bu)$_2$(py)$_2$(OTf) reacts with LiO-t-Bu or LiN(SiMe$_3$)$_2$ in THF to yield the four-coordinate complexes, Os(C-t-Bu)(CH$_2$-t-Bu)$_2$(O-t-Bu) and Os(C-t-Bu)(CH$_2$-t-Bu)$_2$(N(SiMe$_3$)$_2$), respectively, in 60-80% yield. Os(C-t-Bu)(CH$_2$-t-Bu)$_2$(N(SiMe$_3$)$_2$) is a crystalline brown-red solid which is exceedingly soluble in pentane. It can be recrystallized from ether/acetonitrile mixtures at -40°C. The two trimethylsilyl groups are equivalent in the NMR time scale at 25°C in C$_6$D$_6$.

Os(C-t-Bu)(CH$_2$-t-Bu)$_2$(O-t-Bu) is a brown oil. Attempts to sublime Os(C-t-Bu)(CH$_2$-t-Bu)$_2$(O-t-Bu) were unsuccessful, resulting in extensive decomposition. To our knowledge, Os(C-t-Bu)(CH$_2$-t-Bu)$_2$(N(SiMe$_3$)$_2$) and Os(C-t-Bu)(CH$_2$-t-Bu)$_2$(O-t-Bu) are the first four-coordinate osmium carbyne complexes, regardless of oxidation state.

Os(C-t-Bu)(CH$_2$-t-Bu)$_2$(py)$_2$(OTf) reacts with NaC$_5$H$_5$ in THF to yield yellow, 18-electron Os(C-t-Bu)(CH$_2$-t-Bu)$_2$(η$^5$-C$_5$H$_5$), an alkylidyne analog of Os(N)(η$^5$-
C$_5$H$_5$)(CH$_2$SiMe$_3$)$_2$. Analogous reactions between Os($C$-t-Bu)(CH$_2$-t-Bu)$_2$(py)$_2$(OTf) and Na[CpCo(P(O)(OE)$_2$)$_3$] (NaL$_3$OE) or sodium trispyrazolylborate (NaHBpz$_3$) in THF yield Os($C$-t-Bu)(CH$_2$-t-Bu)$_2$(L$_3$OE)$_2$ or Os($C$-t-Bu)(CH$_2$-t-Bu)$_2$(HBpz)$_3$, respectively, in 60-80% yields. These compounds are thermally stable pink solids and are air- and water-stable as well. The reaction of Os($C$-t-Bu)(CH$_2$-t-Bu)$_2$(py)$_2$(OTf) with Li(C$_5$(CH$_3$)$_5$) or NaHBpz'$_3$ (pz' = 3-methylpyrazolyl) in THF was unsuccessful; the resulting complexes would likely be too crowded.

Os($C$-t-Bu)(CH$_2$-t-Bu)(py)$_2$X$_2$ (X = Cl, Br) does not react with NaC$_5$H$_5$, KO-t-Bu, or NaHBpz$_3$ in THF or CH$_2$Cl$_2$. The pyridine and halide ligands are tightly bound in Os($C$-t-Bu)(CH$_2$-t-Bu)(py)$_2$X$_2$, resulting in low reactivity. The reaction of Os($C$-t-Bu)(CH$_2$-t-Bu)(py)$_2$X$_2$ with 2 equivalents of RLi (R = CH$_2$-t-Bu, CH$_2$SiMe$_3$) results in the formation of mixtures containing syn, anti- and anti, anti-Os(CH$_3$-t-Bu)$_2$(R)$_2$.

**X-Ray Structure Determination of Os($C$-t-Bu)(CH$_2$-t-Bu)$_2$(HBpz$_3$)**

Crystals of Os($C$-t-Bu)(CH$_2$-t-Bu)$_2$(HBpz$_3$) suitable for X-ray diffraction were obtained by cooling a pentane solution of Os($C$-t-Bu)(CH$_2$-t-Bu)$_2$(HBpz$_3$) to -40°C. The structure of Os($C$-t-Bu)(CH$_2$-t-Bu)$_2$(HBpz$_3$) was solved by Dr. Rhett Kempe and is shown in Figure 3.1. The Os≡C bond length (1.73 (2) Å) is comparable to that found in [Os(CC$_6$H$_5$)(NH$_3$)$_3$]$^{3+}$ (1.73 (1) Å), while the relatively small Os-C(15)-C(16) angle can be ascribed to steric interactions between tert-butyl groups. The Os-N distances (2.18 (2) Å, 2.20 (2) Å) for the pyrazolyls trans to the two neopentyl groups are significantly shorter than that for the pyrazolyl trans to the neopentyldiyne (2.30 (2) Å) due to the weakened trans influence of the alkylidyne. Other bond lengths and angles are shown in Tables 3.1 and 3.2, and the crystallographic data is summarized in Table 3.4.
Figure 3.1 A drawing of Os(C-t-Bu)(CH₂-t-Bu)₂(HBpz)₃ generated using atomic coordinates obtained by X-ray crystallography.
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Table 3.4: Crystal Data for Os(HBpz3)(C-t-Bu)(CH2-t-Bu)2.

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Reactions of the Os(VI) Neopentyldiyne Complexes with Alkynes

Many d⁰ alkylidyne complexes of molybdenum, tungsten, and rhenium metathesize alkynes.¹ In contrast, typical mid- and late-transition metal carbyne complexes do not react metathetically with alkynes. We were interested in comparing the reactivity of the d² osmium neopentyldiyne complexes with the d⁰ alkylidyynes and the known carbyne complexes of osmium.

None of the osmium neopentyldiyne complexes react with internal alkynes such as 2-butyne. Likewise, the 18-electron complexes Os(C-t-Bu)(CH₂-t-Bu)₂(L) (L = Cp, LOEt, HBpz₃) and Os(C-t-Bu)(CH₂-t-Bu)(py)₂X₂ (X = Cl, Br) do not react with terminal alkynes such as phenylacetylene or tert-butylacetylene, even at elevated temperatures. No evidence for formation of η²-acetylene adducts was observed.

Os(C-t-Bu)(CH₂-t-Bu)₂(py)₂(OTf) reacts with tert-butylacetylene in CD₂Cl₂ to yield neopentane and the η¹-acetylide complex, Os(C-t-Bu)(CH₂-t-Bu)(CC-t-Bu)(py)₂(OTf). Os(C-t-Bu)(CH₂-t-Bu)(CC-t-Bu)(py)₂(OTf) is stable for several hours in CD₂Cl₂ at 25°C. However, it is somewhat unstable in the solid state. Addition of 1 equivalent of bpy prior to isolation results in isolation of red, crystalline Os(C-t-Bu)(CH₂-t-Bu)(CC-t-Bu)(bpy)(OTf).

The reactivity of Os(C-t-Bu)(CH₂-t-Bu)₂(py)₂(OTf) is closely linked to the lability of the pyridine ligands. Os(C-t-Bu)(CH₂-t-Bu)₂(bpy)(OTf) reacts with excess tert-butyl acetylene in CD₂Cl₂ over several days to form Os(C-t-Bu)(CH₂-t-Bu)(CC-t-Bu)(bpy)(OTf); the reaction is complete in minutes when Os(C-t-Bu)(CH₂-t-Bu)₂(py)₂(OTf) is used. A likely mechanism is dissociation of pyridine and coordination of tert-butylacetylene, followed by σ-bond metathesis to form neopentane and Os(C-t-Bu)(CH₂-t-Bu)(CC-t-Bu)(py)₂(OTf). The other possibility, direct protonation of a neopentyl group by the relatively acidic acetylenic proton, seems
unlikely in view of the fact that Os(C-\text{-t-Bu})(\text{CH}_2-\text{t-Bu})_2(\text{py})_2(\text{OTf}) is stable to proton sources such as water or pyHOTf.

Bis(acetylide) complexes could not be isolated. It appears that reaction with a second equivalent of \textit{tert}-butylacetylene occurs, but the resulting bis(acetylide) was unstable. The \textit{tert}-butylacetylide group affords much less steric protection than a neopentyl group, leaving the complex vulnerable to bimolecular decomposition.

The four-coordinate alkylidyne complexes, Os(C-\text{-t-Bu})(\text{CH}_2-\text{t-Bu})_2(O-\text{-t-Bu}) and Os(C-\text{-t-Bu})(\text{CH}_2-\text{t-Bu})_2(\text{N(SiMe}_3)_2), do not react with excess phenylacetylene at room temperature in C_6D_6. At elevated temperatures, decomposition occurs, and \textit{tert}-butanol and HN(SiMe}_3)_2, respectively, were the only identifiable products observed.
Discussions and Conclusions

The synthesis of the Os(VI) neopentylidyne complexes Os(C-t-Bu)(CH$_2$-t-Bu)$_2$(py)$_2$(OTf) and Os(C-t-Bu)(CH$_2$-t-Bu)(py)$_2$X$_2$ provides the first examples of α-hydrogen abstraction reactions at osmium. Prior to this work, Roper et al. had prepared benzylidyne complexes such as OsCl$_2$(NCS)(CC$_6$H$_4$NMe$_2$)(PPh$_3$)$_2$ by the reaction of osmium dihalocarbene complexes with 2 equivalents of an appropriate aryl lithium reagent. Although one possible mechanism for this transformation may be an α-halo abstraction reaction, the details are still unknown.

The driving force for the α-hydrogen abstraction appears to spring from the requirement that Os(VI) complexes have more than one metal-ligand π-bond. Thus, intermediate “Os(CH-t-Bu)(CH$_2$-t-Bu)$_3$(OTf)” and “Os(CH-t-Bu)(CH$_2$-t-Bu)$_2$X$_2$” are unstable and cannot even be observed. In the presence of coordinating ligands, α-hydrogen abstraction can occur, but in the absence of strongly coordinating ligands, decomposition occurs.

The reactivity of the metal-carbon triple bond of the osmium(VI) neopentylidyne complexes was investigated and found to resemble neither the Fischer (electrophilic at C$_\alpha$) nor Schrock (nucleophilic at C$_\alpha$) extremes. Both of these extremes have been observed for osmium carbynes, and predictions cannot be made based on formal oxidation state alone. For example, the “Os(VI)” benzylidyne, [Os(CPh)(NH$_3$)$_3$]$^{3+}$ is electrophilic at C$_\alpha$, reacting with propylamine to form [Os(C(Ph)(NHCH$_2$CH$_2$CH$_3$)(NH$_3$)]$^{3+}$. The “Os(IV)” benzylidyne, Os(CC$_6$H$_4$CH$_3$)Cl(CO)(PPh$_3$)$_2$ is nucleophilic at C$_\alpha$, reacting with HCl to form the stable benzylidene OsCl$_2$(CHC$_6$H$_5$CH$_3$)(CO)(PPh$_3$)$_2$. The metal-carbon triple bond in the neopentylidyne complexes appears to be fairly unreactive. Instead, ligand substitution reactions occur at the metal center.
The instability of the transient osmium(VI) mono(alkylidene) complexes towards α-hydrogen abstraction reactions and decomposition suggests that another metal-ligand π-bond is necessary to stabilize an Os(VI) alkylidene. This criteria would be met by an oxo, alkylidyne, or imido ligand. Attempts to prepare \( L_n\text{OsO}(\text{CHR}) \) and \( L_n\text{Os}(\text{C-}t\text{-Bu})(\text{CHR}) \) were unsuccessful, so we turned our efforts to preparing a variety of Os(VI) mono(arylimido) complexes as potential precursors to \( L_n\text{Os} (\text{CH-}t\text{-Bu})(\text{NAr}) \). These results are described in Chapter 4.
Experimental

General details can be found at the end of Chapter 2. Ta(CH-t-Bu)(py)₂Cl₃ was prepared by literature methods, and Ta(CH-t-Bu)(py)₂Br₃ was prepared from Ta(CH₂-t-Bu)₂Br₃ and pyridine in a manner analogous to that used in the preparation of Ta(CH-t-Bu)(py)₂Cl₃. NaLOEt was provided by Dr. R. D. Simpson. All other reagents were purchased from Aldrich and purified by standard methods.

Os(C-t-Bu)(CH₂-t-Bu)₂(py)₂(O₃SCF₃). Os(CH-t-Bu)₂(CH₂-t-Bu)₂ (83 mg, 0.176 mmol) was dissolved in 3 mL of ether and 1 mL of pyridine was added, followed by solid pyridinium triflate (42 mg, 0.183 mmol) The resulting red-orange mixture was allowed to stir for three hours and the solvents were then removed in vacuo and the solid was washed with pentane (5 mL) and ether (5 mL). The resulting orange solid (109 mg, 87%) was pure by ¹H and ¹⁹F NMR. An analytical sample was recrystallized from a mixture of dichloromethane and ether at -40°C: ¹H NMR (CD₂Cl₂) δ 8.60 (d, 4, py), 7.86 (br t, 2, py), 7.40 (br t, 4, py), 3.80 (d, 2, J₉H = 12, OsCH₉H₉-t-Bu), 2.94 (d, 2, J₉H = 12, OsCH₉H₉-t-Bu), 1.38 (s, 9, OsC-t-Bu), 1.02 (s, 18, OsCH₂-t-Bu); ¹³C NMR (CD₂Cl₂) δ 275.9 (OsC-t-Bu), 152.0, 138.8, 125.4 (py), 57.5, 37.0 (CMe₃), 37.5 (OsCH₂-tBu), 33.3, 25.3 (CMe₃); ¹⁹F NMR (CD₂Cl₂) δ -77.0; IR (nujol) cm⁻¹ 1303 (coordinated OTf). Anal. Calcd for OsC₂₆H₄₁N₂F₃O₃S: C, 44.05; H, 5.83; N, 3.95. Found: C, 43.76; H, 5.64; N, 3.62.

Os(C-t-Bu)(CH₂-t-Bu)(py)₂Cl₂. OsO₂(CH₂-t-Bu)₂(py)₂(OTf) (100 mg, 0.27 mmol) was dissolved in 3 mL of dichloromethane, pyridine (50 μL, 0.63 mmol) was added, and the resulting solution was cooled to -40°C. Ta(CH-t-Bu)Cl₃(py)₂ was dissolved in 2 mL of dichloromethane and the solution was cooled to -40°C and added to the cold solution of OsO₂(CH₂-t-Bu)₂ dropwise with stirring. The mixture became
red-orange immediately, and was stirred at room temperature for two hours. Dichloromethane was removed in vacuo and the resulting orange solid was washed with pentane, extracted with benzene and filtered through celite. Benzene was removed in vacuo from the filtrate, leaving an orange solid (128 mg, 82%): \( ^1H \text{NMR (C}_6\text{D}_6 \delta 9.6, 9.2 \text{ (br d, 2 each, py), 7.4, 7.2 \text{ (br t, 1 each, py), 6.8, 6.6 \text{ (br t, 2 each, py), 4.37 (O} \text{sCH}_2-t-\text{Bu)}, 1.64, 1.13 (t-Bu)} \)); \( ^{13}C \text{NMR (CD}_2\text{Cl}_2 \delta 285.7 \text{ (O} \text{sC-t-Bu), 152.9, 150.1, 138.4, 137.1, 124.6, 123.9 \text{ (py), 57.8 (O} \text{sCH}_2-t-\text{Bu), 36.8, 32.1 (CMe}_3, 32.6, 22.4 (CMe}_3 \).}

\textbf{Os}(t-Bu)(CH}_2-t-\text{Bu} (py)_2\text{Br}_2. \text{ OsO}_2(\text{CH}_2-t-\text{Bu})_2 (110 mg, 0.302 mmol) was dissolved in 5 mL CH}_2\text{Cl}_2 and 100 \mu\text{L of pyridine was added. The solution was chilled to -40°C and solid Ta(CH-t-Bu)(py)_2Br}_3 was added. The mixture became red-brown immediately and was allowed to warm to room temperature and was stirred for 1 hour. Dichloromethane was removed in vacuo and the solid was washed with pentane (5 mL), extracted with Et}_2\text{O (10 mL) and filtered. Ether was removed in vacuo from the filtrate, yielding an orange solid (135 mg, 71%).} \text{ }^1H \text{NMR (C}_6\text{D}_6 \delta 9.6, 9.1 \text{ (br d, 2 each, py), 6.9, 6.6 \text{ (br t, 1 each, py), 6.4, 6.25 (br t, 2 each, py) 4.56 (s, 2, O} \text{sCH}_2-t-\text{Bu), 1.65, 1.17 (s, 9 each, t-Bu). Anal. Calcd for OsC}_2\text{H}_3\text{ON}_2\text{Br}_2: C, 37.04; H, 6.59; N, 4.32. Found: C, 36.99; H, 4.51; N, 4.02.}

\textbf{Os}(C-t-Bu)(CH}_2-t-\text{Bu})_2(N(SiMe}_3)_2 \). A solution of Os(C-t-Bu)(CH}_2-t-\text{Bu})_2(py)_2(O}_3\text{SCF}_3 \) (70 mg, 0.099 mmol) in 5 mL THF was cooled to -40°C. A THF solution of LiN(SiMe}_3)_2 \) (0.10 mmol) was added and the mixture was warmed to room temperature and stirred for 45 minutes. Solvent was removed in vacuo and the resulting brown-red solid was extracted with pentane and the solution was filtered through celite. Pentane was removed in vacuo, leaving a crystalline brown solid (42 mg, 75%) that was pure by \textbf{H} NMR: \textbf{H} NMR (C}_6\text{D}_6 \delta 4.79 \text{ (d, 2, } J_{HH} = 12,
OsCH₆Hₓ₉₋ₓ-t-Bu), 2.78 (d, 2, JHH = 12, OsCH₆Hₓ₉₋ₓ-t-Bu), 1.26 (s, 18, OsCH₂-t-Bu), 1.13 (s, 18, OsCH₂-t-Bu), 0.36 (s, 18, SiMe₃); ¹³C NMR (C₆D₆) δ 267.9 (OsCCMe₃), 53.7 (OsCCMe₃), 39.6 (OsCH₂-t-Bu), 35.0 (OsCH₂CMe₃), 33.4 (OsCH₂CMe₃), 25.6 (OsCCMe₃), 6.7 (SiMe₃).

Os(C-t-Bu)(CH₂-t-Bu)₂(O-t-Bu). Os(C-t-Bu)(CH₂-t-Bu)₂(py)₂(O₃SCF₃) (95 mg, 0.135 mmol) was dissolved in 5 mL THF and solid LiO-t-Bu (11 mg, 0.14 mmol) was added and the brown mixture was stirred 45 minutes. THF was removed in vacuo and the resulting brown-red solid was extracted with pentane and the solution was filtered. Pentane was removed in vacuo, leaving a brown oil (40 mg, 62%) that was pure by ¹H NMR: ¹H NMR (C₆D₆) 4.70 (d, 2, JHH = 12 Hz, OsCH₆Hₓ₉₋ₓ-t-Bu), 3.14 (d, 2, JHH = 12 Hz, OsCH₆Hₓ₉₋ₓ-t-Bu), 1.42 (s, 9, O-t-Bu), 1.27 (s, 18, OsCH₂-t-Bu), 1.14 (s, 9, OsC-t-Bu); ¹³C NMR (C₆D₆) δ 261.4 (OsC-t-Bu), 79.5 (OCMe₃), 54.6 (OsCH₂-t-Bu), 36.0, 35.1 (CMe₃), 33.1, 29.4, 26.6 (CMe₃).

Os(η⁵-C₅H₅)(C-t-Bu)(CH₂-t-Bu)₂. Os(C-t-Bu)(CH₂-t-Bu)₂(py)₂(O₃SCF₃) (40 mg, 0.057 mmol) was dissolved in 3 mL of THF and a THF solution of sodium cyclopentadienide (0.070 mmol) was added. The resulting red-brown mixture was stirred for two hours at room temperature, and then the THF was removed in vacuo and the resulting solid was extracted with pentane to yield a yellow-brown solid (18 mg, 68%) that was pure by ¹H NMR. An sample for elemental analysis was prepared by passing a pentane solution of Os(η⁵-C₅H₅)(C-t-Bu)(CH₂-t-Bu)₂ through silica gel; pentane was then removed in vacuo to yield a yellow solid that was analytically pure: ¹H NMR (C₆D₆) δ 5.08 (s, 5, η⁵-C₅H₅), 2.25 (AB quartet, 4, OsCH₂-t-Bu), 1.26 (s, 18, OsCH₂-t-Bu), 0.99 (s, 9, OsC-t-Bu); ¹³C NMR (C₆D₆) δ 272.8 (OsC-t-Bu), 89.2 (η⁵-C₅H₅), 54.1 (OsCCMe₃), 35.7 (OsCH₂CMe₃), 34.5 (OsCH₂CMe₃), 26.7
(OsCCMe\textsubscript{3}), 19.3 (OsCH\textsubscript{2}-t-Bu). Anal. Calcd for OsC\textsubscript{20}H\textsubscript{36}: C, 51.47; H, 7.77. Found: C, 51.28; H, 7.47.

Os(L\textsubscript{OEt})(C-t-Bu)(CH\textsubscript{2}-t-Bu\textsubscript{2}). Os(C-t-Bu)(CH\textsubscript{2}-t-Bu\textsubscript{2})(py\textsubscript{2})(O\textsubscript{3}SC\textsubscript{F}\textsubscript{3}) (52 mg, 0.073 mmol) was dissolved in 3 mL of THF and solid Na[CpCo(P(O)(OEt\textsubscript{2})\textsubscript{3}) (42 mg, 0.075 mmol) was added. The red-orange solution was stirred for 3 hours at room temperature and the solvent was then removed in vacuo. The orange-pink solid was extracted with 10 mL of ether. The solvent was then removed in vacuo from the extract to yield orange-pink crystals (45 mg, 66%): \textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}) \delta 4.88 (s, 5, Cp), 4.38 (d, 2, J\textsubscript{HH} = 12, OsCH\textsubscript{a}H\textsubscript{b}-t-Bu\textsubscript{2}), 4.2, 4.1 (br m, 12 total, POCH\textsubscript{2}CH\textsubscript{3}), 3.32 (d, 2, J\textsubscript{HH} = 12, OsCH\textsubscript{a}H\textsubscript{b}-t-Bu\textsubscript{2}), 1.51 (s, 18, CH\textsubscript{2}-t-Bu\textsubscript{2}), 1.40 (s, 9, C-t-Bu\textsubscript{2}), 1.2 (br m, 18, POCH\textsubscript{2}CH\textsubscript{3}); \textsuperscript{13}C NMR (C\textsubscript{6}D\textsubscript{6}) \delta 266.1 (OsC-t-Bu\textsubscript{2}), 89.5 (Cp), 60.7, 60.5 (POCH\textsubscript{2}CH\textsubscript{3}), 55.7 (OsCH\textsubscript{2}-t-Bu\textsubscript{2}), 37.3 (CH\textsubscript{2}CM\textsubscript{e}\textsubscript{3}), 33.4 (CH\textsubscript{2}CM\textsubscript{e}\textsubscript{3}), 28.8 (CM\textsubscript{e}\textsubscript{3}), 23.8 (CM\textsubscript{e}\textsubscript{3}), 16.9, 16.7 (POCH\textsubscript{2}CH\textsubscript{3}). Anal. Calcd for CoOsC\textsubscript{32}H\textsubscript{56}O\textsubscript{9}P\textsubscript{3}: C, 41.02; H, 7.10. Found: C, 41.39; H, 6.78.

Os(HBpz\textsubscript{3})(C-t-Bu)(CH\textsubscript{2}-t-Bu\textsubscript{2}). Os(C-t-Bu)(CH\textsubscript{2}-t-Bu\textsubscript{2})(py\textsubscript{2})(O\textsubscript{3}SC\textsubscript{F}\textsubscript{3}) (80 mg, 0.11 mmol) was dissolved in 5 mL of THF and solid Na[HBpz\textsubscript{3}] (26 mg, 0.11mmol) was added. The orange solution was stirred for 2 hours at room temperature and the solvent was then removed in vacuo. The remaining orange-pink solid was extracted with 10 mL of pentane and the solvent was then removed in vacuo to yield a crystalline orange-pink solid. (58 mg, 83%). \textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}) \delta 8.15 (d, 2, J\textsubscript{HH} =1.8, N=CH), 7.87 (d, 1, J\textsubscript{HH} = 2, N=CH), 7.35 (d, 2, J\textsubscript{HH} = 2.4, NCH=CH), 7.21 (d, 1, J\textsubscript{HH} =2.4, NCH=CH), 5.91(t, 2, CHCHCH), 5.78 (t, 1, CHCHCH), 3.59 (d, 2, J\textsubscript{HH} =12, OsCH\textsubscript{a}H\textsubscript{b}-t-Bu\textsubscript{2}), 2.86 (d, 2, J\textsubscript{HH} =12, OsCH\textsubscript{a}H\textsubscript{b}-t-Bu\textsubscript{2}), 1.31 (s, 18, CH\textsubscript{2}-t-Bu\textsubscript{2}), 1.09 (s, 9, C-t-Bu\textsubscript{2}); \textsuperscript{13}C NMR (C\textsubscript{6}D\textsubscript{6}) \delta 280.1 (OsC-t-Bu\textsubscript{2}), 146.7, 141.1, 135.0, 134.6, 105.6,
105.2 (pz), 56.5 (OsCH₂-t-Bu), 36.4 (OsCH₂CMe₃), 33.9 (OsCH₂CMe₃), 32.6 (OsCCMe₃), 24.3 (OsCCMe₃).

X-ray Structure of Os(HBpz₃)(C-t-Bu)(CH₂-t-Bu)₂. Crystals of Os(HBpz₃)(C-t-Bu)(CH₂-t-Bu)₂ were grown from pentane at -40°C. A red crystal of OsBC₂₄H₄₁N₆ having approximate dimensions of 0.16 x 0.36 x 0.36 mm was mounted on a glass fiber. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo Kα radiation. Cell constants and an orientation matrix for data collection, obtained from a least squares refinement using the setting angles of 25 carefully centered reflections in the range 18.00 < 2θ < 26.00° corresponded to a monoclinic cell with dimensions: a = 10.5759 (9) Å, b = 13.549 (2) Å, c = 19.598 (3) Å, β = 104.20 (1)°, V = 2722 (1) Å³. For Z = 4 and F. W. = 614.64, the calculated density is 1.500 g/cm³. Based on the systematic absences of h0l ≠ 2θ, 0k0 ≠ 2θ and the successful solution and refinement of the structure, the space group was determined to be P2₁/n.

The data were collected at a temperature of 25 ± 1°C using the ω - 2θ scan technique to a maximum 2θ value of 44.9°. Omega scans of several intense reflections, made prior to data collection, had an average width at half height of 0.60° with a take-off angle of 2.8°. Scans of (1.05 + 0.35tanθ) were made at speeds ranging from 16.9 to 1.9°/min (in omega). Moving crystal moving counter background measurements were made by scanning an additional 25% above and below the scan range. The counter aperture consisted of a variable horizontal slit with a width ranging from 2.0 to 2.5 mm and a vertical slit set to 2.0 mm. The diameter of the incident beam collimator was 0.7 mm and the crystal to detector distance was 21 cm. For intense reflections an attenuator was automatically inserted in front of the detector.
Of the 3983 reflections which were collected, 3807 were unique \((R_{int} = 0.183)\). The intensities of three representative reflections which were measured after every 60 minutes of X-ray exposure time declined by -7.90%. A linear correction factor was applied to the data to account for this phenomena. The linear absorption coefficient for Mo Kα is 47.1 cm\(^{-1}\). An analytical absorption correction was applied which resulted in transmission factors ranging from 0.22 to 0.54. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 0.29980 x 10\(^{-7}\)).

The structure was solved by direct methods. The non-hydrogen atoms were refined either anisotropically or isotropically. The final cycle of full-matrix least-squares refinement was based on 1883 observed reflections \((I > 4.00\sigma(I))\) and 240 variable parameters and converged (lowest parameter shift was 0.14 times its esd) with unweighted and weighted agreement factors of \(R = 0.060\) and \(R_w = 0.064\). The standard deviation of an observation of unit weight was 1.92. The weighting scheme was based on counting statistics and included a factor \((p = 0.03)\) to downweight the intense reflections. Plots of \(\Sigma w (|F_o| - |F_c|)^2\) versus \(|F_o|\), reflection order in data collection, \(\sin\theta/\lambda\), and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 2.29 and -2.08e/Å\(^3\). Neutral atom scattering factors were taken from Cromer and Waber. Anomalous dispersion effects were included in \(F_{calc}\); the values for \(\Delta f'\) and \(\Delta f''\) were those of Cromer. All calculations were performed using the TExSAN crystallographic software package of Molecular Structure Corporation.

\[
\text{Os(C-t-Bu)(CH}_2\text{-t-Bu)(CC-t-Bu) (b p y ) (O T f ) . \quad \text{Os(C-t-Bu)(CH}_2\text{-t-Bu)}_2(p y )_2(\text{OTf}) (42 mg, 0.60 mmol) was dissolved in 5 mL of dichloromethane and pyridine (20 \(\mu\)L) was added. The solution was chilled to -40°C, and t-butylacetylene}
\]
(20 µL, 0.17 mmol)) was added. The resulting mixture was stirred for 2 hours at room temperature, and solid bpy (9 mg, 0.57 mmol) was added. The mixture became red immediately. After allowing the mixture to stir 20 minutes, dichloromethane and pyridine were removed in vacuo, and the resulting red solid was washed with pentane and recrystallized from a CH₂Cl₂/pentane mixture at -40°C: ¹H NMR (CD₂Cl₂) δ 7.5 - 9.7 (m, 8 total, bpy), 2.53, 1.96 (d, 2 each, JHH = 12 Hz, OsCH₂-t-Bu), 1.42, 1.18, 0.99 (s, 9 each, t-Bu); ¹³C NMR (CD₂Cl₂) δ 294.3 (OsCt-Bu), (bpy) 84.0, 82.0 (OsCC and OsCC), 57.0 (OsCH₂-t-Bu), 33.0, 32.9, 23.1 (CMe₃), 35.9, 29.8, 25.0 (CMe₃). IR (Nujol, cm⁻¹) 2359 (CC stretch), 1285 (coordinated OTf).

Os(C-t-Bu)(CH₂-t-Bu)₂(bpy)(OTf). Os(C-t-Bu)(CH₂-t-Bu)₂(py)₂(OTf) (47 mg, 0.067 mmol) was dissolved in 5 mL of dichloromethane and solid 2,2'-bipyridyl (10 mg, 0.07 mmol) was added. The mixture immediately became red and was stirred for 1 hour at 25°C. Following removal of dichloromethane and pyridine in vacuo, a crystalline red solid was isolated. Recrystallization from a CH₂Cl₂/pentane mixture at -40°C yielded red needles which were collected, washed with pentane, and dried. (45 mg, 96%). ¹H NMR (CD₂Cl₂) δ 9.7 - 7.2 (m, 8 total, bpy), 3.5 (overlapping d, 3 total, OsCH₂H₂-t-Bu), 2.2 (d, 2, JCH = 12 Hz, OsCH₂H₂-t-Bu), 1.61, 0.88, 0.55 (t-Bu). Note: the two neopentyl groups are non-equivalent.
CHAPTER 4: IMIDO COMPLEXES OF OSMIUM(VI)
Introduction

The sterically demanding 2, 6-diisopropylphenylimido ligand ("NAr") has been widely used as a means of stabilizing monomeric transition metal complexes in relatively high oxidation states. Examples include complexes that contain niobium or tantalum,\textsuperscript{52,53} molybdenum or tungsten,\textsuperscript{54,55} technetium or rhenium,\textsuperscript{56-58} and osmium.\textsuperscript{2} The original route to all of the osmium arylimido complexes involved the synthesis of trigonal planar Os(NAr)_3 from OsO_4 and three equivalents of ArNCO, a reaction that proceeds in 50% yield.\textsuperscript{2} A higher yield route was later developed which utilized a molybdenum imido complex as an imido/oxo exchange reagent. Os(NAr)_2O_2 and Os(NAr)_3O are readily synthesized in >70% yield from OsO_4 and Mo(NAr)(O-\textit{t}-Bu)_2.\textsuperscript{14} However, multi-step routes were still required for most potentially useful Os(VI) organometallic complexes, including Os(NAr)_2(CH_2-\textit{t}-Bu)_2. Furthermore, mono(imido) complexes were not accessible by this route. As mentioned at the end of Chapter 3, we were interested in preparing imido-alkylidene complexes of Os(VI), and so we began to investigate the reactivity of Os(VI) imido-alkyl complexes as potential precursors to the imido-alkylidene complexes. In this chapter, imido/oxo exchange reactions of Os(VI) are described and the reactivity of a variety of Os(VI) mono(imido) complexes is described.

Synthesis of Ta(NAr)(O-\textit{t}-Bu)_3

It was necessary to develop a synthetic route to tantalum imido complexes appropriate for use as imido/oxo exchange reagents. Alkoxides were chosen as supporting ligands due to their low cost, the ease with which early transition metal alkoxide complexes can be removed from reaction mixture, and the prior success of the imido/oxo exchange reactions between OsO_4 and Mo(NAr)_2(O-\textit{t}-Bu)_2. Wigley and co-
workers had reported the synthesis of TaCl3(NAr)(DME) and Ta(NAr)(OAr)3.52 TaCl3(NAr)(DME) can be easily synthesized from TaCl5 and ArNHTMS in > 90% yield in large (10 - 20 grams) quantities. This synthetic methodology could be extended to TaCl3(NAr')(DME) (Ar' = 2,6-dimethylphenyl) with equally good results. The reaction of TaCl3(NAr)(DME) with 3 equivalents of LiO-t-Bu in THF cleanly yields Ta(NAr)(O-t-Bu)3 as a white, pentane-soluble solid. Attempts to synthesize Ta(NAr')(OR)3 were unsuccessful, perhaps due to the smaller size of the 2,6-dimethylphenylimido ligand.

**Synthesis of OsO(NAr)R2 and Os(NAr)2R2.**

A variety of reactions were tried in an attempt to convert OsO2(CH2-t-Bu)2 to OsO(NAr)(CH2-t-Bu)2 or the known compound Os(NAr)2(CH2-t-Bu)2. Traditional routes used to synthesize d0 imido complexes were unsuccessful. OsO2(CH2-t-Bu)2 does not react with excess ArNCO in toluene-d8 at 100°C for several days. Likewise, OsO2(CH2-t-Bu)2 does not react with mixtures of 2,6-diisopropylaniline, trimethylsilylchloride and pyridine (or lutidine) in varying proportions, nor does it react with neat t-butylamine or t-butylamine/trimethylsilylchloride mixtures. A 1/1 mixture of OsO2(CH2-t-Bu)2 and Os(NAr)2(CH2-t-Bu)2 in C6D6 did not disproportionate to OsO(NAr)(CH2-t-Bu)2. Molybdenum imido complexes such as Mo(NAr)2(O-t-Bu)2 or Mo(NAr)(CH-t-Bu)(O-t-Bu)2 do not react with OsO2(CH2-t-Bu)2 in C6D6 at temperatures up to 70°C. Since tantalum alkylidenes had reacted readily with OsO2(CH2-t-Bu)2, the reaction of OsO2(R)2 with tantalum imido complexes was explored.

OsO2R2 (CH2-t-Bu, CH2CMe2Ph, CH2SiMe3, mesityl) reacts readily with 2 equivalents of Ta(NAr)(O-t-Bu)3 in pentane or toluene to form Os(NAr)2R2. TaO(O-t-
Bu)₃ is removed by passing the reaction mixture through silica gel. This reaction represents a much easier route to the potentially useful compounds, Os(NAr)₂R₂. Previously, the synthesis of Os(NAr)₂(CH₂-t-Bu)₂ required 5 steps and proceeded in 16% overall yield from OsO₄.² This route requires 2 steps from (OsO₂Cl₄)(PPh₄)₂ and proceeds in approximately 40% overall yield (based on osmium).

\[
\text{OsO}_2R_2 + 2 \text{Ta(NAr)(O-t-Bu)}_3 \xrightarrow{\text{pentane}} \text{Os(NAr)}_2R_2 - 2 \text{TaO(O-t-Bu)}_3
\]

\[
R = \text{CH}_2t-\text{Bu} \quad \text{CH}_2\text{CMe}_2\text{Ph} \quad \text{CH}_2\text{SiMe}_3 \quad \text{mesityl}
\]

When 1 equivalent of Ta(NAr)(O-t-Bu)₃ is reacted with OsO₂R₂ (R = CH₂-t-Bu, CH₂CMe₂Ph) in THF, purple OsO(NAr)R₂ is formed in 60 - 70% yield. When [OsO₂(CH₂SiMe₃)₂]ₙ and one equivalent of Ta(NAr)(O-t-Bu)₃ are combined in THF at -40°C, a mixture of OsO(NAr)(CH₂SiMe₃)₂ and Os(NAr)₂(CH₂SiMe₃)₂ is formed. Since [OsO₂(CH₂SiMe₃)ₙ] is oligomeric in solution, the first imide/oxo exchange may occur with the oligomeric complex and the rate is perhaps slower than imide/oxo exchange involving a monomeric osmium oxo. Following the formation of monomeric OsO(NAr)(CH₂SiMe₃)₂, the second imide/oxo exchange occurs rapidly to form Os(NAr)₂(CH₂SiMe₃)₂. OsO(NAr)R₂ are probably structurally analogous to distorted tetrahedral OsO(N-t-Bu)(mesityl)₂, which is synthesized in 5% yield from OsO₃(N-t-Bu) and dimesitylmagnesium.⁵⁹
OsO₂R₂ + Ta(NAr)(O-τ-Bu)₃ ⇌ THF → OsO(NAr)R₂

- TaO(O-τ-Bu)₃

R = CH₂-τ-Bu
CH₂CMe₂Ph
mesityl

The reaction of OsO₂(CH₂-τ-Bu)₂ and OsO(NAr)(CH₂-τ-Bu)₂ with Ta(NAr)(O-τ-Bu)₃ under a variety of conditions was investigated by ³¹H NMR. Qualitatively, several generalizations about the exchange reactions can be made. First, coordinating solvents such as THF significantly slow the rate of the imido/oxo exchange reaction. The reaction of OsO(NAr)(CH₂-τ-Bu)₂ with Ta(NAr)(O-τ-Bu)₃ in toluene-d₈ was essentially complete after a few minutes at -40°C, while no reaction was observed in THF-d₈ until the sample was warmed to 35°C. Unfortunately, reliable kinetic data for these systems could not be obtained. In a d⁰ system, the kinetics of imido/oxo exchange between Mo(NAr)₂(O-τ-Bu)₂ and MoO₂(O-τ-Bu)₂ was investigated and the results obtained were consistent with a mechanism involving an ordered, bimetallic transition state.¹³ It is likely that the imido/oxo exchange reactions described here proceed via a similar mechanism.

Synthesis of Os(NAr)(CH₂-τ-Bu)₂X₂ (X = Cl, I)

OsO(NAr)(CH₂-τ-Bu)₂ is a potentially useful starting material for a variety of Os(VI) mono(imido) complexes. In mixed oxo, imido complexes, the oxo group is typically more reactive than the imido group,²⁰ and it was hoped that it could be derivatized.

OsO(NAr)(CH₂-τ-Bu)₂ reacts with 2 equivalents of HCl in DME to yield water and yellow OsCl₂(NAr)(CH₂-τ-Bu)₂. Water does not react with OsCl₂(NAr)(CH₂-τ-
Bu)₂ and is readily removed in vacuo. Red, crystalline OsI₂(NAr)(CH₂-t-Bu)₂ is formed in the reaction of Os(NAr)(CH₂-t-Bu)₂Cl₂ with 2 equivalents of TMSI in CH₂Cl₂, or by the reaction of OsO(NAr)(CH₂-t-Bu)₂ with 2 equivalents of TMSI in CH₂Cl₂ or DME. It is unclear whether the latter reaction is catalyzed by traces of HI or proceeds via direct attack of TMSI. ¹H NMR reveals that the methylene protons on C₆ are diastereotopic, which suggests that Os(NAr)(CH₂-t-Bu)₂X₂ has either a square pyramidal structure with a cis orientation of the neopentyl groups or a trigonal bipyramidal structure with the neopentyl groups in two of the equatorial positions. The two possibilities are shown below.

![Diagram of Os(NAr)(CH₂-t-Bu)₂X₂ structures]

**Synthesis of Os(NAr)(CH₂-t-Bu)₂(OSiMe₃)(X) (X = Cl, OTf)**

The reaction of OsO(NAr)(CH₂-t-Bu)₂ with TMSCl or TMSOTf in CH₂Cl₂ yields green, crystalline Os(NAr)(CH₂-t-Bu)₂(OSiMe₃)(Cl) or Os(NAr)(CH₂-t-Bu)₂(OSiMe₃)(OTf), respectively. ¹H NMR data for these complexes reveals that the two tert-butyl groups of the neopentyl ligands are equivalent, and the methylene protons are diastereotopic, suggesting that the neopentyl ligands are related by a mirror plane. This data suggests that the complexes adopt a trigonal bipyramidal structure, with the neopentyl groups occupying two of the equatorial sites. The orientation of the trimethylsiloxide and chloride or triflate ligands is not known. In the ¹H NMR, the peaks associated with the methylene and isopropyl resonances of Os(NAr)(CH₂-t-Bu)₂(OSiMe₃)(OTf) are broad at 25°C in C₆D₆ suggesting that dissociation and
recoordination of the triflate ion are occurring in solution. In contrast, Os(NAr)(CH$_2$-t-Bu)$_2$(OTMS)(Cl) shows no evidence of fluxional behavior at 25°C in C$_6$D$_6$.

One interesting feature of the dineopentyl complexes of osmium is the wide range of $^1$H chemical shifts observed for H$_\alpha$. The chemical shifts for a variety of complexes containing the Os(NAr)(CH$_2$-t-Bu)$_2$ core is summarized in Table 4.1, and range from 3.40 in Os(NAr)(CH$_2$-tBu)$_2$(CH$_3$)$_2$ to 9.29 ppm in Os(NAr)(CH$_2$-t-Bu)$_2$I$_2$. Data for several osmium oxo and alkylidene complexes is included for comparison. The complexes containing two electronegative substituents such as halide or triflate have H$_\alpha$ resonances from 5-10 ppm, those containing an additional oxo or imido ligand have H$_\alpha$ resonances at 4-5 ppm, and those containing additional hydrocarbon substituents have H$_\alpha$ resonances from 2-4 ppm. This trend is useful for comparing complexes containing the Os(NAr)(CH$_2$-t-Bu)$_2$ core and analyzing reaction mixtures.

Table 4.1: Selected $^1$H Chemical Shifts of H$_\alpha$ in L$_n$Os(CH$_2$-t-Bu)$_2$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$ H$_\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>anti, anti-Os(CH$_2$-t-Bu)$_2$(CH$_2$-t-Bu)$_2$</td>
<td>2.09</td>
</tr>
<tr>
<td>syn, anti-Os(CH$_2$-t-Bu)$_2$(CH$_2$-t-Bu)$_2$</td>
<td>2.65</td>
</tr>
<tr>
<td>trans-Os(NAr)(CH$_2$-tBu)$_2$(CH$_3$)$_2$</td>
<td>3.63</td>
</tr>
<tr>
<td>OsO$_2$(CH$_2$-t-Bu)$_2$</td>
<td>4.22</td>
</tr>
<tr>
<td>Os(NAr)$_2$(CH$_2$-t-Bu)$_2$</td>
<td>4.43</td>
</tr>
<tr>
<td>OsO(NAr)(CH$_2$-t-Bu)$_2$</td>
<td>4.52, 4.21</td>
</tr>
<tr>
<td>Os(NAr)(CH$_2$-t-Bu)$_2$(OSiMe$_3$)(Cl)</td>
<td>6.31, 5.15</td>
</tr>
<tr>
<td>Os(NAr)(CH$_2$-t-Bu)$_2$(OSiMe$_3$)(OTf)</td>
<td>7.5, 5.8</td>
</tr>
<tr>
<td></td>
<td>(broad at 25°C)</td>
</tr>
<tr>
<td>Os(NAr)(CH$_2$-t-Bu)$_2$Cl$_2$</td>
<td>8.90, 6.78</td>
</tr>
<tr>
<td>Os(NAr)(CH$_2$-t-Bu)$_2$I$_2$</td>
<td>9.29, 7.21</td>
</tr>
</tbody>
</table>
Reactions of the Mono(imido) complexes with Donor Ligands and Nucleophiles

The reactivity of Os(NAr)(CH₂-t-Bu)₂(X)₂ (X = Cl, I) and Os(NAr)(CH₂-t-Bu)₂(OSiMe₃)(X) (X = Cl, OTf) was investigated. In particular, it was hoped that these complexes would undergo intramolecular α-hydrogen abstraction reactions to form "Os(NAr)(CH-t-Bu)(X)(Y)" which would be d² analogs of the family of molybdenum and tungsten imido-allylidenes. Deprotonation of Cα to form "Os(NAr)(CH-t-Bu)(CH₂-t-Bu)(X)" is another possible route to imido-alkylidene complexes of Os(VI).

Addition of excess pyridine to a toluene solution of Os(NAr)(CH₂-t-Bu)₂(OTMS)(OTf) yields a precipitate of green Os(NAr)(CH₂-t-Bu)₂(py)(OTMS)(OTf) in 80% yield. In CDCl₃ at 25°C, the isopropyl and pyridine peaks of Os(NAr)(CH₂-t-Bu)₂(py)(OTMS)(OTf) are extremely broad, and the resonances associated with the methylene protons could not even be located. Possible fluxional processes that could occur in Os(NAr)(CH₂-t-Bu)₂(py)(OTMS)(OTf) include dissociation of the triflate and or pyridine ligands. No evidence for α-hydrogen abstraction reactions is seen in Os(NAr)(CH₂-t-Bu)₂(py)(OTMS)(OTf), even when a CDCl₃ solution is heated for 1 hour at 70°C.

Os(NAr)(CH₂-t-Bu)₂(OTMS)(Cl) does not react with pyridine in C₆D₆ at 25°C. Likewise, no reaction was observed when pyridine was added to C₆D₆ or CD₂Cl₂ solutions of Os(NAr)(CH₂-t-Bu)₂(X)₂ (X = Cl, I) or when Os(NAr)(CH₂-t-Bu)₂(X)₂ was dissolved in pyr-d₅. No reaction was observed when these solutions were heated or photolyzed.

The complexes Os(NAr)(CH₂-t-Bu)₂(X)₂ (X = Cl, I) and Os(NAr)(CH₂-t-Bu)₂(OSiMe₃)(X) (X = Cl, OTf) were readily reduced by trimethylphosphine in C₆D₆.
or CD$_2$Cl$_2$. Neopentane formation was observed by $^1$H NMR, but no controlled α-hydrogen abstractions occurred. It should be noted that very few phosphine containing organometallic complexes of Os(VI) are known.$^{2,4}$

**Synthesis of trans-Os(NAr)(CH$_2$-t-Bu)$_2$(CH$_3$)$_2$**

OsO(NAr)(CH$_2$-t-Bu)$_2$ reacts cleanly with 2 equivalents of AlMe$_3$ in pentane to yield red trans-Os(NAr)(CH$_2$-t-Bu)$_2$(CH$_3$)$_2$ in 80% yield. The mixture is readily purified by passing the reaction mixture through silica gel to remove any aluminum-containing byproducts and impurities. $^1$H NMR reveals that the complex is h运转nly symmetric in solution, with equivalent methyl and tert-butyl groups. All four methylene hydrogens of the tert-butyl groups are also equivalent, suggesting that the complex adopts a square pyramidal structure with a trans orientation of the neopentyl ligands, as shown. The high symmetry of the molecule, elemental analysis data, the $^1$H chemical shift of the methyl protons (3.40 ppm) and its stability to silica gel suggest that it is not a trimethyl aluminum adduct of the formula "Os(OAlMe$_3$)(NAr)(CH$_2$-t-Bu)$_2"$.

![Reaction diagram]

**Reactions of OsO(NAr)R$_2$ with Alkylidene/Oxo Exchange Reagents**

The reaction of OsO(NAr)R$_2$ with tantalum alkylidene complexes was investigated. However, all attempts to isolate "Os(NAr)(CH-CH$_2$-t-Bu)(CH$_2$-t-Bu)$_2"$ were unsuccessful. The reaction of OsO(NAr)(CH$_2$-t-Bu)$_2$ with Ta(CH-t-Bu)(CF$_2$-t-Bu)$_3$ in
pentane results in precipitation of \([\text{TaO(CH}_2\text{-t-Bu)}_3]_n\) and isolation of a diamagnetic red oil which can be crystallized as dark red plates from ether/acetonitrile mixtures at -40°C. When the reaction is done in \(\text{C}_6\text{D}_6\) and monitored by \(^1\text{H}\) NMR, 2,2,6,6-tetramethylhexane is also observed. \(^1\text{H}\) and \(^{13}\text{C}\) NMR and elemental analysis data are consistent with the formulation \([\text{Os}_2\text{O}_2(\text{NAr})_2(\text{CH}_2\text{-t-Bu})_2(\eta^2\text{-t-BuCHCH-t-Bu})]\). The two imido ligands are non-equivalent (not merely diastereotopic), yet the two neopentyl groups are equivalent, with diastereotopic protons on \(\text{C}_6\), suggesting that the dimer is not symmetric. A possible structure is shown below.

\[
\begin{align*}
&\text{Os} \\
&\text{NAr} \\
&\text{ArN} = \text{Os} \\
&\text{O} \\
&\text{O} \\
&\text{CH}_2\text{-t-Bu} \\
&\text{CH}_2\text{-t-Bu} \\
&\text{t-Bu} \\
&\text{t-Bu}
\end{align*}
\]

The mechanism for formation of \([\text{Os}_2\text{O}_2(\text{NAr})_2(\text{CH}_2\text{-t-Bu})_2(\text{t-BuCHCH-t-Bu})]\) from \(\text{OsO(NAr)}(\text{CH}_2\text{-t-Bu})_2\) is not obvious and in view of the low yields obtained, any mechanistic proposals are guesses at best. Nonetheless, the retention of the \(\text{OsO(NAr)}(\text{CH}_2\text{-t-Bu})_2\) core on one half of the dimer suggests that unreacted \(\text{OsO(NAr)}(\text{CH}_2\text{-t-Bu})_2\) is attacked during the course of the reaction. However, attempts to isolate "\(\text{Os(NAr)(CH-t-Bu)(CH}_2\text{-t-Bu})_2\)" by using a less oxophilic tantalum alkylidene complex such as \(\text{Ta(CH-t-Bu)(O-t-Bu)}_3\), addition of THF or pyridine to reaction mixtures, or reversing the order of addition were unsuccessful. Likewise, the reaction of \(\text{OsO(NAr)}R_2\) \((R = \text{mesityl}, \text{CH}_2\text{CMMe}_2\text{Ph})\) with \(\text{Ta(CH-t-Bu)(CH}_2\text{-t-Bu)}_3\) failed to yield any tractable products.
Discussion and Conclusions

The synthetic methodology of imido/oxo exchange reactions was extended to Os(VI) dioxo complexes. The main difference between the exchange reactions of Os(VIII) and Os(VI) appears to be that a more oxophilic metal, tantalum, is required for the exchange reactions of Os(VI). On a similar note, electron-withdrawing alkoxides significantly slow the rate of the imido/oxo exchange reaction. This result could be attributed to a stronger Ta=N bond which disfavors exchange to yield the more electron-deficient Ta=O moiety.

As is the case in the alkylidene/oxo exchange reactions, the ancillary ligands on both tantalum and osmium must be chosen with care. Alkyl groups appear to be ideal ligands due to their inertness, but this limits the scope of the exchange reactions. Alkoxide ligands on tantalum are suitable ancillary ligands, since they are unlikely to be transferred to osmium. Conversely, osmium alkoxides and diolates are unsuitable since exchange of the alkoxide or diolate ligands can occur with early transition metal imido complexes. For instance, in the reaction of OsO(OCH₂CH₂O)₂(py)₂ with one equivalent of Os(NAr)(O-t-Bu)₃ in THF, Os(NAr)₃ is the only osmium-containing product isolated. The presence of halide ligands on the transfer reagent usually results in halide/oxo exchange reactions as well as the desired imido/oxo exchange reaction. Thus, in the reaction of OsO₂(CH₂-t-Bu)₂ with one equivalent of Ta(NAr)Cl₃(DME) in C₆D₆, Os(NAr)(CH₂-t-Bu)₂Cl₂ forms slowly, and OsO(NAr)(CH₂-t-Bu)₂ is not observed by ¹H NMR.

The mixed oxo, imido complex, OsO(NAr)(CH₂-t-Bu)₂ exhibits enhanced reactivity of the oxo linkage relative to the arylimido group, as is evidenced by the selective syntheses of OsX₂(NAr)(CH₂-t-Bu)₂ and trans-Os(NAr)(CH₂-t-Bu)₂(CH₃)₂. Comparisons between the reactivity of OsO₂(CH₂-t-Bu)₂ and OsO(NAr)(CH₂-t-Bu)₂
can also be made. The arylimido group activates the oxo group towards attack by acids and electrophiles and stabilizes the products formed - the dioxo complex, OsO₂(CH₂-t-Bu)₂ does not react with HCl, TMSCl, or triflic acid in DME. The arylimido group also provides steric and electronic protection of the metal center during alkylation reactions. OsO(NAr)(CH₂-t-Bu)₂ reacts with 2 equivalents of Me₃Al to form trans-Os(NAr)(CH₂-t-Bu)₂(CH₃)₂ with no net reduction, but OsO₂(CH₂-t-Bu)₂ is reduced under identical conditions, forming dimeric [Os(CH₂-t-Bu)₂(CH₃)]₂.

In Chapter 3, the conversion of transient OsX₂(CH-t-Bu)(CH₂-t-Bu)₂(py)ₙ (X = Cl, Br) to Os(C-t-Bu)(CH₂-t-Bu)(py)₂X₂ was described. It is interesting to note that the imido complexes, Os(NAr)(CH₂-t-Bu)₂X₂ (X = Cl, I) show no evidence for controlled α-hydrogen abstraction reactions in the presence of coordinating ligands. This result can be interpreted by rationalizing that the metal center is more electron-rich in the imido complexes, and is thus less prone to undergo α-hydrogen abstraction reactions. The general requirement that Os(VI) complexes require at least two metal-ligand π-bonds is already fulfilled in Os(NAr)(CH-t-Bu)₂X₂. Additionally, for a given metal, a neopentyl group is much less likely to undergo an α-hydrogen abstraction reaction than is a neopentylidene ligand. Likewise, moving from a d⁰ metal center (M = Mo, W) to a d² metal center shuts down the α-hydrogen abstraction reaction in the mono-imido complexes. Transient "M(NAr)(CH₂R)₂(OTf)₂" (M = Mo, W) loses alkane to form M(NAr)(CHR)(OTf)₂(DME) but the d² analog, Os(NAr)(CH₂-t-Bu)₂X₂, is inert.

In conclusion, the chemistry of a variety of Os(VI) mono(imido) complexes was investigated in hopes of synthesizing complexes of the general formula LnOs(NAr)(CH-t-Bu). Such complexes would be d² analogs of the molybdenum and tungsten imido alkylidenes that have been extensively studied in the Schrock group, and would allow comparisons to be made between the d⁰ and d² systems. However, the osmium imido alkylidene complexes could not be synthesized because of the difficulty
with which osmium neopentyl complexes undergo controllable \( \alpha \)-hydrogen abstraction reactions.
Experimental

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres HE-43 dry box 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 CaCl₂, 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 Isotopes. Tetrahydofuran-d₈ was vacuum transferred from sodium benzophenone ketyl. C₆D₆, CD₂Cl₂, CDCl₃, CD₃CN, and pyridine-d₅ were stored over activated molecular sieves in the dry box.

Ta(NAr)Cl₃(DME) was prepared as described in the literature.⁵² OsO₂R₂ were prepared from (OsO₂Cl₄)(PPh₄)₂ and R₂Zn in CH₂Cl₂. Triflic acid, triflic anhydride, chlorotrimethylsilane, trimethylsilyl triflate, and iodonitrilomethylsilane were purchased from Aldrich and used without further purification. Lithium-tert-butoxide was purchased from Strem. Silica gel was typically 70-230 mesh (Aldrich) or 230-400 mesh (Bodman).

NMR spectra were recorded on either a Bruker WM-250, Varian XL-300, or Varian UNITY-300 spectrometer. ¹H and ¹³C data are listed in parts per million downfield from tetramethylsilane and were referenced by the residual solvent proton peak. 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.

**Ta(NAr)(O-t-Bu)₃.** A slurry of Ta(NAr)Cl₃(DME) (5.27 g, 9.5 mmol) in 50 mL THF was cooled to -40°C. Solid LiO-t-Bu (2.30 g, 28.8 mmol) was added and the mixture was allowed to warm to room temperature and stir for three hours. The solution became pale yellow as the reaction proceeded. THF was removed in vacuo from the reaction mixture, leaving a beige solid which was extracted with pentane (40 mL). The extracts were filtered through celite and pentane was then removed in vacuo from the filtrate. A beige waxy solid was isolated and recrystallized from pentane at -40°C and two crops of colorless crystals of Ta(NAr)(O-t-Bu)₃ were isolated and dried (2.79g, 51%) Note: the high solubility of Ta(NAr)(O-t-Bu)₃ in non-polar solvents such as pentane results in relatively low isolated yields. The crude material obtained upon extraction with pentane is pure by ¹H NMR and can be used in the imido/oxo exchange reactions without any problems. ¹H NMR (C₆D₆) δ 7.17 (br s, 2, Ar), 6.92 (t, 1, Ar), 4.22 (sept, 2, CHMe₂), 1.36 (d, 12, CHMe₂), 1.28 (s, 27, OCMc₃); ¹³C NMR (C₆D₆) δ 152.1, 143.1, 122.4, 121.8 (Ar), 80.0 (OCMe₃), 32.3 (OCMe₃), 27.6 (CHMe₂), 24.4 (CHMe₂). Anal. Calcd for TaC₂₄H₄₄NO₃: C, 50.08; H, 7.70; N, 2.43. Found: C; 50.13; H, 7.96; N, 2.41.

**Os(NAr)₂(CH₂-t-Bu)₂.** OsO₂(CH₂-t-Bu)₂ (77 mg, 0.21 mmol) was dissolved in 5 mL of pentane and the solution was cooled to -40°C. Solid Ta(NAr)(O-t-Bu)₃ was added and the mixture immediately became orange-green. The mixture was allowed to warm to room temperature and stir for 1 hour, and then it was filtered through silica gel to remove TaO(O-t-Bu)₃. Solvent was removed in vacuo from the filtrate, yielding orange, crystalline Os(NAr)₂(CH₂-t-Bu)₂ (80 mg, 57%). Spectral data matched the reported values.
Os(NAr)$_2$(CH$_2$CMe$_2$Ph)$_2$. Os(NAr)$_2$(CH$_2$CMe$_2$Ph)$_2$ was prepared from OsO$_2$(CH$_2$CMe$_2$Ph)$_2$ in a manner similar to that used for Os(NAr)$_2$(CH$_2$-t-Bu)$_2$, except toluene was used as the solvent. $^1$H NMR (C$_6$D$_6$) $\delta$ 7.4 - 6.8 (m, 16 total, Ph + NAr), 4.63 (s, 4, OsCH$_2$CMe$_2$Ph), 3.62 (sept, 4, CHMe$_2$), 1.44 (s, 12, CMe$_2$Ph), 1.28 (d, 24, CHMe$_2$Ph); $^{13}$C NMR (C$_6$D$_6$) $\delta$ 154.3, 151.1, 145.2, 126.9, 126.0, 125.7, 123.3 (Ph + Ar; one peak is apparently obscured by the solvent peak), 44.4 (CMe$_2$Ph), 31.7 (CMe$_2$Ph), 29.0 (CHMe$_2$), 24.1 (CHMe$_2$). Anal. Calcd for OsC$_{44}$H$_{60}$N$_2$: C, 65.47. H, 7.49. N, 3.47. Found: C, 65.40. H, 7.65. N, 3.51.

Os(NAr)$_2$(CH$_2$SiMe$_3$)$_2$. Os(NAr)$_2$(CH$_2$SiMe$_3$)$_2$ was prepared from [OsO$_2$(CH$_2$SiMe$_3$)$_2$)$_2$]$_n$ and 2 equivalents of Ta(NAr)(O-t-Bu)$_3$ (per Os) in a manner identical to that used for Os(NAr)$_2$(CH$_2$-t-Bu)$_2$ (yield = 60%). Spectral data matched the reported values.

Os(O)(NAr)(CH$_2$-t-Bu)$_2$. OsO$_2$(CH$_2$-t-Bu)$_2$ (105 mg, 0.288 mmol) was dissolved in 10 mL THF and cooled to -40°C. A prechilled solution of Ta(N-2,6-i-Pr-C$_6$H$_3$)(O-t-Bu)$_3$ (170 mg, 0.300 mmol) in THF was then added dropwise. The mixture became purple-red as it warmed and was stirred for 1 hour. The mixture was passed through silica gel to remove Ta(O)(O-t-Bu)$_3$ and the resulting solution was reduced to dryness. The purple solid was extracted into pentane (2 mL) and recrystallized at -40°C. (98 mg, 65%): $^1$H NMR (C$_6$D$_6$) $\delta$: 7.20 (t, 1, Ar), 6.86 (d, 2, Ar), 4.52 (d, 2, J$_{H-H}$ = 12 Hz, OsCH$_8$H$_8$-t-Bu), 4.21 (d, 2, J$_{H-H}$ = 12 Hz, OsCH$_8$H$_8$-t-Bu), 3.66 (sept, 2, CHMe$_2$), 1.21 (d, 12, J$_{H-H}$ = 7 Hz, CHMe$_2$), 1.15 (s, 18, CH$_2$-t-Bu); $^{13}$C NMR (C$_6$D$_6$) $\delta$ 152.2 (C$_{ipso}$), 144.9 (C$_{ortho}$), 129.4 (C$_{para}$), 123.6 (C$_{meta}$), 35.6 (CH$_2$CMe$_3$), 32.1 (CMe$_3$), 30.5 (CH$_2$-t-Bu), 29.1 (CHMe$_2$), 23.3 (CHMe$_2$); IR (Nujol) cm$^{-1}$ 925 (Os=O). Anal. Calcd for OsC$_{22}$H$_{39}$NO: C, 50.45; H, 7.51; N, 2.67. Found: C, 50.37; H, 7.40; N, 2.50.
OsO(NAr)(CH₂CMe₂Ph)₂. OsO(NAr)(CH₂CMe₂Ph)₂ was prepared from OsO₂(CH₂CMe₂Ph)₂ and Ta(NAr)(O-t-Bu)₃ in a manner identical to that used in the preparation of OsO(NAr)(CH₂-t-Bu)₂. ¹H NMR (C₆D₆) δ 6.8 - 7.4 (m, 13 total, Ph + NAr), 4.69 (d, 2, OsCH₃Hb, JHH = 12 Hz), 4.50 (d, 2, OsCH₃Hb, JHH = 12 Hz), 3.23 (sept, 2, CHMe₂), 1.49, 1.44 (s, 6 each, CMe₂Ph), 1.12 (d, 12, CHMe₂); IR (Nujol) cm⁻¹ 928 (Os=O).

Os(NAr)(CH₂-t-Bu)₂Cl₂. Os(NAr)(O)(CH₂-t-Bu)₂ (132 mg, 0.25 mmol) was dissolved in 5 mL of DME and cooled to 0°C. A 1.0 M solution of HCl in Et₂O (1.0 mL, 1.0 mmol) was added to the stirred solution by syringe and the reaction mixture became yellow-brown. The solution was allowed to warm to room temperature and stirred for 1 hour. DME was removed in vacuo and the yellow-brown solid was extracted with pentane (10 mL), the volume of the solution was reduced to 1 mL, and the solution was cooled to -40°C. Yellow-green prisms formed and were collected and dried (115 mg, 79%): ¹H NMR (CD₂Cl₂) δ 8.90 (d, 2, JHH = 12 Hz, OsCH₃Hb-t-Bu), 7.95 (t, 1, Ar), 7.08 (d, 2, Ar), 6.78 (d, 2, JHH = 12 Hz, OsCH₃Hb-t-Bu), 2.98 (sept, 2, CHMe₂), 1.28 (d, 12, CHMe₂), 1.10 (s, 18, t-Bu); ¹³C NMR (CDCl₃) δ 153.5, 145.4, 132.7, 126.5 (Ar), 57.0 (OsCH₂-t-Bu), 41.4 (CMe₃), 32.8 (CMe₃), 32.2 (CHMe₂), 23.9 (CHMe₂). Anal. Calcd for OsC₂₅H₃₉NCl₂: C, 45.66; H, 6.79; N, 2.42. Found: C, 45.88; H, 7.07; N, 2.29.

Os(NAr)(CH₂-t-Bu)₂I₂. OsO(NAr)(CH₂-t-Bu)₂ (60 mg, 0.115 mmol) was dissolved in 3 mL of dichloromethane and the solution was cooled to -40°C. TMSI (34 μL, 0.24 mmol) was added. The solution became red immediately. After warming to room temperature, the solution was stirred for 1.5 hours. Dichloromethane was removed in vacuo, and the resulting red oily solid was extracted with pentane (10 mL), filtered, and the volume of the filtrate was reduced to 2 mL and cooled to -40°C. Dark
red crystals formed after several days and were collected and dried (66 mg, 75%): \(^1\)H NMR (toluene-\(d_8\)) \(\delta\) 9.29 (d, 2, J\(_{CH}\) = 12 Hz, OsCH\(_3\)H\(_3\)-t-Bu), 7.25 (t, 1, Ar), 7.21 (d, 2, J\(_{CH}\) = 12 Hz, OsCH\(_3\)H\(_3\)-t-Bu), 6.46 (d, 2, Ar), 3.05 (sept, 2, CHMe\(_2\)), 1.11 (d, 12, CHMe\(_2\)), 1.09 (s, 9, t-Bu); \(^{13}\)C NMR (toluene-\(d_8\)) 153.0, 141.6, 130.6, 126.0 (Ar), 63.3 (OsCH\(_2\)-t-Bu), 38.8 (CMe\(_3\)), 33.6 (CMe\(_3\)), 31.7 (CHMe\(_2\)), 23.1 (CHMe\(_2\)). Anal. Calcd for OsC\(_{25}\)H\(_{39}\)NI\(_2\): C, 34.70; H, 5.14; N, 1.84. Found: C, 34.69; H, 5.14; N, 2.01.

Os(NAr)(CH\(_2\)-t-Bu\(_2\))(OSiMe\(_3\))Cl. OsO(NAr)(CH\(_2\)-t-Bu\(_2\)) (81 mg, 0.15 mmol) was dissolved in 5 mL of dichloromethane and the solution was chilled to -40°C. Trimethylsilylchloride (25 \(\mu\)L, 0.19 mmol) was added and the resulting green solution was allowed to warm to 25°C and stir for 1 hour. Dichloromethane was removed in vacuo and the resulting green solid was recrystallized from Et\(_2\)O/pentane at -40°C. Dark green prisms were collected and dried (2 crops, 64 mg, 66%): \(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta\) 7.14 (t, 1, Ar), 6.60 (d, 2, Ar), 6.31 (d, 2, OsCH\(_4\)H\(_3\)-t-Bu), 5.15 (d, 2, OsCH\(_3\)H\(_3\)-t-Bu), 3.5 (sept, 2, CHMe\(_2\)), 1.30 (s, 18, t-Bu), 1.18 (d, 12, CHMe\(_2\)), 0.47 (s, 9, OSiMe\(_3\)). \(^{13}\)C NMR (C\(_6\)D\(_6\)) \(\delta\) 153.1, 146.3, 130.4, 125.6 (Ar), 50.5 (OsCH\(_2\)-t-Bu), 39.3 (CHMe\(_2\)), 32.5 (CMe\(_3\)), 30.8 (CMe\(_3\)), 24.0 (CHMe\(_2\)), 2.9 (SiMe\(_3\)). Anal. Calcd for OsC\(_{25}\)H\(_{48}\)NCIOSi: C, 47.48; H, 7.65; N, 2.21. Found: C, 47.42; H, 7.65; N, 2.17.

Os(NAr)(CH\(_2\)-t-Bu\(_2\))(OSiMe\(_3\))(OTf). OsO(NAr)(CH\(_2\)-t-Bu\(_2\)) (108 mg, 0.21 mmol) was dissolved in 5 mL of dichloromethane and the solution was chilled to -40°C. Trimethylsilyltriflate (42 \(\mu\)L, 0.21 mmol) was added and the resulting green solution was allowed to warm to 25°C and stir for 1 hour. Dichloromethane was removed in vacuo and the resulting olive-green solid was washed with pentane and dried (121 mg, 77%): \(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta\) 7.5 (br d, 2, OsCH\(_4\)H\(_3\)-t-Bu), 7.14 (t, 1, Ar), 6.62 (d, 2, Ar), 5.8 (br d, 2, OsCH\(_4\)H\(_3\)-t-Bu), 3.25 (br m, 2, CHMe\(_2\)), 1.27 (d, 12, CHMe\(_2\)), 1.13 (s, 18, t-Bu), 0.33 (s, 9, OSiMe\(_3\)); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 153.8, 146.7,
132.0, 125.3 (Ar), 43 (br, OsCH₂t-Bu), 40.0 (CMe₃), 31.9 (CMe₃), 31.3 (CHMe₂), 23.8 (CHMe₂), 2.3 (OSiMe₃). Anal. Calcd for OsC₂₆H₄₈NF₃O₄SiS: C, 41.86; H, 6.49; N, 1.88. Found: C, 41.59; H, 6.90; N, 1.90.

Os(NAr)(CH₂-t-Bu)₂(py)(OSiMe₃)(OTf) was prepared in 80% yield by addition of excess pyridine to a toluene solution of Os(NAr)(CH₂-t-Bu)₂(OSiMe₃)(OTf). The resulting green precipitate was washed with pentane and dried. ¹H NMR (CDCl₃) δ 8.6 (br, d, 2, py), 8.15 (t, 1, Ar), 7.75 (br, t + d, 3, py), 3.0 (br, CHMe₂), 1.15 (br, 12, CHMe₂), 1.00 (s, 18, t-Bu), 0.38 (s, 9, SiMe₃) Note: The methylene protons could not be located due to considerable broadening. ¹³C NMR (CDCl₃) δ 152.5, 147.1, 141.7, 129.3, 128.4, 126.7, 125.5 (py + Ar), 46 (br, OsCH₂-t-Bu), 39 (br, CMe₃), 32.0 (CMe₃), 31.3 (CHMe₂), 23.6 (CHMe₂), 2.7 (SiMe₃). Anal. Calcd for OsC₃₁H₅₃N₂F₃O₄SSi: C, 45.13; H, 6.47; N, 3.40. Found: C, 44.44; H, 6.54; N, 3.43.

trans-Os(NAr)(CH₃)₂(CH₂-t-Bu)₂. Os(NAr)(O)(CH₂-t-Bu)₂ (55 mg, 0.105 mmol) was dissolved in 5 mL of pentane and the solution was chilled to -40°C. A solution of trimethylaluminum in hexane (0.24 mmol) was added. The reaction mixture became red and then orange as it warmed to room temperature. After 30 minutes, the solution was filtered, the volatiles were removed in vacuo, and then a pentane solution of the crude product was passed through silica gel. After removal of solvent in vacuo, a crystalline orange solid (47 mg, 83%) was obtained. ¹H NMR (C₆D₆) δ 7.01 (t, 1, Ar), 6.72 (d, 2, Ar), 3.63 (s, 4, OsCH₂-t-Bu), 3.40 (s, 6, OsCH₃), 3.31 (sept, 4, CHMe₂), 1.27 (s, 18, CH₂-t-Bu), 1.12 (d, 12, J₉H =7 Hz, CHMe₂); ¹³C NMR (C₆D₆) δ 146.4 (Cipso), 142.5 (Cortho), 127.0 (Cpara), 124.5 (Cmeta), 74.2 (OsCH₂-t-Bu), 40.7 (OsCH₃), 40.4 (CH₂CMe₃), 34.1 (CH₂CMe₃), 29.0 (CHMe₂), 23.8 (CHMe₂). Anal. Calcd for OsC₂₄H₄₅N: C, 53.60; H, 8.43; N, 2.60. Found: C, 53.92; H, 8.79; N, 2.56.
Os₂O₂(NAr)₂(CH₂-t-Bu)₂(t-BuCHCH-t-Bu). OsO(NAr)(CH₂-t-Bu)₂ (125 mg, 0.24 mmol) was dissolved in 5 mL of pentane and the solution was cooled to -40°C. Excess Ta(CH₂-t-Bu)(CH₂-t-Bu)₃ (155 mg, 0.33 mmol) was dissolved in 1 mL of pentane and the solution was cooled to -40°C and then added dropwise to the stirring solution of OsO(NAr)(CH₂-t-Bu)₂. The red-brown mixture was allowed to warm to room temperature and stirred for 1 hour. The solution was passed through silica gel and pentane was removed in vacuo. The resulting red oil was crystallized from Et₂O/CH₃CN at -40°C. Dark red needles were collected and dried (45 mg, 35%): ¹H NMR (C₆D₆) δ 7.31, 7.21 (t, 1 each, ArH), 6.89, 6.74 (d, 2 each, ArH), 6.20 (s, 2, t-BuCHCH-t-Bu), 5.57 (d, 2, JHH = 12, OsCH₂H₂t-Bu), 3.99, 3.44 (sept, 2H each, CHMe₂), 3.72 (d, 2, JHH = 12, OsCH₃H₂t-Bu), 1.47, 1.22 (s, 9 each, t-Bu), 1.28, 1.10 (d, 12 each, CHMe₂); ¹³C NMR (C₆D₆) δ 152.6, 152.2 (Ar Cipso), 141.4, 139.9 (Ar Cortho), 127.2, 127.1 (Ar Cpara), 123.8, 123.7 (Ar Cmeta), 77.5 (tBuCHCH-t-Bu), 51.6 (OsCH₂-t-Bu), 37.7, 36.5 (CHMe₂), 33.81 (CMe-3; the two tert-butyl resonances are apparently coincidental), 30.1, 29.3 (CMe₃), 24.1, 23.7 (CHMe₂); Anal. Calcd for Os₂C₄₄H₇₆N₂O₂: C; 50.55. H; 7.32. N; 2.67. Found: C; 50.85. H; 7.30. N; 2.57.
References for Chapters 2-4


APPENDIX I: ORGANIZATION OF NOTEBOOKS, SPECTRA, AND OTHER DATA

Experiments are recorded in 10 notebooks (AML-1 - AML-10). A few early osmium experiments are recorded in notebook AML-X (February - April 1992). NMR data are labeled according to notebook number and page number (e.g AML-3-45), and if more than one spectrum was obtained on a page, the spectra are labeled a, b, c, etc. (e.g AML-3-45-a). The spectra are stored in binders (spectra from AML-1-3 are combined in one binder, and those from AML-4-10 are stored in a separate binder for each notebook.) Typically, NMR data from clean compounds or particularly interesting reactions are recorded in the notebook for simplicity, or a photocopy of the spectrum is taped into the notebook on the page following the experiment. Each $^{13}$C spectrum is listed in the table of contents in the lab notebooks, and all $^{13}$C data is recorded in the notebook. Results from elemental analyses are recorded in a section in the back of each lab notebook.
APPENDIX II: MISCELLANEOUS COMPOUNDS
List of Compounds

1. \[ \text{Re(}t\text{-Bu)}(\text{CH}_2t\text{-Bu})(2-t\text{-Bu, 6-(CH}_2\text{NMe}_2)C_6H_3O)\text{(Cl)} \]
2. \[ \text{Re(}t\text{-Bu)}(\text{CH}_2t\text{-Bu})(2-t\text{-Bu, 6-(CH}_2\text{NMe}_2)C_6H_3O)\text{(OTf)} \]
3. \[ \text{Re(}t\text{-Bu)}(\text{CH}_2t\text{-Bu})\text{(N(Ts)(CH}_2)_2\text{NMe}_2)\text{(Cl)} \]
4. \[ \text{WO(}t\text{-Bu)}(\text{DABP(SiMe}_3)_2\text{)(PMe}_3) \]
(DABP = 2,2'-diaminobiphenyl)
5. \[ \text{WO(}t\text{-Bu)}(\text{BINO(SiPh}_3)_2\text{)(PMe}_3) \]
(BINO = 2,2'-binaphthol)

(Ts = p-tolylsulfonyl)
Experimental

\[ \text{Re(C-t-Bu)(CH-t-Bu)(O-2,6-Ph}_2\text{C}_6\text{H}_3)_2 \] (1). Solid KO-2,6-Ph\text{H}_2\text{C}_6\text{H}_3 (0.495 g, 1.74 mmol) was added to a stirred solution of \([\text{Re(C-t-Bu)(CH-t-Bu)Cl}_2]_x\) (0.322 g, 0.813 mmol) in 10 mL of THF. The resulting maroon solution was stirred at room temperature for 1.5 hours, and the solvent was removed in vacuo, leaving a yellow-brown powder, which was extracted with toluene (50 mL). The solution was filtered through Celite, solvent was then removed in vacuo from the filtrate, and an analytically pure bright yellow powder (300 mg, 42%) was obtained by washing the resulting solid with a 2/1 mixture of cold ether/pentane. \(^1\)H NMR (\text{C}_6\text{D}_6) \delta 9.71 (s, 1, CHt-Bu); 6.5-8 (mult., 26, aryl), 0.61, 0.59 (s, 9 each, t-Bu). Anal. Calcd for ReC\text{46}H\text{45}O\text{2}: C, 67.70; H, 5.56. Found: C, 67.85; H, 5.71.

2-t-Bu, 6-(CH\text{2NM}e\text{2})\text{C}_6\text{H}_3\text{OH} (2). 2-t-butylphenol (15 grams, 0.1 mol) was slurried in 100 mL of water. Dimethylamine (13 mL of a 40% solution in H\text{2O}) and formaldehyde (10 mL of a 37% solution in H\text{2O}) were added and the red heterogeneous mixture was stirred for 1.5 h at 25\text{oC}. The solution was extracted with 100 mL of \text{Et}_2\text{O}, the ether extract was dried over MgSO\text{4}, and ether was removed in vacuo to yield a pale pink oil (12.5 g, 60%) \(^1\)H NMR (CDCl\text{3}) \delta 7.3 - 6.6 (m, 4, Ar), 3.60 (s, 2, CH\text{2NM}e\text{2}), 2.29 (s, 6, NMe\text{2}), 1.40 (s, 9, t-Bu).

\[ \text{Re(C-t-Bu)(CH-t-Bu)(2-t-Bu, 6-CH}_2\text{NM}e\text{2-C}_6\text{H}_3\text{O})(\text{Cl}) \] (3). [Re(C-t-Bu)(CH-t-Bu)Cl\text{2}]x (362 mg, 0.91 mmol) was dissolved in 5 mL of THF and the solution was cooled to -40\text{oC}. (2-t-Bu, 6-CH\text{2NM}e\text{2-C}_6\text{H}_3\text{Cl})-(\text{Et}_2\text{O}) (272 mg, 0.95 mmol) was dissolved in 3 mL of THF and the solution was cooled to -40\text{oC} and then added to the chilled solution of [Re(C-t-Bu)(CH-t-Bu)Cl\text{2}]x. The reaction mixture was allowed to warm to room temperature and was stirred for 45 minutes. THF was removed in vacuo and the solid was extracted with toluene and filtered through Celite.
After removal of toluene in vacuo, the brown solid was washed with pentane and dried. (yield: 330 mg, 65%): $^1$H NMR (CD$_6$D$_6$) $\delta$ 13.58 (s, 1, ReCH-$t$-Bu), 7.55 (d, 1, Ar), 6.82 (t, 1, Ar), 6.69 (d, 1, Ar), 3.38, 3.21 (br. d., 1 each, CH$_2$H$_b$NMe$_2$), 2.23, 2.13 (s, 3 each, NMe$_2$), 1.88, 1.21, 1.19 ($t$-Bu). Anal. Calcd for ReC$_{23}$H$_{39}$: C, 48.70; H, 6.88; N, 2.47. Found: C, 48.68; H, 7.03; N, 2.30.

Re(C-$t$-Bu)(CH-$t$-Bu)(2-$t$-Bu, 6-CH$_2$NMe$_2$-C$_6$H$_3$O)(O$_3$SCF$_3$) (4). To a stirred solution of Re(C-$t$-Bu)(CH-$t$-Bu)(2-$t$-Bu, 6-CH$_2$NMe$_2$-C$_6$H$_3$O)(Cl) (78 mg, 0.134 mmol) in 10 mL of Et$_2$O, solid silver triflate was added. The mixture was stirred for one hour at room temperature, and then it was filtered. The ether was removed in vacuo to yield a light brown powder, which was washed with pentane (10 mL) and dried. The resulting pale beige powder was pure by $^1$H NMR (65 mg, 60%). An analytical sample was recrystallized from toluene/pentane at -40°C: $^1$H NMR (CD$_6$D$_6$) $\delta$ 14.03 (s, 1, ReCH$^4$Bu), 7.51 (d, 1, H$_{aryl}$), 6.82 (t, 1, H$_{aryl}$), 6.60 (d, 1, H$_{aryl}$), 3.38 (br. d., 1, CH$_2$H$_b$NMe$_2$), 2.90 (br. d., 1, CH$_2$H$_b$NMe$_2$), 2.12, 1.91 (s, 3 each, NMe$_2$), 1.26, 1.21 (s, 9 each, $t$-Bu). Anal. Calcd for ReC$_{24}$H$_{39}$NF$_3$O$_4$S: C, 42.34; H, 5.77; N, 2.06. Found: C, 42.81; H, 5.80; N, 1.79.

TsNH(CH$_2$)$_2$NMe$_2$ (5). N-tosylaziridine (1.656 g, 8.38 mmol) was dissolved in 20 mL of THF. Dimethylamine (1.5 mL of a 40% solution in H$_2$O, 13.33 mmol) was added. The mixture became yellow and was allowed to stir overnight. THF was removed in vacuo and the resulting beige solid was extracted with dichloromethane, the solution was dried over Na$_2$SO$_4$ and dichloromethane was removed in vacuo. The solid was washed with pentane, leaving 1.44 g TsNH(CH$_2$)$_2$NMe$_2$ (71%). $^1$H NMR (CDCl$_3$) $\delta$ 7.73 (d, 2, Ar), 7.28 (d, 2, Ar), 2.92 (t, 2, TosNHCH$_2$), 2.40 (s, 3, ArCH$_3$), 2.28 (t, CH$_2$NMe$_2$), 2.01 (s, 6, NMe$_2$).

Re(C-$t$-Bu)(CH-$t$-Bu)(TsNCH$_2$CH$_2$NMe$_2$)Cl (6). [Re(C-$t$-Bu)(CH-$t$-Bu)Cl$_2$]$_x$ (506 mg, 1.28 mmol) was dissolved in 20 mL of THF. To this solution 3 mL of triethylamine was added, followed by solid N, N-dimethyl, N'-p-toluenesulfonyl,
ethanediamine (300 mg, 1.25 mmol). The brown solution was stirred at room temperature overnight. The volatiles were then removed \textit{in vacuo} and the brown solid was extracted with toluene (20 mL) and filtered through celite. The solvent was removed \textit{in vacuo} and the solid was washed with pentane (10 mL) to yield a tan powder that was pure by \textsuperscript{1}H NMR (596 mg, 77%). An analytically pure sample was recrystallized from toluene/pentane at -40°C: \textsuperscript{1}H NMR (CD\textsubscript{2}Cl\textsubscript{2}) \( \delta \) 12.81 (s, 1, ReCH\textsubscript{t}-Bu), 7.66 (d, 2, Ar), 7.23(d, 2, Ar) 3.44, 3.25, 3.10, 2.84 (m, 1 each, CH\textsubscript{2}), 2.9, 2.5 (br. s., 3 each N(CH\textsubscript{3})\textsubscript{2}), 1.33, 1.32 (s, 9 each, t-Bu); \textsuperscript{13}C NMR (CD\textsubscript{2}Cl\textsubscript{2}) \( \delta \) 290.8 (ReCH\textsuperscript{t}Bu, J\textsubscript{CH} =110 Hz.), 286.9 (ReC-t-Bu), 142.1, 138.3, 129.1, 127.6 (C\textsubscript{aromatic}), 63.0, 50.0 (N(CH\textsubscript{3})\textsubscript{2}), 48.6 (CMe\textsubscript{3}), 30.5, 29.2 (CMe\textsubscript{3}), 21.3 (ArCH\textsubscript{3}). Anal. Calcd for C\textsubscript{21}H\textsubscript{36}N\textsubscript{2}Cl\textsubscript{2}SRe: C, 41.88; H, 6.03; N, 4.65. Found: C, 41.86; H, 5.84; N, 4.85.

2, 2’-(N(SiMe\textsubscript{3})(Li))\textsubscript{2}biphenyl-(Et\textsubscript{2}O)\textsubscript{2} (7). 2,2’-diaminobiphenyl (1.09 g, 5.93 mmol) was dissolved in ether and the solution was cooled to -40°C. A solution of n-BuLi in hexane (13.6 mmol) was added. The mixture became yellow and a precipitate formed. The mixture was allowed to warm to 25°C and was stirred for 1 hour and then cooled to -40°C. TMSCl (1.52 g, 14 mmol) was added and the mixture became colorless and a precipitate of LiCl formed. The mixture was allowed to warm to 25°C and was stirred for 1 hour and then filtered through celite and the filtrate was cooled to -40°C. A solution of n-BuLi in hexane (13.6 mmol) was added and the mixture was allowed to warm to 25°C and was stirred for one hour. Ether was removed in vacuo and the waxy beige solid was crystallized from pentane at -40°C. Beige crystals were collected (713 mg, 32%). Ether is slowly lost in vacuo: \textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}) \( \delta \) 7.0 - 6.5 (m, 8 total, Ar), 3.0 (br m, 8, OCH\textsubscript{2}CH\textsubscript{3}), 0.95 (br m, 6, OCH\textsubscript{2}CH\textsubscript{3}), 0.04 (s, 18, SiMe\textsubscript{3}).

WO(CH-t-Bu)(DABP(TMS)\textsubscript{2})(PMe\textsubscript{3}) (8). WO(CH-t-Bu)Cl\textsubscript{2}(PMe\textsubscript{3})\textsubscript{2} (63 mg, 0.13 mmol) was slurred in 4 mL of Et\textsubscript{2}O and the mixture was cooled to -40°C. [DABP(TMS)\textsubscript{2}Li\textsubscript{2}](Et\textsubscript{2}O)\textsubscript{2} (63 mg, 0.13 mmol) was dissolved in 1 mL of Et\textsubscript{2}O and the
solution was cooled to -40°C and added dropwise to the stirring solution of WO(CH-t-Bu)Cl2(PMe3)2. The reaction mixture was initially a clear yellow solution, but a white precipitate formed after the mixture had warmed to room temperature. The reaction mixture was allowed to stir for 45 minutes, and then the ether was removed in vacuo and the resulting yellow solid was extracted with pentane and filtered. Pentane was removed in vacuo from the filtrate to yield a yellow glassy solid (85 mg, 97%) which was pure by 1H NMR but was impossible to recrystallize. 1H NMR (C6D6) δ 10.61 (s, 1, WCH-t-Bu), 7.5 - 6.7 (overlapping M, 8 total, Ar), 1.32 (s, 9, t-Bu), 0.82 (d, 9, PMe3, JPH = 12 Hz), 0.33, 0.18 (s, 9 each, SiMe3); 13C NMR (C6D6) δ 272.1 (OsCH-t-Bu, JCH = 113 Hz, JCW = 11 Hz), 156.0, 147.3, 141.3, 140.2, 136.0 (Ar, (one Ar C peak is presumably buried under the solvent peak), 45.0 (CMe3), 34.2 (CMe3), 16.2 (PMe3), 4.4, 3.4 (SiMe3).

WO(CH-t-Bu)(Bino(SiPh3)2)(PMe3) (9) WO(CH-t-Bu)Cl2(PMe3)2 (0.250 g, 0.51 mmol) was dissolved in THF (50 mL) and the solution was cooled to -40°C. To this solution was added solid (Bino(SiPh3)2K2)(THF) (482 mg, 0.51 mmol). The bright yellow suspension was stirred at 25°C for 12 hr, after which time the solid had dissolved and a precipitate of KCl had formed. KCl was removed by filtration through a bed of Celite, and THF was removed in vacuo to yield a greenish solid which was dissolved in CH2Cl2 and precipitated by addition of pentane. The off-white solid was collected and dried in vacuo (510 mg, 87%). The material is insoluble in Et2O and pentane, sparingly soluble in THF, DMSO and C6H6, and soluble in CH2Cl2. 1H NMR (CD2Cl2) δ 8.77 (d and dd, 1, CH-t-Bu, 3J(PH) = 3 Hz, 2J(WH) = 10 Hz). 8.07 (s, 1, Bino); 7.22 - 7.77 (m, 36, Bino and/or SiPh3), 6.99 - 7.19 (m, 2, Bino or SiPh3) and 6.53 - 6.56 (m, 1, Bino or SiPh3); 0.79 (d, 9, PMe3, 2J(PH) = 10.2 Hz); 0.60 (s, 9 t-Bu). 13C NMR (CD2Cl2) δ 283.4 (WCH-t-Bu, JCP = 10 Hz), 117.4, 119.1, 122.3, 123.4, 125.0, 125.9, 126.5, 126.6, 126.9, 127.5, 128.4, 128.5, 128.8, 129.3, 129.9, 135.8, 135.96, 136.1, 136.1, 136.5, 136.8, 137.5, 141.6, 142.7, 145, 147. (Ar. The two signals
due to the two ipso carbon atoms in the triphenyl...yl groups are expected to be weak and were not observed.), 43.1 (CMe₃), 31.8 (CMe₃), 15.0 (PMe₃); ³¹P (CD₂Cl₂) δ 3.90 (relative to 85 % H₃PO₄) (¹J(WP) = 406.9 Hz). IR (Nujol, cm⁻¹) 956 (W=O); Anal. Calcd for WC₆₄H₇₉O₃PSi₂: C, 67.01; H, 5.18. Found: C, 67.36; H, 5.18.

WO(CH-t-Bu)(2,6-Ph₂C₆H₃O)₂(PPh₂Me). WO(CH-t-Bu)(PPh₂Me)₂Cl₂ (411 mg, 0.55 mmol) was dissolved in 15 ml of THF. Solid 2,6-Ph₂C₆H₃OK (330 mg, 1.16 mmol) was added. The yellow-green mixture was allowed to stir for 12 hours at room temperature. THF was removed in vacuo and a yellow solid was obtained which was triturated with ether (10 ml) and pentane (10 ml). A pale yellow solid was isolated which was washed with 50 ml of pentane to remove residual PPh₂Me. The solid was then extracted with 30 ml of toluene, filtered through celite, and toluene was then removed in vacuo from the filtrate. The crude material was recrystallized from CH₂Cl₂/pentane mixture at -40°C overnight. Yellow blocks (240 mg, 45%) were collected, washed with pentane and dried. ¹H NMR (CDCl₃) δ 10.00 (s, 1, WCH-t-Bu), 7.5 - 6.8 (br m, 36 total, Ar + Ph), 0.95 (d, 3, PPh₂Me ) 0.38 (s, 9, t-Bu). ¹³C NMR (CDCl₃) δ 287.4 (WCH-t-Bu, JCH = 118 Hz), 140.7, 132.4, 130.5, 129.6, 128.6, 128.5, 128.2, 126.4, 119.9 (Ar; the three peaks due to C(ipso) are expected to be weak and were not observed), 43.8 (CMe₃), 31.6 (CMe₃), 11.5 (PPh₂Me, ¹JCₚ = 49 Hz); ³¹P NMR (relative to 85% H₃PO₄; CDCl₃, 20°C) δ 12.2.
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So admit it, you didn’t look at my thesis at all except to see how long it was and to read the acknowledgments.

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