PART 1: MOLYBDENUM AMIDOPHENOLATES AND CATECHOLATES FOR NONCLASSICAL OXYGEN ACTIVATION AND ATOM TRANSFER REACTIONS

PART 2: SILICON-CARBON BOND ACTIVATION IN ARYLOXY-IMINOQUINONES AND ENHANCED REACTIVITY OVER TIN ANALOGUES

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Sukesh Shekar

Seth N. Brown, Director

Graduate Program in Chemistry and Biochemistry
Notre Dame, Indiana
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Abstract

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Part 1: The tetradentate ligand \( t^\text{BuClipH}_4 \) \((t^\text{BuClipH}_4 = 4,4'-\text{di}-\text{tert}-\text{butyl}-N,N'-\text{bis}(3,5-\text{di}-\text{tert}-\text{butyl}-2\text{-hydroxyphenyl})-2,2'-\text{diaminobiphenyl})\) forms molybdenum(VI) complexes with a varying number (0-2) of terminal oxo groups. The doubly deprotonated cis-dioxo complex \((t^\text{BuClipH}_2)\text{MoO}_2\) readily loses water to form a series of monooxo complexes \((t^\text{BuClip})\text{MoO}(L)\) in the presence of donor ligands. \((t^\text{BuClipH}_2)\text{MoO}_2\) also reacts with 3,5-di-\text{tert}-butylcatechol to form oxo-free \((t^\text{BuClip})\text{Mo}(3,5-\text{tBu}_2\text{Cat})\). The facile formation and interconversion of these species highlights the ability of the amidophenoxide ligand to stabilize the high-valent molybdenum metal center by strong \(\pi\)-donation. \((t^\text{BuClip})\text{Mo}(3,5-\text{tBu}_2\text{Cat})\) has lower Lewis acidity compared to oxo and catecholate analogues \((t^\text{BuClip})\text{MoO}, \text{Mo}(3,5-\text{tBu}_2\text{Cat})_3,\) and \((3,5-\text{tBu}_2\text{Cat})_2\text{MoO},\) which is apparent from rates of pyridine dissociation. These amidophenolate ligands enable
oxygen atom abstraction by the molybdenum(VI) in a "nonclassical" fashion, as the required reducing equivalents for oxygen reduction are drawn from ligand oxidation and not the molybdenum center. This generates a reactive intermediate, tentatively identified as (tBuClipSQ)MoO₂, with oxidizing equivalents stored in a bis-semiquinone ligand. (tBuClipSQ)MoO₂ can be deoxygenated by dimethylphenylphosphine, establishing a closed loop cycle for catalytic oxygen atom transfer.

Part 2: Silylation of the oxidized ligand in lead(II) bis(3,5-di-tert-butyl-1,2-quinone-(3,5-di-tert-butyl-2-oxy-1-phenyl)imine), Pb(ONO²)₂, with chlorosilanes RSiX₂Cl (R = Me, Ph; X = Me, Ph, Cl) results in tetracyclic, pentacoordinate silicon compounds X(Y)Si(ON[R]O) in which the aryloxyiminoquinone ligand is irreversibly reduced. The trigonal bipyramidal silicon products of migration in some cases form kinetic isomers, R(Cl)Si(ON[R]O) with an equatorial chlorine substituent, which isomerize to their thermodynamically stable stereoisomers, Cl(R)Si(ON[R]O), in which the chlorine is axial. The kinetic stereoselectivity in these reactions is determined not only by relative barriers of migration from isomeric octahedral silicon intermediates, but also from the reversibility in isomerization of κ³-R(X)(Y)Si(ONO²) isomers via the tetrahedral κ¹-R(X)(Y)Si(ONO²).

In reaction of Me₃MCl (M = Si or Sn) with H(DOPO²) (DOPO = 2,4,6,8-tetra-tert-butyl-1-oxo-1H-phenoxazin-9-olate), tetrahedral intermediates κ¹-Me₃M(ONO²) can be isolated or spectroscopically identified. The rates of methyl migration from these intermediates indicates that migration from tetrahedral tin is 10⁴ times faster than migration from silicon. In stark contrast, methyl migration from silicon in the octahedral
intermediate $\kappa^3$-$\text{MeCl}_2\text{Si(DOPO)}^0$ is at least $10^7$ time faster than migration from tin. The enhanced reactivity of the silicon-carbon bond in monomethyl compounds results from the increased stability of the $\kappa^3$ intermediate relative to $\kappa^1$. This inference can used to the drive the desired reactivity of silicon and tin.
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CHAPTER 1:

THE Π BONDING CONTINUUM OF MOLYBDENUM(VI) AMIDOPHENOLATES

“ The Chemical Bond Defined – there is a chemical bond between two atoms or groups of atoms in case that the forces acting between them are such as to lead to the formation of an aggregate with sufficient stability to make it convenient for the chemist to consider it as an independent molecular species. Linus Pauling – The Nature of the Chemical Bond. “1

1.1 Introduction

1.1.1 Redox-active ligands.

Linus Pauling’s simple yet fundamental definition suggests that bonds exist when atoms are significantly attracted to each other. The formation of a bond in a coordination compound must involve some redistribution of electron density between the metal center and ligand. The magnitude of this electron density redistribution determines if a bond is dative, covalent, or ionic. The oxidation state is a formalism of valence bond theory that is eminently useful for balancing redox reactions and understanding chemical properties of compounds. The coordination chemist Jørgensen coined the term ‘innocent ligand’ to describe the situation where the sum of all ligands’ formal oxidation states accurately represents the complementary oxidation state of the bound metal (as an integer value).2 In such cases the oxidation state of the metal center is in accordance with its spectroscopic and magnetic properties. Non-innocent ligands
can exist as ligand-centered radicals or closed shell species, which causes ambiguity in assigning oxidation states. Non-innocent ligands such as nitrosyl or 1,2-dithiolenes exhibit a significant charge transfer to the metal and increase the covalency of the metal ligand bond. A strong mixing of ligand and metal frontier orbitals makes the assignment of a physical oxidation state as integers impossible because the degree of electron density distribution between ligand and metal is a continuum. Therefore, many π acceptor ligands like carbonyls, alkenes, and alkynes can be classified as non-innocent in covalent metallic compounds. The term ‘non-innocent’ is used interchangeably with redox-active, though the latter phrase makes the ligands seem less culpable and more aptly describes redox events which occur in concert with the metal center. In one of the most fundamental reactions that sustain aerobic life, cytochrome P450 Compound I is a heme Fe(IV) oxo thiolate complex that is formed by a two electron oxidation. One of these oxidizing equivalents is supplied by the oxidation of Fe(III) to Fe(IV) and the second is delocalized over the porphyrin and thiolate ligands. Redox-active ligands are truly ambi-valent, often spanning multiple oxidation states. A recent forum issue in Inorganic Chemistry highlights the uses of redox active ligands as electron reservoirs.

1.1.2 Oxidation states and π bonding of catechol.

Catechols are the poster child of redox active ligands and encompass three integer oxidation states: a fully reduced dianionic catecholate, a monoanionic semiquinone, and fully oxidized neutral quinone. The Lewis structures (Figure 1.1) of different oxidation states have distinct structural variations. In the dianionic closed-shell catecholate, the six-membered ring is aromatic, with C–C bonds intermediate between
double and single bonds and carbon-heteroatom single bonds. In the neutral quinone oxidation state, there are carbon-heteroatom double bonds. The semiquinone has an intermediate geometry.

![Chemical structure of oxidation states of catecholates](image)

Figure 1.1 Oxidation states of 3,5-di-tert-butyl catecholate (3,5-
\textsuperscript{t}Bu\textsubscript{2}Cat).

The geometric changes accompanying ligand oxidation have been used qualitatively to assign the oxidation states of the ligands in metal complexes.\textsuperscript{6} A quantitative measure of catechol and analogous amidophenol ligand oxidation can be provided by a metrical oxidation state.\textsuperscript{7} This recently developed metric uses a least squares fit of all eight independently observable (five for catecholates) bond distances for each ring (Figure 1.3). These crystallographically determined C–O, C–N, and ring C–C distances were gathered from a large number of structures where the physical oxidation states of metal and ligand were unambiguous. Equivalent bond distances (say, all C\textsubscript{1}–O distances) were averaged across all structures with a given ligand oxidation state and plotted as a function of ligand oxidation state. Linear correlations between bond distance and oxidation state exist for all bond distances except C\textsubscript{1}–C\textsubscript{2}, which shows a quadratic fit.
Figure 1.2 Bond distances used to calculate MOS values in catecholates and amidophenoxides.\(^7\)

Using these correlations, an empirical single numerical value called the metrical oxidation state (MOS) can be determined.

Figure 1.3 Analogous bonding interactions in metal oxo and catecholate complexes.

Catecholate and amidophenolates are also unusually strong π bonding ligands. They form two σ bonds, similar to the σ and one π bond of the oxo ligand (Figure 1.2).  

The second π interaction of the oxo is analogous to donation from the \(B_1\)-symmetric donor orbital of the catecholate, which is raised in energy by its interaction with a filled benzene π-bonding orbital.\(^8\) These π bonding interactions lead to a depletion of electron density in the HOMO of catecholate/amidophenolate, which causes structural
changes that are indistinguishable geometrically from ligand oxidation. The MOS calculation can be used to discern variations in structures which correspond to non integer oxidation states. A MOS value of -2 indicates a fully reduced form whereas more positive values indicate increased covalency of the π bonds or electron transfer.

This chapter reports the preparation, characterization, and π bonding continuum of molybdenum complexes of 4,4'-di-tert-butylbiphenyl-2,2'-bis((2-hydroxy-3,5-di-tert-butylphenyl)amine), 'BuClipH₄. This tetradentate ligand is bridged by a biphenyl backbone and has two ligating amidophenoxide groups. 2-Amidophenoxides are isoelectronic with catecholates but even stronger π donors because of the increased basicity of nitrogen compared to oxygen. They are also more easily oxidized than catecholates to form iminosemiquinones or iminoquinones.

1.2 Results

1.2.1 Preparation and metalation of 4,4'-di-tert-butyl-2,2'-bis((2-hydroxy-3,5-di-tert-butylphenyl)amino)biphenyl ('BuClipH₄).¹⁰

Preparation of the 4,4'-di-tert-butyl-2,2'-biphenyl-bridged bis(aminophenol) ligand 'BuClipH₄ is carried out in three steps from commercially available 4,4'-di-tert-butylbiphenyl. The bis(aminophenol) ligand with a 2,2'-biphenyl backbone has been reported by Mukherjee.¹¹ Nitration of the biphenyl and reduction of the dinitrophenyl are carried out in accordance with procedures described by Tashiro and Yamato.¹² The

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¹ The preparation of 'BuClipH₄ was developed by S. N. Brown.
diamine condensation with 3,5-di-tert-butylcatechol is catalyzed by triethylamine and takes place in high yield to produce \(^{1}\text{BuClipH}_4\).

The bis(aminophenol) ligand \(^{1}\text{BuClipH}_4\) reacts with MoO\(_2\)(acac)\(_2\) in chlorinated solvents in 48 h to deposit sparingly soluble, bright yellow, microcrystalline \((^{1}\text{BuClipH}_2)\text{MoO}_2\) (Figure 1.4).\(^8\) Free acetylacetone is a byproduct of the reaction and is evident \textit{in situ} by \(^1\text{H}\) NMR spectroscopy. The \(^1\text{H}\) NMR spectrum of the product is symmetrical, suggesting a \textit{cis}-\(\alpha\) geometry, and IR spectroscopy indicates the presence of a typical \textit{cis}-dioxomolybdenum unit with Mo=O stretches at 935 and 900 cm\(^{-1}\), as well as an NH stretch at 3216 cm\(^{-1}\). The NH protons resonate at \(\delta\) 6.69 (CDCl\(_3\)), and couple weakly \((J = 0.5\) Hz\) with the aminophenoxide aromatic peak at \(\delta\) 6.30.\(^9\)

1.2.2. Formation of a bridging nitrido complex.

Nitridomolybdenum(VI) tris(tert-butoxide), NMo(O\(^{13}\text{Bu})_3\),\(^{13}\) reacts with \(^{1}\text{BuClipH}_4\) to form \((^{1}\text{BuClipH})\text{MoN}\) in high yields as judged by NMR. \((^{1}\text{BuClipH})\text{MoN}\) is a violet diagmagnetic compound and shows ten aromatic resonances and six \textit{tert}-butyl resonances in its \(^1\text{H}\) NMR spectrum indicative of an unsymmetrical ligand environment. The resonance at \(\delta\) 4.69 is of the NH proton and two NH stretches in the infrared spectrum (3305 and 3395 cm\(^{-1}\)) suggest that a monomeric structure is unlikely. Furthermore, a dimeric structure is suggested by an ESI MS peak of 1624.8271, which is double the mass of the empirical formula.

\(^8\) The preparation of \(^{1}\text{BuClipH}_2\text{MoO}_2\) was developed by J.A. Kopec and S. N. Brown.
Figure 1.4 Molybdenum complexes of 4,4'-di-tert-butylbiphenyl-2,2'-bis((2-hydroxy-3,5-di-tert-butylphenyl)amine) (tBuClipH₄) containing 0-3 π Bonds
X-ray crystallography confirms the dimeric structure of $t$BuClipHMoN and its formulation as ($t$BuClip)Mo($\mu$-N)($\mu$-NH$_2$)Mo($t$BuClip). This compound has fully deprotonated bis(amidephenolate) ligands with a novel $\mu$-nitrido/$\mu$-amido dimolybdenum core (Figure 1.5). The amide and nitride groups are easily distinguishable with short nitride bonds (Mo-N$_5$ = 1.848(2) Å avg.), and considerably longer bonds to the amide (Mo-N$_6$ = 2.138(15) Å avg.). The two hydrogens on the bridging amide were found on the difference Fourier map. An approximate $C_2$ axis contains the nitride and amide nitrogens atoms. Substantial trigonal twist angles$^{14}$ of 35 ± 11° indicate distortions between an octahedron and a trigonal prism for the molybdenum centers.

Similar structures are observed in the oxo-catecholate complexes MoO($3,6$-$t$Bu$_2$C$_6$H$_2$O$_2$)$_2$(L) (L = C$_5$H$_5$NO, Me$_2$SO, Ph$_3$AsO).$^{15}$ The bridging nitride has an acute Mo-N-Mo angle of 109.49(10)°. Unconstrained bridging nitrides of molybdenum are typically linear and this angle is greater than 144° even in 6-membered ring nitrides.$^{16}$ The Mo($\mu$-N)($\mu$-NH$_2$)Mo core structure is novel, although Mo(VI) $\mu$-nitrido complexes with alternating triple ($\sim$1.67 Å) and single ($\sim$2.15 Å) bonds are known in tetramers of Mo(N)Cl$_3$$^{17}$ as well as in other structures.$^{18,19}$ Two bimetallic compounds with W$_2$(\(\mu\)-N)$_2$ cores and acute W-N-W angles ($\sim$95°) are also known, but show alternating single and multiple bonds to nitrogen.$^{20}$ The Mo-(\(\mu\)-N) distances in ($t$BuClip)Mo($\mu$-N)($\mu$-NH$_2$)Mo($t$BuClip) are typical of molybdenum-nitrogen double bonds,$^{21}$ even though the bending at nitrogen allows for the formation of only one $\pi$ bond and subsequently a Mo-N bond order of only 1.5.
Figure 1.5 Thermal ellipsoid plot of (tBuClip)Mo(μ-N)(μ-NH₂)Mo(tBuClip). Hydrogen atoms (except those on N6), methyl groups, and lattice solvent have been omitted for clarity.

The amidophenoxides that are located cis to the bridging nitride donate less effectively to the molybdenum because of competing π donation from the bridging nitride. Consequently, their donor orbitals are higher in energy as compared to the amidophenoxides located trans to the bridging nitride (ΔE ≈ 0.45 eV, from DFT calculations). The cyclic voltammogram of (tBuClip)Mo(μ-N)(μ-NH₂)Mo(tBuClip) shows one reversible ligand-centered oxidation at –0.03 V (vs. Cp₂Fe⁺/Cp₂Fe). Several irreversible oxidations are perceptible between ~ 0.8-1.1 V, and one reversible metal-centered reduction is seen at –1.12 V.
1.2.3 Synthesis and characterization of monooxo molybdenum(VI) complexes\textsuperscript{c}.

\((\text{tBuClipH}_2)\text{MoO}_2\) readily loses water on treatment with bases to form mono-oxo complexes \((\text{tBuClip})\text{MoO}(L)\), which exhibit predominantly a \textit{cis}-\textit{β} geometry with an aryloxide \textit{trans} to the oxo group. The \textit{cis}-\textit{β} geometry is suggested by an unsymmetrical NMR and confirmed by a solid state structure of \((\text{tBuClip})\text{MoO}(\text{Lut})\).

\textsuperscript{c}Synthesis, characterization, and DFT calculations of \((\text{tBuClip})\text{MoO}(\text{Py}/\text{Lut})\) were carried out by J. A. Kopec and S.N. Brown but are included in this section for the sake of continuity and completeness.
In the solid state, \((\text{tBuClipH}_2)\text{MoO}_2\) is yellow, indicative of an octahedral \textit{cis-}\textit{dioxomolybdenum(VI)} complex where all three \(d\pi\) orbitals are \(\text{Mo} = \text{O} \pi^*\) in character and thus high in energy. The aryloxide-to-metal charge transfer bands are higher energy transitions absorbing light of a short wavelength. Solutions of the complex quickly turn vibrant green or brown in THF or with added DMSO, suggesting that the dioxo complex is in equilibrium with \((\text{tBuClip})\text{Mo}(\text{O})(\text{L})\) complexes, where \(\text{L} = \text{base}\). Solutions of the complex quickly turn olive green hues in the absence of basic donors, suggesting small equilibrium concentrations of an oxo-hydroxo \((\text{tBuClipH})\text{Mo}(\text{O})(\text{OH})\) or oxo-aquo \((\text{tBuClip})\text{Mo}(\text{O})(\text{OH}_2)\) complex. Addition of triphenylsilanol to \((\text{tBuClipH}_2)\text{MoO}_2\) results in an 80% isolated yield of \((\text{tBuClipH})\text{Mo}(\text{O})(\text{OSiPh}_3)\). The same product can also be
independently generated from the reaction of ligand \( ^t\text{BuClip}H_4 \) and \((\text{Ph}_3\text{SiO})_2\text{MoO}_2\).\(^{22}\)

Stronger donors such as pyridine, 3,5-lutidine, or phenyldimethylphosphine yield monooxo adducts \((^t\text{BuClip})\text{Mo}(O)(L)\) in quantitative yield as judged by NMR spectroscopy. Isolable material where \( L = \text{pyridine or lutidine} \) can be obtained in moderate yields by crystallization from the reaction mixture in the presence of excess ligand, and infrared spectroscopy shows the absence of N-H stretches and a single molybdenum-oxo stretch (901 cm\(^{-1}\) for the pyridine adduct, 907 cm\(^{-1}\) for the lutidine adduct). The \(^1\text{H} \) NMR spectrum of \((^t\text{BuClip})\text{Mo}(\text{PMe}_2\text{Ph})\) indicates a \( C_1 \)-symmetric product with \textit{cis}-\( \beta \) geometry analogous to \((^t\text{BuClip})\text{Mo}(\text{lut})\). The solid-state structure of the 3,5-lutidine adduct \((^t\text{BuClip})\text{Mo}(O)(\text{lut})\) (Figure 1.7) is very similar to that of each molybdenum center in \((^t\text{BuClip})\text{Mo}(\mu-N)(\mu-NH_2)\text{Mo}(^t\text{BuClip})\), with the oxo group in place of the bridging nitride and the lutidine in place of the bridging amide (Figure 1.5). The oxo complex shows a short metal-oxygen multiple bond \( (d_{\text{Mo}=\text{O}} = 1.7098(19) \text{ Å}) \), consistent with a molybdenum-oxygen triple bond.\(^{23}\) Its \textit{cis}-\( \beta \) geometry with amidophenolate oxygen \textit{trans} to oxo is also favored in solution, but traces (~3%) of a minor isomer are observed. DFT calculations on \((\text{Clip})\text{Mo}(O)(\text{py})\) (B3LYP, SDD basis set for Mo, 6-31G* for all other atoms) indicate that all three \textit{cis} isomers are local minima, with the crystallographically observed isomer energetically more stable by 5.4 kcal mol\(^{-1}\) in comparison with the \textit{cis}-\( \alpha \) geometry. The other \textit{cis}-\( \beta \) geometry (with amide \textit{trans} to oxo) is also 12 kcal mol\(^{-1}\) higher in energy.
1.2.4 Synthesis and structure of oxo-free dialkoxytungsten(VI) complexes.

The loss of a single oxo from a dioxoaluminum complex is often observed, but complete deoxygenation of dioxoaluminum complexes is rare regardless of how they are made. The reaction of \((tBuClipH_2)MoO_2\) with methanol or isopropanol leads to the loss both oxo ligands and the formation of bis(alkoxide) complexes \((tBuClip)Mo(OR)_2\) (Figure 1.4). The oxo-bridged bis(catecholate) complex \((3,6-tBu_2C_6H_2O_2)_2Mo(\mu-O))_4\) is known to react in a similar fashion.\(^{15}\) In situ NMR spectroscopy indicates the formation of these bis(alkoxide) compounds in high yields, although isolated yields are low. The addition of water to isolated \((tBuClip)Mo(OR)_2\), in the absence of excess alcohol, causes hydrolysis to \((tBuClipH_2)MoO_2\). Preparations of the alkoxides are most convenient when using the nitrido complex \((tBuClip)Mo(\mu-N)(\mu-NH_2)Mo(tBuClip)_2\), which also reacts with alcohols to form the bis(alkoxide) complexes. NMR spectra of \((tBuClip)Mo(OR)_2\) indicate \(C_2\) symmetric complexes. The \(^1H\) NMR spectrum of \((tBuClip)Mo(OCH_3)_2\) is unchanged even at \(-60^\circ\)C and suggests a \(cis-\alpha\) geometry.

The solid-state structure of \((tBuClip)Mo(OiPr)_2\) (Figure 1.8) confirms the \(cis-\alpha\) structure. The differences in the conformations of the two isopropoxide groups (O5-Mo-O6-C62 and O6-Mo-O5-C52 dihedral angles are 50.0° and 91.4°, respectively) and differences (~0.02 Å) between the pairs of analogous metal-ligand distances lower the symmetry from the \(C_2\) structure displayed in solution.
Figure 1.8 Thermal ellipsoid plot of (\(\text{\textsuperscript{t}BuClip}\))Mo(O\(\text{\textsuperscript{Pr}}\))\(_2\)•2 CH\(_3\)CN, with solvent molecules and hydrogen atoms omitted for clarity.
TABLE 1.1.

CRYSTAL DATA FOR (tBuClip)$_2$MO$_2$($\mu$-N)($\mu$-NH$_2$)•0.5 Et$_2$O,

(tBuClip)MO(O)(LUT)•CH$_3$CN, AND (tBuClip)MO(O'Pr)$_2$•2 CH$_3$CN

<table>
<thead>
<tr>
<th>(tBuClip)$_2$Mo$_2$($\mu$-N)($\mu$-NH$_2$)•0.5 Et$_2$O</th>
<th>(tBuClip)Mo(O'Pr)$_2$•2 CH$_3$CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{38}$H$</em>{135}$Mo$_2$N$<em>6$O$</em>{4.5}$</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>100(2)</td>
</tr>
<tr>
<td>$\lambda$Å</td>
<td>1.54178 (Cu Kα)</td>
</tr>
<tr>
<td>Space group</td>
<td>$P\overline{1}$</td>
</tr>
<tr>
<td>Total data collected</td>
<td>44466</td>
</tr>
<tr>
<td>No. of indep reflns.</td>
<td>15691</td>
</tr>
<tr>
<td>$R_{int}$</td>
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</tr>
<tr>
<td>Obsd. refls. [I &gt; 2σ(I)]</td>
<td>13443</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>14.7223(2)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>15.4117(3)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>21.2348(4)</td>
</tr>
<tr>
<td>$\alpha$ (deg)</td>
<td>88.7516(8)</td>
</tr>
<tr>
<td>$\beta$ (deg)</td>
<td>84.1354(8)</td>
</tr>
<tr>
<td>$\gamma$ (deg)</td>
<td>75.3810(7)</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>4637.66(14)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Cryst size (mm)</td>
<td>0.34 × 0.25 × 0.11</td>
</tr>
<tr>
<td>No. refined params.</td>
<td>1028</td>
</tr>
<tr>
<td>$R$ indices [I &gt; 2σ(I)]</td>
<td>$R1 = 0.0352$, $wR2 = 0.0898$</td>
</tr>
<tr>
<td>$R$ indices (all data)</td>
<td>$R1 = 0.0438$, $wR2 = 0.0953$</td>
</tr>
<tr>
<td>Goodness of fit</td>
<td>1.017</td>
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</table>
TABLE 1.2.

SELECTED BOND DISTANCES (Å) AND ANGLES (DEG) IN $^{7}$BUCLIP)$_2$MO$_2$(μ-N)(μ-NH$_2$)$\cdot$0.5 ET$_2$O, AND $^{7}$BUCLIP)MO(O$^3$Pr)$_2\cdot$2 CH$_3$CN.

<table>
<thead>
<tr>
<th></th>
<th>(BuClip)$_2$MO$_2$(μ-N)(μ-NH$_2$)$\cdot$0.5 Et$_2$O</th>
<th>(BuClip)MO(O$^3$Pr)$_2\cdot$2 CH$_3$CN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mo$_1$$^a$</td>
<td>Mo$_2$$^{a,b}$</td>
</tr>
<tr>
<td>Mo-O1</td>
<td>2.0109(17)</td>
<td>2.0118(17)</td>
</tr>
<tr>
<td>Mo-O2</td>
<td>1.9800(17)</td>
<td>1.9825(17)</td>
</tr>
<tr>
<td>Mo-N1</td>
<td>2.015(2)</td>
<td>2.013(2)</td>
</tr>
<tr>
<td>Mo-N2</td>
<td>2.035(2)</td>
<td>2.028(2)</td>
</tr>
<tr>
<td>Mo-N5</td>
<td>1.847(2)</td>
<td>1.848(2)</td>
</tr>
<tr>
<td>Mo-N6</td>
<td>2.148(2)</td>
<td>2.127(2)</td>
</tr>
<tr>
<td>Mo-O5</td>
<td></td>
<td>1.8863(16)</td>
</tr>
<tr>
<td>Mo-O6</td>
<td></td>
<td>1.9027(17)</td>
</tr>
<tr>
<td>O1-Mo-N1</td>
<td>74.95(8)</td>
<td>74.47(8)</td>
</tr>
<tr>
<td>O1-Mo-O2</td>
<td>107.21(7)</td>
<td>107.53(7)</td>
</tr>
<tr>
<td>O1-Mo-N2</td>
<td>99.00(8)</td>
<td>99.04(8)</td>
</tr>
<tr>
<td>O1-Mo-N5</td>
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<td>143.94(8)</td>
</tr>
<tr>
<td>O1-Mo-O5</td>
<td></td>
<td>81.18(7)</td>
</tr>
<tr>
<td>O1-Mo-N6</td>
<td>79.23(7)</td>
<td>80.66(8)</td>
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<tr>
<td>O1-Mo-O6</td>
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<td>89.58(7)</td>
</tr>
<tr>
<td>O2-Mo-N2</td>
<td>77.18(8)</td>
<td>77.14(8)</td>
</tr>
<tr>
<td>O2-Mo-N1</td>
<td>161.80(8)</td>
<td>162.71(8)</td>
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<tr>
<td>O2-Mo-N5</td>
<td>98.35(8)</td>
<td>98.30(8)</td>
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<tr>
<td>O2-Mo-O5</td>
<td></td>
<td>92.04(7)</td>
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<tr>
<td>O2-Mo-N6</td>
<td>77.39(8)</td>
<td>77.96(8)</td>
</tr>
<tr>
<td>N1-Mo-N2</td>
<td>84.63(9)</td>
<td>85.58(8)</td>
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<tr>
<td>N1-Mo-N5</td>
<td>89.22(9)</td>
<td>88.26(9)</td>
</tr>
<tr>
<td>N1-Mo-O5</td>
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<td>150.47(8)</td>
</tr>
<tr>
<td>N1-Mo-N6</td>
<td>120.40(9)</td>
<td>119.04(8)</td>
</tr>
<tr>
<td>N1-Mo-O6</td>
<td></td>
<td>90.12(8)</td>
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<tr>
<td>N2-Mo-N5</td>
<td>113.42(9)</td>
<td>111.14(9)</td>
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<td>153.74(9)</td>
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<tr>
<td>N2-Mo-O6</td>
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<td>N5-Mo-N6</td>
<td>80.08(8)</td>
<td>80.62(8)</td>
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<tr>
<td>Mo1-N5-Mo2</td>
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<tr>
<td>Mo1-N6-Mo2</td>
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<td>89.79(8)</td>
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<tr>
<td>Mo-O5-C52</td>
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</tr>
<tr>
<td>Mo-O6-C62</td>
<td></td>
<td>130.37(15)</td>
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</tbody>
</table>

$^a$For Mo$_2$, the analogous atom labels are O3=O1, O4=O2, N3=N1, N4=N2.
1.2.5 Metrical oxidation states of (tBuClip)Mo complexes.

Since each bond length in a catecholate or amidophenoxide complex correlates with the ligand oxidation state, we can calculate the oxidation state for the ligand given its metrical data using a least squares fitting procedure.\(^7\)

The results of the MOS analysis of the tBuClip complexes (Table 1.3) provide further insights into the variability of their structures. The ring cis to the oxo in (tBuClip)Mo(O)(lut) has an MOS value of $-2.00(9)$, while the ring trans to the oxo has a value of $-1.34(12)$. The nitrido complex shows an analogous pattern, but with less variation between the ligands ($-1.57(10)$ and $-1.50(11)$ for rings 1 and 5, trans to the nitride, and $-1.88(12)$ and $-1.87(10)$ for rings 4 and 8, cis to the nitride). The two rings in the isopropoxide display MOS values of $-1.43(9)$ and $-1.58(11)$. The amidophenolate groups cis to the multiply bonded ligands show little or no deviation from their expected structures, while the groups trans to the multiply bonded ligands or alkoxides do show significant metrical changes consistent with partial oxidation by $\pi$ donation.

![Figure 1.9 Calculated MOS values of molybdenum amidophenolates.](image-url)
TABLE 1.3

METRICAL OXIDATION STATE (MOS) ANALYSIS OF MOLYBDENUM AMIDOPHENOLATES
AND CATECHOLATES. NUMBERING SYSTEM IS AS SHOWN IN FIGURE 1.3.

<table>
<thead>
<tr>
<th>Ring</th>
<th>C–O</th>
<th>C–N</th>
<th>C1-C2</th>
<th>C2-C3 a</th>
<th>C6–C1 a</th>
<th>C3–C4 a</th>
<th>C5–C6 a</th>
<th>C4–C5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trans to oxo (Ring 1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcd, MOS = –1.36</td>
<td>1.316(3)</td>
<td>1.378(4)</td>
<td>1.411(4)</td>
<td>1.418(4)</td>
<td>1.422(4)</td>
<td>1.384(4)</td>
<td>1.375(4)</td>
<td>1.411(4)</td>
</tr>
<tr>
<td>Cis to oxo (Ring 4)</td>
<td>1.357(3)</td>
<td>1.415(3)</td>
<td>1.406(4)</td>
<td>1.392(4)</td>
<td>1.403(4)</td>
<td>1.399(4)</td>
<td>1.405(4)</td>
<td>1.390(5)</td>
</tr>
<tr>
<td>Calcd, MOS = –2.00</td>
<td>1.366</td>
<td>1.402</td>
<td>1.410</td>
<td>1.391</td>
<td>1.397</td>
<td>1.396</td>
<td>1.404</td>
<td>1.389</td>
</tr>
<tr>
<td>(BuClip)Mo(O)(µ-N)(µ-NH)2Mo(BuClip)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trans to µ-N, Ring 1</td>
<td>1.336(3)</td>
<td>1.386(3)</td>
<td>1.398(4)</td>
<td>1.405(4)</td>
<td>1.412(4)</td>
<td>1.377(4)</td>
<td>1.387(4)</td>
<td>1.412(4)</td>
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<tr>
<td>Ring 5</td>
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<td>1.399(4)</td>
<td>1.419(4)</td>
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<td>1.384(4)</td>
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<td>1.411</td>
<td>1.385</td>
<td>1.392</td>
<td>1.407</td>
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<tr>
<td>Cis to µ-N, Ring 4</td>
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<td>1.399(4)</td>
<td>1.390(4)</td>
<td>1.402(4)</td>
<td>1.396(4)</td>
<td>1.390(4)</td>
<td>1.400(5)</td>
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<tr>
<td>Ring 8</td>
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<td>1.395(4)</td>
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<td>1.401(4)</td>
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<td>1.401</td>
<td>1.393</td>
<td>1.401</td>
<td>1.394</td>
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<tr>
<td>(BuClip)Mo(OiPr)2</td>
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<td></td>
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<tr>
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<td>1.405(3)</td>
<td>1.403(3)</td>
<td>1.408(3)</td>
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<td>1.383(4)</td>
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</tr>
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<td>1.414</td>
<td>1.382</td>
<td>1.389</td>
<td>1.411</td>
</tr>
<tr>
<td>Ring 4</td>
<td>1.337(3)</td>
<td>1.381(3)</td>
<td>1.395(3)</td>
<td>1.402(4)</td>
<td>1.411(3)</td>
<td>1.375(4)</td>
<td>1.386(4)</td>
<td>1.408(4)</td>
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<td>1.400</td>
<td>1.410</td>
<td>1.386</td>
<td>1.393</td>
<td>1.405</td>
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*Calculated values are generated from MOS correlations.
1.3 Discussion

Molybdenum-amidophenoxide $\pi$ bonding exerts a powerful influence on the structure and reactivity of the (tBuClip)Mo complexes in the following ways:

1.3.1 Stabilization of metal complexes with and without ligands that form multiple binds to the metal center.

High valent complexes of early transition metals are stabilized by multiply bonded ligands such as oxo, nitride and amides. In contrast to this usual affinity of molybdenum(VI), ligation of the metal center to the tetradeutate tBuClip ligand allows for a remarkable interconversion between structures containing containing two, one, or zero oxo ligands under mild conditions (Figure 1.4). (tBuClipH$_2$)MoO$_2$ has two multiply bonded oxo groups whereas the family of (tBuClip)MoO(L) compounds only has one. The facile association of neutral ligands with the concomitant loss of water is favored with increasing basicity of the neutral donors. While the reaction of Ph$_3$SiOH with (tBuClipH$_2$)MoO$_2$ leads to a monooxo product, (tBuClipH)MoO(OSiPh$_3$), oxo-free compounds (tBuClip)Mo(OR)$_2$ (R = Me, $^1$Pr) are generated from the analogous reaction with either MeOH or $^1$PrOH. Formation of (tBuClip)Mo(μ-N)(μ-NH$_2$)Mo(tBuClip) from $^1$BuClipH$_4$ and Mo(N)(O$^1$Bu)$_3$ involves the conversion of two terminal nitrides into a $\sigma$-only bridging amide and a highly bent μ-nitride capable of forming only one $\pi$ bond among two molybdenums, and can be formally considered a ligand having half a multiply bonded ligand per metal center. The structural elasticity shown by (tBuClip)Mo compounds can be compared to the isoelectronic bis(catecholate)molybdenum fragment (3,6-$^1$Bu$_2$C$_6$H$_2$O$_2$)$_2$Mo described by Pierpont and coworkers.$^{15}$ The
bis(catecholate) complexes also readily form mono-oxo complexes as well as complexes lacking terminal oxo groups, such as the μ-oxo tetramer $\{(3,6^{-1}Bu_2C_6H_2O_2)_2Mo(\mu-O)\}_4$ and the bis(alkoxide) $(3,6^{-1}Bu_2C_6H_2O_2)_2Mo(OiPr)_2$.

1.3.2 Spectroscopic, structural, and dynamic effects.

The amidophenoxide and catecholate ligands are analogous, although observations indicate that amidophenoxides are stronger donors than catecholates. The amidophenoxide complexes ($^tBu$Clip)MoO(L) show lower-frequency Mo=O stretches (901-907 cm$^{-1}$) than do $(3,6^{-1}Bu_2C_6H_2O_2)_2MoO(L)$ (916-929 cm$^{-1}$). The oxo-amidophenoxide complexes ($^tBu$Clip)MoO(L) also show enhanced lability of the neutral donors in comparison to their catecholate analogues. No exchange is observed between free and bound Me$_2$SO resonances in the oxo-dimethyl sulfoxide complex $(3,6^{-1}Bu_2C_6H_2O_2)_2MoO(OSMe_2)$ even at ambient temperatures, whereas ($^tBu$Clip)MoO(py) shows facile dissociative loss of pyridine. These observations indicate that amidophenoxide is a stronger donor than catecholate but do not distinguish between $\sigma$- and $\pi$-donating abilities of these ligands. The more acute Mo-O-C angles of the alkoxides (133(4)$^\circ$ vs. 143(2)$^\circ$) compared to $(3,6^{-1}Bu_2C_6H_2O_2)_2Mo(OiPr)_2$$^{15}$ indicate that the greater donation from the amidophenoxides has a significant $\pi$ component. $^{24}$

1.3.3 Stereochemical effects.

The stereochemistry of ($^tBu$Clip)Mo complexes) can be rationalized on the basis of the π-bonding predilections of the amidophenoxide ligand. In ($^tBu$Clip)MoO(Lut), the amidophenoxide is aligned so that it can donate into $d\pi$ orbitals not involved in $\pi$-
bonding with the oxo ligand, and is in an orientation that maximizes overlap of this dπ orbital with the nitrogen of the amidophenoxide, which contributes more to the ligand’s π-donor orbital than the oxygen (Figure 1.10).

Figure 1.10 Kohn-Sham HOMO–1 in (Clip)Mo(O)(py).

The observed energy order calculated for cis isomers of (Clip)MoO(py) is consistent with the trans influence, with the less basic aryloxide trans to oxo and pyridine trans to amide. While the trans influence undoubtedly contributes to the relative energies of the structures, π bonding effects are more important. The isoelectronic but geometrically unconstrained bis(catecholate) complexes of Mo(3,6-DTBCat)₂(O)(L) adopt a cis geometry,¹⁵ which does not obey the trans influence (oxo is trans to the catecholate rather than to the more weakly bound neutral donor) but is favored on the grounds of π bonding. The observed cis-β configuration of (′BuClip)Mo(μ-N)(μ-NH₂)Mo(′BuClip) is uniquely adopted among the three possible ways of wrapping the ligand around molybdenum, placing an aryloxide (rather than amide) trans to the bridging nitride. This geometry maximizes the π overlap of the amido nitrogens with the
lowest-lying Mo dπ orbitals and is consistent with the nitride’s strong trans influence. The relative configuration of the two molybdenum atoms could give a complex of overall C₂ or C₅ symmetry, but the latter is excluded for steric reasons (the biphenyl bridges would be angled directly at one another).

1.4 Experimental

Unless otherwise noted, all procedures were carried out under an inert atmosphere in a nitrogen-filled glovebox or on a vacuum line. When dry solvents were needed, chlorinated solvents and acetonitrile were dried over 4 Å molecular sieves, followed by CaH₂. Benzene and toluene were dried over sodium, and ether and tetrahydrofuran over sodium benzophenone ketyl. Alcohols were dried over 4 Å molecular sieves. Deuterated solvents were obtained from Cambridge Isotope Laboratories, dried using the same procedures as their protio analogues, and stored in the drybox prior to use. ′BuClipH₄ and (′BuClipH₂)MoO₂ are prepared as described.¹⁰ Nitridotri(tert-butoxy)molybdenum(VI) was prepared from MoCl₄(CH₃CN)₂ and was purified by sublimation.²⁵ All other reagents were commercially available and used without further purification. NMR spectra were measured on a Varian VXR-300 or Bruker DPX-400 spectrometer. Chemical shifts for ′H and ′³C{′H} spectra are reported in ppm downfield of TMS, with spectra referenced using the known chemical shifts of the solvent residuals. Infrared spectra were recorded as nujol mulls between NaCl plates on a Thermo Nicolet Nexus 470 ESP FT-IR spectrometer. ESI mass spectra were obtained using a Bruker micrOTOF-II mass spectrometer, and peaks reported are the mass
number of the most intense peak of isotope envelopes. Samples were injected as
dichloromethane solutions, preceded and followed by methanol. In all cases, the
observed isotope patterns were in good agreement with calculated ones. UV-visible
spectra were measured using dichloromethane solutions in 1-cm quartz cuvettes with a
Beckman DU-7500 diode array spectrophotometer. Elemental analyses were performed
by M-H-W Laboratories (Phoenix, AZ) or Midwest Microlab, LLC (Indianapolis, IN).

1.4.1 X-ray Crystallography

Crystals of (tBuClip)Mo(μ-N)(μ-NH₂)Mo(tBuClip)•0.5 Et₂O were grown by slow
cooling of a concentrated solution of the complex in ether, while crystals of
(tBuClip)Mo(OiPr)₂•2 CH₃CN were grown by diffusion of acetonitrile into benzene
solutions. Crystals were placed in inert oil before transferring to the cold N₂ stream of a
Bruker Apex II CCD diffractometer. Data were reduced, correcting for absorption, using
the program SADABS. The bridging nitride structure was solved using direct methods,
while (tBuClip)Mo(OiPr)₂•2 CH₃CN, was solved using a Patterson map. All nonhydrogen
atoms not apparent from the initial solutions were found on difference Fourier maps,
and all heavy atoms were refined anisotropically.

The ether in (tBuClip)Mo(μ-N)(μ-NH₂)Mo(tBuClip)•0.5 Et₂O was disordered
equally about the center of inversion, which was at the midpoint of a C-O bond. Two of
the tert-butyl groups in this structure, those centered on C37 and C48, were disordered
in two different orientations. Disordered tert-butyl groups were modeled by
constraining the thermal parameters of the methyl carbons to be equal to those of the
carbons opposite them in the other orientation, and allowing the occupancy of the two
orientations to refine. All hydrogen atoms in (\(^t\)BuClip)Mo(\(\mu\)-N)(\(\mu\)-NH\(_2\))Mo(\(^t\)BuClip)•0.5 Et\(_2\)O were placed in calculated positions, except the amido hydrogens which were found on difference Fourier maps and refined isotropically. Hydrogen atoms in (\(^t\)BuClip)Mo(O\(^i\)Pr)\(_2\)•2 CH\(_3\)CN were found on difference Fourier maps and refined isotropically, except for solvent and tert-butyl hydrogens, which were placed in calculated positions. Calculations used SHELXTL (Bruker AXS),\(^{26}\) with scattering factors and anomalous dispersion terms taken from the literature.\(^{27}\)

1.4.2 (\(\mu\)-Nitrido)(\(\mu\)-amido)bis(4,4\(^{1}\)-di-tert-butyldiphenyl-2,2\(^{1}\)-bis((2-oxy-3,5-di-tert-butylphenyl)amido)dimolybdenum(VI), (\(^t\)BuClip)Mo(\(\mu\)-N)(\(\mu\)-NH\(_2\))Mo(\(^t\)BuClip).

NMo(O\(^t\)Bu)\(_3\) (0.3447 g, 1.05 mmol) and \(^t\)BuClipH\(_4\) (0.7385 g, 1.05 mmol) were dissolved in 50 mL ether and allowed to stir for 3 h. After 3 d standing at RT, a violet precipitate had formed. It was suction filtered to yield 458 mg (54%) of the bridging nitride complex. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 0.68, 0.99, 1.03, 1.05, 1.09, 1.40 (s, 18H each, \(^t\)Bu), 4.69 (s, 2H, NH\(_2\)), 5.63 (d, 2 Hz, 2H, ArH), 5.94 (d, 2 Hz, 2H, ArH), 6.55 (d, 2 Hz, 2H, H-3), 6.61 (d, 2 Hz, 2H, ArH), 6.72 (d, 2 Hz, 2H, ArH), 6.77 (dd, 8, 2 Hz, 2H, H-5), 6.93 (d, 8 Hz, 2H, H-6), 7.02 (dd, 8, 2 Hz, 2H, H-5), 7.14 (d, 8 Hz, 2H, H-6), 7.17 (d, 2 Hz, 2H, H-3).

\(^{13}\)C\(^{1}\)H NMR (CDCl\(_3\)): \(\delta\) 29.67, 29.89, 31.20, 31.31, 31.77, 31.96 (C(CH\(_3\))\(_3\)), 34.43, 34.57, 34.58, 34.62, 34.68, 34.88 (C(CH\(_3\))\(_3\)), 111.74, 111.89, 118.10, 120.04, 120.53, 122.15, 123.43, 123.49, 126.59, 129.16, 131.46, 132.35, 134.34, 134.72, 140.41, 142.93, 143.12, 145.40, 148.64, 149.26, 151.45, 153.28, 159.49, 165.16. IR: 3395 (m, v\(_{\text{NH}}\)), 3305 (m, v\(_{\text{NH}}\)), 1377 (s), 1360 (s), 1304 (m), 1258 (w), 1234 (w), 1199 (m), 1169 (m), 1131(w), 1021 (w), 992 (w), 947 (w), 931 (w), 910 (m), 853 (m), 833 (m), 812 (m), 780 (w), 767 (w), 743 (w), 24
722 (w), 702 (w), 647 (s), 620 (m), 592 (m). ESI-MS: m/z = 1624.8271 (M⁺, calcd 1624.8292). Anal. Calcd for C₉₆H₁₃₀Mo₂N₆O₄: C, 71.00; H, 8.07; N, 5.17. Found: C, 70.05; H, 7.40; N, 4.76.

1.4.3 (tBuClip)MoO(PMe₂Ph).

A solution of (tBuClipH₂)MoO₂ (8.0 mg, 0.0608 mmol) and PMe₂Ph (2.0 µL, 0.12 mmol, 2.0 equiv) in CDCl₃ (0.6 mL) was mixed for 5 h at room temperature by rotating the NMR tube. Quantitative conversion was observed in situ. The peaks associated with free PMe₂Ph was slightly broaded suggesting exchange on the NMR timescale. ¹H NMR (CDCl₃): δ 0.98, 1.04, 1.09, 1.17, 1.38, 1.43 (s, 9H ea., tBu), 1.93, 1.96 (br s, 3H each, P(CH₃)₂), 5.84 (d, 2 Hz, 1H, ArH), 6.13 (d, 2 Hz, 1H, ArH), 6.61 (d, 2 Hz, 1H, ArH), 6.73 (m, 3H, ArH), 6.89 (d, 8 Hz, 1H, H-6), 7.29 (d, 2 Hz, 1H, ArH), 7.30 (br s, 1H, p-PMe₂Ph), 7.37 (m, 1H, ArH) 7.39 (d, 2 Hz, 1H, ArH), 7.47 (v br t, 2H, m-PMe₂Ph), 7.69 (br s, 2H, o-PMe₂Ph). UV-Vis (CH₂Cl₂): λmax = 460, 570, 800 nm (ε = 4200, 3800, 1100 M⁻¹cm⁻¹).

1.4.4 (tBuClipH)MoO(OSiPh₃).

A solution of (tBuClipH₂)MoO₂ (8.0 mg, 0.0608 mmol) and Ph₃SiOH (3.0 mg, 0.12 mmol, 2.0 equiv) in CDCl₃ (0.6 mL) was mixed for 20 h at room temperature. Approximately 80% of product was observed in situ as an equilibrium mixture. ¹H NMR (CDCl₃): δ 0.97, 1.00, 1.07, 1.16, 1.33, 1.42 (s, 9H ea., tBu), 3.48 (d, 5 Hz, 1H, NH), 5.62 (d, 2 Hz, 1H, ArH), 6.34 (d, 2 Hz, 1H, ArH), 6.39 (d, 2 Hz, 1H, ArH), 6.70 (d, 2 Hz, 1H, ArH), 6.78 (d, 8 Hz, 1H, H-6), 6.84 (d, 2 Hz, 1H), 6.96 (br s, 1H, ArH), 7.22 (t, 8 Hz, 6H, m-Ph), 7.29 (tt, 8, 2Hz, 3H, p-Ph), 7.38 (m, 3H), 7.71 (dd, 7, 1 Hz, 6H, o-Ph).
1.4.5 \((t^\text{BuClip})\text{Mo(O}^\text{iPr})_2\).

\((t^\text{BuClip})\text{Mo(\mu-N)(\mu-NH}_2\text{)Mo(t^\text{BuClip}) (166 mg, 0.181 mmol) was dissolved in 5 mL}

chloroform. After adding 1 mL dry isopropanol, the reaction mixture was stirred 25 h

under N\(_2\). The solvent was evaporated in vacuo to yield 168 mg crude

\((t^\text{BuClip})\text{Mo(O}^\text{iPr})_2\), which was recrystallized from CH\(_2\)Cl\(_2\) (2 mL) layered with acetonitrile

(3 mL) to yield 45 mg (27%) pure diisopropoxide. The analytical sample contained one
equivalent of CH\(_2\)Cl\(_2\). \(^1\)H NMR (CDCl\(_3\)): \(\delta 1.11\) (s, 18H, \(^t^\text{Bu}\)), 1.14 (s, 18H, \(^t^\text{Bu}\)), 1.22 (d,

6 Hz, 6H, OCH(CH\(_3\))(CH\(_3\))), 1.34 (d, 6 Hz, 6H, OCH(CH\(_3\))(CH\(_3\))), 1.35 (s, 18H, \(^t^\text{Bu}\)), 5.59 (sept,

6 Hz, 2H, OCH(CH\(_3\))), 5.80 (d, 2 Hz, 2H, ArH) 6.65 (d, 2 Hz, 2H, H-3), 6.72 (d, 2 Hz, 2H,

ArH), 7.05 (dd, 8, 2 Hz, 2H, H-5), 7.10 (d, 8 Hz, 2H, H-6). \(^{13}\text{C}^\text{\{1H\}}\) NMR (CDCl\(_3\)): \(\delta 24.73,

25.81\) (OCH(CH\(_3\))(CH\(_3\))), 29.99, 31.31, 31.84 (C(CH\(_3\)))\(_3\)), 34.48, 34.73, 34.92 (C(CH\(_3\)))\(_3\)),

76.94 (OCH(CH\(_3\))C(CH\(_3\))), 108.20, 120.00, 121.47, 123.58, 127.47, 130.95, 135.64, 144.42,

145.11, 149.96, 150.51, 156.75. IR: 3170 (w), 1605 (m), 1585 (m), 1556 (m), 1376 (s),

1364 (s), 1303 (m), 1256 (w), 1201 (m), 1166 (m), 1108 (s), 966 (s), 853 (s), 820 (s), 594

(s). ESI-MS: \(m/z = 939.4880 \text{ (M}^+\text{+Na, calcd 939.4922). Anal. Calcd for C}_{55}\text{H}_{80}\text{Cl}_2\text{MoN}_2\text{O}_4:\n
\text{C, 66.05; H, 8.06; N, 2.80. Found: C, 66.53; H, 8.13; N, 2.98.}

1.4.6 \((t^\text{BuClip})\text{Mo(OCH}_3)_2\).

The methoxide complex was generated analogously by treatment of

\((t^\text{BuClip})\text{Mo(\mu-N)(\mu-NH}_2\text{)Mo(t^\text{BuClip}) with CH}_3\text{OH in chloroform; evaporation of the}

volatiles produced a dark purple oil. \(^1\)H NMR (CDCl\(_3\)): \(\delta 1.10, 1.15, 1.36 \text{ (s, 18H ea., }^t^\text{Bu}),

4.74 \text{ (s, 6H, OCH}_3\), 5.82 \text{ (d, 2Hz, 2H, ArH)}, 6.64 \text{ (s, 2H, H-3)}, 6.71 \text{ (d, 2 Hz, 2H, ArH)}, 7.07

(m, 4H, H-5 and H-6). \(^{13}\text{C}^\text{\{1H\}}\) NMR (CDCl\(_3\)): \(\delta 29.77, 31.20, 31.71 \text{ (C(CH}_3)_3\), 34.38, 34.57,
34.98 \((\text{CH}_3)_3\), 65.08 \((\text{OCH}_3)\), 108.50, 120.74, 121.39, 123.82, 127.29, 130.89, 135.54, 143.45, 145.98, 150.01, 150.77, 156.79.
CHAPTER 2:
MIXED MOLYBDENUM(VI) AMIDOPHENOLATE-CATECHOLATES – STRUCTURE,
STEREODYNAMICS, AND LEWIS ACIDITY

2.1 Introduction

The previous chapter described the remarkable flexibility of molybdenum(VI) ligated by the 2,2'-biphenyl-bridged bis(amidophenoxide) ligand tBuClip$^4$ to bind and relinquish multiply bonded ligands such as terminal oxo, bridging nitrido, and alkoxide ligands.$^{10}$ This rich coordination chemistry invites the possibility of performing metal-mediated oxygen atom transfer reactions in a nonclassical manner wherein redox equivalents originate in the ligands while the oxidation state of the metal remains unhanged.$^{28,29}$ The tris(catecholato)molybdenum fragment (3,5-tBu$_2$Cat)$_3$Mo likewise reacts either with dioxygen$^{30}$ or pyridine-$N$-oxide$^{31}$ to form oxomolybdenum(VI) compounds and 3,5-di-tert-butyl-1,2-benzoquinone. This reaction relies on the oxophilicity of Mo(VI) and the reducing power of the catecholates to achieve net oxygen atom transfer.

A serious limitation of the above reactions is the lability of the quinone ligands in their oxidized form. In no cases can an oxidized ligand coordinated to the metal center be observed; instead, free benzoquinone dissociates rapidly. This obviates the possibility of catalysis since the oxidized metal complex does not persist long enough to transfer its
oxygen atom to a substrate. Replacing two catecholates with a single 'BuClip ligand may lead to increased stability of complexes by preventing the loss of partially oxidized intermediates due to the chelate effect. Precedents exist for stable bis(iminoquinonate) complexes of early transition metals.\(^{32}\)

This chapter describes the preparation and characterization of monomeric (\(\text{'}\)BuClip)\(\text{Mo}(3,5\text{-}^1\text{Bu}_2\text{Cat})\), which contains both catecholate and amidophenoxide ligands.\(^{33}\) Although it is unsymmetrical in the solid state and solution, variable-temperature NMR data indicate that several diastereomers interconvert at low temperature. A high-temperature fluxional process exchanges the ends of the \(\text{'}\)BuClip, making them equivalent at ambient temperatures. Also described is an unsymmetrical dimolybdenum complex, (\(\text{'}\)BuClip)\(\text{Mo}(|\mu-(3,5\text{-}^1\text{Bu}_2\text{Cat})_2\text{MoO}(3,5\text{-}^1\text{Bu}_2\text{Cat})\), which is effectively a structural hybrid of (\(\text{'}\)BuClip)\(\text{Mo}(3,5\text{-}^1\text{Bu}_2\text{Cat})\) and a \(\text{MoO}(3,5\text{-}^1\text{Bu}_2\text{Cat})_2\) fragment and which contains both six- and seven-coordinate molybdenum. (\(\text{'}\)BuClip)\(\text{Mo}(3,5\text{-}^1\text{Bu}_2\text{Cat})\) binds pyridine to form an isolable seven-coordinate adduct, (\(\text{'}\)BuClip)\(\text{Mo}(3,5\text{-}^1\text{Bu}_2\text{Cat})(\text{py})\), which exists as a mixture of unsymmetrical isomers in solution. (\(\text{'}\)BuClip)\(\text{Mo}(3,5\text{-}^1\text{Bu}_2\text{Cat})\) binds pyridine relatively slowly but has similar rates of dissociation as other adduct analogues.

2.2 Results and Discussion

2.2.1 Synthesis, structure, and bonding of (\(\text{'}\)BuClip)\(\text{Mo}(3,5\text{-}^1\text{Bu}_2\text{Cat})\)

The dioxomolybdenum bis(aminophenoxide) complex (\(\text{'}\)BuClip\(\text{H}_2\)\(\text{MoO}_2\))

\((\text{'}\text{BuClip}_4 = 4,4'\text{-di-tert-buty}-2,2'\text{-bis}((2\text{-hydroxy}-3,5\text{-di-tert-}

\text{H}_2\text{Bu})_2)\)
butylphenyl)aminobiphenyl) serves as a useful precursor for many molybdenum(VI) complexes containing the $^{1}$BuClip$^{4-}$ ligand including those with no multiply bonded ligands (Chapter 1). ($^{1}$BuClipH$_{2}$)MoO$_{2}$ reacts with one equivalent of 3,5-di-tert-butylcatechol, 3,5-$^{1}$Bu$_{2}$CatH$_{2}$, over the course of a few minutes at room temperature in chloroform or benzene to give ($^{1}$BuClip)Mo(3,5-$^{1}$Bu$_{2}$Cat) as the major product. The same product is formed on reaction of 3,5-$^{1}$Bu$_{2}$CatH$_{2}$ with the bridging nitride complex ($^{1}$BuClip)Mo($^{1}$-N)($^{1}$-NH$_{2}$)Mo($^{1}$BuClip). The $^{1}$H NMR spectrum of the product establishes a 1:1 ratio of $^{1}$BuClip:$^{1}$Bu$_{2}$Cat in the product. Confirmation of the monomeric nature of the complex is provided by observation of the parent ion in the electrospray mass spectrum and by the solid-state structure determined by X-ray crystallography (Figure 2.1).

The solid-state structure of ($^{1}$BuClip)Mo(3,5-$^{1}$Bu$_{2}$Cat) is roughly octahedral, with some distortion toward a trigonal prismatic geometry, as previously observed for six-coordinate complexes of the $^{1}$BuClip ligand$^{10}$ and the analogous bis(amidophenoxide) ligand bridged by an unsubstituted 2,2$^1$-biphenyl linker. $^{34}$ The structure is isoelectronic with (3,5-$^{1}$Bu$_{2}$Cat)$_{3}$Mo which forms a seven-coordinate molybdenum dimer in the solid state. $^{31}$ Although the $^{1}$BuClip ligand is not well-suited to bridging because of the tert-butyl groups ortho to the aryloxides, the catecholate could conceivably bridge, as in Mo$_{2}$(3,5-$^{1}$Bu$_{2}$Cat)$_{6}$. The monomeric structure is therefore an electronic consequence of enhanced donation from the amidophenoxide ligands compared to catecholate.
Figure 2.1 Thermal ellipsoid plot of (^tBuClip)Mo(3,5-^tBuCat)•1.5 C_6H_6, with hydrogen atoms and lattice solvent omitted for clarity. Only the major orientation of the tert-butyl groups bonded to C24 and C45 are shown.
Table 2.1.
CRYSTAL DATA FOR (tBuClip)Mo(3,5-tBu2Cat)•1.5 C6H6, (tBuClip)Mo(m-(3,5-
tBu2Cat)2)MoO(3,5-tBu2Cat)•1.5 C6H6 AND Mo2O2(3,5-tBu2Cat)4•2 C6H6.

<table>
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<tr>
<th></th>
<th>(tBuClip)Mo(3,5-tBu2Cat)•1.5 C6H6</th>
<th>(tBuClip)Mo(m-(3,5-tBu2Cat)2)MoO(3,5-tBu2Cat)•1.5 C6H6</th>
<th>Mo2O2(3,5-tBu2Cat)4•2 C6H6</th>
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<td>120(2)</td>
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<tr>
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<td>λ/Å</td>
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<td>0.71073 (Mo Kα)</td>
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<td>37715</td>
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<td>16.5304(4)</td>
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<td>90</td>
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<td>519</td>
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<td>Goodness of fit</td>
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# Table 2.2.

BOND DISTANCES (Å) AND ANGLES (DEG) FOR (\(^{\text{BuClip}}\)Mo(3,5-\(^{7}\) Bu\(_2\)Cat),

\((^{\text{BuClip}}\)Mo(\(\mu\)-(3,5-\(^{7}\) Bu\(_2\)Cat))\(_2\))Mo(3,5-\(^{7}\) Bu\(_2\)Cat) AND Mo\(_2\)O\(_2\)(3,5-\(^{7}\) Bu\(_2\)Cat)\(_4\).
The bis(amidophenoxide) ligand is sterically constrained to adopt a cis configuration, and in this complex it adopts a structure where the aryloxide oxygen O2 is trans to one of the amido nitrogen atoms (N1), the cis-β isomer, though cis-α compounds (with the aryloxide oxygens mutually trans) can also be formed by this ligand (Figure 2.2).

Figure 2.2. Possible geometric isomers of (tBuClip)Mo(3,5-tBu2Cat) with stereochemistry about biphenyl and metal center.

There are two possible cis-β isomers of the complex. The one that is observed in the solid state (cis-β1) has the more electron-rich oxygen of the catecholate (O4, ortho and para to the tert-butyl groups) trans to aryloxide. (tBuClip)Mo(3,5-iBu2Cat) additionally contains two elements of chirality: axial chirality of the 2,2'-disubstituted biphenyl moiety and chirality at the metal center. However, the axial chirality of the biphenyl is tightly coupled to the configuration at the metal as has been observed with biphenyl-bridged bis(β-diketonates). The physical limitations of the tBuClip ligand in an
octahedral tris-chelate environment restrict each geometric isomer to only one enantiomeric pair: \((S,\Delta)/(R,\Lambda)\) \(cis-\alpha\) or \((S,\Lambda)/(R,\Delta)\) \(cis-\beta\). The alternative diastereomers are not geometrically accessible due to unreasonably high ground state energies and are also universally unobserved in octahedral \(cis-\alpha\)\(^{37}\) and \(cis-\beta\)\(^{38}\) complexes bearing 2,2'-biphenyl- or binaphthyl-bridged bis(salicylaldimine) ligands. DFT calculations (gas-phase, B3LYP) on all three possible geometric isomers of \((t\text{BuClip})\text{Mo}(3,5-t\text{Bu}_2\text{Cat})\) suggest that the two \(cis-\beta\) isomers are very similar in energy (Figure 2.3). The \(cis-\alpha\) isomer is significantly higher in energy.

![Figure 2.3 Calculated structures and relative energies (B3LYP, SDD (Mo)/6-31G*) of \((t\text{BuClip})\text{Mo}(3,5-t\text{Bu}_2\text{Cat})\) isomers: (a) \(cis-\alpha\), (b) \(cis-\beta_1\) and (c) \(cis-\beta_2\)](image)

The greater stability of the \(cis-\beta\) isomers compared to the \(cis-\alpha\) isomer can be rationalized by an orbital mismatch of the ligand donors in the quasi-\(C_2\) symmetric \(cis-\alpha\) isomer (only symmetrical \(^t\text{Bu}\) substituents on the catecholate would make the \(cis-\alpha\) truly \(C_2\) symmetric). The ligand \(\pi\) donor orbitals transform as \(A + 2B\), while the metal \(d\pi\) orbitals transform as \(2A + B\) (Figure 2.4).\(^{39}\) The Lewis acidity of the analogous
tris(catecholate)molybdenum(VI) has been attributed to the inability of the $A_2^{-}$ symmetry ligand $\pi$ combination to donate to any of the metal $d\pi$ orbitals, which leaves the $d_{z^2}$ orbital low in energy.\textsuperscript{31}

![Diagram](image)

**Figure 2.4** Kohn-Sham LUMO, $\pi^{\text{nb}}$ orbital of $A$ symmetry in $(i\text{BuClip})\text{Mo}(3,5\text{-di-iBuCat})$. (a) $\text{Cis-}\alpha$ isomer. (b) $\text{Cis-}\beta1$ isomer.

The stability of the $cis-\beta1$ geometry may be attributed to the trans influence where the more basic amidophenolate nitrogen is located trans to the less electron rich oxygen of the catecholate. The less electron rich catecholate oxygen lies *meta* to both of its *tert*-butyl groups. The crystallographically unobserved $cis-\beta2$ would have an arylamide arm trans to the more electron rich catecholate arm, which is ortho and para to its *tert*-butyl groups.

Metrical oxidation states (MOS)\textsuperscript{7} for each ligand donor were calculated to quantify the degree of $\pi$ donation. In $(i\text{BuClip})\text{Mo}(3,5\text{-iBu2Cat})$, MOS values of $-1.44(7)$ and $-1.87(11)$ were calculated for amidophenoxy rings 1 and 4, respectively. The
bound catecholate shows bond distances typical of fully reduced catecholates with little
π bonding, MOS = −1.85(12). Only ring 1 shows significant π donation with an
appreciably positive MOS value. The surprising difference between the two
amidophenoxide donors is mirrored by the gas-phase calculation on the cis-β1 isomer
which gives a similar incongruence (MOS = −1.42(6) and −1.70(10) for the two rings) and
suggests a genuine electronic effect.⁷

2.2.2 Stereodynamics of (tBuClip)Mo(3,5-tBu₂Cat)

NMR spectroscopic measurements show a highly symmetric structure for
(tBuClip)Mo(3,5-tBu₂Cat) in solution at room temperature, with seven aromatic
resonances and five tert-butyl resonances observed in the \(^1\)H NMR spectrum in CD₂Cl₂
(Figure 2.5a). This apparent symmetry must result from a fluxional process because
every possible geometric isomer is C₁-symmetric and should show twelve aromatic and
eight tert-butyl resonances, as seen at −40 °C (Figure 2.5c). Lineshape simulation of the
tert-butyl region between −30 and +10 °C gives ΔH\(^{‡}\) = 14.5 ± 0.3 kcal mol\(^{-1}\) and ΔS\(^{‡}\) = +8.5
± 1.3 cal mol\(^{-1}\) K\(^{-1}\) for the process that exchanges the two halves of the tBuClip ligand in
this temperature range. At temperatures below −40 °C, peaks of the tBuClip broaden
and shift significantly, but no decoalescence is observed. The peaks due to the
catecholate are also broadened by the temperature changes, in contrast to their
behavior above −40 °C, where they are sharp. This behavior indicates rapid equilibration
between isomers whose rate is reduced at lower temperatures; however, no
decoalescence of 3,5-tBu₂Cat peaks is observed and (tBuClip)Mo(3,5-tBu₂Cat) remains is a
mixture of isomers that can equilibrate rapidly on the NMR timescale even at -80 °C.
Figure 2.5. Variable-temperature $^1$H NMR spectra ($\delta$ 0.0-1.8 and 6.0-8.0 ppm) of ($^t$BuClip)Mo(3,5-$^t$Bu$_2$Cat) (500 MHz, CD$_2$Cl$_2$). (a) 21.5 °C; (b) –20 °C; (c) –40 °C; (d) –80 °C. Peaks due to bound catecholate (o) and CHCl$_3$ (*) are marked on the room-temperature spectrum. The vertical scale of the upfield region is reduced relative to the downfield region, but the horizontal scale is the same throughout the spectra.
As mentioned earlier, (tBuClip)Mo(3,5-tBu2Cat) contains two elements of chirality: axial chirality of the 2,2'-disubstituted biphenyl moiety and chirality at the metal center. Along with the asymmetry of the 3,5-di-tert-butylcatecholate, this allows for four stereoisomers per geometric isomer (of which there are three).

Typically, molybdenum catecholate complexes undergo stereoisomerization by trigonal twist mechanisms,\textsuperscript{15,29} which cause an inversion of configuration at the metal center after each trigonal twist. This means that (S,\Lambdalpha)-cis-\beta 1 and (S,\Lambdalpha)-cis-\beta 2 isomers can only interconvert via the intermediacy of the (S,\Deltaalpha)-cis-\alpha isomer in a series of two consecutive trigonal (Ray-Dutt) twists (Scheme 2.2a). These twists are likely to be facile and may account for the \textsuperscript{1}H NMR spectrum of (tBuClip)Mo(3,5-tBu2Cat) below \(-40 ^\circ C\), as two or three stereoisomers equilibrate in a temperature-dependent ratio (causing large temperature-dependence of chemical shifts) and at a moderate rate (causing appreciable broadening of some peaks). Symmetrization of the NMR spectra above \(-40 ^\circ C\) cannot be explained by isomerization alone because all three isomers are C\textsubscript{1}-symmetric and would not exchange the ends of the tBuClip ligand. The high-temperature behavior can only be explained by racemization, which requires an inversion of stereochemistry of the ligand backbone, as well as a trigonal twist. Since twisting about the biphenyl axis is geometrically precluded if the configuration at the metal is maintained, both twists must occur simultaneously. A plausible transition state in such a process is illustrated in Scheme 2.1. The observed barrier for this process (\(\Delta G^\ddagger \approx 12 \text{ kcal mol}^{-1}\)) is low, compared to the sum of the barriers for a Bailar twist (\(\Delta G^\ddagger \approx 9 \text{ kcal mol}^{-1}\) in oxobis(catecholates),\textsuperscript{15,29} and racemization of 2,2'-disubstituted biphenyls
(e.g., \( \Delta G^\ddagger \approx 14 \text{ kcal mol}^{-1} \) for racemization in titanium\(^{39a} \) and germanium\(^{40} \) 2,2'-biphenoxides). However, the two events are likely to be strongly coupled. In particular, the N–N distance will likely decrease in the trigonal prism, and the barrier to twisting in 2,2'-disubstituted biphenyls decreases sharply with decreasing equilibrium distance between the substituents.\(^{41} \) Additionally, it is possible for \((S,\Lambda)-\text{cis-}\beta\)2 and \((R,\Delta)-\text{cis-}\beta\)2 isomers to interconvert directly via a Ray-Dutt twist coupled to a biphenyl epimerization (Scheme 2.2b). The two isomerizations depicted in Scheme 2.2 occurring sequentially would also account for the racemization seen at room temperature. The mechanism shown in Scheme 2.1 is favored because NMR spectra below – 40 °C do not show multiple sets of \('\text{Bu peaks from } 3,5-'\text{Bu}_2\text{Cat. The coupled epimerization required to symmetrize these peaks across diastereomers is unlikely to occur at temperatures below – 40 °C.}
Scheme 2.1 Stereodynamics of (BuClip)Mo(3,5-Bu₂Cat), racemization by coupled Bailar twist and epimerization of the biphenyl linker.
Scheme 2.2 (a) Interconversion of geometric isomers via cis-\( \beta \)

\[ S,\tau^-\text{cis-}\overline{\beta} \leftrightarrow S,\tau^-\text{cis-}\beta \]

(b) Direct conversion of cis-\( \beta \) geometric isomers by a single Ray-Dutt twist coupled with epimerization of axial chirality of the biphenyl linker.

\[ S,\tau^-\text{cis-}\overline{\beta} \leftrightarrow R,\tau^-\text{cis-}\beta \]
2.2.3 Preparation, characterization, and bonding of (tBuClip)Mo(μ-(3,5-tBuCat)_2)Mo(O)(3,5-tBuCat).

Addition of excess 3,5-tBuCatH_2 to (tBuClipH_2)MoO_2 does not increase the yield of (tBuClip)Mo(3,5-tBuCat) but leads to the formation of free tBuClipH_4 and a molybdenum-containing byproduct as observed by ^1H NMR. This byproduct was first observed as a minor product in the reaction of (tBuClipH_2)MoO_2 with 3,5-tBuCatH_2. It shows sixteen clearly distinguishable aromatic resonances in unity ratios including one set of diagnostic unsymmetrical tBuClip peaks and three inequivalent di-tert-butylcatecholate ligands. Formulation of the product as a dimolybdenum monooxo complex, Mo_2(O)(tBuClip)(3,5-tBuCat)_3, is supported by the observation of a parent ion in its electrospray mass spectrum. The compound is conveniently prepared by self-assembly from dioxomolybdenum bis(acetylacetonate), tBuClipH_4, and 3,5-tBuCatH_2 in a 2:1:3 ratio. The dimer is formed in this reaction in nearly quantitative yield, as judged by in situ NMR spectroscopy, though isolation is subject to solubility losses. The NMR spectrum of (tBuClip)Mo(μ-(3,5-tBuCat)_2)MoO(3,5-tBuCat) shows only one isomer and is static in solution. A catecholate analogue, Mo_2O(3,5-tBuCat)_5, was reported in solution as an intermediate in oxygenations of Mo_2(3,5-tBuCat)_6. X-ray crystallography (Figure 2.6) confirms the dimeric nature of this mixed amidophenolate and its formulation as (tBuClip)Mo(μ-(3,5-tBuCat)_2)Mo(O)(3,5-tBuCat) with fully deprotonated bis(amidophenolate) and catecholate ligands and a bis-μ-3,5-tBuCat bridged dimolybdenum core. The molybdenum fragment containing the oxo group is an octahedron, whilst the tBuClip ligand is incorporated into a seven-coordinate distorted...
pentagonal bipyramidal molybdenum center. The bridging catecholate trans to oxo forms a longer bonds (Mo1-O21 = 2.215(3) Å) than other bridging catecholates (Mo1-O11 = 2.042(2), Mo2-O11 = 2.159(2), Mo2-O21 = 2.146(2) Å).

Figure 2.6 Thermal ellipsoid plot of (tBuClip)Mo(μ-(3,5-tBu2Cat)2)Mo(O)(3,5-tBu2Cat)·1.5 C6H6. Solvent molecules, hydrogen atoms, and methyl groups are omitted for clarity.

The structure of (tBuClip)Mo(μ-(3,5-tBu2Cat)2)Mo(O)(3,5-tBu2Cat) is a fusion between half of the tris(catecholate) dimer Mo3(3,5-tBu2Cat)6 and half of the oxobis(catecholate) dimer Mo2O2(3,5-tBu2Cat)4. Pierpont and coworkers first reported...
the 3,5-di-tert-butylcatecholate bridged molybdenum dimer as a toluene solvate in the triclinic space group \( PT \).\(^{42}\) The same compound is also shown here (Figure 2.7) and was crystallized as a bis(benzene) solvate in the monoclinic space group \( P2_1/c \). The molecular structure and bond distances and angles (Table 2.2) show no major variability from the toluene solvate.

Figure 2.7 Thermal ellipsoid plot of \( \text{Mo}_2\text{O}_2(3,5^{-\text{tBu}_2\text{Cat}})_4\cdot 2 \text{C}_6\text{H}_6 \).
Solvent molecules and hydrogen atoms are omitted for clarity.

All bridged 3,5-di-tert-butylcatecholate structures have a steric preference to bridge from the less encumbered oxygen not adjacent to the tert-butyl group.\(^{43}\) In an
attempt to prepare a monomeric oxo molybdenum catecholate, 3,6-di-tert-butyl-1,2-benzoquinone was used in a reaction with Mo(CO)$_6^{15}$ as tertiary butyl groups adjacent to both oxygen atoms would prevent dimerization.$^{44}$ The resultant tetrameric {MoO(3,6-tBu$_2$Cat)$_4$} with bridging oxo groups illustrates the overriding preference of catecholate bridges. This preference precludes the tetradentate $^5$BuClip from forming a bridge across the metal centers. A molybdenum center containing both $^5$BuClip and a terminal oxo would require additional bridging catecholates and would render the other molybdenum center severely Lewis acidic; therefore, the oxo group must be mutually exclusive to the molybdenum fragment containing the $^5$BuClip ligand.

The plane of the bridging catecholates in the oxomolybdenum dimer Mo$_2$O$_2$(3,5-$^5$Bu$_2$Cat)$_4$ are acutely inclined with respect to the Mo$_2$O$_2$ diamond core (angle between planes = $55.8^\circ$ in the toluene solvate,$^{42}$ $51.9^\circ$ in the benzene solvate). The bridging catecholate supplied by the oxomolybdenum fragment in the asymmetric dimer ({$^5$BuClip}Mo(µ-(3,5-$^5$Bu$_2$Cat)$_2$)MoO(3,5-$^5$Bu$_2$Cat)) similarly makes an angle to the Mo1-O11-Mo2-O21 mean plane of $50.2^\circ$. In contrast, the bridging catecholate supplied by the seven-coordinate Mo2 center is inclined by only $9.1^\circ$ to this plane, a nearly coplanar arrangement seen in Mo$_2$(3,5-$^5$Bu$_2$Cat)$_6$ and most other M$_2$(µ-3,5-$^5$Bu$_2$Cat)$_2$ complexes.$^{43}$ The nonbridging catecholate on Mo1 has its ortho tert-butyl group away from the second molybdenum, as observed in Mo$_2$O$_2$(3,5-$^5$BuCat)$_4$. Electronically, a bridging catecholate oxygen trans to the oxo group, with its nonbridging counterpart donating into the otherwise $\pi^{nb}$ metal $d_{xy}$ orbital allows for the most stable configuration around the oxo-containing molybdenum metal center. The amidophenolate ligands are strongly
engaged in π donation to Mo2, as judged from their MOS values -1.37(7) for the ring containing N1 and -1.39(11) for the ring containing N2). These values are significantly more positive than those observed in the six-coordinate (t-BuClip)Mo(3,5-tBu2Clip), and are close to that observed in the amidophenoxide trans to oxo in (t-BuClip)MoO(3,5-lutidine) (MOS = -1.34(12)), consistent with π donation of each of the amidophenolates into a dπ orbital where there is no competition from other π-donor ligands.

2.2.4 (t-BuClip)Mo(3,5-tBu2Cat)(NC6H5): Structure and bonding.

(t-BuClip)Mo(3,5-tBu2Cat) is isolable as a six-coordinate monomer, but undergoes facile addition of pyridine to form seven-coordinate adducts. The 1H NMR spectrum of this reaction in CD2Cl2 (Figure 2.9) shows peaks that are broad at ambient temperature, but sharp at temperatures below -20 °C. Integration of the signals due to bound pyridine is consistent with one pyridine per molybdenum center. (t-BuClip)Mo(3,5-tBu2Cat)(py) was crystallographically characterized and most closely resembles a capped octahedral structure, but shows significant distortions. The pyridine is bound along the pseudo-C3 axis and caps the face containing atoms N1 and O2 (from different amidophenoxide rings) as well as atom O4 (from catecholate). The bound pyridine distance (Mo–N6 = 2.226(2) Å) corresponds well to pyridines bonded to Mo(VI) that are not subject to substantial trans influences. Our group has reported an analogous tris(catecholate) structure, (3,5-tBu2Cat)3Mo(py),31 whose Mo–py distance is 2.274(2) Å; however, the tris(catecholate) exhibits a near perfect capped octahedral geometry and is not restricted by a biphenyl linked backbone. More recently, our group reported a
heptadentate, triarylamine linked tris(amidophenoxide), Mo(MeClamp)\textsuperscript{45} which also forms a capped octahedron with a Mo–NAr\textsubscript{3} distance of 2.274(2) Å. In (\textsuperscript{t}BuClip)Mo(3,5-\textsuperscript{t}Bu\textsubscript{2}Cat)(NC\textsubscript{6}H\textsubscript{3}), the amidophenoxides and catecholate span the capped and uncapped octahedral faces. The two nitrogen atoms of the \textsuperscript{t}BuClip ligand do not both occupy the same face because it is substantially expanded to accommodate the pyridine ligand (O2-Mo-N1 = 126.01(9)°, O2-Mo-O4° = 80.168, and O4-Mo-N1 = 137.92(8)°) and the uncapped face is substantially contracted (N2-Mo-O3 = 78.56(8)°, O1-Mo-O3 = 80.43(8)°, and O1-Mo-N2 = 123.17(9)°). The 2,2'-biphenyl group bridges between the capped and uncapped faces showing a cis-\textalpha-like structure (O1-Mo-O2 = 159.27(8)°). It could also bridge both the nitrogen atoms on the same uncapped face (cis-\textbeta-like) (Scheme 2.3). The two amidophenoxides show noticeable π-donation (MOS = −1.31(11), −1.60(15) for rings 1 and 2 respectively and the catecholate shows negligible donation (MOS = −1.94(10)). The dπ orbitals in the capped octahedral geometry (d\textsubscript{xy} and d\textsubscript{x\textsuperscript{2}−y\textsuperscript{2}}) overlap more strongly with the nitrogen atom on the capped face (N1), which may explain the stronger π interaction in amidophenoxide ring 1. The catecholate also has its electron-rich oxygen (O4, ortho and para to \textsuperscript{t}Bu) on the capped face.
Figure 2.8 Thermal ellipsoid plot of (\textsuperscript{1}BuClip)Mo(3,5-\textsuperscript{2}Bu\textsubscript{2}Cat)(py).
Hydrogen atoms are omitted for clarity.
TABLE 2.3.

CRYSTAL DATA AND SELECTED BOND DISTANCES (Å) AND ANGLES (DEG) FOR

\((^7\text{BUCLIP})\text{MO}(3,5-^7\text{BU}_2\text{CAT})(\text{PY})\)

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Figure 2.9. Partial $^1$H NMR spectra (δ 4.8-8.7 ppm, 500 MHz, CD$_2$Cl$_2$) of (tBuClip)Mo(3,5-$^t$Bu$_2$Cat) in the presence of pyridine at (a) 10 °C and (b) –30 °C. Key: Major isomer(s) of (tBuClip)Mo(3,5-$^t$Bu$_2$Cat)(py) (o), minor isomer(s) (*), free pyridine (‡), benzene (B), and dimethyl terephthalate (S, added as an internal standard).

2.2.5 VT-NMR, mechanism of pyridine exchange, and $K_{eq}$ for binding in (tBuClip)Mo(3,5-$^t$Bu$_2$Cat)(py).

The $^1$H NMR spectrum of (tBuClip)Mo(3,5-$^t$Bu$_2$Cat)(py) at low temperature (Figure 2.9) displays two sets of signals in unequal amounts (2.3:1 at –30 °C). Each set consists of resonances due to an unsymmetrical tBuClip ligand, one catecholate ligand, and one pyridine. Each set of signals represent a single isomer ($^\sim$cis-$\alpha$ and $^\sim$cis-$\beta$) or a rapidly equilibrating pair of isomers (each cis isomer family has two geometrical isomers because of the bound asymmetrical catecholate). In one scenario, the cis-$\alpha$ isomers
could be rapidly equilibrating with each other, and slowly interconverting with the two 
 cis-β isomers. The presence of multiple isomers interconverting rapidly is preceded in 
 (3,5-^tBu_2Cat)_3Mo(py), which shows only a single catecholate environment by ^1H NMR 
 even at –70 °C despite the crystallization of the compound as the unsymmetrical 
 isomer. \(^31\) A large temperature dependence of the chemical shifts of the resonances in 
 (^tBuClip)Mo(3,5-^tBuCat)(py) from –50 °C to 0 °C suggests a fast equilibration of isomers 
 within each discrete set of signals. At higher temperatures, ^1H NMR spectra of 
 (^tBuClip)Mo(3,5-^tBuClip)(py) indicate that free and bound pyridine are exchanging on 
 the NMR timescale (Figure 2.9). The linewidth of the resonances due to bound pyridine 
 are independent of the concentration of free pyridine in the slow exchange regime and 
 indicate a dissociative mechanism of exchange.

Scheme 2.3 Structural families of seven-coordinate isomers after 
 pyridine association. ^tBu groups in red indicate asymmetry of 
 bound ^tBu_2Cat.

Quantitative lineshape simulation of the bound and free pyridine resonances at 
 0 °C gives similar dissociation rate constants for the pyridines associated with the major
and minor sets of isomers \( k_{\text{diss}} = 25 \pm 3 \text{ s}^{-1}, \Delta G^\ddagger_{\text{diss}} = 14.2 \text{ kcal mol}^{-1} \). The dissociation of pyridine results in exchange between isomers; however, the activation parameters could not be determined because additional intramolecular pathways that also result in isomerization could not be excluded in the fast-exchange regime.

The equilibrium constant for pyridine binding can be determined by UV-visible spectroscopy. Titration of solutions of \((\text{tBuClip})\text{Mo}(3,5\text{-}^1\text{Bu}_2\text{Cat})\) in \( \text{CH}_2\text{Cl}_2 \) with pyridine under anaerobic conditions results in a color change from dull to vibrant purple with corresponding changes in the optical spectrum (Figure 2.10). In particular, the three features in the visible spectrum of \((\text{tBuClip})\text{Mo}(3,5\text{-}^1\text{Bu}_2\text{Cat})\) at \( \lambda_{\text{max}} = 743 \text{ nm} \) (\( \varepsilon = 5400 \text{ L mol}^{-1} \text{ cm}^{-1} \)), 496 nm (18000 L mol\(^{-1}\) cm\(^{-1}\)), and 403 nm (11000 L mol\(^{-1}\) cm\(^{-1}\)) shift on addition of pyridine to longer wavelengths (\( \lambda_{\text{max}} = 767 \text{ nm}, 550 \text{ nm}, \) and a shoulder at 450 nm). Analysis of the spectra as a function of added pyridine allows calculation of the binding constant of pyridine, and its variation from 284–308 K gives thermodynamic parameters for binding of \( \Delta H^\circ = -10.9 \pm 0.7 \text{ kcal mol}^{-1} \) and \( \Delta S^\circ = -23.9 \pm 2.4 \text{ cal mol}^{-1} \text{ K}^{-1} \) (Figure 2.10, inset). From the equilibrium binding data for \((\text{tBuClip})\text{Mo}(3,5\text{-}^1\text{Bu}_2\text{Cat})(\text{py})\) (Figure 2.10), the van’t Hoff plot can be used to calculate \( \Delta G^\circ_{\text{binding, 273K}} = -4.4 \text{ kcal mol}^{-1} \) and activation parameters for pyridine binding, \( \Delta G^\ddagger_{\text{binding, 273K}} = 9.8 \text{ kcal mol}^{-1} \) (\( k_{\text{assoc}} = 8 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1} \)).
Figure 2.10. UV-visible titration of (tBu Clip)Mo(3,5-tBu Cat) (5 × 10⁻⁵ mol L⁻¹) with pyridine (CH₂Cl₂, 24 °C). The thick solid line is the initial spectrum of (tBu Clip)Mo(3,5-tBu Cat) and the thick dashed line is the final (calculated) spectrum of (tBu Clip)Mo(3,5-tBu Cat)(py). Thin solid lines correspond to successive additions of
2.2.6 Comparative Lewis acidity of Mo(VI) complexes bound by 3,5-‘Bu₂Cat, ‘BuClip, and oxo groups.

\[(‘\text{Bu}²\text{Cat})_₂\text{Mo} \rightarrow (‘\text{Bu}²\text{Cat})_₂\text{MoO} \rightarrow (‘\text{Bu}²\text{Cat})₃\text{Mo} \text{ Associative} \rightarrow (‘\text{Bu}²\text{Cat})_₂\text{MoO} \rightarrow (‘\text{BuClip})\text{MoO} \rightarrow (‘\text{BuClip})\text{MoO}(‘\text{Bu}²\text{Cat}) \text{ Dissociative} \rightarrow (‘\text{BuClip})\text{MoO}\text{Ox} \rightarrow (‘\text{BuClip})\text{MoO(‘Bu}²\text{Cat}) \text{ Slow Dissociative} \]

Figure 2.11 Comparison of Lewis acidity of analogous compounds based on rate and type of exchange of bound pyridine donors.

\[(‘\text{BuClip})\text{Mo}(3,5-‘\text{Bu}²\text{Cat})\] is the least Lewis acidic fragment compared to its analogues \((3,5-‘\text{Bu}²\text{Cat})₂\text{MoO}, (3,5-‘\text{Bu}²\text{Cat})₃\text{Mo}, \) and \((‘\text{BuClip})\text{MoO},\) since only the mixed amidophenoxide-catecholate can be observed as a stable monomeric compound. The lower Lewis acidity of \((‘\text{BuClip})\text{Mo}(3,5-‘\text{Bu}²\text{Cat})\) is caused by its higher coordination number of six, which makes ligand binding less favorable compared to the five-coordinate oxo analogues that dimerize readily or add donor ligands such as pyridine or pyridine-\(N\)-oxide. \((‘\text{BuClip})\text{Mo}(3,5-‘\text{Bu}²\text{Cat})\) is less Lewis acidic than its tris(catecholate) analogue because amidophenolate is a stronger electron donor than catecholate. By the same rationale in the reverse direction, \((3,5-‘\text{Bu}²\text{Cat})₂\text{MoO}\) is the most Lewis acidic. Pyridine substitution in \((3,5-‘\text{Bu}²\text{Cat})₂\text{MoO(py)}\) is much slower than in any of the other three adducts and takes place by an associative mechanism.\(^{29}\) In contrast, bound
pyridine peaks in (3,5-^t^Bu_2Cat)_3Mo(py) show coalescence with free pyridine, but line
broadening is independent of the concentration of free pyridine, indicating a
dissociative mechanism, consistent with the observed activation parameters (0–50 °C,
\( \Delta H^\ddagger = 15.4 \pm 0.6 \text{ kcal mol}^{-1}, \Delta S^\ddagger = +6.6 \pm 2.0 \text{ cal mol}^{-1} \text{ K}^{-1}. \)) \(^{31} \) H NMR spectra of
(^t^BuClip)Mo(O)(L) (L = pyridine, 3,5-lutidine) were analyzed quantitatively and show a
zero order pyridine dependence and positive entropies of activation (\( \Delta H^\ddagger = 17.2(7) \)
kcal/mol, \( \Delta S^\ddagger = 9(2) \text{ cal mol}^{-1} \text{ K}^{-1} \) for pyridine exchange, \( \Delta H^\ddagger = 20.9(6) \text{ kcal mol}^{-1}, \Delta S^\ddagger = 17(2) \text{ cal mol}^{-1} \text{ K}^{-1} \) for 3,5-lutidine exchange). \(^{10} \)

The lower degree of Lewis acidity of the mixed amidophenolate-catecholate
complex is not completely evident in pyridine dissociation rates from (^t^BuClip)Mo(3,5-
^t^Bu_2Cat)(py) (\( \Delta G^\ddagger_{273K} = 14.2 \text{ kcal mol}^{-1} \)), which is similar to (^t^BuClip)MoO(py) (\( \Delta G^\ddagger_{273K} = 14.7 \text{ kcal mol}^{-1} \)) \(^{10} \) and (3,5-^t^Bu_2Cat)_3Mo(py) (\( \Delta G^\ddagger_{273K} = 13.6 \text{ kcal mol}^{-1} \)). \(^{31} \)
(^t^BuClip)MoO(py) dissociates pyridine approximately 10 times slower than (3,5-
^t^Bu_2Cat)_3Mo(py) at 22 °C indicating the lower Lewis acidity of the latter in comparison
to the five-coordinate (^t^BuClip)MoO, although the overall span of dissociation rates
among them is within an order of magnitude.

The kinetics of dissociative ligand substitution in six coordinate complexes is
generally attributed to the relative thermodynamic stability of reactant and five-
coordinate intermediate. This phenomenon prevails because ligand rebinding to the
five-coordinate intermediate is very fast (\( \Delta G^\ddagger_{\text{rebinding}} \approx 0 \)). \(^{46,47} \) 1H NMR data of pyridine
exchange in (^t^BuClip)MoO(py) show evidence of a short lived five-coordinate
intermediate, as stereoisomers of the product do not interconvert during
dissociation/reassociation of pyridine.\textsuperscript{10} The comparatively slow binding kinetics of pyridine to the six-coordinate \((^1\text{BuClip})\text{Mo}(3,5-^2\text{Bu}_2\text{Cat})\) suggests that \(\Delta G_{\text{rebinding}}^\dagger \neq 0\) for dissociative reactions of seven-coordinate species. The coordination of the pyridine ligand to unsaturated \((^1\text{BuClip})\text{Mo}(3,5-^2\text{Bu}_2\text{Cat})\) is affected by steric encumbrance and greater ligand rearrangement. Its low thermodynamic affinity for pyridine is expressed mainly as a low rate of association rather than a high rate of dissociation from \((^1\text{BuClip})\text{Mo}(3,5-^2\text{Bu}_2\text{Cat})(\text{py})\) (Figure 2.12).

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure2_12.png}
\caption{Comparative kinetics and thermodynamics of pyridine binding in \((3,5-^2\text{Bu}_2\text{Cat})_3\text{Mo}\) and \((^1\text{BuClip})\text{Mo}(3,5-^2\text{Bu}_2\text{Cat})\).}
\end{figure}

2.3 Experimental

Unless otherwise noted, all procedures were carried out under an inert atmosphere in a nitrogen-filled glovebox or on a vacuum line. When dry solvents were needed, chlorinated solvents and acetonitrile were dried over 4 Å molecular sieves, followed by \(\text{CaH}_2\). Benzene and toluene were dried over sodium, and tetrahydrofuran over sodium benzophenone ketyl. Deuterated solvents were obtained from Cambridge Isotope Laboratories, dried using the same procedures as their protio analogues, and
stored in the drybox prior to use. The ligand $^1$BuClipH$_4$ (4,4'-di-tert-butylbiphenyl-2,2'-bis((2-hydroxy-3,5-di-tert-butylphenyl)amine)), ($^1$BuClipH$_2$)MoO$_2$, and ($^1$BuClip)Mo($\mu$-N)($\mu$-NH$_2$)Mo($^1$BuClip) were prepared as previously described.$^{10}$ All other reagents were commercially available and used without further purification. Routine NMR spectra were measured on Varian VXR-300 spectrometer or Bruker Avance DPX 400 spectrometers. Variable-temperature NMR spectra were measured on a Varian Inova 500 spectrometer. Chemical shifts for $^1$H and $^{13}$C($^1$H) spectra are reported in ppm downfield of TMS, with spectra referenced using the known chemical shifts of the solvent residuals. Infrared spectra were recorded as nujol mulls between NaCl plates on a Jasco 6300 FT-IR spectrometer. ESI mass spectra were obtained using a Bruker micrOTOF-II mass spectrometer, and peaks reported are the mass number of the most intense peak of isotope envelopes. Samples were injected as dichloromethane solutions, preceded and followed by methanol. In all cases, the observed isotope patterns were in good agreement with calculated ones. Elemental analyses were performed by Roberstson Microlit Labs (Ledgewood, NJ) or Midwest Microlab, LLC (Indianapolis, IN).

2.3.1 (4,4'-Di-tert-butylbiphenyl-2,2'-bis((2-oxy-3,5-di-tert-butylphenyl)amido))(3,5-di-tert-butylcatecholato)molybdenum(VI), ($^1$BuClip)Mo(3,5-$^1$Bu$_2$Cat).

($^1$BuClipH$_2$)MoO$_2$ (0.1544 g, 0.185 mmol) and 3,5-di-tert-butylcatechol (3,5-$^1$Bu$_2$Cat$_2$; Aldrich, 0.0421 g, 0.189 mmol) were weighed in the drybox and dissolved in 4 mL THF. The reaction mixture was stirred for 18 h at room temperature in a sealed reaction vessel. After evaporation of the THF from the dark purple solution in vacuo, the crude product was dissolved in 2 mL benzene, filtered through a plug of sand, and
layered with 4 mL acetonitrile in a 20 mL scintillation vial. The crystalline product was isolated by filtration, and two subsequent crops were combined to yield 0.1614 g of (**BuClip**)**Mo(3,5-**Bu**2**Cat**) (85%). $^1$H NMR (CDCl$_3$, 20 °C, 400 MHz): δ 0.58, 1.15 (s, 9H each, C(CH$_3$)$_3$ from **Bu**2**Cat**), 1.11, 1.19, 1.43 (s, 18H each, C(CH$_3$)$_3$ from **BuClip**), 6.29 (d, 2 Hz, 1H, ArH from **Bu**2**Cat**), 6.47 (br s, 2H, ArH from **BuClip**), 6.59 (d, 2 Hz, 1H, ArH from **Bu**2**Cat**), 6.81 (d, 2 Hz, 2H, H-3), 7.10 (d, 2 Hz, 2H, ArH from **BuClip**), 7.22 (dd, 8, 2 Hz, 2H, H-5), 7.51 (d, 8 Hz, 2H, H-6). $^{13}$C($^1$H) NMR (CDCl$_3$, 20 °C, 100.62 MHz): δ 29.69, 29.77, 31.22, 31.75, 31.96 (C(CH$_3$)$_3$), 33.95, 34.68, 34.83, 34.98, 35.39 (C(CH$_3$)$_3$), 109.30, 110.10, 110.23, 113.41, 121.31, 124.91, 124.93, 125.48, 131.14, 131.51, 134.18, 136.74, 145.03, 146.83, 151.56, 157.10, 158.48, 159.28. IR (cm$^{-1}$): 1601 (w), 1584 (m), 1362 (s), 1307 (m), 1259 (m), 1200 (m), 1169 (s), 1150 (s), 1099 (s), 1026 (m), 992 (s), 944 (m), 912 (m), 853 (m), 762 (m), 721 (w). ESI-MS: 1019.5575 (M+H, calcd 1019.5563). Anal. Calcd for C$_{62}$H$_{84}$MoN$_2$O$_4$ • 1.5 C$_6$H$_6$: C, 75.17; H, 8.26; N, 2.47. Found: C, 74.83; H, 8.38; N, 2.42.

2.3.2. (4,4'-di-tert-butylbiphenyl-2,2'-bis((2-oxy-3,5-di-tert-butylphenyl)amido)bis-µ-(3,5-di-tert-butylcatecholato)oxo(3,5-di-tert-butylcatecholato)dimolybdenum(VI), (**BuClip**)**Mo(µ-(3,5-**Bu**2**Cat**))$_2$MoO(3,5-**Bu**2**Cat**).

In a 20 mL scintillation vial in the drybox were weighed 0.1772 g (**BuClip**)$_4$ (0.251 mmol), 0.1639 g dioxomolybdenum bis(acetylacetonate) (Strem, 0.503 mmol, 2.00 equiv), and 0.1672 g 3,5-**Bu**2**Cat**$_2$H$_2$ (0.752 mmol, 3.00 equiv). The mixture was dissolved in 5 mL benzene and stirred 48 h. The reaction mixture was filtered through a glass frit and layered with 4 mL dry acetonitrile to yield crystalline product, which was isolated by filtration and washed with 2 × 2 mL acetonitrile. A second crop was isolated from the
filtrate on standing to give a total yield of 114.4 mg (29%). $^1$H NMR (CDCl$_3$): $\delta$ 0.64, 0.72, 0.79 (s, 9H each, $^t$Bu), 0.93 (s, 18H, 2 $\times$ $^t$Bu), 1.01 (s, 27H, 3 $\times$ $^t$Bu), 1.15, 1.17, 1.34, 1.43 (s, 9H each, $^t$Bu), 4.79 (d, 2Hz, 1H, ArH), 5.21 (d, 2 Hz, 1H, ArH), 5.45 (d, 2 Hz, 1H, ArH), 6.37 (d, 2 Hz, 1H, ArH), 6.48 (d, 2 Hz, 1H, H-3), 6.55 (m, 3H, H-3, 2 $\times$ ArH), 6.73 (d, 2 Hz, 1H, ArH), 6.93 (d, 2 Hz, 1H, ArH), 6.98 (d, 2 Hz, 1H, ArH) 7.05 (dd, 8, 2 Hz, 2H, H-5), 7.21 (d, 8 Hz, 1H, H-6), 7.31 (dd, 8, 2 Hz, 1H, H-5), 7.58 (d, 2 Hz, 1H, H-6), 7.82 (d, 2 Hz, 1H, ArH). $^{13}$C($^1$H) NMR (CDCl$_3$): $\delta$ 29.93, 29.95, 30.11, 30.17, 30.57, 31.08, 31.31, 31.35, 31.42, 31.65, 32.00, 32.08 (C(CH$_3$)$_3$), 34.34, 34.40, 34.56, 34.59, 34.65, 34.74, 34.81, 34.82 (2C), 34.85, 34.88, 35.25 (C(CH$_3$)$_3$), 107.53, 107.64, 108.86, 110.56, 115.02, 116.08, 116.52, 118.42, 121.78, 123.41, 123.57, 124.37, 124.99, 125.27, 126.16, 129.96, 130.57, 130.64, 134.33, 135.31, 136.56, 138.26, 138.49, 140.69, 143.44, 143.83, 145.22, 146.90, 148.27, 149.94, 150.01, 151.34, 152.07, 153.08, 153.54, 153.69, 154.65, 155.88, 158.81, 161.64, 163.04, 164.71. IR (cm$^{-1}$): 1583 (m), 1551 (w), 1410 (m), 1387 (m), 1361 (s), 1307 (s), 1253 (m), 1201 (s), 1174 (m), 1149 (w), 1105 (w), 1026 (m), 973 (s), 944 (s), 914 (m), 890 (w), 865 (m), 834 (m), 753 (s), 722 (w), 687 (m), 651 (m), 595 (w), 588 (w). ESI-MS: 1573.7506 (M+H, calcd 1573.7491). Anal. Calcd for C$_{90}$H$_{124}$Mo$_2$N$_2$O$_9$: C, 68.86; H, 7.96; N, 1.78. Found: C, 68.72; H, 7.67; N, 1.60.

2.3.3 Variable-temperature NMR spectroscopy

NMR spectra of ($^t$BuClip)Mo(3,5-$^t$Bu$_2$Cat) were recorded between −95 and +21.5 °C in CD$_2$Cl$_2$ on a Varian VXR-500 NMR spectrometer. The line shapes of the ligand tert-butyl resonances were simulated using the program gNMR$^{48}$ to generate calculated lineshapes and superimpose them on the observed spectra for temperatures from −30
to +10 °C. NMR spectra of (tBuClip)Mo(3,5-tBu2Cat)(py), generated in situ from (tBuClip)Mo(3,5-tBu2Cat) and pyridine, were recorded between –40 and +30 °C in CD$_2$Cl$_2$ on a Varian VXR-500 NMR spectrometer. To determine the rate of dissociation of pyridine at 0° C, the region from δ 7.4-8.6 ppm, containing peaks due to the 2,6- and 4-H signals of bound and free pyridine, were simulated using the program iNMR (http://www.inmr.net). In addition to exchange between each of the two sets of bound pyridine signals with free pyridine, a minor amount of direct exchange between the bound pyridine signals was required to achieve a satisfactory fit.

2.3.4 UV-visible titration of (tBuClip)Mo(3,5-tBu2Cat) with pyridine

A solution of 2.0 mL of 5 × 10^{-5} M (tBuClip)Mo(3,5-tBu2Cat) in CH$_2$Cl$_2$ was prepared in the drybox and sealed in a 1-cm quartz screw-cap cuvette using a Teflon-backed silicone rubber septum. Spectra were obtained on a Thermo Scientific Evolution Array UV-Visible spectrophotometer. The cuvette was equilibrated in the instrument's multicell changer, with the temperature controlled by circulation of ethylene glycol/water mixture through the cell holder and measured using a thermocouple inserted in a dummy cuvette. The titration was carried out by sequential injection of aliquots of pyridine dissolved in dichloromethane through the Teflon-backed silicone septum of the cuvette. Binding constants were extracted from simulation of the absorbance data from 300-1000 nm for each titration. The spectrum of (tBuClip)Mo(3,5-tBu2Cat) was fixed as equal to the initial spectrum in the titration, and the spectrum of the pyridine adduct was removed as an independent parameter using linear least-squares fitting as described in the literature.$^{49}$ The binding constant $K_{eq}$ was optimized.
as the sole adjustable parameter by nonlinear least-squares fitting using the Solver routine in Microsoft Excel.\(^{50}\) A van’t Hoff plot of ln(K\(_{eq}\)) vs. 1/T in the range of 284-308 K was used to calculate thermodynamic parameters for binding.

2.3.5 DFT Calculations

Geometry optimizations and orbital calculations were performed on all three geometric isomers of (\(^{t}\)BuClip)Mo(3,5-\(^{t}\)Bu\(_2\)Cat). The crystal structure of (\(^{t}\)BuClip)Mo(3,5-\(^{t}\)Bu\(_2\)Cat) was used as the starting geometry in calculations on the cis-\(\beta\)1 isomer, and the starting structure of the cis-\(\beta\)2 isomer was created by shifting the positions of the tert-butyl groups on the 3,5-\(^{t}\)Bu\(_2\)Cat ligand. The crystal structure of (\(^{t}\)BuClip)Mo(O\(^{t}\)Pr)\(_2\)\(^{10}\) was modified to use as a starting structure for the cis-\(\alpha\) isomer. Calculations used the hybrid B3LYP method, with an SDD basis set for molybdenum and a 6-31G* basis set for all other atoms, using the Gaussian09 suite of programs.\(^{51}\) The optimized geometries were confirmed as minima by calculation of vibrational frequencies.

2.3.6 X-ray crystallography

Crystals of (\(^{t}\)BuClip)Mo(3,5-\(^{t}\)Bu\(_2\)Cat)•1.5 C\(_6\)H\(_6\), (\(^{t}\)BuClip)Mo(\(\mu\)-3,5-\(^{t}\)Bu\(_2\)Cat)\(_2\)MoO(3,5-\(^{t}\)Bu\(_2\)Cat)•1.5 C\(_6\)H\(_6\), and (\(^{t}\)BuClip)Mo(3,5-\(^{t}\)Bu\(_2\)Cat)(py) were grown by layering concentrated solutions in benzene with acetonitrile. Crystals of Mo\(_2\)O\(_2\)(3,5-\(^{t}\)Bu\(_2\)Cat)\(_4\)•2 C\(_6\)H\(_6\) formed on attempted recrystallization of (\(^{t}\)BuClip)Mo(\(\mu\)-3,5-\(^{t}\)Bu\(_2\)Cat)\(_2\)MoO(3,5-\(^{t}\)Bu\(_2\)Cat) from a benzene/acetonitrile mixture that was exposed to air. Crystals were placed in inert oil before transferring to the cold N\(_2\) stream of a Bruker Apex II CCD diffractometer. Data were reduced, correcting for absorption, using the
program SADABS. The structures were solved using direct methods. All nonhydrogen atoms not apparent from the initial solutions were found on difference Fourier maps, and all heavy atoms were refined anisotropically. The crystal of (tBuClip)Mo(3,5-tBu2Cat)•1.5 C6H6 was found to be twinned by examination using the TwinRotMat function in the program PLATON.52 The twin law was found to be [ -1 0 0 0 -1 0 1 0 1 ], and refinement of the batch structure factor indicated that the extent of twinning was 0.064. Inclusion of this twin law drastically improved the model and eliminated all of the inconsistent equivalents. Two of the tert-butyl groups in (tBuClip)Mo(3,5-tBu2Cat), those bonded to C24 and C45, were disordered in two different orientations, as was the tert-butyl group bonded to C18 in Mo2O2(3,5-tBu2Cat)4. Disordered tert-butyl groups were modeled by constraining the thermal parameters of the methyl carbons to be equal to those of the carbons opposite them in the other orientation, and allowing the occupancy of the two orientations to refine. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms in Mo2O2(3,5-tBu2Cat)4•2 C6H6, except for those on the disordered tert-butyl group, were found on difference maps and refined isotropically. All other hydrogen atoms were placed in calculated positions, with thermal parameters for the hydrogens tied to the isotropic thermal parameters of the atoms to which they are bonded (1.5 × for methyl, 1.2 × for all others). Calculations used SHELXTL (Bruker AXS),26 with scattering factors and anomalous dispersion terms taken from the literature.27 Further details about the structures are in Tables 2.1 and 2.3.
CHAPTER 3:

NONCLASSICAL OXYGEN ACTIVATION AND ATOM TRANSFER USING MOLYBDENUM OXO AMIDOPHENOLATES AND CATECHOLATES.

3.1 Introduction

3.1.1 The chemistry of oxygen and oxo groups.

Oxygen is the most abundant element in the earth’s crust. Biological systems of all aerobic organisms utilize oxygen as the terminal electron acceptor and mediate oxidation reactions selectively. Oxygenases are such a class of enzymes that accomplish these reactions by cleaving the the O-O bond in O₂. These reactions often involve a metal center and a single oxygen molecule being converted to a metal oxo fragment, formally a 2e⁻ oxidation of the metal center and a 4e⁻ reduction of oxygen. The cleavage of the oxygen bond in oxygenases occurs in sequential uni-electron steps via the formation of high energy (M-{O₂}⁻, M-{O₂}^{2⁻}) intermediates. Metal oxo’s are also integral intermediates in mechanisms of water oxidation and oxygen evolution during photosynthesis. The thermodynamics of the oxygen reduction reaction are very favorable {ΔE°(O₂/H₂O) = +1.23V}, although kinetic barriers impede such a direct conversion upon interaction with organic substrates. The O=O bond has a homolytic bond dissociation energy of 119 kcal mol⁻¹ and early transition metal oxo’s have high
bond dissociation enthalpies of > 95 kcal mol\(^{-1}\).\(^{55}\) Formation of a metal oxo bond is a 2 e\(^-\) reduction and transfer of a reduced oxygen atom to a substrate is also a net 2e\(^-\) redox process. First row transition metals preferably effect stepwise single electron transfers, whereas coordinatively unsaturated 4d and 5d metals can undergo direct two electron transfers in oxygen reduction reactions and stabilize the resulting terminal oxo group.

3.1.2 Nonclassical oxygen activation.

Our group is interested in exploring homogeneous catalysts that consist of a single molybdenum metal center surrounded by redox active amidophenolate and catecholate ligands. The chemistry of molybdenum(VI) is dominated by strong \(\pi\) donors such as oxo, imido, and nitrido ligands. The isolobal catecholate (Figure 1.2) and its analogues are apt candidates to displace the hegemony of oxo groups on molybdenum(VI). These strong \(\pi\) donors stabilize the Lewis acidic metal and achieve saturated electron counts by forming multiple bonds. The general reaction depicted in Scheme 3.1 involves the four electron reduction of \(\text{O}_2\). The four electron reduction at a single metal center is challenging due to electronic restrictions of symmetry.\(^{56}\) In classical systems, the metal supplies the reducing electrons and acts as the electron reservoir, whereas in nonclassical\(^{57}\) systems oxidation is mediated by the metal center without a formal change of oxidation state. The reducing equivalents are supplied by the oxidation of ligands that can span multiple oxidation states.
Scheme 3.1 Nonclassical oxygen activation utilizing redox equivalents from ligands.

Precedents for nonclassical oxygen activation have been reported by Pierpont \(^{58}\) and Abu-Omar.\(^{59}\) In a recent report, our group demonstrated a nonclassical oxygen atom transfer reaction, in which oxomolybdenum(VI) bis(3,5-di-tert-butylcatecholate) deoxygenates pyridine-N-oxide.\(^{57}\) A transient dioxomolybdenum complex, \((SQ)_2 MoO_2\), containing two 3,5-di-\(^{1}\)BuCat ligands with a net \(2^-\) charge, is a proposed intermediate of this reaction.

Scheme 3.2 Nonclassical oxygen atom transfer utilizing Mo(VI) catecholates. \(^{5}\)Bu groups on catechol are omitted.
Nonclassical oxygen activation and atom transfer involving redox active ligands such as catechol or its derivatives can proceed through a variety of mechanisms that involve reactive intermediates such as (SQ)$_2$MoO$_2$ that have stored oxidizing power. The redox equivalents stored in these intermediates may prove critical in performing nonclassical oxygen atom transfer to organic substrates such as olefins.

This chapter describes the deoxygenation of $N$-methylmorpholine-$N$-oxide by the ($^t$BuClip)MoO(py) complex. Mechanistic data indicate that this reaction takes place by nonclassical oxygen atom transfer to generate a reactive intermediate with a limited lifetime. The stored oxidizing power can be transferred to dimethylphenylphosphine with the concomitant regeneration of $^t$BuClipMoO(L), establishing a closed loop of oxygen atom transfer in which the molybdenum metal center retains its $d^5$ electron configuration and all electronic changes are exported to the ligand. A similar reaction of oxo-free mixed catecholate amidophenoxide Mo(VI) with NMO or O$_2$ yielding disparate reactive intermediates is also outlined.

3.2 Results and Discussion

3.2.1 Attempted generation of the oxidized intermediate ($^t$BuClip$^{SQ}$)MoO$_2$ from dioxomolybdenum precursors.

The molybdenum complex (SQ)$_2$MoO$_2$ is proposed as an intermediate in the reaction of ($^t$Bu$_2$Cat)$_2$MoO with pyridine-$N$-oxide. Our strategy to protect the (SQ)$_2$MoO$_2$ intermediate from further oxidation and loss of quinone involves the tetradeinate bisaminophenoxide $^t$BuClipH$_4$ ligand. Multiple schemes for metal incorporation and
ligand oxidation were investigated for the generation of the reactive intermediate

\((\text{tBuClip}^\text{SO})\text{MoO}_2\) with harvestable stored oxidizing power.

The simplest scheme involves a double deprotonation of \((\text{tBuClipH}_2)\text{MoO}_2\)
followed by a 2e\(^-\) outer sphere oxidation (Scheme 3.3). \((\text{tBuClipH}_2)\text{MoO}_2\) was reacted
with two equivalents of KH in THF-\(d_8\) to give a mixture of products by NMR;

\(\text{K}_2[\text{tBuClipMoO}_2]\) is not formed cleanly.

Scheme 3.3 Synthetic strategies for generation of

\((\text{tBuClip}^\text{SO})\text{MoO}_2\).

Alternatively, preoxidizing the ligand to \(\text{tBuClipH}_2\) with oxidants such as

\(\text{PhI(OAc)}_2\), followed by reaction with a Mo(VI) dioxo precursor such as \(\text{MoO}_2(\text{OSiPh}_3)_2\)
could yield the desired intermediate. This reaction leads to an unoxidized mono-oxo
product, \((\text{tBuClipH})\text{MoO}(\text{OSiPh}_3)_2\). The same product is also generated from the reaction
of unoxidized ligand \(\text{tBuClipH}_2\) and \((\text{Ph}_3\text{SiO})_2\text{MoO}_2\) or independently from the reaction of

\((\text{tBuClipH}_2)\text{MoO}_2\) and triphenylsilanol.
3.2.2 Oxidation of \(^{1}\)BuClipMoO(Py) with \(N\)-methylmorpholine-\(N\)-oxide and regeneration upon oxygen atom transfer to dimethylphenyl phosphine

A third strategy for generation of the oxidized intermediate \(^{1}\)BuClip\(^{SC}\)MoO\(_2\) involves the oxidation of adducts \(^{1}\)BuClipMoO(L) by the stoichiometric addition of oxygen atom transfer reagents such as \(N\)-methylmorpholine-\(N\)-oxide. This was demonstrated by Jason A. Kopec.\(^{60}\) He found that the reaction proceeds via an NMO adduct \(^{1}\)BuClipMoO(NMO) which decays to a brown intermediate assigned as \(^{1}\)BuClip\(^{SC}\)MoO\(_2\). Rate constants for NMO deoxygenation were measured and the reaction was found to proceed via the first order decay of \(^{1}\)BuClipMoO(NMO). The oxidized species generated in situ can be deoxygenated by PMe\(_2\)Ph to produce the corresponding phosphine oxide and regenerate starting material \(^{1}\)BuClipMoO(py) in the presence of excess pyridine (Scheme 3.4, Figure 3.1).
Scheme 3.4 Cyclic nonclassical oxidation and atom transfer.
3.2.3 Characterization of oxidized intermediate (tBuClipSQ)MoO₂

In situ generation of (tBuClipSQ)MoO₂ leads to the disappearance of the sharp NMR signals of the (tBuClip)MoO(py) starting material (Figure 3.2). Three sets of signals representing tBuClipQ, free pyridine, and reduced N-methylmorpholine are apparent in
the spectrum. A broad set of three signals in a 1:1:3 ratio that gradually reduce in intensity over the course 4 h are tentatively assigned to an isomeric mixture of (tBuClipSQ)MoO₂. Mo(VI) dioxo complexes are invariably cis, but there are two possible isomers of the tBuClip ligand (Chapter 2). A broad NMR spectrum limits the ability to interpret its spectroscopic behavior, although the upfield peaks (δ 10.05, 5.12) of equal intensity most likely represent the biphenyl tBu groups of a cis-β isomer, whereas as the downfield peak (δ 1.58) represents the symmetric cis-α isomer.

![Figure 3.2. In situ ¹H NMR spectra (CDCl₃, 400 MHz) reaction of tBuClipMoO(py) with NMO. Bottom: t = 15 min; Middle: t = 1 h Top: t = 4 h. Key: □ = (tBuClipSQ)MoO₂; ○ = Clip,Q; ◊ = pyridine; ◈ = N-methylmorpholine; $ = std; # = solvent residual.](image)

The longevity of (tBuClipSQ)MoO₂ was determined by tracking the decrease in % yield of the normalized sum of integrals assigned to tBu groups of its isomers (Figure 3.3). The same stock solutions of NMO and (tBuClip)MoO(py) combined in situ and
separated into equal aliquots. The periodic addition of 2μL of PMe$_2$Ph to these individual aliquots generated generated O=PMe$_2$Ph in decreasing amounts as a function of time (Figure 3.3). A sharp doublet at δ 1.74 (J = 8 Hz) represents the methyl peaks of O=PMe$_2$Ph that is generated by the reduction of (tBuClip$^\text{SQ}$)MoO$_2$ to (tBuClipH$_2$)MoO$_2$, which quickly converts to (tBuClipH$_2$)MoO(py) in the presence of excess pyridine. The half-life of tBuClipMoO$_2$ is approximately 50 min.

Figure 3.3 Percent yield of (tBuClip$^\text{SQ}$)MoO$_2$ determined from (a) normalized sum of broad tBu integrals and (b) generation O=PMPMe$_2$Ph.

(tBuClip$^\text{SQ}$)MoO$_2$ was generated for analysis by mass spectrometry from the in situ reaction of (tBuClip)MoO(py) and 1 equiv. of NMO in CH$_2$Cl$_2$. A sample solution of (tBuClipH$_2$)MoO$_2$, 10$^{-3}$ M was generated as a control in the dry box and analyzed within 15 min. ESI-MS: (tBuClipH$_2$)MoO$_2$ (C$_{46}$H$_{66}$MoN$_2$O$_4$) = 815.4055 (M$^+$−OH, calcd 831.4056) (Figure 3.4).
Figure 3.4 ESI-MS of ion peaks from ($t$BuClip)MoO$_2$ (control).

Peaks corresponding to ($t$BuClip$^{SQ}$)MoO$_2$ and $t$BuClip and were detected from the 	extit{in situ} generated solution of $t$BuClipMoO(py) and NMO, with no discernable formation $t$BuClipH$_2$MoO$_2$ (Figure 3.5). ESI-MS: ($t$BuClip$^{SQ}$)MoO$_2$ ($C_{48}H_{64}MoN_{2}O_{4}$) = 831.4033 (M+H$^+$, calcd 831.4005), 814.4057 (M+H$^+$–H$_2$O); ($t$BuClip$^Q$) ($C_{48}H_{64}N_{2}O_{4}$) = 701.5042 (M+H$^+$, calcd 701.5041).
A series of solution cell IR spectra of (tBuClip_H2)MoO₂, (tBuClip)MoO(py), and (tBuClip^SQ)MoO₂ were collected in CH₂Cl₂, but the relevant M=O stretches overlapped with solvent peaks and the experiement proved inconclusive.

3.2.4 Kinetics of (tBuClip^SQ)MoO₂ reacting with PMe₂Ph

(tBuClip^SQ)MoO₂ was generated in situ from the reaction of (tBuClip)MoO(py) and NMO. Its reaction with dimethylphenylphosphine was monitored by UV-vis spectroscopy (Figure 3.6). The reaction proceeds cleanly (four isosbestic points) with the appearance of (tBuClip)MoO(PMe₂Ph), whose absorption spectrum is very similar to that of (tBuClip)MoO(py). This reaction follows a pseudo first order rate law in the presence of excess phosphine. The same reaction was carried out at various concentrations of phosphine to yield a first order dependence on phosphine concentration (Figure 3.6 inset. The second order rate constant, k = 11.6 ± .4 M⁻¹ s⁻¹.
3.2.5 Reaction of \((\text{tBuClip})\text{Mo}(3,5-\text{tBu}_2\text{Cat})\) with NMO

\((\text{tBuClip})\text{Mo}(3,5-\text{tBu}_2\text{Cat})\) upon addition of NMO gives a paramagnetic product within 15 min at ambient temperature, whose \(^1\text{H} \text{NMR}\) shows the same characteristic broad peaks in an approximately 1:1:3 ratio. This spectrum is consistent with the isomeric mixture of \((\text{tBuClip}^{\text{SQ}})\text{MoO}_2\). The quinone 3,5-\text{tBu}_2\text{Q} is also formed along with 2.5 equiv. of \(N\)-methylmorpholine. Quantitative conversion of \((\text{tBuClip})\text{Mo}(3,5-\text{tBu}_2\text{Cat})\) requires at least one equiv. of NMO. The second oxidizing equivalent leads to the generation of the same oxidized intermediate \((\text{tBuClip}^{\text{SQ}})\text{MoO}_2\).
Figure 3.7 Multi-wavelength kinetics of $({}^{t}BuClip)Mo(3,5-^{t}Bu_2Cat)$ ($5 \times 10^{-5}$ mol L$^{-1}$) with NMO ($5 \times 10^{-4}$ mol L$^{-1}$) (CH$_2$Cl$_2$, 21 °C). Inset: Plot of $k_{obs}$ vs [NMO], $2.5 \times 10^{-4}$ - $2 \times 10^{-3}$ M

When the reaction is monitored by UV-vis spectroscopy, a sharp isosbestic point is observed at 370 nm, which indicates a clean conversion to the product of oxidation, whose spectrum is consistent with that of $({}^{t}BuClip^{SO})MoO_2$ observed in the reaction of NMO with $({}^{t}BuClip)MoO(py)$. Multiwavelength spectra show no accumulation of a 7 coordinate adduct at these concentrations. The oxidation kinetics of $({}^{t}BuClip)Mo(3,5-^{t}Bu_2Cat)$ with NMO is a second order reaction that proceeds with a rate constant of $k = 16.7 \pm 0.26$ M$^{-1}$ s$^{-1}$ with a first order dependence on both reactants.
Scheme 3.5 Oxidation of '('BuClip)Mo(3,5-{'Bu2Cat}) with NMO.

The experimentally determined rate expression is $R = k[('BuClip)Mo(3,5-{'Bu2Cat})][NMO]$. Applying a steady state approximation to '('BuClip)Mo(3,5-{'Bu2Cat})(NMO) results in $k_{obs} = k_1 k_2 / (k_1 + k_2)$ assuming a low steady state concentration of the 7-coordinate NMO adduct. In Chapter 2, it was established that '('BuClip)Mo(3,5-{'Bu2Cat}) binds to pyridine with a rate $k_{assoc} = 8 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ and dissociates with a rate $k_{diss} = 25 \text{ s}^{-1}$. Given that $k_{obs} << k_{assoc}$, then $k_1 >> k_2$ and therefore N-O bond cleavage is rate determining. A 5 coordinate '('BuClip)MoO species would be highly Lewis acidic and immediately bind available donors and lead to further products of addition or oxidation.
3.2.6 Kinetics of (tBuClip)Mo(3,5-tBu_2Cat) reacting with O_2

Figure 3.8. Multi-wavelength kinetics of (tBuClip)Mo(tBuCat) (5 × 10^{-5} mol L^{-1}) with O_2 (0.2 atm)

The chief interest in (tBuClip)Mo(3,5-tBu_2Cat) is its reaction with O_2. The reaction of (tBuClip)Mo(3,5-tBu_2Cat) with ambient atmospheric oxygen proceeds with disappearance of its NMR signals and appearance of free 3,5-di-tert-butylquinone. The broad signals characteristic of (tBuClipSO)MoO_2 are not observed. The reaction rates for the oxygenation reaction were measured by UV-Vis spectroscopy and found to follow a second order rate expression R = k[(tBuClip)Mo(tBuCat)][O_2] being first order in molybdenum as well as oxygen. The reaction is facile in air with k_{obs} = 0.030(2) s^{-1} with t_{1/2} = 20 s. The reaction kinetics were measured at two different oxygen concentrations, ambient air (0.2 atm) and 1 atm of oxygen. The reaction proceeds approximately 5
times faster under a 1 atm pressure of oxygen as compared to air. Characterization attempts of metal-containing products of this reaction did not prove fruitful by crystallization or NMR. The products of oxygenation are disparate from those in the oxidation by NMO as judged by NMR and UV vis spectroscopy.

While the addition of NMO proceeds via a 7 coordinate adduct, the reaction with oxygen could proceed via an 8 coordinate adduct (tBuClip)Mo(3,5-tBu2Cat)(O2). Our lab has also synthesized an unprecedented 8 coordinate dioxo complex (DOPO²)₂MoO₂ that shows considerable reactivity.⁶⁹

![Figure 3.9 Single-wavelength kinetics plot of (tBuClip)Mo(3,5-tBu₂Cat) (5 × 10⁻⁵ mol L⁻¹) with O₂ (0.2 atm) in CH₂Cl₂, 22.4 °C.](image)
3.2.7 Reactions of oxidized intermediates with organic substrates

The compound (BuClip)MoO\textsubscript{2} reacts with dimethylphenylphosphine to give phosphine oxide. Oxidation of other substrates was also of interest. Reaction with olefins might form diolates, which could also be independently synthesized by reacting diols with (BuClipH\textsubscript{2})MoO\textsubscript{2} or the alkoxides (BuClip)Mo(OR)\textsubscript{2}. Diolate cleavage of (BuClip)Mo(OCR\textsubscript{2}CR\textsubscript{2}O) would be an interesting observation upon reaction with oxidants such as quinones or O\textsubscript{2}. 
TABLE 3.1

SUBSTRATE REACTIVITY STUDIES ON (tBuCLIP)MO COMPLEXES.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Substrate</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>(tBuClipH₂)MoO₂</td>
<td>Pinacol</td>
<td>?</td>
</tr>
<tr>
<td>(tBuClipH₂)MoO₂</td>
<td>Benzopinacol</td>
<td>?</td>
</tr>
<tr>
<td>(tBuClip)Mo(OiPr)₂</td>
<td>Mesohydrobenzoin</td>
<td>X</td>
</tr>
<tr>
<td>(tBuClip)Mo(OiPr)₂</td>
<td>Pinacol</td>
<td>X</td>
</tr>
<tr>
<td>(tBuClip)Mo(OMe)₂</td>
<td>Pinacol</td>
<td>X</td>
</tr>
<tr>
<td>(tBuClipSQ)MoO₂</td>
<td>Benzopinacol</td>
<td>X</td>
</tr>
<tr>
<td>(tBuClipSQ)MoO₂</td>
<td>4,4’-Dimethylstilbene</td>
<td>X</td>
</tr>
<tr>
<td>(tBuClipSQ)MoO₂</td>
<td>PPh₃</td>
<td>X</td>
</tr>
<tr>
<td>(tBuClipSQ)MoO₂</td>
<td>PMe₂Ph</td>
<td>O=PMe₂Ph + (tBuClip)MoO(PMe₂Ph)</td>
</tr>
<tr>
<td>(tBuClipH₂)MoO₂</td>
<td>Py</td>
<td>(tBuClip)MoO(py)¹⁰</td>
</tr>
<tr>
<td>(tBuClipH₂)MoO₂</td>
<td>3,5-Lut</td>
<td>(tBuClip)MoO(3,5-Lut)¹⁰</td>
</tr>
<tr>
<td>(tBuClipH₂)MoO₂</td>
<td>Ph₃SiOH</td>
<td>(tBuClip)MoO(OSiPh₃)</td>
</tr>
<tr>
<td>(tBuClipH₂)MoO₂</td>
<td>THF</td>
<td>(tBuClip)MoO(THF)</td>
</tr>
<tr>
<td>(tBuClipH₂)MoO₂</td>
<td>DMSO</td>
<td>(tBuClip)MoO(DMSO)</td>
</tr>
</tbody>
</table>

NR = no reaction; ? = reaction progresses without cleanly identifiable products by NMR. (tBuClipSQ)MoO₂ was generated in situ from the reaction of (tBuClip)MoO(py) and NMO, followed by substrate addition.

Unfortunately, reactions of (tBuClipH₂)MoO₂ or (tBuClip)Mo(OR)₂ with diols did not lead to the formation of diolates. In situ generated (tBuClipSQ)MoO₂ did not oxidize 4,4’-dimethylstilbene, benzopinacol, or even PPh₃. The reactivity of (tBuClipSQ)MoO₂ therefore appears to be quite low.
3.3 Experimental

Unless otherwise noted, all procedures were carried out in the drybox or on the vacuum line. Chloroform and methylene chloride were dried over 4 Å molecular sieves, followed by CaH$_2$. Benzene and toluene were dried over sodium and tetrahydrofuran (THF) over sodium benzophenone ketyl. Deuterated solvents were obtained from Cambridge Isotope Laboratories, dried using the same procedures as their protio analogues, and were stored in the dry box prior to use. $^7$BuClipH$_4$, ($^7$BuClipH$_2$)MoO$_2$, ($^7$BuClip)MoO(py), and ($^7$BuClip)Mo(3,5-$^7$Bu$_2$Cat) were prepared as described.$^{10,33}$ All other reagents were commercially available and used without further purification.$^1$H and $^{13}$C{$^1$H} NMR spectra were measured as CDCl$_3$ solutions on a Varian Inova 500 or Bruker Avance DPX 500/400 spectrometers and are reported in ppm downfield of TMS, with spectra referenced using the known chemical shifts of the solvent residuals. UV-Visible spectra were obtained as solutions in CH$_2$Cl$_2$ on Beckman DU-7500. Infrared spectra were recorded in a solution cell with KBr windows in CH$_2$Cl$_2$ on a Jasco FT/IR-6300 spectrometer. ESI mass spectra were obtained using a Bruker micrOTOF-II mass spectrometer, and peaks reported are the mass number of the most intense peak of isotope envelopes. Samples were injected as dichloromethane or acetonitrile solutions, preceded and followed by methanol. In all cases, the observed isotope patterns were in good agreement with calculated ones.

3.3.1 Reaction kinetics of ($^7$BuClip$^{5Q}$)MoO$_2$ with PMe$_2$Ph.

In a typical experiment, $^7$BuClipMoO(py) (4.7 mg) was dissolved in 5 mL of CH$_2$Cl$_2$ to generate a 10$^{-3}$ M stock solution. NMO (5.85 mg) was dissolved in 5 mL CH$_2$Cl$_2$ to
generate a $10^{-2}$ M stock solution. 200 µL $^t$BuClipMoO(py) and 18 µL NMO (0.9 equiv) were added sequentially via syringe to 2mL CH$_2$Cl$_2$ in a 1.0 cm air tight quartz cuvette to yield $10^{-4}$ M ($^t$BuClip$^{SQ}$)MoO$_2$. The initial spectrum was acquired to confirm its UV-Vis signature and PMe$_2$Ph (20 µL, $10^{-1}$ M) was injected, leading to a resultant $10^{-3}$ M phosphine solution. The reaction progress was monitored by UV-vis spectroscopy (300-800 nm) for 20 min at 20 s intervals. Single wavelength kinetics were measured at 560 nm at 21.0 °C and $5 \times 10^{-5}$ M ($^t$BuClip)MoO$_2$. The amount of PMe$_2$Ph injected was varied to give a $10^{-3} - 4 \times 10^{-3}$ M phosphine solution. The cuvette was placed in a multicell UV-vis cell holder with a recirculating bath and reaction kinetics were monitored for 3-12 min at 3-30 s intervals.

3.3.2 Reaction kinetics of ($^t$BuClip)Mo(3,5-$^t$Bu$_2$Cat) with NMO.

A multi-wavelength kinetics measurement was made in a 1.0 cm air tight quartz cuvette by charging it with $5 \times 10^{-5}$ M ($^t$BuClip)Mo(3,5-$^t$Bu$_2$Cat) in methylene chloride. The initial spectrum was acquired to confirm its UV-Vis signature and 10 equiv NMO was injected to give a $5 \times 10^{-4}$ M NMO solution. The reaction progress was monitored by UV-vis spectroscopy (300-800 nm) for 45 min at 30 s intervals. Single wavelength kinetics were measured at 490 and 780 nm at 21.3 °C and $5 \times 10^{-5}$ M ($^t$BuClip)Mo(3,5-$^t$Bu$_2$Cat). The amount of NMO injected was varied in different sets of experimental runs to furnish $2.5 \times 10^{-4} - 2 \times 10^{-3}$ M NMO concentrations. The cuvette was placed in a multi-cell holder and reaction kinetics were monitored for 3-10 min at 3-20 s intervals.
3.3.3 Reactions of (tBuClip)Mo(3,5-tBu2Cat) with O2.

In a representative NMR reaction, 5-10 mg (tBuClip)Mo(tBuCat) and 1-2 mg of a standard (dimethylterephthalate) were dissolved in CDCl₃ in the dry box and transferred to a J. Young NMR tube with a Teflon valve. The tube was connected to a high vacuum line and the nitrogen evacuated with two freeze pump thaw cycles. Oxygen was then introduced into the solution via the vacuum line and the tube was shaken vigorously to allow for sufficient mixing.

In the UV-Vis kinetics run of (tBuClip)Mo(3,5-tBu2Cat) under 1 atm of oxygen, a 1.0 cm quartz cuvette fitted with a septum cap was sealed with 2.5 mL CH₂Cl₂ under N₂. The solution was oxygenated by bubbling oxygen through the cuvette for 5 min with a needle without over pressurizing it by venting through another needle. The reaction was initiated by injecting a stock solution to give 5 × 10⁻⁵ M (tBuClip)Mo(3,5-tBuCat). Spectra were recorded for 1 min at half second intervals. For the kinetics run under atmospheric concentrations of oxygen (0.2 atm), ambient CH₂Cl₂ was utilized without any modification and spectra were recorded for 5 min at 3 s intervals.
CHAPTER 4:
MIGRATIONS OF ALKYL AND ARYL GROUPS FROM SILICON TO NITROGEN IN SILYLATED ARYLOXYIMINOQUINONES

4.1 Introduction

4.1.1 The redox active ONO ligand.

The previous three chapters encompassed the chemistry of bidentate catecholates and tetradeative bis amidophenoxides engendered by their redox activity. A similar tridentate ligand, 3,5-di-tert-butyl-1,2-quinone-(3,5-di-tert-butyl-2-hydroxy-1-phenyl)imine), abbreviated as ONO, is also of interest because of its ability to adopt multiple oxidation states. This ligand centered redox activity can be combined with substrate reduction or oxidation at a metal center. A recent report from our group has outlined a net nonclassical oxygen atom transfer, where a two-electron reduction of the [ONO\textsuperscript{O}]\textsuperscript{-} ligand is accompanied by the cleavage of a rhenium-oxo bond and an oxygen atom transfer to a phosphine.\textsuperscript{61} The redox activity of the ONO ligand originates from its highest energy \(\pi\) orbital (\(B_2\) symmetry in the \(C_{2v}\) point group). This \(5b_2\) orbital is raised in energy due to antibonding interactions of in phase heteroatom \(p\) orbitals with filled \(\pi_b\) orbitals of the benzene rings (Figure 4.1).\textsuperscript{62} The ONO ligand has three commonly accessible oxidation states, analogous to catecholates and amidophenoxides, that can
be explained by population of the $5b_2$ orbital. When this orbital is fully occupied, the
ONO ligand is trianionic and looks like a catecholate $[\text{ONO}^{\text{Cat}}]^{3-}$; a singly occupied $5b_2$
orbital corresponds to a one-electron oxidized dianionic iminosemiquinone $[\text{ONO}^{\text{SQ}}]^{2-}$; and an empty $5b_2$ orbital is a two-electron oxidized monoanionic iminoquinone $[\text{ONO}^\text{Q}]^-$.  

![5b_2 Redox Active Orbital](image)

\[ \begin{align*}
[\text{ONO}^{\text{Cat}}]^{3-} & \xrightarrow{\text{e}^-} [\text{ONO}^{\text{SQ}}]^{2-} & \xrightarrow{\text{e}^-} [\text{ONO}^\text{Q}]^- 
\end{align*} \]

Figure 4.1 The ONO ligand’s redox-active orbital and its common oxidation states.

4.1.2 Metal Complexes of the ONO ligand.

Neutral homoleptic complexes of the form $\text{M(ONO)}_2$, where $\text{M} = \text{Mg, Fe, Cu, Ni, Zn, Cd; } \text{Al, Ga, Ca, Ba; } \text{Mn, Co; Ti, V, Ge, Sn; } \text{and Pb}$ are prepared by self-assembly from ammonia and 3,5-di-tert-butylcatechol or 3,5-di-tert-butyl-1,2-benzoquinone. These complexes do not show notable reactivity towards substrate oxidation and reduction, though tungsten and molybdenum homologues investigated by our group reduce amine-$N$-oxides. Early transition metals in bis-ONO complexes such as titanium and vanadium are in their highest oxidation states with a $d^0$ configuration, whereas late transition metals such as copper and zinc adopt divalent oxidation states. Our group has recently reported the preparation of group 6 $\text{M(ONO)}_2$ ($\text{M} = \text{Cr, Mo, W}$) and group 8 $\text{Ru(ONO)}_2$ and $\text{Os(ONO)}_2$ complexes from the reaction of
divalent metal halide precursors with Pb(NO\textsubscript{2})\textsubscript{2}.\textsuperscript{123} Quantitative analysis of the intraligand bond lengths of ONO complexes also furnished a metrical oxidation state (MOS) calculator that can be used to compare structure and bonding in these ONO complexes.

I was originally interested in preparing (2-trialkylsiloxy-3,5-di-tert-butylphenyl)imino-4,6-di-tert-butyl-1,2-benzoquinone as a useful synthetic precursor to install the ONO ligand onto metal centers by reaction with metal halides. Monoligated complexes have been prepared by self-assembly\textsuperscript{70} but with synthetic difficulty. A silylated ligand R\textsubscript{3}Si(NO\textsubscript{2}) would supplement the available ONO sources such as the fully reduced H\textsubscript{3}[ONO\textsubscript{Cat}]\textsuperscript{71} or the oxidized H[ONO\textsubscript{Q}]\textsuperscript{72} or K[ONO\textsubscript{Q}].\textsuperscript{73}

4.1.3 ONO transmetalation with Sn or reduction by R group migration to nitrogen.

In a previous study of tin halides with the ONO ligand, it was reported that butyltrichlorostannane undergoes transmetalation with Zn(NO\textsubscript{2})\textsubscript{2} to give octahedral (ONO\textsubscript{O})SnCl\textsubscript{2}Bu. Mono- and diarylstannanes PhSnCl\textsubscript{2} and Ph\textsubscript{2}SnCl\textsubscript{2} were reported to both give the transmetalation product, (ONO\textsubscript{O})SnCl\textsubscript{2}Ph. In contrast, dialkyldichlorostannanes with Zn(NO\textsubscript{2})\textsubscript{2} resulted in transfer of one alkyl group from tin to nitrogen and formation of tin complexes of the reduced ligand Cl(R)Sn[ON[R]O].\textsuperscript{74}
Figure 4.2. Reaction of Zn(ONO)$^2_2$ with alkyl or aryl-chlorosilanes.

<table>
<thead>
<tr>
<th>R</th>
<th>X</th>
<th>R</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>nBu</td>
<td>Cl</td>
</tr>
<tr>
<td>Ph</td>
<td>Cl</td>
<td>Cl</td>
<td>CH$_3$ CH$_3$</td>
</tr>
</tbody>
</table>

0.5 Zn(ONO)$^2_2$ + R(X)SnCl$_2$ → 0.5 ZnCl$_2$  

R$_3$Si(ONO)$^2_2$ → R$_3$Sn(ON[R]O)

Alkyl- and aryltin compounds readily undergo C-Sn bond cleavage and are used in Stille couplings as sources of carbon nucleophiles.$^{75}$ On the other hand, silicon-carbon bonds are non-polar and strong, with silicon-carbon bond dissociation energies over 85 kcal/mol,$^{76}$ and are thus inert. This greater lability of silicon-heteroatom bonds has led to widespread use oftrialkylsilyl groups as protecting groups in organic chemistry, where R$_3$Si groups can be installed and removed leaving the substituents unchanged.$^{77}$ Given the much greater tendency of tin than silicon to donate its alkyl group, and the fact that migration in (ONO)-stannanes was not universal, silylation was not expected to be accompanied by migration.

In fact, the attempted silylation of the (ONO)$^2_2$- group with methyl- or phenylsilyl chlorides universally results in migration of alkyl or aryl groups from silicon to nitrogen.$^{78}$ The analogous migration of phenyl groups from tin to nitrogen is also described.
4.2 Results and Discussion

4.2.1 Silylation of Pb(ONO\textsubscript{Q})\textsubscript{2} to form products of silicon-to-nitrogen migration.

Silylation of the oxidized ligand in Pb(ONO\textsubscript{Q})\textsubscript{2} with trimethylchlorosilane in chlorinated solvents leads to precipitation of lead chloride and formation of the diamagnetic pentacoordinate silicon product, Me\textsubscript{2}Si(ON[Me]O) (Figure 4.2) in which the ONO ligand has been modified by migration of a methyl group from silicon to nitrogen. Silylation with other silanes result in in pentacoordinate products with corresponding substituents. These silylations proceed more slowly in benzene solution and in situ NMR monitoring indicates that the migrated products are usually formed in good to excellent yields, but isolated yields are modest due to solubility losses.

![Figure 4.3 Reaction of Pb(ONO\textsubscript{Q})\textsubscript{2} with trimethylchlorosilane.](image)

Although stannylated compounds of the ONO ligand have been prepared by reaction of Zn(ONO\textsubscript{Q})\textsubscript{2} with chlorostannanes,\textsuperscript{74} the Pb(ONO\textsubscript{Q})\textsubscript{2} complex is a more efficient source of [ONO\textsubscript{Q}]\textsuperscript{-}. The lead complex reacts completely with PhMe\textsubscript{2}SiCl in CDCl\textsubscript{3} in about 4 h at room temperature, whereas silylation of Zn(ONO\textsubscript{Q})\textsubscript{2} is only about 10% complete over 20 h under the same conditions. Pb(ONO\textsubscript{Q})\textsubscript{2} is prepared by self-assembly
from PbF₂, 3,5-di-tert-butylcatechol, 3,5-di-tert-butyl-1,2-benzoquinone, and aqueous ammonia in a procedure described by McGarvey,⁶⁷ which is modified by the extraction of the crude product into chloroform to remove inorganic lead salts that coprecipitate from ethanol. The reaction rates of silylation and net migration correlate with the reactivity of the chlorosilanes as silylating agents. Reactions of phenyldimethylsilyl chloride take several hours to go to completion, trimethylsilyl chloride and phenylmethyldichlorosilane are complete in less than an hour, while dimethyldichlorosilane and methyltrichlorosilane react immediately at room temperature. The least reactive chlorosilane, triphenylsilyl chloride, requires several days of heating at 70 °C to react completely with Pb(ONO₂)₂. The reactions proceed equally well in ambient light or in the dark and are therefore thermal rather than photochemical. Multinuclear NMR spectroscopy provides strong support for the formulation of the products as containing five-coordinate silicon with a reduced, N-alkylated tridentate ON[R]O ligand. The ¹H and ¹³C NMR spectra of the product of reaction with Me₃SiCl show three distinct chemical shifts for the methyl groups, with two methyl groups showing upfield shifts characteristic of Si-CH₃ groups (¹H δ 0.34, 0.46, ¹³C δ 0.71, 2.81 ppm), and the third methyl group resonating more downfield (¹H δ 2.98, ¹³C δ 45.62 ppm), consistent with its formulation as an N-CH₃ group. The reduction in the ligand can be assessed by the chemical shift of the aromatic carbon attached to oxygen⁶⁴ which is at δ 148.32 ppm in Me₂Si(ON[Me]O) and far upfield of δ 177.36 observed for the quinonoid ligand in Pb(ONO₂)₂.
The observation of two distinct Si-CH₃ resonances in Me₂Si(ON(CH₃)O) is strongly suggestive of a five-coordinate silane with inequivalent axial and equatorial methyl groups. The ²⁹Si resonance at δ −16.11 ppm is 10 ppm upfield of the four-coordinate analogue Me₂Si(OPh)₂ (δ −6.8 ppm), and suggests the retention of the N-Si interaction in solution. This 10 ppm upfield shift is typical of compounds with sp³-hybridized nitrogen donors. There is crystallographic and NMR evidence for the presence of a transannular N-Si interaction in dialkylsilyl diethanolamine complexes, Me₂Si(OCH₂CH₂N[Me]CH₂CH₂O) where ²⁹Si resonates at δ −10.1. In contrast, the five-coordinate silane Me₂Si(2,6-[OCAr₂]₂C₆H₃N) with an sp²-hybridized nitrogen donor atom resonates at δ −57 ppm. The larger negative shifts for sp² donors compared to sp³ corresponds to the shorter Si–N distances; correlation between ²⁹Si chemical shift and the silicon-nitrogen distance in silatranes has been observed.

When both phenyl and methyl groups are present in the silane (PhMe₂SiCl, PhMeSiCl₂), only methyl migration is observed on reaction with Pb(ONO)₂, as judged by the appearance of the characteristic NCH₃ signals in the ¹H NMR spectrum. In situ monitoring of reactions shows no signs of products in which phenyl migration has taken place. If, however, silanes containing only phenyl groups are used (Ph₃SiCl, Ph₂SiCl₂), then migration of phenyl groups is observed. Ph₃SiCl reacts with Pb(ONO)₂ to give Ph₂Si(ON[Ph]O), in which three different phenyl environments (NPh, equatorial SiPh, and axial SiPh) are observed by ¹H and ¹³C NMR spectroscopy. Exclusive observation of methyl in preference to phenyl migration is unusual because only cases of exclusive or moderate preference of phenyl over methyl migration are known. There are also
known instances of a moderate preference of methyl over phenyl migration, but there are no instances of exclusive thermal 1,2-methyl migrations in competition with phenyl migration. Selective photochemical 1,3-migration of alkyl groups from silicon in preference to phenyl groups has been reported, although photochemical migration of phenyl groups is observed if no alkyl groups are present.

4.2.2 Structures and stereochemical preferences of (X)(Y)Si(ON[R]O).

The solid-state structures of six of the products of silylation and migration (Table 4.1, Figure 2) were determined by single crystal X-ray diffraction. The structures confirm the connectivity and geometry inferred from spectroscopic data. While the unmodified ONO ligand is rigid and adopts a mer geometry in its complexes, alkylation at nitrogen forces the ligand into a fac-type geometry, with O–Si–O angles in the range of 115–125°, close to the 120° expected for an ideal trigonal bipyramid. Silicon has two aryloxide oxygens in equatorial positions and the methylated or phenylated amine nitrogen occupying one of the axial positions ($d(Si-N) = 2.3$-$2.9$ Å). If present, chlorine occupies
the other axial position (X) in preference to methyl or phenyl, which occupy the
remaining equatorial position (Y = Me or Ph). The same basic structure was observed for
the tin analogue Cl(Bu)Sn(ON(Bu)O) formed from reaction of Bu₂SnCl₂ with Zn(NO₃)₂.⁷⁰

Figure 4.5 Thermal ellipsoid plot of Me₂Si(ON[Me]O). Hydrogen
atoms are omitted for clarity. Only one of the two
crystallographically inequivalent molecules is depicted.
Figure 4.6 Thermal ellipsoid plot of Cl(Me)Si(ON[Me]O)•2 C₆H₆.
Hydrogen atoms and solvent molecules are omitted for clarity.
Figure 4.7 Thermal ellipsoid plot of Cl(Ph)Si(ON[Me]O). Hydrogen atoms and minor orientations of disordered tert-butyl groups are omitted for clarity.
Figure 4.8 Thermal ellipsoid plot of Cl(Ph)Si(ON[Ph])O. Hydrogen atoms and minor orientation of disordered tert-butyl group are omitted for clarity.
Figure 4.9 Thermal ellipsoid plot of Me(Ph)Si(ON[Me]O).
Hydrogen atoms and solvent molecules are omitted for clarity.
Figure 4.10 Thermal ellipsoid plot of $\text{Ph}_2\text{Si(ON[Ph]O)}$. Hydrogen atoms are omitted for clarity. Only one of the two crystallographically inequivalent molecules is depicted.
The major difference between the structures is how tightly the amine nitrogen is bonded to silicon. In compounds with ON[Me]O chelates, the silicon-nitrogen distances increase with decreasing trans group influences. Bond distances increase in the order of \(\text{trans-Cl (Si-N = 2.302(2), 2.3042(16) \text{ Å}) < trans-CH}_3 \) (Si-N = 2.605(2), 2.617(2), 2.5393(11) Å) \(\approx \text{trans-\(\mu\)-O (Si-N = 2.585(2), 2.675(2) \text{ Å, vide infra})}.\) Silicon-nitrogen binding in \(\text{Ph}_2\text{Si(ON[Ph]O)}\) is even weaker (Si-N = 2.7516(12), 2.9184(13) Å for the two crystallographically independent molecules), because of the lowered Lewis basicity of nitrogen on substituting methyl for phenyl. The variation in bond distances between the same bonds in the crystallographically inequivalent molecules of \(\text{Ph}_2\text{Si(ON[Ph]O)}\) and the chemically equivalent but crystallographically distinct silicons in \((\text{ON}[\text{Me}]\text{O})\text{Si}(\text{Me})(\mu\text{-O})\text{Si}(\text{Me})(\text{ON}[\text{Me}]\text{O}))\) suggests weak silicon-nitrogen interactions with a shallow potential energy surface. The much shorter distance trans to Cl indicates strong donation of the amine to the Si-Cl \(\sigma^*\) orbital. Invariant Si-N bond distances in \(\text{Cl}(\text{Me})\text{Si(ON[Me]O)}\) and \(\text{Cl}(\text{Ph})\text{Si(ON[Me]O)}\) reflect the strength of this interaction. The degree of silicon-nitrogen interaction is also reflected in the degree of pyramidalization at nitrogen, where the chloro compounds show strongly pyramidalized nitrogen atoms (sum of C-N-C angles = 335.4°, 336.7°) while \(\text{Ph}_2\text{Si(ON[Ph]O)}\) shows a nearly planar nitrogen atom (sum of C-N-C angles = 355.3°, 347.9°).

The silicon-nitrogen distances are longer than those observed for analogous silatranes with dative N\(\rightarrow\)Si interactions. Silatranes with apical chlorides, \(\text{N}[\text{CH}_2\text{CH}_2\text{O}]_3\text{SiCl (Si-N = 2.026(10) \text{ Å})}^{89}\) and \(\text{N}[\text{CH}_2\text{C}_6\text{H}_2-3\text{-tBu}_2-5\text{-Me}-2\text{-O}]_3\text{SiCl (Si-N = 2.046(2) \text{ Å})}^{90}\) show Si-N distances over 0.25 Å shorter than those observed in
Cl(R)Si(ON[Me]O). Silatranes are tricyclic rather than bicyclic, but even bicyclic
diethanolamine derivatives can show significantly shorter Si-N distances;
F(Ph)Si([OCH₂CH₂]₂NCH₃) has \( d(\text{Si-N}) = 2.1751(7) \text{ Å} \), \( 91 \) 0.13 Å shorter than the
corresponding distance in Cl(Ph)Si(ON[Me]O). The greater basicity of the trialkyl amine
donor in the diethanolamine ligand is balanced by torsional strain suffered in the boat-
boat conformation of the saturated dioxasilocane ring needed for strong nitrogen-to-
silicon donation. \( N \)-aryldiethanolamines have decreased nitrogen basicity and adopt a
crown-crown conformation with scission of the Si-N bond, \( d(\text{Si-N}) > 3.0 \text{ Å} \). \( 89,92 \)

In compounds Cl(R)Si(ON[Me]O), the chlorine is apical in the crystallographically
classified product. This is in agreement with the well-known preference for more
electronegative groups to preferentially adopt the apical positions in trigonal
bipyramidal compounds of the main group elements due to the greater ionic character
of the apical bonds. \( 93 \) The chloro compounds are also observed in solution to form only
one stereoisomer at equilibrium. In the case of Cl(Ph)Si(ON[Me]O), NMR data support
the stereochemical assignment of an equatorial phenyl located syn to the upfield N-CH₃
resonance (\( \delta 2.23 \)), where the methyl group is in the shielding cone of the equatorial
phenyl group. In comparison, migrated methyl groups resonate at \( \delta 2.98 \) and \( \delta 3.02 \) in
Me₄Si- and Cl(Me)Si(ON[Me]O), respectively, where no Si-Ph group is present. A similar
upfield shift of the NCH₃ resonance has been observed in X(Ph)Si([OCH₂CH₂]₂NCH₃) with
equatorial phenyl groups at low temperature. \( 94 \)

In the solid state, Me(Ph)Si(ON[Me]O) has an apical methyl group and an
equatorial phenyl group. In solution, this compound shows two stereoisomers at
equilibrium in a 8.7:1 ratio. The major isomer in solution has an equatorial phenyl, based on the upfield shift of its N-methyl group (δ NCH₃ 1.99 major, δ 3.04 minor), and is the same isomer characterized crystallographically. The apical preference for the methyl group is unexpected because of the greater electronegativity of \( sp^2 \) carbons over \( sp^3 \) carbons, but literature comparisons suggest that these preferences are modest and subject to subtle aspects of ligand structure. For example, in the solid state, (CH₂=CHCH₂)(Ph)Si(OCH₂CH₂)₂N(CH₃)₃ shows a 1.5:1 preference (at −90 °C) for an axial methyl group.\(^{94}\)

The two isomers of Me(Ph)Si(ON[Me]O) equilibrate within 15 minutes after dissolution of the solid in CDCl₃. This equilibration is not fast on the NMR timescale at room temperature, however, as the two isomers give separate sharp signals; similarly, the two SiMe resonances in the \(^1\)H and \(^{13}\)C NMR spectra of Me₂Si(ON[Me]O) are separate and sharp as well. The mechanism of exchange between axial and equatorial substituents is accomplished by scission of the Si-N bond followed by an inversion of the boat-boat configuration of the 8 membered ring. The mechanism is discussed in detail in the following chapter.
### Table 4.1

**BOND DISTANCES (Å) AND ANGLES (°) IN CHLORINATED FIVE-COORDINATE PRODUCTS**

\[(X)\text{Y} \text{Si(ON}\text{Z})\text{O}\]

<table>
<thead>
<tr>
<th></th>
<th>Cl(Me)Si(ON[Me]O)</th>
<th>Cl(Ph)Si(ON[Ph]O)</th>
<th>Cl(Ph)Si(ON[Me]O)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(X = \text{Cl})</td>
<td>(X = \text{Cl})</td>
<td>(X = \text{Cl})</td>
</tr>
<tr>
<td></td>
<td>(Y = \text{C3})</td>
<td>(Y = \text{C41})</td>
<td>(Y = \text{C31})</td>
</tr>
<tr>
<td></td>
<td>(Z = \text{C1})</td>
<td>(Z = \text{C31})</td>
<td>(Z = \text{C1})</td>
</tr>
<tr>
<td>Si-O1</td>
<td>1.651(2)</td>
<td>1.6318(10)</td>
<td>1.6467(13)</td>
</tr>
<tr>
<td>Si-O2</td>
<td>1.642(2)</td>
<td>1.6303(10)</td>
<td>1.6520(13)</td>
</tr>
<tr>
<td>Si-X</td>
<td>2.1442(10)</td>
<td>2.0554(5)</td>
<td>2.1176(7)</td>
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<tr>
<td>Si-Y</td>
<td>1.856(3)</td>
<td>1.8424(14)</td>
<td>1.847(2)</td>
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<tr>
<td>Si-N</td>
<td>2.302(2)</td>
<td>2.7146(12)</td>
<td>2.3043(16)</td>
</tr>
<tr>
<td>N-C11</td>
<td>1.455(3)</td>
<td>1.4506(17)</td>
<td>1.460(2)</td>
</tr>
<tr>
<td>N-C21</td>
<td>1.463(3)</td>
<td>1.4456(17)</td>
<td>1.464(2)</td>
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<tr>
<td>N-Z</td>
<td>1.486(3)</td>
<td>1.4277(17)</td>
<td>1.485(2)</td>
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<tr>
<td>O1-Si-O2</td>
<td>117.67(11)</td>
<td>114.35(5)</td>
<td>124.64(7)</td>
</tr>
<tr>
<td>O1-Si-X</td>
<td>93.52(7)</td>
<td>101.13(4)</td>
<td>93.98(5)</td>
</tr>
<tr>
<td>O1-Si-Y</td>
<td>119.25(13)</td>
<td>116.68(6)</td>
<td>115.26(8)</td>
</tr>
<tr>
<td>X-Si-Y</td>
<td>120.65(14)</td>
<td>107.93(5)</td>
<td>117.24(8)</td>
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<tr>
<td>O2-Si-X</td>
<td>91.83(7)</td>
<td>99.68(4)</td>
<td>92.78(5)</td>
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<tr>
<td>O2-Si-Y</td>
<td>100.10(11)</td>
<td>114.31(6)</td>
<td>100.55(7)</td>
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<tr>
<td>O1-Si-N</td>
<td>81.82(9)</td>
<td>73.03(4)</td>
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<tr>
<td>O2-Si-N</td>
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<td>80.80(6)</td>
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<tr>
<td>X-Si-N</td>
<td>169.24(6)</td>
<td>167.21(3)</td>
<td>167.31(5)</td>
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<td>Y-Si-N</td>
<td>90.63(12)</td>
<td>84.83(5)</td>
<td>92.14(7)</td>
</tr>
<tr>
<td>C11-N-C21</td>
<td>112.37(19)</td>
<td>112.06(10)</td>
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<tr>
<td>C11-N-Z</td>
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<td>117.54(11)</td>
<td>112.17(14)</td>
</tr>
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<td>C21-N-Z</td>
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<td>118.07(11)</td>
<td>110.00(14)</td>
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<td>C11-N-Si</td>
<td>100.98(15)</td>
<td>93.40(7)</td>
<td>102.01(11)</td>
</tr>
<tr>
<td>C21-N-Si</td>
<td>101.52(15)</td>
<td>95.03(8)</td>
<td>110.00(14)</td>
</tr>
<tr>
<td>Z-N-Si</td>
<td>118.26(16)</td>
<td>115.84(8)</td>
<td>116.49(12)</td>
</tr>
<tr>
<td>C12-O1-Si</td>
<td>123.67(17)</td>
<td>128.62(9)</td>
<td>125.16(12)</td>
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<tr>
<td>C22-O2-Si</td>
<td>124.08(17)</td>
<td>132.83(9)</td>
<td>124.64(11)</td>
</tr>
</tbody>
</table>

**NOTE:** \(X\) = axial substituent, \(Y\) = equatorial substituent, \(Z\) = migrated group
## TABLE 4.2
### CRYSTAL DATA FOR CHLORINATED FIVE-COORDINATE PRODUCTS

<table>
<thead>
<tr>
<th>Identification code</th>
<th>Cl(Ph)Si(ON[Ph]O)</th>
<th>Cl(Me)Si(ON[Me]O)</th>
<th>Cl(Ph)Si(ON[Me]O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{40}$H$</em>{50}$ClN$_2$O$_2$Si</td>
<td>C$<em>{42}$H$</em>{58}$ClNO$_2$Si</td>
<td>C$<em>{35}$H$</em>{48}$ClNO$_2$Si</td>
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<tr>
<td>Formula weight</td>
<td>640.35</td>
<td>672.43</td>
<td>289.14</td>
</tr>
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<td>T/K</td>
<td>120(2) K</td>
<td>121(2) K</td>
<td>150(2) K</td>
</tr>
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<td>λ/Å</td>
<td>0.71073 Å</td>
<td>0.71073 Å</td>
<td>0.71073 Å</td>
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<tr>
<td>Crystal system</td>
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<td>Orthorhombic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
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<td>P2(1)2(1)2(1)</td>
<td>P-1</td>
</tr>
<tr>
<td>a (Å)</td>
<td>37.394(2) Å</td>
<td>9.7339(6)</td>
<td>10.7842(10)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>10.6766(6) Å</td>
<td>17.7599(11)</td>
<td>10.7966(9)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>18.4173(10) Å</td>
<td>23.0354(14)</td>
<td>14.8554(13)</td>
</tr>
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<td>α (deg)</td>
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<td>74.145(2)</td>
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<td>β (deg)</td>
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<td>79.789(2)</td>
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<td>γ (deg)</td>
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<td>90</td>
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<td>1608.4(2) Å$^3$</td>
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<td>Z</td>
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<td>1.122 g.cm$^{-3}$</td>
<td>1.194 g.cm$^{-3}$</td>
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<td>Crystal size</td>
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<td>20537</td>
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<tr>
<td>Independent reflections</td>
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<td>7025</td>
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<td>$R_{int}$</td>
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<td>0.0582</td>
<td>0.0387</td>
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<tr>
<td>$R_1$, $wR_2$ [I &gt; 2σ(I)]</td>
<td>R$_1$ = 0.0342, wR$_2$ = 0.0938</td>
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<td>Goodness-of-fit on $F^2$</td>
<td>1.051</td>
<td>0.999</td>
<td>1.009</td>
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TABLE 4.3

BOND DISTANCES (Å) AND ANGLES (°) IN UNCHLORINATED HYDROCARBYL FIVE-COORDINATE PRODUCTS (X)(Y)SI(ON[Z]O)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Me₂Si(ON[Me]O) (Molecule 1)a</th>
<th>MePhSi(ON[Me]O)</th>
<th>Ph₂Si(ON[Ph]O) (Molecule 1)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-O1</td>
<td>1.6599(15)</td>
<td>1.6539(9)</td>
<td>1.6454(10)</td>
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<tr>
<td>Si-O2</td>
<td>1.6541(17)</td>
<td>1.6577(9)</td>
<td>1.6515(10)</td>
</tr>
<tr>
<td>Si-X</td>
<td>1.848(3)</td>
<td>1.8533(14)</td>
<td>1.8622(14)</td>
</tr>
<tr>
<td>Si-Y</td>
<td>1.843(3)</td>
<td>1.8563(13)</td>
<td>1.8519(15)</td>
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<tr>
<td>Si-N</td>
<td>2.605(2)</td>
<td>2.5393(11)</td>
<td>2.9184(13)</td>
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<tr>
<td>N-C11</td>
<td>1.449(3)</td>
<td>1.4472(14)</td>
<td>1.4272(17)</td>
</tr>
<tr>
<td>N-C21</td>
<td>1.442(3)</td>
<td>1.4514(15)</td>
<td>1.4395(18)</td>
</tr>
<tr>
<td>N-Z</td>
<td>1.475(3)</td>
<td>1.4773(15)</td>
<td>1.4163(18)</td>
</tr>
<tr>
<td>O1-Si-O2</td>
<td>115.32(8)</td>
<td>120.24(5)</td>
<td>115.44(5)</td>
</tr>
<tr>
<td>O1-Si-X</td>
<td>100.20(10)</td>
<td>99.65(6)</td>
<td>101.10(6)</td>
</tr>
<tr>
<td>O1-Si-Y</td>
<td>114.62(12)</td>
<td>113.40(5)</td>
<td>116.36(6)</td>
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<tr>
<td>X-Si-Y</td>
<td>107.59(13)</td>
<td>115.47(5)</td>
<td>107.63(6)</td>
</tr>
<tr>
<td>O2-Si-X</td>
<td>99.41(10)</td>
<td>98.21(6)</td>
<td>105.22(6)</td>
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<tr>
<td>O2-Si-Y</td>
<td>116.56(11)</td>
<td>105.73(6)</td>
<td>110.31(6)</td>
</tr>
<tr>
<td>O1-Si-N</td>
<td>74.50(7)</td>
<td>75.84(4)</td>
<td>66.79(4)</td>
</tr>
<tr>
<td>O2-Si-N</td>
<td>73.31(7)</td>
<td>75.68(4)</td>
<td>66.50(4)</td>
</tr>
<tr>
<td>X-Si-N</td>
<td>167.29(10)</td>
<td>168.53(5)</td>
<td>157.21(5)</td>
</tr>
<tr>
<td>Y-Si-N</td>
<td>85.08(10)</td>
<td>85.72(4)</td>
<td>92.48(5)</td>
</tr>
<tr>
<td>C11-N-C21</td>
<td>115.26(16)</td>
<td>115.03(9)</td>
<td>116.88(11)</td>
</tr>
<tr>
<td>C11-N-Z</td>
<td>111.07(17)</td>
<td>113.24(9)</td>
<td>119.84(11)</td>
</tr>
<tr>
<td>C21-N-Z</td>
<td>113.74(17)</td>
<td>111.42(9)</td>
<td>118.61(11)</td>
</tr>
<tr>
<td>C11-N-Si</td>
<td>95.76(12)</td>
<td>99.26(7)</td>
<td>93.10(8)</td>
</tr>
<tr>
<td>C21-N-Si</td>
<td>98.41(12)</td>
<td>98.42(7)</td>
<td>88.06(8)</td>
</tr>
<tr>
<td>Z-N-Si</td>
<td>121.21(15)</td>
<td>118.33(7)</td>
<td>109.97(8)</td>
</tr>
<tr>
<td>C12-O1-Si</td>
<td>128.66(13)</td>
<td>130.50(8)</td>
<td>136.66(9)</td>
</tr>
<tr>
<td>C22-O2-Si</td>
<td>130.71(14)</td>
<td>129.82(7)</td>
<td>128.65(9)</td>
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</table>
4.2.3 Silylation of Pb(ONO\textsuperscript{O})\textsubscript{2} to form unalkylated or hydrolysis products.

The reactions of silylation proceed with a color change from the dark green of Pb(ONO\textsuperscript{O})\textsubscript{2} to a much lighter purple or magenta color. The isolated products are
colorless, and the purple colors indicate the formation of small amounts of compounds containing unalkylated ONO ligands. This has been confirmed by the crystallization of Me$_2$Si(ONO$^{SQ}$)$_2$ from the reaction of Me$_2$SiCl$_2$ (Figure 4.9) and the crystallization of Si(ONO$^{SQ}$)$_2$ from the reaction with MeSiCl$_3$ (Figure 4.10). Both these compounds are paramagnetic with the ONO ligand exhibiting a 2- charge in the [ONO$^{SQ}$]$^{2-}$ form. They exhibit short Si-N bond distances of 1.8731(1) Å for Me$_2$Si(ONO$^{SQ}$) and 1.8627(10), 1.8558(10) Å for Si(ONO$^{SQ}$), respectively, which are typical of Si-N bond lengths to sp$^2$ hybridized nitrogens.

Products lacking Si–Cl bonds are air- and moisture-stable solids, while products retaining one or more Si–Cl bonds are susceptible to hydrolysis. (ON[Me]O)SiMe(μ-O)SiMe(ON[Me]O) is formed by hydrolysis of ClMeSi(ON[Me]O) (Figure 4.11). It also shows the previously mentioned preference for the electronegative μ-O to be located trans to the apical nitrogen and is structurally consistent with the unbridged chloro analogue, ClMeSi(ON[Me]O). The Si-N bond distances (2.585(2), 2.675(2) Å) are much longer than in the Si(ONO$^{SQ}$)$_2$ complex. All three of these compounds were not isolated as bulk samples but rather single crystals from the aformentiaoned reaction solutions and were not characterized further by other techniques.
Figure 4.11 Thermal ellipsoid plot of Me$_2$Si(ONO$_{5O}$). Hydrogens are omitted for clarity.
Figure 4.12. Thermal ellipsoid plot of Si(ONO$^{SO_2}$)$_2$. Hydrogen atoms and the minor orientation of the tert-butyl group centered at C280 are omitted for clarity.
Figure 4.13. Thermal ellipsoid plot of (ON[Me]O)SiMe(µ-O)MeSi(ON[Me]O)•2 C₆H₆. Hydrogen atoms and solvent molecules are omitted for clarity.
### TABLE 4.5.

CRYSTAL DATA FOR ME₂Si(ONO\(^{3}O\)), Si(ONO\(^{3}O\))₂, AND (ON[ME]O)SiMe(µ-O)MeSi(ON[ME]O)•2 C₆H₆.

<table>
<thead>
<tr>
<th></th>
<th>Me₂Si(ONO(^{3}O))</th>
<th>Si(ONO(^{3}O))₂</th>
<th>(ON[ME]O)SiMe(µ-O)MeSi(ON[ME]O)•2 C₆H₆</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C₃₀H₄₆NO₂Si</td>
<td>C₅₈H₈₆N₂O₄Si</td>
<td>C₇₂H₁₃₄N₂O₄Si₂</td>
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<tr>
<td><strong>Formula weight</strong></td>
<td>480.77</td>
<td>873.32</td>
<td>1133.75</td>
</tr>
<tr>
<td><strong>T (K)</strong></td>
<td>100(2)</td>
<td>120(2)</td>
<td>120(2)</td>
</tr>
<tr>
<td><strong>λ (Å)</strong></td>
<td>0.71073 (Mo Kα)</td>
<td>0.71073 (Mo Kα)</td>
<td>0.71073 (Mo Kα)</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
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<tr>
<td><strong>Space group</strong></td>
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<td>P₁</td>
<td>P₁</td>
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<tr>
<td><strong>Refls. collected</strong></td>
<td>21176</td>
<td>60966</td>
<td>28757</td>
</tr>
<tr>
<td><strong>Indep. refls.</strong></td>
<td>5863</td>
<td>12665</td>
<td>9590</td>
</tr>
<tr>
<td><strong>R_{int}</strong></td>
<td>0.0267</td>
<td>0.0287</td>
<td>0.0305</td>
</tr>
<tr>
<td><strong>Obsd. refls. [I&gt;2σ(I)]</strong></td>
<td>4774</td>
<td>10082</td>
<td>7469</td>
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<tr>
<td><strong>a (Å)</strong></td>
<td>5.9995(3)</td>
<td>11.1944(10)</td>
<td>13.041(3)</td>
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<tr>
<td><strong>b (Å)</strong></td>
<td>9.4458(4)</td>
<td>12.1836(11)</td>
<td>15.124(3)</td>
</tr>
<tr>
<td><strong>c (Å)</strong></td>
<td>26.4122(11)</td>
<td>20.7527(18)</td>
<td>18.205(4)</td>
</tr>
<tr>
<td><strong>α (deg)</strong></td>
<td>80.198(2)</td>
<td>90.909(2)</td>
<td>72.58(3)</td>
</tr>
<tr>
<td><strong>β (deg)</strong></td>
<td>84.4337(19)</td>
<td>104.408(2)</td>
<td>84.92(3)</td>
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<tr>
<td><strong>γ (deg)</strong></td>
<td>81.1163(18)</td>
<td>103.912(2)</td>
<td>89.92(3)</td>
</tr>
<tr>
<td><strong>V (Å(^3))</strong></td>
<td>1453.39(11)</td>
<td>2652.3(4)</td>
<td>3411.4(12)</td>
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<tr>
<td><strong>Z</strong></td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td><strong>Crystal size, mm</strong></td>
<td>0.53 × 0.15 × 0.07</td>
<td>0.48 × 0.26 × 0.14</td>
<td>0.38 × 0.28 × 0.06</td>
</tr>
<tr>
<td><strong>No. refined params.</strong></td>
<td>481</td>
<td>862</td>
<td>741</td>
</tr>
<tr>
<td><strong>R indices [I&gt;2σ(I)]</strong></td>
<td>R1 = 0.0429, wR2 = 0.1008</td>
<td>R1 = 0.0432, wR2 = 0.1082</td>
<td>R1 = 0.0516, wR2 = 0.1256</td>
</tr>
<tr>
<td><strong>R indices (all data)</strong></td>
<td>R1 = 0.0564, wR2 = 0.1087</td>
<td>R1 = 0.0590, wR2 = 0.1195</td>
<td>R1 = 0.0688, wR2 = 0.1383</td>
</tr>
<tr>
<td><strong>Goodness-of-fit</strong></td>
<td>1.034</td>
<td>1.004</td>
<td>1.031</td>
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</table>
4.2.4 Phenyl migration from tin to nitrogen.

In the reaction of Pb(ONO\textsuperscript{O})\textsubscript{2} with Ph\textsubscript{3}SnCl, phenyl migration takes place from tin to nitrogen to give Ph\textsubscript{2}Sn(ON[Ph]O) (Figure 4.14). Migration and consequent reduction of the ONO\textsuperscript{O} ligand is demonstrated by the presence of three inequivalent phenyl groups in Ph\textsubscript{2}Sn(ON[Ph]O), by the upfield shift of the OC\textsubscript{Ar} resonances in the \textsuperscript{13}C NMR spectrum, and by the fact that the product is colorless.

![Figure 4.14 Reaction of Pb(ONO\textsuperscript{O})\textsubscript{2} with triphenylchlorosilane.]

The analogous migrations of alkyl groups from tin to nitrogen were reported upon reaction of R\textsubscript{2}SnCl\textsubscript{2} with Zn(ONO\textsuperscript{O})\textsubscript{2} to form Cl(R)Sn(ON[R]O) (R = Me, Bu).\textsuperscript{74} However, mono aryl and alkyl groups were not observed to migrate in a similar fashion, yielding transmetalation products (ONO\textsuperscript{O})Sn(R)Cl\textsubscript{2} (R = Ph, \textsuperscript{6}Bu) instead. Thus the major factor in distinguishing whether stannanes react with sources of [ONO\textsuperscript{O}]\textsuperscript{−} by simple transmetalation or transmetalation followed by migration appears to be the number of ancillary chlorides present, not whether the migrating group is aryl or alkyl. Ph\textsubscript{3}SnCl, Bu\textsubscript{2}SnCl\textsubscript{2}, and Me\textsubscript{2}SnCl\textsubscript{2} all undergo migration, while PhSnCl\textsubscript{3} and BuSnCl\textsubscript{3} undergo only transmetalation. An investigation into the details of the migration mechanism in silicon,
and the magnitude and origin of differences in reactivity between silicon and tin, are discussed in the following chapters.

4.3 Experimental Section

All procedures were carried out under an inert atmosphere in a nitrogen-filled glovebox or on a vacuum line. Chlorinated solvents and acetonitrile were dried over 4 Å molecular sieves, followed by CaH₂. Benzene was dried over sodium, and ether over sodium benzophenone ketyl. Alcohols were dried over 4 Å molecular sieves. Deuterated solvents were obtained from Cambridge Isotope Laboratories, dried using the same procedures as their protio analogues, and stored in the drybox prior to use. Zn(ONO₂)₂ was prepared as described. Other reagents were commercially available and used without further purification. ¹H and ¹³C{¹H} NMR spectra were measured as CDCl₃ solutions on a Varian VXR-300 or Bruker Avance DPX 400 spectrometers. ²⁹Si{¹H} and ¹¹⁹Sn{¹H} NMR spectra were measured on Varian Inova 500 spectrometer. Chemical shifts for ¹H, ¹³C{¹H} and ²⁹Si{¹H} spectra are reported in ppm downfield of TMS, and ¹¹⁹Sn{¹H} chemical shifts are reported in ppm downfield of Me₄Sn. Infrared spectra were recorded as neat solids (except as otherwise noted) between NaCl plates. ESI mass spectra were obtained using a Bruker micrOTOF-II mass spectrometer, and peaks reported are the mass number of the most intense peak of isotope envelopes. Samples were injected as dichloromethane or acetonitrile solutions, preceded and followed by methanol. In all cases, the observed isotope patterns were in good agreement with calculated ones.
4.3.1 Pb(ONO\textsuperscript{Q})\textsubscript{2}. 

The procedure is adapted from that of McGarvey and coworkers.\textsuperscript{67} Into a 50 mL Erlenmeyer flask were weighed 0.45 g 3,5-di-tert-butyl-1,2-benzoquinone (2.0 mmol), 0.45 g 3,5-di-tert-butylcatechol (2.0 mmol), and 0.25 g lead(II) fluoride (1.0 mmol). After adding 40 mL absolute ethanol and a stirbar, to the stirred suspension of white solids in a brown solution was added 4 mL concentrated aqueous ammonia. The solution rapidly turned dark green and was stirred overnight. The green slurry was suction filtered through a glass frit and the precipitate washed with 5 mL ethanol and the filtrate and wash discarded. The solid was then washed with 3 × 3 mL CHCl\textsubscript{3} to extract the brownish-green lead complex; insoluble white lead salts were left behind on the frit and discarded. The compound was isolated on evaporation of the chloroform filtrate; yield 0.81 g (77%). NMR data do not agree with those in the literature. \textsuperscript{1}H NMR: \(\delta\) 1.22, 1.23 (s, 36H each, \textsuperscript{t}Bu), 6.91, 7.19 (d, 2 Hz, 4H each, ArH). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR: \(\delta\) 29.65, 30.50 (\textsuperscript{C}(CH\textsubscript{3})\textsubscript{3}), 34.86, 35.46 (\textsuperscript{C}(CH\textsubscript{3})\textsubscript{3}), 119.13, 131.62, 143.26, 144.84, 146.17, 177.36 (C\textsubscript{ar}O).

Anal. Calcd for C\textsubscript{56}H\textsubscript{80}N\textsubscript{2}O\textsubscript{4}Pb: C, 63.91; H, 7.66; N, 2.66. Found: C, 64.17; H, 7.34; N, 2.81.

4.3.2 2,4,8,10-Tetra-tert-butyl-6,6,12-trimethyl-12H-dibenzo[d,g][1,3,6,2]diazasasilocine, Me\textsubscript{2}Si(ON[Me]O).

To a solution of 0.2313 g Pb(ONO\textsuperscript{Q})\textsubscript{2} (0.2197 mmol) in 3 mL methylene chloride was added 54.5 µL chlorotrimethylsilane (1.98 equiv) via syringe. Within 5 min stirring at room temperature, the solution changed color to a deep magenta. The reaction was stirred 18 h, and solid lead chloride was removed by filtration. The mother liquor was
layered with methanol and allowed to stand overnight to provide crystals, which were filtered and washed with 2 × 2 mL methanol to yield 0.1100 g Me₂Si(ON[Me]O) (50%).

¹H NMR: δ 0.34, 0.46 (s, 3H each, SiCH₃), 1.27, 1.28 (s, 18H each, t-Bu), 2.98 (s, 3H, NCH₃), 7.33, 7.44 (d, 2 Hz, 2H each, ArH). ¹³C¹H NMR: δ 0.71, 2.81 (SiCH₃), 29.82, 31.77 (C(CH₃)₃), 34.71, 35.24 (C(CH₃)₃), 45.62 (NCH₃), 118.65, 121.31, 138.13, 139.90, 142.90, 148.32 (C₆H₅). ²⁹Si¹H NMR: δ –16.11. IR (cm⁻¹): 3084 (w), 2925 (s), 2859 (s), 1576 (s), 1262 (w), 1205 (w), 1140 (m), 1119 (m), 1070 (m), 1021 (w), 972 (m), 914 (m), 661 (w).

ESI-MS: 496.3591 (M+H⁺, calcd 496.3605). Anal. Calcd for C₃₁H₄₉NO₂Si: C, 75.10; H, 9.96; N, 2.83. Found: C, 75.41; H, 10.15; N, 2.89.

4.3.3 2,4,8,10-Tetra-tert-butyl-6-chloro-6,12-dimethyl-12H-dibenzo[d,g][1,3,6,2]dioxazasilocine, Cl(Me)Si(ON[Me]O).

The compound was prepared analogously using 0.1729 g Pb(ONO₂)₂ (0.1643 mmol) and 45 μL dichlorodimethylsilane (0.3710 mmol) in 4 mL CHCl₃. After stirring overnight, lead chloride was removed by filtration and the filtrate was evaporated to dryness in vacuo. The compound was crystallized by dissolving the crude product in chloroform, layering with acetonitrile, and cooling to –18 °C. The crystals were filtered and washed with 2 × 2 mL acetonitrile to yield 0.0449 g of ClMeSi(ON[Me]O) (27%). ¹H NMR: δ 0.90 (s, 3H, Si-Me), 1.26, 1.36 (s, 18H each, t-Bu), 3.02 (s, 3H, NCH₃), 7.15, 7.33 (d, 2 Hz, 2H each, ArH). ¹³C¹H NMR: δ 3.63 (SiCH₃), 29.52, 31.42 (C(CH₃)₃), 34.56, 35.20 (C(CH₃)₃), 45.92 (NCH₃), 116.72, 122.53, 138.41, 138.75, 144.10, 147.63 (C₆H₅). ²⁹Si¹H NMR: δ –44.89. IR (cm⁻¹): 2958 (s), 2929 (s), 2851 (s), 1605 (m), 1589 (m), 1303 (m), 1258 (w), 1237 (w), 1172 (m), 972 (m), 927 (m), 865 (m). ESI-MS: 498.3382 (M+H⁺ calcd
for Me[OH]Si(ON[Me]O), 498.3398). Anal. Calcd for C_{30}H_{46}ClNO_{2}Si: C, 69.80; H, 8.98; N, 2.71. Found: C, 68.18; H, 8.78; N, 2.61.

4.3.4 2,4,8,10-Tetra-tert-butyl-6,6-dichloro-12-methyl-12H-dibenzo[d,g][1,3,6,2]dioxazasilocine, Cl_{2}Si(ON[Me]O).

This compound was generated in a scintillation vial using 33.8 mg Pb(ONO\textsubscript{0})\textsubscript{2} (0.0321 mmol) and 8.0 µL methyltrichlorosilane (0.068 mmol) in 0.8 mL CDCl\textsubscript{3}. After stirring 5 min, the violet solution was filtered through a plug of sand into a screw cap NMR tube for characterization. \textsuperscript{1}H NMR: δ 1.31, 1.41 (s, 18H each, \textsuperscript{t}Bu), 3.16 (s, 3H, NC\textsubscript{3}H\textsubscript{3}), 7.23, 7.41 (d, 2 Hz, 2H each, ArH). \textsuperscript{13}C\textsubscript{1}H NMR: δ 29.54, 31.62 (C(CH\textsubscript{3})\textsubscript{3}), 34.91, 35.13 (C(CH\textsubscript{3})\textsubscript{3}), 50.09 (NCH\textsubscript{3}), 116.10, 123.17, 136.90, 138.03, 144.96, 145.61. \textsuperscript{29}Si\textsubscript{1}H NMR: δ –80.41. IR (evaporated film, cm\textsuperscript{-1}): 2958 (s), 2917 (s), 2868 (m), 2851(m), 1486 (s), 1458 (s), 1413 (m), 1360 (s), 1294 (m), 1266 (m), 1245 (w), 1209 (w), 1188 (w), 1102 (m), 1061 (m), 963 (m), 927 (m), 894 (w), 878 (w), 853 (m), 780 (w).

4.3.5 2,4,8,10-Tetra-tert-butyl-6-chloro-12-methyl-6-phenyl-12H-dibenzo[d,g][1,3,6,2]dioxazasilocine, Cl(Ph)Si(ON[Me]O).

After reaction as described above (0.2511 g Pb(ONO\textsubscript{0})\textsubscript{2}, 78 µL PhMeSiCl\textsubscript{2}, 4 mL CH\textsubscript{2}Cl\textsubscript{2}, 18 h) and removal of lead chloride by filtration, the brown-red filtrate was allowed to stand for two days. Light pink crystals deposited from CH\textsubscript{2}Cl\textsubscript{2} and were isolated by filtration to produce 0.1219 g of Cl(Ph)Si(ON[Me]O) (44%). \textsuperscript{1}H NMR: δ 1.29, 1.51 (s, 18H each, \textsuperscript{t}Bu), 2.23 (s, 3H, NCH\textsubscript{3}), 7.23 (d, 2 Hz, 2H, ArH), 7.34 (m, 5H, ArH, m-, p-Ph), 7.50 (m, 2H, o-Ph). \textsuperscript{13}C\textsubscript{1}H NMR: δ 29.69, 31.77 (C(CH\textsubscript{3})\textsubscript{3}), 35.36, 35.91 (C(CH\textsubscript{3})\textsubscript{3}),
48.66 (NCH₃), 117.08, 122.84, 128.39, 129.85, 130.80, 135.70, 137.99, 138.23, 144.36, 147.23 (CₐO). ²⁹Si{¹H} NMR: δ –62.16. IR (nujol, cm⁻¹): 3076 (w), 1482 (s), 1409 (m), 1376 (m), 1360 (m), 1258 (s), 1237 (m), 1213 (w), 1196 (w), 1164 (w), 1119 (m), 1057 (m), 1025 (w), 947 (s), 886 (m), 792 (w), 775 (m), 739 (m), 722 (m), 657 (w), 620 (w). ESI-MS: 542.3464 (M⁺–Cl, calcd 542.3449. The analytical sample was purified by crystallization from chloroform/hexane and analyzed as a hemichloroform solvate. Anal. Calcd for C₃₅H₄₈ClN₂O₂Si•0.5 CHCl₃: C, 66.83; H, 7.66; N, 2.20. Found: C, 66.77; H, 7.07; N, 2.20.

4.3.6 2,4,8,10-Tetra-tert-butyl-6,12-dimethyl-6-phenyl-1H-dibenzo[d,g][1,3,6,2]dioxazasilocine, Me(Ph)Si(ON[Me]O).

After reaction as described above (0.1118 g Pb(ONO)₂ (0.1062 mmol), 2 mL CHCl₃, PhMe₂SiCl (38.5 µL, 2.05 equiv), 18 h) and removal of lead chloride by filtration, the red-brown filtrate was layered with 3 mL methanol and stored at –36 °C for 3 d. The white crystalline solid was filtered and washed with 2 × 1 mL CH₃OH to yield 0.0664 g Me(Ph)Si(ON[Me]O) (56%). The ¹H NMR spectrum shows a 8.7:1 ratio of isomers; only peaks due to the major isomer are reported below. ¹H NMR: δ 0.40 (s, 3H, SiC₃H₃), 1.22, 1.42 (s, 18H each, ³Bu), 1.99 (s, 3H, NCH₃), 7.10 (d, 2 Hz, 2H, ArH), 7.24 (m, 3H, m,p-Ph), 7.27 (d, 2 Hz, 2H, ArH), 7.40 (m, 2H, o-Ph). ¹³C{¹H} NMR δ 2.85 (SiC₃H₃), 29.83, 31.75 (C(CH₃)₃), 34.70, 35.33 (C(CH₃)₃), 45.92 (NCH₃), 119.11, 121.57, 127.49, 127.93, 131.27, 137.84, 137.95, 139.84, 143.15, 148.15 (CₐO). ²⁹Si{¹H} NMR: δ –32.34. IR (nujol, cm⁻¹): 3068 (m), 3052 (m), 1580 (w), 1421 (m), 1388 (m), 1372 (m), 1352 (s), 1266 (s), 1241 (m), 1176 (m), 1127 (s), 1074 (m), 1025 (w), 976 (m), 947 (s), 886 (s), 874 (s), 804...
(s), 784 (m), 767 (w), 739 (w), 710 (s), 694 (s), 641 (w), 604 (w), 620 (w). ESI-MS: 558.3757 (M+H⁺, calcd 558.3762). Anal. Calcd for C₃₆H₅₁NO₂Si: C, 77.50; H, 9.21; N, 2.51. Found: C, 77.42; H, 9.28; N, 2.42.

80B 2,4,8,10-Tetra-tert-butyl-6-chloro-6,12-diphenyl-1H-dibenzo[d,g][1,3,6,2]dioxazasilocine, Cl(Ph)Si(ON[Ph]O).

After reaction and filtration of lead chloride as described above (0.2014 g Pb(NO₃)₂ (0.2140 mmol), 4 mL CHCl₃, 81.0 µL Ph₂SiCl₂ (0.384 mmol, 2.0 equiv), 18 h), the filtrate was evaporated to dryness, redissolved in minimal CHCl₃, and layered with acetonitrile. Crystals of the product were isolated by filtration after 3 d, washed with 2 × 2 mL acetonitrile, and vacuum dried to give 0.1034 g ClPhSi(ON[Ph]O) (43%). ¹H NMR: δ 1.35, 1.66 (s, 18H each, ‑Bu), 6.05 (d, 8 Hz, 2H, o-NPh), 6.61 (t, 7 Hz, 1H, p-NPh), 6.78 (t, 8 Hz, 2H, m-NPh), 6.96 (t, 8 Hz, 2H, m-SiPh), 7.15 (t, 8, 1Hz, 1H, p-SiPh), 7.21 (d, 7 Hz, 2H, o-SiPh), 7.31 (d, 2 Hz, 2H, ArH), 7.42 (d, 2 Hz, 2H, ArH). ¹³C{¹H} NMR: δ 29.52, 31.28 (C(CH₃)₃), 34.51, 35.11 (C(CH₃)₃), 117.48, 120.13, 122.43, 122.77, 127.51, 127.75, 129.52, 130.84, 131.08, 135.23, 138.81, 145.27, 148.60, 149.73. ²⁹Si{¹H} NMR: δ -49.86. IR (evaporated film, cm⁻¹): 3068 (w), 2958 (s), 2868 (s), 1593 (m), 1572 (m), 1474 (s), 1454 (m), 1446 (m), 1413 (w), 1388 (s), 1360 (s), 1307 (m), 1245 (s), 1204 (w), 1155 (w), 1123 (s), 1082 (m), 963 (s), 935 (s), 898 (s), 792 (m), 759 (w), 730 (m) 690 (m), 583 (w). ESI-MS: 604.3631 (M⁺–Cl, calcd 604.3605). Anal. Calcd for C₄₀H₅₀ClNO₂Si: C, 75.02; H, 7.87; N, 2.19. Found: C, 74.66; H, 7.56; N, 2.22.
4.3.8 2,4,8,10-Tetra-tert-butyl-1,7,7-triphenyl-12H-dibenzo[d,g][1,3,6,2]dioxazasilocine, 
Ph$_2$Si(ON[Ph]O).

A solution of 0.2074 g Pb(ONO$_2$)$_2$ (0.1979 mmol) and 0.1162 g 
triphenylchlorosilane (0.3940 mmol, 1.99 equiv) in 5 mL CHCl$_3$ in a 20 mL scintillation 
vial sealed with a Teflon-lined cap was stirred and heated for 4 d in a 70 °C oil bath.

After filtration of lead chloride, the solution was layered with acetonitrile and allowed to 
stand for 3 d. Crystals of the product were filtered to give 0.0975 g Ph$_2$Si(ON[Ph]O) 
(36%). $^1$H NMR: δ 1.25, 1.42 (s, 18H each, $^3$Bu), 5.87 (d, 8 Hz, o-NPh), 6.53 (tt, 7, 2 Hz, 
1H, p-NPh), 6.66 (t, 8 Hz, 2H, m-NPh), 6.85 (t, 8 Hz, 2H, m-SiPh), 7.05 (tt, 8, 1Hz, 1H, p- 
SiPh), 7.14 (d, 8 Hz, 2H, o-SiPh), 7.23 (d, 2 Hz, 2H, ArH), 7.28 (d, 2 Hz, 2H, ArH), 7.29 (t, 8 
Hz, 2H, m-SiPh), 7.36 (tt, 7, 1.6 Hz, 1H, p-SiPh), 7.71 (d, 8 Hz, 2H, o-SiPh). $^{13}$C($^1$H) NMR: δ 
29.78, 31.39 (C(CH$_3$)$_3$), 34.48, 35.16 (C(CH$_3$)$_3$), 116.50, 118.48, 122.39, 123.69, 127.31, 
127.38, 127.65, 128.79, 129.38, 131.10, 132.14, 134.65, 135.68, 136.87, 139.11, 144.49, 
149.43, 150.59. $^{29}$Si($^1$H) NMR: δ –38.74. IR (cm$^{-1}$): 3101 (w), 3076 (m), 2929 (s), 2864 (s), 
2708 (w), 1593 (s), 1446 (s), 1311 (m), 1237 (m), 1127 (m), 1041 (m), 927 (m), 845 (w), 
780 (w), 681 (w), 600 (w). ESI-MS: 681.3985 (M$^+$, calcd 681.3997). Anal. Calcd for 
C$_{46}$H$_{55}$NO$_2$Si: C, 81.01; H, 8.13; N, 2.05. Found: C, 77.79; H, 8.11; N, 1.83.

4.3.9 2,4,8,10-Tetra-tert-butyl-6,6,12-triphenyl-12H- 
dibenzo[d,g][1,3,6,2]dioxazastannocine, Ph$_2$Sn(ON[Ph]O).

Triphenyltin chloride (0.1332 g, 0.3455 mmol, 2.0 equiv) was added to a 4 mL 
chloroform solution of 0.1818 g Pb(ONO$_2$)$_2$ (0.1727 mmol). The dark green solution 
changed color to brown within two minutes of stirring. The reaction was allowed to stir
overnight and lead chloride was removed by filtration. The mother liquor was cooled to
−20 °C to furnish microcrystalline aggregates of Ph₂Sn(ON[Ph]O) (0.1614 g, 60%). ¹H
NMR: δ 1.32, 1.57 (s, 18H each, ¹Bu), 6.29 (d, 8 Hz, o-Ph), 6.79 (m, 3H, m,p-Ph), 7.04
(d, 8 Hz, 2H, o-Ph), 7.11 (t, 8 Hz, 2H, m-Ph), 7.23 (tt, 8 Hz, 1 Hz, 1H, p-Ph), 7.31 (d, 2 Hz,
2H, ArH), 7.36 (d, 2Hz, 2H, ArH), 7.43 (m, 3H, Ph), 7.80 (d, 8 Hz, 2H, o-Ph), 7.11 (t,
8 Hz, 2H, m-Ph), 7.23 (tt, 8 Hz, 1 Hz, 1H, p-Ph), 7.31 (d, 2 Hz, 2H, ArH), 7.36 (d, 2Hz, 2H, ArH), 7.43 (m, 3H, Ph), 7.80 (m, 2H, Ph). ¹³C{¹H} NMR: δ
29.92, 31.81 (C(C(CH₃)₃), 34.61, 35.63 (C(C(CH₃)₃), 120.77, 121.74, 122.48, 122.53, 127.83,
128.44, 128.68, 129.37, 129.58, 134.14, 134.40, 135.95, 137.95, 138.32, 140.31, 144.37,
149.47, 153.43. ¹¹⁹Sn{¹H} NMR: δ −204.06. IR (nujol mull, cm⁻¹): 3067 (w), 3046 (w), 1597
(w), 1565 (w), 1411 (m), 1387 (m), 1378 (m), 1361 (m), 1298 (s), 1260 (s), 1238 (s), 1200
(m), 1190 (m), 1155 (w), 1127 (m), 1078 (m), 1032 (m), 1003 (m), 956 (w), 915 (w), 897
(w), 883 (w), 866 (w), 839 (s), 780 (m), 768 (s), 726 (s), 685 (s), 676 (m), 656 (w), 641 (w),
551 (m), 534 (m). ESI-MS: 796.3186 (M+Na⁺, calcd 796.3157). Anal. Calcd for
C₄₆H₅₅NO₂Sn: C, 71.51; H, 7.17; N, 1.81. Found: C, 71.67; H, 7.40; N, 1.66.

4.3.10 X-ray Crystallography.

Crystals of Me₂Si(ON[Me]O) and Me(Ph)Si(ON[Me]O) were grown by layering a
concentrated dichloromethane solution of each complex with methanol, while crystals
of Cl(Me)Si(ON[Me]O)•2 C₆H₆ were grown from a concentrated solution of the
compound in benzene. Crystals of Cl(Ph)Si(ON[Me]O) and Ph₂Si(ON[Ph]O) were grown
by layering concentrated solutions of the complex in CDCl₃ with hexane and acetonitrile,
respectively. Crystals of Cl(Ph)Si(ON[Ph]O) were grown by layering concentrated
solutions of the complex in CHCl₃ with acetonitrile. Crystals of (ONO⁵Q)SiMe₂ deposited
from the crude reaction mixture of Pb(ONO⁵Q)₂ with Me₂SiCl₂ in CH₂Cl₂, after filtration to
remove PbCl₂ at −20 °C. Crystals of (ON[Me]O)Si(Me)(μ-O)Si(Me)(ON[Me]O)•2 C₆H₆ deposited from a crude sample of ClMeSi(ON[Me]O) dissolved in C₆H₆ and layered with CH₃CN. Crystals of (ONO⁵Q₂)₂Si were formed when the reaction mixture of MeSiCl₃ with Pb(ONO⁵Q)₂, after filtration and concentration to dryness, was dissolved in CDCl₃ and layered with hexane.

Crystals were placed in inert oil before transferring to the cold N₂ stream of a Bruker Apex II CCD diffractometer. Data were reduced, correcting for absorption, using the program SADABS. The structures were solved using direct methods. All non-hydrogen atoms not apparent from the initial solutions were found on difference Fourier maps, and all heavy atoms were refined anisotropically. The TWIN command was used to address a 27% racemic twin in the refinement of Cl(Me)Si(ON[Me]O)•2 C₆H₆.

The tert-butyl group centered on C150 on in Me(Ph)Si(ON[Me]O) was disordered in two different orientations, as were the tert-butyl groups centered on C150 and C250 in Me₂Si(ON[Me]O), on C28 in (Cl)(Ph)Si(ON[Ph]O), and on C280 in Si(ONO⁵Q)₂. Disordered tert-butyl groups were modeled by constraining the thermal parameters of the methyl carbons to be equal to those of the carbons opposite them in the other orientation, and allowing the occupancy of the two orientations to refine. Hydrogens on the disordered methyl groups were placed in calculated positions, while all other hydrogen atoms were found on difference Fourier maps and refined isotropically, except for those in Cl(Me)Si(ON[Me]O)•2 C₆H₆ and (ON[Me]O)Si(Me)(μ-O)Si(Me)(ON[Me]O)•2 C₆H₆, which were all placed in calculated positions. Calculations
used SHELXTL (Bruker AXS),\textsuperscript{26} with scattering factors and anomalous dispersion terms taken from the literature.\textsuperscript{27} Further details about the individual structures are given in Tables 4.2, 4.3 and 4.5.
5.1 Introduction

The previous chapter described that silylation of the oxidized ligand in Pb(ONO\textsuperscript{O})\textsubscript{2} with a slew of chlorosilanes R(X)(Y)SiCl (R = Me, Ph; X,Y = Me, Ph, Cl) results in tetracyclic, pentacoordinate compounds X(Y)Si(ON[R]O) (X = axial, Y= equatorial) with a reduced, dianionic amine-bisphenolate ligand in which the methyl or phenyl group has migrated to nitrogen (Scheme 5.1).

![Scheme 5.1 Silylation of Pb(ONO\textsuperscript{O})_{2} results in pentacoordinate products (X)(Y)Si(ON[R]O)](image)

This chapter reports an investigation into the mechanism of these methyl and phenyl migrations that cleave the silicon-carbon bond. Insights into the unusual
preference for methyl migrations in comparison to phenyl groups are substantiated. The trigonal bipyramidal silicon products of migration in some cases form kinetic isomers with an equatorial chlorine that isomerize to their thermodynamically stable forms with an axial chlorine. The chemo- and stereoselectivity of migrated products is determined not only by relative rates of methyl and phenyl migration from octahedral silicon, which is facile, but also from the reversibility in isomerization of $\kappa^3$-$R(X)(Y)Si(ONO^Q)$ isomers via the tetrahedral intermediate $\kappa^1$-$R(X)(Y)Si(ONO^Q)$. \textsuperscript{97}

5.2 Results

5.2.1 Crossover experiment illustrating a mechanistic pathway.

While tetrahedral silyl species are not isolable in silylation reactions of Pb(ONO$^Q$)$_2$, they must occur as an initial intermediate of these reactions prior to migration (Scheme 5.1). One plausible mechanism of migration involves formation of carbon based radicals which are subsequently captured by the adjacent nitrogen. Although homolytic scission of the strong carbon silicon bond seems unlikely, the associated redox chemistry of the ONO ligand elicits an investigation of this mechanism (Scheme 2.2). The previous chapter lists the formation of Me$_2$Si(ONO$^{SQ}$) in trace amounts from the silylation reactions utilizing Me$_2$SiCl$_2$. 

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The mechanism was investigated by reacting an equimolar mixture of \((\text{CH}_3)_3\text{SiCl}\) and \((\text{CD}_3)_3\text{SiCl}\) with \(\text{Pb}(\text{ONO}^\text{O})_2\). Silylation of the ligand in \(\text{Pb}(\text{ONO}^\text{O})_2\) with trimethylchlorosilane in chlorinated solvents leads to precipitation of lead chloride and formation of \(\text{Me}_2\text{Si}([\text{ON}\text{Me}]\text{O})\) within 15 minutes. An ESI MS of the \textit{in situ} reaction mixture shows peaks with high intensities (Figure 5.1) representing the migrated products of \(d^0\) and \(d^9\) isotopomers \((\text{CH}_3)_2\text{Si}([\text{ON}\text{CH}_3]\text{O})\) and \((\text{CD}_3)_2\text{Si}([\text{ON}\text{CD}_3]\text{O})\). The mixed \((d^3\text{ and } d^6)\) isotopomers account for less than 5% of the signal intensity. The amounts of mixed isotopomers do not change after 48 h at room temperature and suggest that crossover does not occur due to exchange of the \([\text{ON}\text{Me}]\text{O}^{2-}\) ligand between \(\text{Me}_2\text{Si}^{2+}\) fragments after migration. Even if some of the \((\text{ONO}^\text{SQ})\text{SiMe}_2\) radical is formed, it does not appear to intervene significantly on the pathway to the migrated product \(\text{Me}_2\text{Si}([\text{ON}\text{Me}]\text{O})\).

A general outline for silylation of the ONO ligand followed by alkyl or aryl migration is shown in Scheme 5.2). The mechanism initially must proceed by silylation to
form a tetrahedral intermediate $\kappa^1$-R(X)(Y)Si(ONO$Q$). Tetrahedral conformers should be able to interconvert crossing small energetic barriers by free rotation along the silicon oxygen bond. Each tetrahedral conformer would have a unique transition state $\kappa^1$-TS-$\kappa^3$ that precedes ring closure and formation of an octahedral intermediate $\kappa^3$-R(X)(Y)Si(ONO$Q$) (X trans to R, Y trans to N). A 1,2-alkyl/aryl migration from octahedral silicon to nitrogen leads to the formation of pentacoordinate products (X)(Y)Si(ON[R]O).
Figure 5.1. ESI mass spectrum of crossover experiment after reaction time of 15 minutes.

Scheme 5.3 General mechanism after silylation leading to migration in aryloxyiminoquinones.
The stereochemistry of the migrated product elucidates the octahedral intermediate from which migration occurs. The migrating substituent R must occupy a position cis to the nitrogen in the $\kappa^3$ intermediate. The X substituent trans to the R group in the octahedral intermediate ends up axial in the migrated product, trans to nitrogen. The Y group trans to nitrogen in the octahedral intermediate ends up equatorial in the final product, cis to the nitrogen and syn to the R group that has migrated to the nitrogen.

5.2.2 Stereoselectivity of migration reactions.

*In situ* monitoring of the reaction of PhMeSiCl$_2$ with Pb(ONO$_2$)$_2$ (Figure 5.2) shows a kinetic product of migration, Ph(Cl)Si(ON(Me)O), in which chlorine is equatorial (Figure 5.3), forms with a kinetic stereoselectivity $> 6:1$. The kinetic product then isomerizes to the thermodynamic product Cl(Ph)Si(ON(Me)O) with axial chlorine over 12 hours in chlorinated solvents. Confident assignment of the *in situ* $^1$H NMR spectra can be made due to the distinct change in chemical shift of the downfield $N$-methyl at $\delta$ 3.17 in the kinetic product that shifts upfield to $\delta$ 2.23 in the thermodynamic product due its position in the shielding cone of the adjacent phenyl group (Figure 4.7).
Figure 5.2 *In situ* $^1$H NMR spectra (CDCl$_3$, 300 MHz) of the reaction of Pb(ONO$_Q$)$_2$ with Ph(Me)SiCl$_2$. Bottom: $t = 15$ min. Top: $t = 12$ h. Key: • = Ph(Cl)Si(ON[Me]O) (kinetic isomer); □ = Cl(Ph)Si(ON[Me]O) (thermodynamic isomer); S = Ph(Me)SiCl$_2$; P = \{PbCl(ONO$_Q$)\}$_n$.

The first order rate constant for isomerization ($k_{\text{isom}} = 8.0(11) \times 10^{-5}$ s$^{-1}$ in CD$_2$Cl$_2$ at 21 °C, $\Delta G^\ddagger = 22.7(2)$ kcal mol$^{-1}$, Figure 5.4) was determined from concentration data derived from a plot of integral ratios of $N$-methyl groups of the thermodynamic and kinetic products. The identity of the kinetic product illustrates that the octahedral isomer from which migration occurs, $\kappa^3$-Me(Cl)(Ph)Si(ONO$_Q$), has mutually trans hydrocarbyl groups, as shown in Figure 5.3 in square brackets preceding the kinetic product.
Figure 5.3 Formation of kinetic and thermodynamic products after silylation of the ONO ligand with (a) PhMeSiCl₂; (b) Ph₂SiCl₂; (c) Me₂SiCl₂.

*In situ* NMR monitoring of the reaction of Ph₂SiCl₂ with Pb(ONOQ)₂ within 15 minutes at room temperature indicates that formation of the thermodynamic product of migration with an apical chlorine, (Cl)(Ph)Si(ON[Ph]O), is preceded by the formation of a kinetic product (Ph)(Cl)Si(ON[Ph]O) (kinetic stereoselectivity > 5:1). The kinetic product has the same chemical composition and coupling patterns in the ^1^H NMR spectra as the thermodynamic product, but a discernible upfield shift of peaks associated with N-phenyl groups.
Figure 5.4. Plot of concentration vs. time data for isomerization of Ph(Cl)Si(ON[Me]O) (CD₂Cl₂, 21.0 °C).

Figure 5.5 ᵃ¹H NMR spectra (400 MHz) of the reaction of Ph₂SiCl₂ with Pb(ONO₃)₂ (CDCl₃, 20 °C). (a) t = 20 min. (b) t = 22 h. Key: • = Ph(Cl)Si(ON[Ph]O) (kinetic isomer); ▲ = Cl(Ph)Si(ON[Ph]O) (thermodynamic isomer); S = Ph₂SiCl₂; P = {PbCl(ONO₃)}ₙ.
supports this assignment. *In situ* NMR monitoring of the reaction indicates an approximate half life of 50 min for isomerization, which is three times shorter than that of Ph(Cl)Si(ON[Me]O).

The analogous reaction with Me₂SiCl₂ (Figure 5c) proceeds differently. Only a single stereoisomer of migration, Cl(Me)Si(ON[Me]O), is formed within 5 min at room temperature. Reactions carried out at −30 °C (at which temperature silylation is complete in ~80 min) also only produces this isomer. The thermodynamic product is also kinetically preferred in this case and originates from the octahedral isomer κ³-Me(Me)(Cl)Si(ONO⁰).

5.2.3 DFT mapping of reaction coordinates.

The energies and optimized structures of intermediates and transition states in the reaction of Me₃SiCl with Pb(ONO⁰)₂ after initial silylation were computed using DFT (Figure 5.6). Calculations were carried out on gas phase species using the B3LYP functional and 6-31G* basis set for all atoms, using a simplified ONO ligand in which the tert-butyl groups were replaced with hydrogens. The four-coordinate κ¹-Me₃Si(ONO⁰) reactant is significantly lower in energy (17 kcal mol⁻¹) than the octahedral intermediate κ³-Me₃Si(ONO⁰). Ring closure has an estimated barrier of 20 kcal mol⁻¹. The mutually trans methyl groups adjacent to the nitrogen then undergo a 1,2- migration (ΔG‡ = 2.1 kcal mol⁻¹) to furnish the N-methylated product Me₂Si(ON[Me]O) containing a reduced and redox inactive ligand. This calculation suggests that migration has a low barrier and is competitive and perhaps faster than ring opening of κ³-Me₃Si(ONO⁰). Therefore, migration could occur before reversion to the tetrahedral intermediate.
Figure 5.6 Energetics of silylation of the ONO ligand with Me₃SiCl with subsequent migration.

5.2.3.1 DFT insights into stereo- and chemoselectivity of migration.

The reaction of Ph(Me)(Cl)Si(ONO₂) is extremely interesting because it allows investigation of both the stereoselectivity and chemoselectivity of the migration reaction. DFT calculations (6-31G*/B3LYP/PCM=CH₂Cl₂) furnished migration barriers and energies of penta-coordinate products (Figure 5.7). Energies and geometries for this and subsequent calculations use a continuum solvation model with dichloromethane (Figures 5.9 and 5.10), but gas-phase calculations yield very similar results. Initial silylation of Ph(ONO₂)₃ with PhMeSiCl₂, forms the tetrahedral intermediate κ¹-
Ph(Me)(Cl)Si(ONO₂) which possesses rotational freedom about the Si-O bond. There are three possible stereoisomeric κ³-Si(ONO₂) intermediates that can form upon ring
Energies of all three optimized octahedral isomers were computed, along with their corresponding transition states for ring closure, $\kappa^1$-TS-$\kappa^3$.

**Figure 5.7** Reaction coordinate of ONO after silylation with PhMeSiCl$_2$. 
Each octahedral intermediate has different carbon nucleophiles in migrating positions that can undergo the 1,2-shift to the iminoquinone nitrogen.

Ph(Me)(Cl)Si(ONO\(^Q\)), \(1-\kappa^3\), with methyl trans to the nitrogen, can only undergo phenyl migration. \(\kappa^3\)-Me(Cl)(Ph)Si(ONO\(^Q\)), \(2-\kappa^3\), with chlorine trans to nitrogen, can migrate either a methyl or a phenyl group. \(\kappa^3\)-R(X)(Y)Si(ONO\(^Q\)), \(3-\kappa^3\), with phenyl trans to nitrogen, can only undergo methyl migration. Four distinct transition states of migration were identified, which in turn lead to unique products of methyl or phenyl migration with different axial and equatorial substituents. The experimentally observed formation of the kinetic product of methyl migration, (Ph)(Cl)Si(ON[Me]O), \(2-\text{N-Me}\) (encircled in Figure 5.7), reveals the octahedral stereoisomer from which it formed, \(\kappa^3\)-Me(Cl)(Ph)Si(ONO\(^Q\)), \(2-\kappa^3\) (boxed in Figure 5.7).

Chemoselective methyl migration from Me(Cl)(Ph)Si(ONO\(^Q\)), \(2-\kappa^3\), can occur in two scenarios that can be distinguished. In the first scenario, \(2-\kappa^3\) would be in rapid equilibrium with other octahedral intermediates, \(1-\kappa^3\) and \(3-\kappa^3\), via reversion to \(\kappa^1\)-Me(Ph)(Cl)Si(ONO\(^Q\)). In this scenario, \(2-\text{TS-NMe}\) would have the lowest absolute energy of any methyl or phenyl transition state, therefore migrating its methyl nucleophile selectively. However, calculations suggest that the transition state for methyl migration, \(3-\text{TS-NMe}\) (\(\Delta G^\ddagger = 8.9\) kcal mol\(^{-1}\)), from the octahedral intermediate \(1-\kappa^3\) has the lowest absolute energy of any of the migration transition states at 2.0 kcal mol\(^{-1}\). This predicts that all methyl migration would occur from isomer \(3-\kappa^3\) if migration were rate-limiting.
In the second scenario, 2-κ³ would form stereoselectively, having the lowest ΔG$^\dagger$ of formation (2-κ¹-TS-κ³). The preferential migration of the methyl over phenyl would occur as long as the migration barrier 2-TS-NMe is lower in energy than 2-TS-NPh. In this scenario, formation of octahedral intermediates would be rate limiting and migration would be fast. The κ¹-TS-κ³ transition states of ring closure that lead to octahedral intermediates have significant activation barriers (ΔG$^\dagger$ = 7.8-15.8 kcal mol⁻¹). The transition state 2-κ¹-TS-κ³ that is part of the experimentally supported reaction path has the lowest barrier to ring closure (ΔG$^\dagger$ = 8.8 kcal mol⁻¹) and lies 6 kcal mol⁻¹ below the analogous barriers of 1-κ¹-TS-κ³ (ΔG$^\dagger$ = 15.8 kcal mol⁻¹) and 3-κ¹-TS-κ³ (ΔG$^\dagger$ = 15.7 kcal mol⁻¹) that lead to 1-κ³ and 3-κ³ respectively. These calculations show that barriers to isomerisation are larger than those of migration, and therefore suggest that scenario two is in effect.

Stereoselective formation of 2-κ³ allows for a direct comparison between the migratory aptitudes of methyl and phenyl groups in 1,2-nucleophilic migrations. Calculations show that the transition state for methyl migration 2-TS-NMe (ΔG$^\dagger$ = 8.6 kcal mol⁻¹) lies below the transition state for phenyl migration 2-TS-NPh (ΔG$^\dagger$ = 11.6 kcal mol⁻¹). This energetic difference (ΔΔG$^\dagger$ = 3.0 kcal mol⁻¹) establishes a chemoselective preference that is quantitatively consistent with the experimentally observed absence of migrated N-phenyl products. The difference in activation barriers between methyl migration from isomer 3-κ³ (3-TS-NMe, ΔG$^\dagger$ = 8.9 kcal mol⁻¹) and phenyl migration from 1-κ³ (1-TS-NPh, ΔG$^\dagger$ = 12.3 kcal mol⁻¹) is similar (ΔΔG$^\dagger$ = 3.4 kcal mol⁻¹). This
suggests that the chemoselective preference for methyl migration is *not* due to a trans effect.
Figure 5.8 Calculated geometries and energies (kcal mol$^{-1}$) of intermediates, transition states, and products in the experimentally supported reaction coordinate that leads to kinetic product (Ph)(Cl)Si(ON[Me]O), 2-N-Me.
The geometries of calculated transition states for migration are best described as early per Hammond’s postulate, with marked resemblance to octahedral intermediates (Figure 5.8). In the transition state for methyl migration (2-TS-NMe), the methyl group shifts towards a pyramidalizing nitrogen that moves closer to silicon (Si-N = 1.90 Å). The N-Si-Cl and Me-Si-Ph bond angles decrease as the methyl group migrates. A similar transition state geometry for phenyl migration is observed in 2-TS-NPh. The mirror plane that bisects the ONO ligand also bisects the plane of the phenyl ring in 2-κ³ and in the transition state 2-TS-NPh.

The calculated energy of the reaction of Ph₂SiCl₂ or Me₂SiCl₂ with Pb(ONOQ)₂ (Figure 5.9) show trends which are qualitatively consistent with experiment as well as in comparison to prior calculations in this section. The observed kinetic products of migration, 4-NPh and 7-NMe, suggest that reaction pathway containing octahedral intermediate 4-κ³ and 7-κ³ are preferred.

5.2.3.2 DFT systematically underestimates the differences in relative rates of migration and relative stabilities of migrated products.

The energies shown in Figure 5.7 suggest that formation of octahedral isomers via ring closure is the rate-limiting step in reaction paths 1 and 3. Calculated transition state energies for ring closure can be used to furnish relative rate constants for methyl migrations from octahedral isomers 2-κ³ and 3-κ³ ([3-TS-κ³]-[2-TS-Me], ΔΔG⁺ = 0.2 kcal mol⁻¹, k_rel = 1.4). This relative rate suggests that almost half of the N-methyl migrated product should form via reaction path 3. In fact, experimentally this ratios is greater
than 6:1. The calculated barriers also predict the formation of 26% N-phenyl product via pathway 1. Experimentally no N-phenyl migration is detected (< 1%). The calculations predict that the five-coordinate product with axial chlorine is more stable than that with axial methyl or phenyl, in agreement with experiment, but the calculated energy differences (~1 kcal mol⁻¹) are small compared to experiment (where only products with axial chlorine are observed at equilibrium, > 30:1 by NMR, ΔG° > 2 kcal mol⁻¹). A systematic underestimation of the apicophilicity of chlorine in trigonal bipyramidal geometries of silicon results from an inadequate description of the hypervalent bonding in silicon by DFT. ⁹⁸

In the reaction of Me₂SiCl₂ with Pb(ONO²)₂, it is empirically observed that the thermodynamically favored isomer, Cl(Me)Si(ON[Me]O), is also kinetically favored by migration; however, calculations suggest equal rates of migration from either octahedral isomer, 6-κ³ or 7-κ³ (ΔΔG‡ = 0, k_rel = 1). Calculations underestimate these relative barriers of migration and isomerization. It is likely, that these energies are similar and either migration or isomerization could be rate limiting.
Figure 5.9 Reaction coordinate of ONO after silylation with (a) \( \text{Ph}_2\text{SiCl}_2 \) and (b) \( \text{Me}_2\text{SiCl}_2 \).
5.2.3.3 The consistent trends of DFT

While quantitative energies are not always in agreement with experiment, some qualitatively consistent trends are observed throughout these calculations. (1) Formation of the \( \kappa^3 \) intermediate is significantly faster when chlorine is in the equatorial position \textit{trans} to nitrogen. The \( \kappa^1\text{-TS}-\kappa^3 \) transition states that lead to these isomers are 6-8 kcal mol\(^{-1}\) lower in energy than the transition states to form the isomers with methyl or phenyl groups in equatorial positions. (2) In contrast to the fastet forming octahedral intermediates, \( \kappa^3 \) intermediates are significantly (~6 kcal mol\(^{-1}\)) more stable when chlorine is an axial position \textit{cis} to nitrogen, \textit{trans} to a hydrocarbyl group. These thermodynamically preferred six-coordinate isomers have the two carbon groups trans to electronegative substituents (nitrogen and chlorine), which helps to maximize bonding in hypervalent species. (3) Migration barriers are not very sensitive to the group \textit{trans} to the migrating group. (4) Barriers to phenyl migration are consistently ~3 kcal/mol higher than barriers to methyl migration. (5) Transition state energies for dechelation and for migration are similar, therefore small changes in the substrate may cause a shift in the rate-limiting step from chelation to migration, in which case kinetic as well as thermodynamic formation of a trigonal bipyramidal product containg the axial chlorine would be observed. Such a case is likely in the reaction of \( \text{Me}_2\text{SiCl}_2 \). (6) In all cases, migration is highly exothermic (\( \Delta G^\circ < -30 \text{ kcal mol}\(^{-1}\) for formation of migrated products from \( \kappa^1 \) silanes).
5.3 Discussion

5.3.1 1,2-Alkyl or -aryl migrations from hypervalent silicon to electron deficient nitrogen.

Nucleophilic rearrangements occur when an electron deficient site is generated in vicinity of a migrating group that has a lone pair or bonding pair of electrons. Wagner-Meerwein shifts (Figure 5.10) are a common type of 1,2-alkyl shifts, which are driven by the formation of a more stable carbocation or by relief of steric strain.°

![Figure 5.10 Carbocation induced nucleophilic rearrangements.](image)

Migrations in $\kappa^3$-$R_3$Si(ONO)$^q$ are nucleophilic rearrangements in which the ONO ligand is reduced and the silicon atom is oxidized. The frontier orbital picture shows that the source of electrons for ligand reduction is the 3-center 4-electron bond of the hypervalent silicon and two mutually trans alkyl groups (Figure 5.11a).° DFT expectedly shows the LUMO of the octahedral intermediate as the unoccupied ONO $5b_2$ orbital with in phase p orbitals on donor atoms. Migration of the carbon nucleophile to the adjacent nitrogen terminus leads to occupation of the high energy $5b_2$ orbital and its resultant stabilization, as well as coordinative saturation at nitrogen.
5.3.2 The greater migratory aptitude of methyl versus phenyl.

The relative facility of methyl versus phenyl migration in the case of $\kappa^3$-Me$_2$Si(ONO$^Q$)$_2$, can be assessed directly because both alkyl and aryl groups are in migrating positions. In well-established cases of 1,2-nucleophilic migrations such as pinacol rearrangements, the ability of the migrating group to delocalize its charge stabilizes the transition state allowing for greater ease of migration. Experimental studies in pinacol-pinacolone rearrangements establish the greater migratory aptitude of phenyl over methyl in these 1,2-rearrangements that proceed via a cationic transition state. Silicon-to-nitrogen migrations in ONO$^Q$ ligand system are electronically different from Wagner-Meerwein shifts, where the migration terminus is a highly reactive empty carbon $\sigma$ orbital. The origin of migration in a Wagner-Meerwein shift is a low energy carbon-carbon $\sigma$ bonding pair of electrons. Therefore, high-lying $\pi$ bonding
orbitals of the phenyl group that stabilize the carbocation increase the facility of migration. In contrast to Wagner-Meerwein shifts, the empty orbital on the ONO\textsuperscript{Q} fragment is not extremely low-lying due to its antibonding character (many compounds of ONO\textsuperscript{Q} ligand are isolable and relatively unreactive). Also, the electrons involved in the migration are in a higher energy silicon σ nonbonding orbital. The three highest occupied orbitals of 2-κ\textsuperscript{3} are phenyl π bonding while the relevant donor orbital is the HOMO-4. Figure 5.12a shows an equal distribution of electron density on both the methyl and phenyl groups. The plane of the phenyl group is roughly perpendicular to the Si–N bond in the κ\textsuperscript{3} intermediate and in the migration transition state (Figure 5.7), which indicates an absence of geometric impediment to charge delocalization. However, the ability of the aryl group to donate π electrons is much less important because of the lower electrophilicity of nitrogen in ONO\textsuperscript{Q} and the higher energy of the σ nonbonding donor orbital. The lack of electron delocalization into the phenyl π system is corroborated computationally by the absence of elongation of the phenyl C1-C2 and C1-C6 bonds in the transtion state. These bonds actually contract slightly in the transition state (1.385 Å vs. 1.410 Å in the reactants), in contrast to the lengthening calculated for aryl-bridged carbocations (to 1.442 Å).\textsuperscript{104}

Since the phenyl π system does not dominate the tendency to migrate, factors that favor methyl migration can be expressed. The sp\textsuperscript{3}-hybridized methyl group is likely to both be more nucleophilic and form a weaker bond to silicon than the sp\textsuperscript{2}-hybridized phenyl group. Both these factors should favor migration of the methyl group.
Figure 5.12. Donor and acceptor orbitals of \( \kappa^3\text{-Me(Cl)(Ph)Si(ONO)} \). (a) HOMO-4 centered on carbon nucleophile. (b) LUMO centered on \( 5b_2 \) ONO orbital.

5.3.3 When are separate kinetic and thermodynamic products observed?

The stereoselectivity of the migration is determined by which step is rate limiting. Either migration itself is rate limiting, or chelation, which leads to formation of the octahedral \( \kappa^3 \) intermediate, is rate-limiting. If chelation is rate limiting, migration would occur faster than the octahedral isomer could isomerize. Chealtion is fastest when the nitrogen is anti to the chlorine, which maximizes interaction of the nitrogen lone pair with the Si–Cl \( \sigma^* \) orbital. Chelation can be thought of as an \( S_N2 \)-like attack of the nitrogen on silicon with chlorine in a pseudo leaving group position.\(^{105, 106}\) The \( \kappa^3 \) isomers that are the fastest to form are also the least stable thermodynamically (by \( \sim 6 \) kcal mol\(^{-1}\)), because the most electronegative substituents (nitrogen and chlorine) are in mutually trans positions, which does not maximize bonding in the hypervalent species. If chelation is rate limiting and migration occurs from the thermodynamically least stable
κ³ isomers, R(Cl)(R’Si(ONO)³), the kinetically formed product of migration is R'(Cl)Si(ON[R]O), possessing an equatorial chlorine. The kinetic isomer stereoisomerizes into the thermodynamic product of migration, Cl(R’Si(ON[R]O), where the chlorine is axially positioned.

Conversely, if κ¹ and κ³ isomers can interconvert before migration, and migration is rate limiting, the product of migration would occur via the lowest-energy transition state for migration. Calculations show that barriers to migration are dominated by the relative energies of the κ³ intermediates. If migration were to occur via the thermodynamically preferred κ³ isomer, R(R')(Cl)Si(ONO³), only a single product of migration would be observed, Cl(R’Si(ON[R]O), which is both kinetically and thermodynamically favored.

5.3.4 Stereoisomerization of trigonal bipyramidal X(Y)Si(ON[R]O) products.

The kinetic product Ph(Cl)Si(ON[Me]O), 2-NMe, formed in the reaction of Pb(NO³)₂ with PhMeSiCl₂ isomerizes to the thermodynamic product Cl(Ph)Si(ON[Me]O), 3-NMe, over twelve hours at room temperature in CDCl₃ (t₁/₂ = 2.5 h). The driving force for isomerization to the thermodynamic products arises from the stabilization of the axial (3 center 4 e⁻) bonds by electronegative chlorine in the position transannular to the donor amine nitrogen. Trigonal bipyramidal geometries are known to isomerize by Berry pseudorotations and turnstile variants. If the Si-N bond were a strong covalent bond that did not break, isomerization would not be observed. The bicyclic nature of the dioxoazasilocine ring and the presence of substituents on both the silicon and nitrogen in the dianionic (ON[R]O)²⁻ chelate render its two faces inequivalent.
and prevent Berry pseudorotations. The rate of isomerization of kinetic to thermodynamic products was measured by NMR (Δ\text{G}^\dagger_{\text{isomerization}} = 22.7(2) \text{ kcal mol}^{-1}) and is greater than similar isomerizations in dibenzodioxasilocine (CH₂(CH₂-3,5-^t\text{Bu}_2-2-O)_₂SiMe₂, (Δ\text{G}^\dagger_{\text{isomerization}} = 13.9 \text{ kcal mol}^{-1})^{108} that lack the Si-N bond, as well as, diethanolamine complexes, RR'Si([OCH₂CH₂]₂NMe) (Δ\text{G}^\dagger_{\text{isomerization}} = 9-13 \text{ kcal/mol}) which have more flexible silocane rings.\textsuperscript{109} The breaking of the Si-N bond in pentacoordinate fluorosilanes with intramolecular coordination of a dimethylamino group accounts for 10-12 \text{ kcal mol}^{-1} of the energetic barrier.\textsuperscript{110}

![Diagram of isomerization mechanism](image)

**Figure 5.13** Mechanism of isomerization of kinetic to thermodynamic products.

In the reaction of the ONO ligand with Ph₂SiCl₂, the kinetic product Ph(Cl)Si(ON[Ph]O) isomerizes approximately three times faster (t\textsubscript{1/2} ≈ 50 \text{ min}) than Ph(Cl)Si(ON[Me]O) (t\textsubscript{1/2} = 150 \text{ min}), consistent with the difference in basicity of nitrogen. The longer Si–NPh bond (2.7146(12) Å) in Cl(Ph)Si(ON[Ph]O) reflects the decreased Lewis basicity of nitrogen in comparison to the shorter Si–NMe bond in Cl(Ph)Si(ON[Me]O) (2.3043(16) Å). This trend in the rates of isomerization of
Ph(Cl)Si(ON[Ph]O) and Ph(Cl)Si(ON[Me]O) suggests that if a kinetic isomer Me(Cl)Si(ON[Me]O) formed in the reaction of Me₂SiCl₂, it would isomerize the most slowly and would be observable. Thus, it is most likely that Cl(Me)Si(ON[Me]O) (Si–NMe₂ = 2.302(2) Å) is both kinetically and thermodynamically favorable.

The favored mechanism of stereoisomerization occurs through two consecutive eight membered ring flips. The stable form of the 8 membered rings is these tetracyclic systems is the boat-boat conformation. A single ring flip would result in a boat-chair conformation and a temporary disruption of the of the silicon nitrogen bond. A second 8 membered ring flip by an umbrella inversion of the amine followed by silicon nitrogen bond formation would lead to another stable boat-boat conformation. The axial substituent on silicon exchanges position with the equatorial substituent located syn to the migrated R group as a result of these consecutive ring flips. The thermodynamic product has the nitrogen substituent syn to a phenyl group and the kinetic product is the other pentacoordinate stereoisomer with the nitrogen substituent located syn to apical chlorine.

In all cases migration of alkyl or aryl groups is facile. Investigations of migration barriers from analogous tin systems are presented in the next chapter. Tin has a larger coordination sphere than silicon, so a hypervalent six-coordinate silicon could prove more reactive than six-coordinate tin. This would have broad implications in reactions that use stannanes as coupling reagents for the generation of carbon nucleophiles. It would be remarkable and synthetically provident to activate the strong silicon-carbon bond for use as a less toxic, highly stable and inexpensive source of carbon nucleophiles.
5.4 Experimental Section

All procedures were carried out under an inert atmosphere in a nitrogen-filled glovebox or on a vacuum line. Chlorinated solvents and acetonitrile were dried over 4 Å molecular sieves, followed by CaH₂. Benzene was dried over sodium, and ether over sodium benzophenone ketyl. Alcohols were dried over 4 Å molecular sieves. Deuterated solvents were obtained from Cambridge Isotope Laboratories, dried using the same procedures as their protio analogues, and stored in the drybox prior to use. Pb(ONO₂)₂ was prepared as described.⁶⁷,⁷⁸ ¹H NMR spectra were measured as CDCl₃ solutions on a Varian Inova 500 spectrometer and chemical shifts are reported in ppm downfield of TMS. Kinetic measurements for the isomerization of Ph(Cl)Si(ON[Me]O) were made in CD₂Cl₂ solutions at room temperature on a Varian Inova 500 spectrometer. ESI mass spectra were obtained using a Bruker microTOF-II mass spectrometer, and peaks reported are the mass number of the most intense peak of isotope envelopes. Samples were injected as acetonitrile solutions, preceded and followed by methanol. In all cases, the observed isotope patterns were in good agreement with calculated ones.

5.4.1 Crossover experiment with protio and deutero chlorotrimethylsilane.

2,4,8,10-Tetra-tert-butyl-6,6,12-trimethyl-12H-dibenzo[d,g][1,3,6,2]dioxazasilocine, Me₂Si(ON[Me]O), is generated in situ from TMSCl and Pb(ONO₂)₂ in chlorinated solvents within ten minutes at ambient temperatures. For the crossover experiment, equal amounts of protio chlorotrimethylsilane (CH₃)₃SiCl (7.2 µL, 0.057 mmol, 1.0 equiv) and its deutero analog (CD₃)₃SiCl (CDN Isotopes) (7.2 µL) were mixed in 0.5 mL of CHCl₃ and syringed into a 1 mL 60 °C chloroform solution of
Pb(ONO\textsubscript{2}) \textsubscript{2} (30.2 mg, 0.028 mmol). The reaction solution was stored at room temperature and analyzed after 15 minutes, 4 h, and 48 h by electrospray mass spectrometry.

5.4.2 2,4,8,10-Tetra-\textit{tert}-butyl-6-chloro-12-methyl-6-phenyl-12H-dibenzo[d,g][1,3,6,2]dioxazasilocine, PhClSi(ON\textsubscript{Me})O kinetic isomer.

In an NMR tube sealed with a septum cap, 0.0105 g (0.010 mmol) of Pb(ONO\textsubscript{2}) \textsubscript{2} was dissolved in 600 µL of CD\textsubscript{2}Cl\textsubscript{2}, 4 µL (0.24 mmol, 1.2 equiv.) of PhMeSiCl\textsubscript{2} was added and a \textsuperscript{1}H NMR spectrum was recorded within 15 min. \textsuperscript{1}H NMR: \(\delta\) 1.33, 1.34 (s, 18H each, \textsuperscript{t}Bu), 3.17 (s, 3H, NCH\textsubscript{3}), 7.20, 7.42 (d, 1.2 Hz, 2H each, ArH), 7.51 (m, 3H, m-,p-Ph), 8.18 (m, 2H, o-Ph).

5.4.3 2,4,8,10-Tetra-\textit{tert}-butyl-6-chloro-6,12-diphenyl-1H-dibenzo[d,g][1,3,6,2]dioxazasilocine, PhClSi(ON\textsubscript{Ph})O kinetic isomer.

In an NMR tube sealed with a septum cap, 0.0099 g (0.009 mmol) of Pb(ONO\textsubscript{2}) \textsubscript{2} was dissolved in 600 µL of CDCl\textsubscript{3}. Ph\textsubscript{2}SiCl\textsubscript{2} (6.5 µL, 0.03 mmol, 1.7 equiv.) was added and a proton spectrum was recorded within 20 min. \textsuperscript{1}H NMR: \(\delta\) 1.28, 1.33 (s, 18H each, \textsuperscript{t}Bu), 6.54 (d, 8 Hz, 2H, o-NPh), 7.17 (m, 3H, p-,m-NPh), 7.29 (d, 2 Hz, 2H, ArH), 7.38 (d, 2 Hz, 2H, ArH), 7.42 (t, 8 Hz, 1H, p-SiPh), 7.45 (t, 8 Hz, 2H, m-SiPh), 7.94 (d, 8 Hz, 2H, o-SiPh).
5.4.4 2,4,8,10-Tetra-tert-butyl-6-chloro-6,12-dimethyl-12H-dibenzo[d,g][1,3,6,2]dioxazasilocine, kinetic and thermodynamic ClMeSi(ON[Me]O).

In an NMR tube 0.0109 g of Pb(ONO\textsuperscript{Q})\textsubscript{2} was dissolved in 600 µL of CDCl\textsubscript{3}, Me\textsubscript{2}SiCl\textsubscript{2} (5 µL) was added and a proton spectrum was recorded within 15 min of silane addition and is as reported in Chapter 4.

5.4.5 Measurement of $k_{\text{isomerization}}$ for conversion of Ph(Cl)Si(ON[Me]O) to Cl(Ph)Si(ON[Me]O).

The kinetic product Ph(Cl)Si(ON[Me]O) in the reaction of phenylmethyl dichlorosilane with Pb(ONO\textsuperscript{Q})\textsubscript{2} was generated in situ in CDCl\textsubscript{3} as described above with added dimethylterephthalate (Aldrich) as a standard. A series of NMR spectra were collected at 10 min intervals for 12 h. The $N$-methyl protons of the kinetic product Ph(Cl)Si(ON[Me]O) appear in decreasing intensity at 3.17 ppm and a resonance due to the thermodynamic isomer, Cl(Ph)Si(ON[Me]O), appears at 2.23 ppm in the $^1$H NMR spectra. Concentration data for the kinetic and thermodynamic products over the time course of isomerization were determined from normalized integrals of the $N$-methyl group versus the internal standard. These concentration data were fit to ascertain a 1\textsuperscript{st} order rate constant of isomerization.

5.4.6 Computational Methods

Geometry optimizations were performed on all complexes using 6-31G* basis set and a B3LYP functional with a PCM solvation model of dichloromethane using the Gaussian09 suite of programs,\textsuperscript{51} except that no solvation model was applied for
optimization of structures in the reaction coordinate that leads to Me₂Si(ON[Me]O).

Energies of optimized geometries are reported as free energies (G, kcal mol⁻¹) with applied thermal and zero point corrections and are standardized relative to χ³ intermediates with mutually trans hydrocarbyl groups. No symmetry constraints were applied during optimization. Stationary points on the potential energy surface were identified as minima with no negative frequencies. Starting geometries for N-alkylated and -arylated five-coordinate structures were obtained by importing the Cartesian coordinates of crystallographically characterized products reported in Chapter 4 into Gaussview and appending their ancillary groups as required. The tert-butyl groups on the ONO ligand backbone were simplified into hydrogens to reduce computational costs without affecting the electronic structure. Starting geometries for the octahedral intermediates were created by modifying the homoleptic complex Si(ONO²S){₂}₇₈.

Transition state calculations for methyl and phenyl migration were performed initially with constrained Si-C and C-N distances to locate the vicinity of the saddle points and check for the appropriate negative frequencies. A transition state search with relaxed constraints was subsequently performed to find the appropriate transition state. Only a single conformation of tetrahedral intermediates was calculated with the assumption that free rotation exists in the Si-O bond. Geometries of each unique transition state that lead to different octahedral intermediates were computed. Plots of calculated Kohn-Sham orbitals were generated using Gaussview (v. 5.0.9) with an isovalue of 0.04.
CHAPTER 6:

INCREASED LABILITY OF THE HYPERVALENT SILICON-CARBON BOND IN CONTRAST TO ANALOGOUS TIN-CARBON BONDS.

6.1 Introduction

6.1.1 Activation of the tin-carbon bond.

Organotin coupling reactions with carbon electrophiles catalyzed by palladium or platinum is a cornerstone strategy in carbon-carbon bond forming reactions. A large collection of organostannanes is commercially available to perform these organic transformations, which take place under mild conditions and often result in high yields. Functional groups including alcohols and aldehydes are tolerated in these reactions, with high turnover numbers observed for the accompanying palladium catalyst.

The key transmetalation step in these reactions is enabled by the nucleophilicity imparted to an R group by an electropositive tin. Conversely, silicon-carbon bonds are typically unreactive. In one particular example highlighting the contrast between tin-carbon bonds and silicon-carbon bonds, $p$-acetylphenyl triflate reacts with $\text{Me}_3\text{SnCH}_2\text{SiMe}_3$ exclusively to effect a methyl transfer from tin and leaving the silicon-methyl bond untouched.
The intramolecular participation of a nitrogen lone-pair has been shown to produce an enhancement of nucleophile reactivity in Stille cross-coupling, and this effect can be further augmented by ligand choice. The cross coupling of furoyl chloride with triphenylmethyl tin, catalyzed by 4 mol% of trans-PhCO(Cl)Pd(PPh₃)₂, requires extensive heating at 65°C to produce furoylbenzene. The related dimethybenzylaminotin reacts smoothly at 40°C to produce the same cross-coupled furoylbenzene (Figure 6.1). The formation of the internally complexed chlorostannane as the sole tin-containing product substantiates the role of the nitrogen in palladation.¹¹³ The authors also studied the effect of steric buttressing by using 1-
dimethylaminobenzyl-2-trimethylsilyl-diphenylmethyltin and saw no influence on reactivity. The silicon-methyl bond unremarkably remains inert, with no methyl-coupled product being observed.

6.1.2 Activation of the silicon-carbon bond.

The sp\textsuperscript{3} carbon-silicon bond can be activated by the formation of hypercoordinate silicon to promote transmetalation. The presence of one or more electron withdrawing groups on silicon such as halides or alkoxides allows for hypercoordination. Transmetalation using tetraorganosilicon is rare and occurs predominantly with vinyl and -arylsilanes.\textsuperscript{114} Hiyama first reported the use of fluoride for formation of pentacoordinate silicon, which facilitates faster transmetalation by enhancing the polarization of the Si-C bond.\textsuperscript{115} Organofluorosilicates with high coordination numbers are established homo- and cross-coupling agents in reactions with activated olefins and allylic halides.\textsuperscript{116} Denmark and coworkers introduced the use of silanolate salts as a mild alternative to the fluoride-based activation method for palladium catalyzed cross coupling reactions.\textsuperscript{117} The formation of cyclic silyl ethers by intramolecular attack also enhances the lability of the silicon-carbon bond allowing for rearrangements and migration. The stereospecific allylation of (Z)-γ-trimethylsilyl allylic alcohols is known to proceed via the intermediacy of a cyclic silyl ether (Figure 6.2a).\textsuperscript{118} Cross-coupling between functionalized aryllithium and aryl halides is also known to be mediated by cyclic silyl ethers (Figure 6.2b).\textsuperscript{119} Hurdlik and co-workers have described the reaction of a γ-oxidopropyl group on α-halosilanes which induces migrations of phenyl, allyl, 2-furyl, and even methyl groups from silicon to the α-carbon (Figure
They also describe the use of the same γ-oxidopropyl group for carbon coupling reactions by desilylation of benzylic or allylic groups with a range of electrophiles. It would be remarkable and synthetically provident to activate the strong silicon-carbon bond for use as a less toxic, highly stable and compatible alternative source of carbon nucleophiles.

A. 

B. 

C. 

\[ Z = \text{Ph, Me, 2-furyl, allyl} \]

Figure. 6.2 Activation of the silicon carbon bond.

Chapter 4 reported that silylation of the oxidized ligand in lead(II) bis(3,5-tert-butyl-1,2-quinone-(3,5-di-tert-butyl-2-hydroxy-1-phenyl)imine), Pb(ONO\(_2\))\(_2\), with chlorosilanes \( RSiX_2Cl \) (\( R = \text{Me, Ph}; \ X = \text{Me, Ph, Cl} \)) results in tetracyclic, pentacoordinate silicon compounds \( X(Y)Si(ON[R]O) \) (\( X = \text{axial, } Y = \text{equatorial} \)) with a reduced, dianionic
amine-bisphenolate ligand in which the methyl or phenyl group has migrated to nitrogen. Chapter 5 detailed the mechanism of these 1,2-migrations that proceed stepwise via silylation of the [ONO\(^Q\)]\(^-\) ligand to form a tetrahedral intermediate \(\kappa^1\)-R(X)(Y)Si-ONO\(^Q\). Ring closure forms an octahedral intermediate \(\kappa^3\)-R(X)(Y)Si(ONO\(^Q\)) (X trans to N; Y trans to R) from which migration results in pentacoordinate products. Contreras and coworkers have also reported that alkylstannanes such as Me\(_2\)SnCl\(_2\) and \(n\)Bu\(_2\)SnCl\(_2\) react with Zn(ONO\(^Q\))\(_2\) to effect alkyl transfer and ligand reduction forming R(Cl)Sn(ON[R]O) (R = CH\(_3\), \(n\)Bu).

In this chapter, the rates of alkyl migrations from silicon are compared to those from tin. While MeSiCl\(_3\) reacts with Pb(ONO\(^Q\))\(_2\) to yield Cl\(_2\)Si(ON[Me]O) upon methyl migration, the analogous reaction with methyltrichlorostannane yields Cl(Me)(Cl)Sn(ONO\(^Q\)), a transmetalation product. A direct comparison of the rates of methyl migration from silicon and tin are furnished by the reaction of H(DOPO\(^Q\)) (DOPO = 2,4,6,8-tetra-tert-butyl-1-oxo-1H-phenoazin-9-olate, Figure 6.5) with mono- and trimethylchlorosilanes as well as -stannanes. The synthesis, characterization, and structures of reduced DOPO compounds with migrated R groups are also reported.
6.2 Results

6.2.1 Methyl migration from silicon but not tin monomethyl dichloro compounds.

Scheme 6.1. Silylation of Pb(ONO$^{Q}$)$_2$ proceeds via tetrahedral and octahedral intermediates to form pentacoordinate products of methyl migration X(Y)Si(ON[R]O)

The net reaction of MeSiCl$_3$ with Pb(ONO$^{Q}$)$_2$ results in methyl migration to give Cl$_2$Si(ON[Me]O). If Pb(ONO$^{Q}$)$_2$ is reacted with MeSiCl$_3$ in CD$_2$Cl$_2$ at -78 °C, a color change from dark green to bright purple is observed immediately, but no silylated intermediates are observed at -50 °C by $^1$H NMR. The color change is attributed to the formation of the lead monochloride complex, PbCl(ONO$^{Q}$), and is verified by changes in chemical shift of the (ONO$^{Q}$) ligand and a decrease in its intensity by 50%. The first equivalent of the ONO$^{Q}$ ligand reacts immediately and the consumption of PbCl(ONO$^{Q}$) is complete as the temperature is raised to -35 °C. The appearance of silylated intermediates is not observed even after complete consumption of the ONO$^{Q}$ ligand. The disappearance of ONO$^{Q}$ ligand signals could be attributed to a fast exchange of silylated intermediates with small amounts of radicals such as Cl(Me)Si(ONO$^{S0}$) on the NMR timescale; Me$_2$Si(ONO$^{S0}$) and Si(ONO$^{S0}$)$_2$ have been reported. Only when the reaction is warmed
to -10 °C is the gradual appearance of migrated product Cl₂Si(ON[Me]O)₂ detected with a yield of 90% by integration relative to an internal standard. The rate of appearance of migrated product was measured as a function of time, \( k_{\text{ProductAppearance}} = 4.3(7) \times 10^{-4} \text{ s}^{-1} \) at -28 °C, CDCl₃. The rate of methyl migration from silylated intermediates cannot be slower than the rate of appearance of migrated product. Therefore, it can be inferred that migration is at least as fast as product appearance, \( \Delta G_{\text{Si-Mig}}^{\ddagger} \leq 17.4 \text{ kcal mol}^{-1} \).

The analogous reaction of MeSnCl₃ with Pb(ONO)₂₂ leads to a product of transmetallation, Cl(CH₃)(Cl)Sn(ONO)², whose octahedral crystal structure is shown in Figure 6.4. The geometry is best described as octahedral with the ligand adopting a mer geometry and chlorines occupying mutually trans positions. The Sn-Me is trans to the
nitrogen with a Sn-N distance of 2.2152(14) Å and trans angles of 149.29(5)°, 178.33(7)° and 169.673(16)°.

The same basic structure was observed for the analogues Cl(R)(Cl)Sn(ONO) (R = nBu, Ph) formed from reaction of Zn(ONO)\(_2\) with BuSnCl\(_3\), PhSnCl\(_3\) or Ph\(_2\)SnCl\(_2\). In the reaction of Pb(ONO)\(_2\) with methyltrichlorostannane, no migration is observed by NMR and only a single isomer of the transmetalation product is observed in situ at -40 °C. The NMR spectrum shows a symmetrical product with a single Sn-Me peak and pairs of \(^1\)Bu and ArH peaks. The chemical shift of Sn-CH\(_3\) (δ 1.54) and \(^{117}\)Sn\(^{1}H\) (δ –365.65) are consistent with an unmigrated methyl group and octahedral tin. Some line broadening is associated with all peaks, which sharpen considerably upon treatment with iodobenzene dichloride. This line broadening is attributed to exchange with radicals such as Me(Cl)Sn(ONOSO).

The isolated octahedral product Cl(Me)(Cl)Sn(ONO) was heated to measure rates of methyl migration from tin. Upon heating at 75 °C for 10 d, at least 90 % of the compound remains intact and no migration is observed, so no more than 10% of the transmetalation product has disintegrated, \(k_{\text{Decomp}} < 3.2 \times 10^{-7} \text{ s}^{-1}\). Since migration is not observed prior to decomposition, a minimum barrier for migration (\(\Delta G^\ddagger_{\text{Sn-Mig}} > 31 \text{ kcal mol}^{-1}\)) can be ascertained on the assumption that no more than 10% of the octahedral product could have migrated. The lack of observed migration from tin indicates that the silicon-carbon bond is at least 10\(^{10}\) times more reactive than the tin-carbon bond for effecting methyl migrations in this system (\(\Delta \Delta G^\ddagger > 14 \text{ kcal mol}^{-1}\)).
Figure 6.4. Thermal ellipsoid plot of Cl(Me)(Cl)Sn(ONO\textsuperscript{3}). Hydrogen atoms and solvent molecules are omitted for clarity.
6.2.2 Silylation or stannylation of the DOPO\(^0\) ligand to form N-migrated products.

![Reaction scheme](image)

Figure 6.5. Silylation of Pb(DOPO\(^0\))\(_2\) or HDOPO\(^0\) to form pentacoordinate products of N-methyl/phenyl migration, \(R_2M(\text{DOPO-}R)\) (\(M = \text{Si, Sn}\); \(R = \text{Me, Ph}\)).

Silylation or stannylation of the dioxophenoxazine, DOPO, ligand from Pb(DOPO\(^0\))\(_2\) or HDOPO\(^0\) with trimethyl- or triphenylsilane or the corresponding stannanes in chlorinated solvents leads to the formation of migration products, \(R_2M(\text{DOPO-}R)\). The reaction to form the N-methylated product, Me\(_2\)Si(DOPO-Me), proceeds in days at room temperature. The reaction solution changes color from indigo of Pb(DOPO\(^0\))\(_2\) or purple HDOPO\(^0\) to a progressively lighter color as migration proceeds.

The \(^1\)H and \(^13\)C NMR spectra show three distinct chemical shifts for the methyl groups, with two methyl groups showing upfield shifts characteristic of Si-CH\(_3\) groups (\(^1\)H \(\delta\) - 0.10, 0.75, \(^{13}\)C \(\delta\) -0.06, 0.35 ppm), and the third methyl group resonating more downfield (\(^1\)H \(\delta\) 2.89, \(^{13}\)C \(\delta\) 46.95 ppm), consistent with its formulation as an N-CH\(_3\) group. The analogous ligand reduction of the ONO compound was also noted to have characteristic upfield and downfield methyl group shifts (\(^1\)H \(\delta\) 0.34, 0.46, and \(\delta\) 2.98).
The observation of two distinct Si-CH₃ resonances in a 2:1 ratio in Me₂Si(DOPO-Me) suggests a trigonal bipyramidal structure. X-ray characterization confirms the reduced nature of the DOPO ligand with an N-methylated substituent. The meridional geometry of the DOPO ligand is maintained upon methylation even though alkylation forces the ligand out of planarity (Figure 6.6). A strong bond in this case is formed with the equatorial nitrogen (Si-N = 1.9324(11) Å), and the aryloxide arms are in mutually trans axial positions (Si–O1 = 1.8611(10) Å; Si–O2, = 1.8336(10) Å) with an obtuse O–Si–O angle of 162.18(4)°. The methylated nitrogen and two Si-CH₃ groups occupy the equatorial positions, N-Si-C2 = 122.83(6)°, N-Si-C3 = 115.72(6)°. The geometry of the five-coordinate structure differs from the analogous Me₂Si(ON[Me]O), in which the methylated amine nitrogen occupies one of the axial positions with a long bond to silicon (Si-N = 2.605(2) Å) and oxygens are equatorial (Si–O1 = 1.6599(15) Å; Si–O2, = 1.6541(17) Å) with shorter bond lengths.

The analogous reaction of Me₃SnCl with HDOPO proceeds much faster (within 2 hours at 5°C). Isoation of pure material was unsuccessful, and in situ reaction yields are modest (60 %). The migrated product shows a single N-CH₃ (δ 2.86, 3H) and two SnCH₃ peaks (δ 0.36, 1.08, 3H each) along with two iBu peaks (δ 1.28, 1.51, 9H each) and a single ArH peak (δ 7.09, 2H). Diamagnetic products of migration are typically colorless, but only red and green crystals were isolated from solution. The green crystals are the unalkylated product Me₂Sn(DOPOSO) (Figure 6.7) analogous to Me₂Si(ONOSO) (Figure 4.11). The red crystals are also a paramagnetic product, Me₂Si(DOP-CH₂-O), that results from insertion of a methylene group into the DOPO backbone (Figure 6.8).
Figure 6.6. Thermal ellipsoid plot of Me₂Si(DOPO-Me). Hydrogen atoms are omitted for clarity.
Figure 6.7 Thermal ellipsoid plot of Me$_2$Sn(DOPO)$^{50}$. Hydrogen atoms are omitted for clarity.
Figure 6.8. Thermal ellipsoid plot of radical product of methylene insertion Me$_2$Sn(DOP-CH$_2$-O). Hydrogen atoms on bridged methylene are shown whereas all others are omitted. Only a single orientation of the disordered CH$_2$O bridge is shown for clarity.

The $N$-phenylated products of the respective reactions of Ph$_3$SiCl or Ph$_3$SnCl with HDOPO$^+$ in the presence of NEt$_3$ were also isolated. The reactions with chlorotriphenylsilane proceeds to completion in 1 d at room temperature and with triphenylstannane in 90 minutes. Ph$_2$Si(DOPO-Ph) exhibits the typical geometry of $N$-alkyl/aryl-ONO complexes such as Ph$_2$Si(ON[Ph]O), with the nitrogen apically positioned in the trigonal bipyramid and the aryloxide arms in equatorial positions (Figure 6.9).
Figure 6.9 Thermal ellipsoid plot of Ph₂Si(DOPO-Ph). Hydrogen atoms are omitted for clarity.

Silicon-nitrogen distances increase from 2.302(2) Å in N-methylated Cl(Me)Si(ON[Me]O) to in Ph₂Si(ON[Ph]O) (Chapter 4). Short Si-N bond distances are rationalized on the basis of amine donation to the Si-Cl σ* orbital and long distances to the absence of electronegative substituents as well as the lowered Lewis basicity of N-phenylated compounds. The strength of the silicon-nitrogen interaction is also reflected in the degree of pyramidalization at nitrogen, where the compounds with transannular chloro substituents show strongly pyramidalized nitrogen atoms (sum of C-N-C angles = 335.4(2) ° in Cl(Me)Si(ON[Me]O), 336.7(2) ° in Cl(Ph)Si(ON[Me]O). Ph₂Si(ON[Ph]O)
exhibits a nearly planar nitrogen atom (avg. of sum of C-N-C angles for two
crystallographic independent molecules = 351.6°) and a very long average Si-N distance
of 2.84 Å. In contrast, Ph₂Si(DOPO-Ph) exhibits a very pyramidalized nitrogen (sum of C-
N-C angles = 333.7(2)°) and a correspondingly short Si-N bond length of 2.493(10) Å. The
O–Si–O angle is 120.81(6)°, close to the ideal angle for equatorial substituents of a
trigonal bipyramid.

In the stannyl congener Ph₂Sn(DOPO-Ph), the DOPO ligand is meridional with the
oxygens occupying apical positions (Figure 6.10) This geometry is thus similar to that of
Me₂Si(DOPO-Me) but different from that of its silicon congener or any ONO analogues.
It can be envisioned to relate to the usual geometry by a Berry pseudorotation along the
Sn-Ph (C₄₁) axis. The O–Sn–O angle 148.77(11)° shows a large deviation from linearity
due to a larger Sn center. A surprisingly short Sn-N bond (2.273(3) Å) results from the
equatorial position of nitrogen. The different geometric arrangements apparently lie on
a shallow potential energy surface.
Figure 6.10 Thermal ellipsoid plot of Ph₂Sn(DOPO-Ph)·CHCl₃. Hydrogen atoms and solvent molecules are omitted for clarity.
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<th>Ph$_2$Sn(DOPO-Ph)</th>
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$Z = N$-migrated substituent; $X =$ substituent syn to $Z$; $Y =$ substituent anti to $Z$
6.2.3 Formation of silyl- and stannyl-DOPQ unmigrated intermediates.

No intermediates prior to migration are observed in the plethora of reactions of the ONO ligand with silanes and stannanes with the exception of Cl(Me)(Cl)Sn(ONOQ), from which migration is not observed. In the reaction of Pb(ONOQ)2 with MeSiCl3, accumulation of an unmigrated silylated intermediate, either κ1- or κ3-MeCl2Si(ONOQ), is implied by the disappearance of ONO ligand signals prior to product formation, but the intermediate could not be characterized by 1H NMR.

While migration in the reaction of Pb(DOPOQ)2 with Me3SiCl takes weeks at room temperature, an intermediate forms rapidly (2 minutes at 65 °C and 30 min at RT). This intermediate is isolable, and spectroscopic data establish that it is four-coordinate κ1-Me3Si(DOPOQ). 1H and 13C NMR spectra of the transmetalated intermediate show that all three silyl-methyl groups are equivalent, but that the two aromatic rings and the four tert-butyl groups are all inequivalent, indicating an unsymmetrical structure. The structure is confirmed by X-ray crystallography (Figure 6.11), which shows a tetrahedral silicon and characteristically shorter carbon-oxygen and -nitrogen bond distances for the iminoquinone (C22–O2 = 1.230(4), N-C21 = 1.299(4) Å) and longer distances for the aryloxide (C12–O1 = 1.348(4), N-C11 = 1.370(4) Å). The silicon is directed towards the central nitrogen atom with a marginal interaction (Si-N = 2.973 Å), an acute O1-Si-C1 angle (100.11(14) °), and slightly expanded O1-Si-C2, O1-Si-C3 angles (110.52(14) °, 111.60(15)°).
Figure 6.11 Thermal ellipsoid plot of silylated intermediate $\kappa^1$-Me$_3$Si(DOPO$^\ominus$)$\cdot$CHCl$_3$. Hydrogen atoms and solvent molecules are omitted for clarity.

*In situ* NMR spectroscopy in the reaction of Pb(DOPO$^\ominus$)$_2$ with MeSiCl$_3$ shows a symmetric $^1$H NMR spectrum at $-10$ °C with a single Si-Me resonance, a pair of $^1$Bu resonances, and a single aromatic resonance. Either a fluxional $\kappa^1$-MeCl$_2$Si(DOPO$^\ominus$) intermediate or any static isomer of $\kappa^3$-MeCl$_2$Si(DOPO$^\ominus$) intermediate could explain this spectrum. VT NMR spectra at lower temperatures show a dramatic downfield shift of
the ArH peak along with broadening and subsequent sharpening without decoalescence. The wide variability in ArH chemical shift (0.44 ppm downfield shift from −0 °C to −80 °C) reflects a change in the in the equilibrium concentration of κ¹ and κ³ isomers.

![Chemical shift variability of ArH](image)

Figure 6.12 Chemical shift variability of ArH in MeCl₂Si(DOPO⁰) (CD₂Cl₂, 500 MHz). Inset, bottom to top T = −65 °C, −50 °C, −30°C, −20 °C.

These observations indicate that the κ¹- and κ³-MeCl₂Si(DOPO⁰) intermediates have similar energies and are in a temperature dependent equilibrium that favors κ¹-MeCl₂Si(DOPO⁰) at higher temperatures, whereas κ³-MeCl₂Si(DOPO⁰) is enthalpically favored. The upfield ArH chemical shift (δ 7.68) is consistent with a κ¹ silane (δ 7.45, 7.57 for each ArH) of κ¹ Me₃Si(DOPO⁰)) representative of the tetrahedral silicon, whereas the downfield shift is representative of a κ³ isomer (δ 8.01 (s, 2H, ArH) for κ³-Cl(Me)(Cl)Sn(DOPO⁰) vide infra).

The reaction of Me₃SnI with either Pb(DOPO⁰)₂ or H(DOPO⁰)/Et₃N at −40 °C also shows a metalated intermediate. The intermediate has one Sn-CH₃ resonance, one aromatic peak, and a pair of ‘Bu resonances. Neither a static κ¹-Me₃Sn(DOPO⁰) (4 ‘Bu, 2
ArH, 1 Sn(CH₃)₃ nor a κ³-Me₃Sn(DOPOQ) (2 ¹Bu, 1 ArH, 2 Sn-Me (2:1 axial:equatorial) intermediate can explain this spectrum, therefore the molecule must be fluxional. Chemical shifts do not vary significantly between – 10 °C and – 95 °C. The ArH resonance decoalesces at – 80 °C, indicating that the ground state structure is . κ¹-Me₃Sn(DOPOQ).

![Figure 6.13 VT ¹H NMR spectra (CD₂Cl₂, 500 MHz) of the reaction of H(DOPOQ)₂ and NEt₃ with Me₃SnI. Bottom: T = -80 °C Middle = – 70 °C Top: T = –15 °C. Key: o = κ¹Me₃Sn(DOPOQ); □ = Me₃SnI; ◊ = NEt₃.](image)

The reaction of MeSnCl₃ with Pb(DOPOQ)₂ leads to a product of transmetalation (Figure 6.14) analogous to the series of ONO structures, Cl(R)(Cl)Sn(ONO) (R = Me, Bu, Ph). The geometry of the DOPO ligand pinches the ligand backbone, shortening the Sn-N bond (2.172(2) Å) and lengthening the Sn–O bond distances (2.1760(13), 2.1925(13) Å) The increase in bond distances is also reflected in a small change of the the O1-Sn-O2 angle to 146.05(5)°. The unconstrained complex Cl(Me)(Cl)Sn(ONO) has a longer Si-N distance (2.2152(14) Å) and shorter Sn-O bonds (2.1229(12), 2.1251(12) Å).
Figure 6.14 Thermal ellipsoid plot of Cl(Me)(Cl)Si(DOPO). Hydrogen atoms are omitted for clarity.
### TABLE 6.3

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<td>6328 ([R_{int} = 0.0435])</td>
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6.2.4 Kinetics of methyl migration in Si/Sn DOPO compounds.

6.2.4.1 Methyl migration from κ¹-Me₃Si(DOPOQ)

The barrier for methyl migration from κ¹-Me₃Si(DOPOQ) were measured by UV-vis kinetics. The tetrahedral intermediate can be generated cleanly at room temperature from a stoichiometric mixture of Me₃SiCl and HDOPOQ with 3 equiv. of NEt₃. The migration proceeds to completion in approximately three weeks at room temperature as measured by ¹H NMR. Decreasing intensity of peaks associated with the tetrahedral intermediate are concurrent with increasing intensity of migrated product. The reaction mixture turns pale brown as the reaction proceeds and rate measurements by UV-vis spectroscopy (55.4 °C, CHCl₃) show two isosbestic points indicating a clean reaction (Figure 6.15). Triplicate measurements provided a rate constant of 0.0058(4) min⁻¹ (Figure 6.16) translates into an activation energy ΔG‡ₘᵢᵍ = 25.3 kcal mol⁻¹.
Figure 6.15. Multiwavelength kinetics plot of methyl migration from $k^1\text{-Me}_3\text{Si(DOPO)}$.

Figure 6.16. First order UV-vis kinetics plot for methyl migration from $k^1\text{-Me}_3\text{Si(DOPO)}$. 
6.2.4.2 Methyl migration from $\kappa^1$-$\text{Me}_3\text{Sn}(\text{DOPO}^\ominus$)

The kinetics of the analogous reaction of $\text{Me}_3\text{SnCl}$ with $\text{HDOP}^\ominus$ (with NEt$_3$) were measured by NMR. The intermediate in this reaction is generated in CDCl$_3$ at -40° C in 70% yield. Decreasing intensity of peaks associated with the $\kappa^1$ intermediate is concurrent with the increasing intensity of the migrated product. Rate measurements were made in a CDCl$_3$ solution by $^1$H NMR at -10 °C. The reaction mixture changes color from a dark green to a pale brown color as the reaction proceeds to completion. The \textit{in situ} yield of the migration product is lowered to 70% by the concomitant formation of radical products, although the decay of the intermediate gives the same rate constant ($k_{\text{obs}} = 0.026(2) \text{ min}^{-1}$) as the growth of the product (Figure 6.17). The yield (65%) and rate constant (0.024(2) min$^{-1}$) constant were measured in the presence of radical inhibitor TEMPO, indicating that migration does not proceed via a radical mechanism.)

Given the \textit{in situ} yield of 70%, the actual rate constant for migration $k_{\text{Mig}}$ is 0.0175 min$^{-1}$, corresponding to an activation energy $\Delta G^\ddagger_{\text{SnMe}_3}$ of 19.5 kcal mol$^{-1}$. 
Figure 6.17. First order NMR kinetics plot for methyl migration from $\kappa^1$-Me$_3$Sn(DOPO)$^Q$, based on disappearance of aromatic proton of $\kappa^1$-Me$_3$Sn(DOPO)$^Q$ (Arl) and appearance of N-Me and aromatic peak (ArP) of product, Me$_2$Sn(DOPO-Me).

6.2.4.3 Methyl migration from $\kappa^3$-MeCl$_2$Si(DOPO)$^Q$

$\kappa^3$-MeCl$_2$Si(DOPO)$^Q$ can be generated in a high yield at temperatures below 0 °C from a stoichiometric reaction of either Pb(DOPO)$^Q$$_2$ or HDOPO$^Q$ (and triethylamine) with MeSiCl$_3$. The peaks associated with the intermediate decrease in intensity over time as the migrated product appears. The $\kappa^3$-intermediate has two possible stereoisomers. The $C_{2v}$ symmetric octahedral isomer, Cl(Me)(Cl)Si(DOPO)$^Q$, would have its methyl group in an equatorial position and cannot undergo direct migration. The $C_3$ symmetric isomer,
MeCl$_2$Si(DOPO$^0$), has its methyl group axial and is capable of 1,2-migration. NMR spectra at 0 °C suggest the preponderance of $\kappa^1$-MeCl$_2$Si(DOPO$^0$) in rapid equilibrium with at least one $\kappa^3$ isomer suggesting that isomerization is faster than migration. The rate of appearance of migrated product was measured by the characteristic appearance of the N-CH$_3$ peak. The reaction mixture turns from a deep navy blue to a pale magenta color as the reaction proceeds to completion. The activation energy of migration was determined to be $\Delta G^\ddagger_{\text{SiMe}} = 20.4$ kcal mol$^{-1}$ with a rate constant 0.016(2) min$^{-1}$.

![Graph showing Cl$_2$SiDOPO-Me Migration at 0°C in CD$_2$Cl$_2$](image)

**Figure 6.18.** First order NMR kinetics plot for methyl migration from MeCl$_2$Si(DOPO$^0$) (CD$_2$Cl$_2$, 0 °C).
6.2.4.4 Attempted observation of methyl migration from $\kappa^3$-Cl(Me)(Cl)Sn(DOPO)$^\text{Q}$.

The reaction of MeSnCl$_3$ with Pb(DOPO)$^\text{Q}_2$ leads to the isolation of $\kappa^3$-Cl(Me)(Cl)Sn(DOPO)$^\text{Q}$, which has its methyl positioned trans to nitrogen and cannot undergo migration directly. *In situ* monitoring of metalation at -40 °C shows only this isomer. Upon heating a CDCl$_3$ solution of $\kappa^3$-Cl(Me)(Cl)Sn(DOPO)$^\text{Q}$ for 10 d at 70 °C, no product of migration is discernible and less than 10% of the starting material has undergone decomposition. The estimated minimum barrier of migration ($\Delta G^\ddagger > 31$ kcal mol$^{-1}$) is a consequence of the observation that less than 10% decomposition of the material occurs in these conditions.

6.2.5 DFT mapping of reaction coordinates.

DFT calculations were carried out for the reactions of MeCl$_2$M(ONO)$^\text{Q}$, MeCl$_2$M(DOPO)$^\text{Q}$ and Me$_3$M(DOPO)$^\text{Q}$ (M = Si and Sn) using the B3LYP functional and a 6-31G* basis set for all atoms except Sn, for which the LANL2DZ basis set was used. A PCM model in CH$_2$Cl$_2$ was applied to all calculations involving DOPO.

The reaction coordinate for Me$_3$M(ONO)$^\text{Q}$ exemplifies the general features of these reactions (Figure 6.19). All transition states were identified including the transition state for ring closure for tin, which closely resembles the geometry of $\kappa^3$-Me$_3$Sn(ONO)$^\text{Q}$. The barrier to methyl migration from Me$_3$Sn(ONO)$^\text{Q}$ is modest ($\Delta G^\ddagger_{\text{calc}} = 14.6$ kcal mol$^{-1}$) and substantially smaller than migration barrier from $\kappa^1$-Me$_3$Si(ONO)$^\text{Q}$ ($\Delta G^\ddagger_{\text{calc}} = 19.3$ kcal mol$^{-1}$).
The substitution of alkyl groups by chlorine (Figure 6.20) strongly stabilizes $\kappa^3$ species ($\Delta \Delta G^\circ = -23.8$ and $-30.9$ kcal mol$^{-1}$ for silicon and tin, respectively). The calculated barriers for migration from $\kappa^1$ species are smaller in $\text{MeCl}_2\text{M(ONO)}^\circ$ than in $\text{Me}_3\text{M(ONO)}^\circ$ compounds ($\Delta \Delta G^\ddagger = -8.1$ and $-10.5$ kcal mol$^{-1}$ for Si and Sn, respectively).
Figure 6.20. Reaction coordinate of ONO after metalation with MeSiCl₃ (top) and MeSnCl₃ (bottom). The transition state for ring closure could not be located for tin.
The ground state stabilization for tin caused by electronegative substituents increases the barrier to migration because the corresponding transition state is stabilized to a lesser degree. Octahedral tin is calculated to have a very large migration barrier, $\Delta G^\ddagger_{\text{cadd}} = 34.4$ kcal mol$^{-1}$, consistent with the high thermal stability of Cl(Me)(Cl)Sn(ONO)$^O$. In the case of silicon, the same substitution inverts the ground state from $\kappa^1$ to $\kappa^3$ and leads to a smaller net barrier of migration, but the difference is modest ($\Delta G^\ddagger_{\text{Me}_3\text{Si}} = 19.3$ kcal mol$^{-1}$ and $\Delta G^\ddagger_{\text{MeCl}_2\text{Si}} = 17.8$ kcal mol$^{-1}$). The experimentally observed $\Delta G^\ddagger_{\text{Mig}} \sim 17$ kcal mol$^{-1}$ for MeCl$_2$Si(ONO)$^O$ is agreement with DFT.

The reactions of Me$_3$M(DOPO)$^O$ are shown in Figure 6.21 on the energy scale calibrated to their respective octahedral intermediates. $\kappa^3$-Me$_3$Si(DOPO)$^O$ exists on a very shallow potential energy surface and easily falls into its tetrahedral resting state. The transition state of ring closure for tin chelation ($5$-$\kappa^1$-TS- $\kappa^3$) that leads to $\kappa^3$-Me$_3$Sn(DOPO)$^O$ could not be located. In accordance with Hammond’s postulate it is mostl likely a late transition state, resembling $5$-$\kappa^3$.

Calculated barriers for migration are larger for DOPO than for ONO ($\Delta \Delta G^\ddagger_{\text{Si}} = 21.0$ kcal mol$^{-1}$, $\Delta \Delta G^\ddagger_{\text{Sn}} = 13.8$ kcal mol$^{-1}$). This substitution also stabilizes the $\kappa^1$ structures relative to the $\kappa^3$ species ($\Delta \Delta G^*_{\text{Si}} = -11.7$ kcal mol$^{-1}$, $\Delta \Delta G^*_{\text{Sn}} = -7.0$ kcal mol$^{-1}$). Theory overestimates migration barriers in silicon and tin by 15 and 9 kcal mol$^{-1}$, respectively, compared to experiment, but correctly predicts that migration from tin is faster.
Figure 6.21. Reaction coordinate of Me$_3$M(DOPO$^q$).
The ground state of MeCl₂Sn(DOPO⁰) is octahedral 10-κ³ (Figure 6.22), whereas κ¹-MeCl₂Si(DOPO⁰) is the most stable intermediate prior to migration for silicon. This is in agreement with experiment for tin, but not for silicon where a temperature dependent equilibrium mixture is observed. As usual, there are two κ³ isomers, and the one that cannot migrate directly is more stable by 6 kcal mol⁻¹. The barrier for methyl migration from 8-κ³ is 27.3 kcal mol⁻¹, again over estimated in comparison to experiment (ΔG‡MeCl₂Si = 20.4 kcal mol⁻¹). The migration barrier from octahedral tin (10-κ³) is prohibitively high at 44.4 kcal mol⁻¹. Theory correctly predicts that migration from octahedral silicon is much faster than from tin (ΔΔG‡Calc = 17.6 kcal mol⁻¹, ΔΔG‡Exp > 10.7 kcal mol⁻¹).

The transition states that lead to octahedral 9-κ³ and 10-κ³ were not located. Even locating a κ¹ minimum by DFT was arduous, as it easily relaxes into the κ³ structure. This suggests that the barrier to chelation is very small in agreement with Hammond’s postulate. In this case the barriers to migration are substantially higher than barriers to isomerization.
Figure 6.22. Reaction coordinate showing MeCl₂M(DOPO⁰).
6.3 Discussion

6.3.1 The greater reactivity of 4 coordinate tin in comparison to 4 coordinate silicon.

The 2,4,6,8-tetra-tert-butyl-1,9- dioxophenoxazinate DOPO ligand is a modified analogue of the ONO ligand with an oxygen bridge between its rings. An exploration of its metal complexes was recently published by our group. The DOPO ligand has an analogous electronic structure to ONO (Figure 6.23), but it is more difficult to reduce DOPO\(^{\text{Q}}\) due to its additional oxygen donor and nominal aromaticity. Additionally, it has restricted flexibility due its oxygen bridge. Both electronic and structural rigidity slow migration and allow for the observation of intermediates. This allows a direct experimental comparison of methyl migration rates from silicon and tin (Figure 6.24).

![Figure 6.23. The redox active orbital and common oxidation states of ONO and DOPO ligands.](image)

The reaction of Pb(DOPO)\(_2\) with Me\(_3\)SiCl proceeds via the isolable four-coordinate intermediate \(\kappa^1\)-Me\(_3\)Si(DOPO\(^{\text{Q}}\)), whose structure is confirmed by X-ray crystallography. 1,2-methyl migration that cleaves the silicon carbon bond occurs over
weeks at room temperature ($\Delta G^\ddagger_{\text{SiMe}_3} = 25.3$ kcal mol$^{-1}$ at 55.4 °C). In comparison, the analogous reaction with Me$_3$SnCl proceeds much faster and is complete in 2.5 h at −10 °C ($\Delta G^\ddagger_{\text{SnMe}_3} = 19.5$ kcal mol$^{-1}$). This difference in reactivity ($\Delta \Delta G^\ddagger = 5.8$ kcal mol$^{-1}$) corresponds to an increased rate of about $10^4$ for tin. DFT calculations on these trimethyl DOPO systems suggest that the difference in reactivity is not due to the intrinsic barrier of migration from the octahedral intermediates, which is 9.5 kcal mol$^{-1}$ lower for silicon (Figure 6.21). Rather, the comparatively slower migration rate from Si is exclusively due to the much greater stability of the tetrahedral silicon intermediate. The calculated migration barrier from tetrahedral silicon 6-$\kappa^1$ ($\Delta G^\ddagger_{\text{SiMe}_3} = 40.3$ kcal mol$^{-1}$) is significantly higher than from tetrahedral tin ($\Delta G^\ddagger_{\text{SnMe}_3} = 28.4$ kcal mol$^{-1}$). The analogous calculations on the ONO ligand with trimethylsilyl or –stannyl groups also mirror this result (Figure 6.19), which suggests that relative energies of tetrahedral ground states dictate faster migration rates from tin.

This conclusion is only valid if both species have tetrahedral ground states. Unsymmetrical $^1$H and $^{13}$C NMR spectra of the Me$_3$Si(DOPO$^\text{Q}$) intermediate confirm that the solid state $\kappa^1$ structure is retained in solution. No symmetrization was observed at a range of temperatures, suggesting that an octahedral structure for Si is high in energy. $^1$H NMR spectra of Me$_3$Sn(DOPO$^\text{Q}$) are symmetrical at all temperatures above −70 °C. Below −70 °C, the ArH peak decoalesces, which implies that the ground state is $\kappa^1$-Me$_3$Sn(DOPO$^\text{Q}$). The coalescence point can be used to estimate the exchange rate$^{124}$ as the two ends of $\kappa^1$-Me$_3$Sn(DOPO$^\text{Q}$) must exchange via $\kappa^3$-Me$_3$Sn(DOPO$^\text{Q}$) ($k = 30$ s$^{-1}$, −70 °C, $\Delta G^\ddagger_{\text{Chelation}} = 10.4$ kcal mol$^{-1}$). In this case both tetrahedral silicon and tin are more
stable than their octahedral structures, although for tin, the $\kappa^3$ species is close in energy to its $\kappa^1$ ground state.

6.3.2 The greater reactivity of 6 coordinate silicon in comparison to 6 coordinate tin.

Replacing methyl groups with electronegative substituents such as chlorine undoubtedly increases the stability of $\kappa^3$ intermediates relative to $\kappa^1$ structures. For MeCl$_2$SnL$^Q$ (L = ONO, DOPO), the $\kappa^3$ species are unambiguously assigned with X-ray structures. DFT implies that these structures are thermodynamically favored by over 20 kcal mol$^{-1}$. For MeCl$_2$Si(DOPO$^Q$), a temperature dependent equilibrium between $\kappa^1$ and $\kappa^3$ species suggests that they are close in energy. The increasingly downfield chemical shift of the ArH peak with decreasing temperature suggests that the $\kappa^3$ form is enthalpically favored, consistent with an entropic preference for the more flexible $\kappa^1$ species at high temperatures. While MeCl$_2$Si(ONO$^Q$) could not be discerned by NMR, DFT shows that $\kappa^3$-Cl(Me)(Cl)Si(ONO$^Q$) is favored energetically ($\Delta G^\text{calc} = -6.6$ kcal mol$^{-1}$). Even qualitatively, the increased structural rigidity of the DOPO$^Q$ ligand in comparison to ONO$^Q$ suggests that $\kappa^3$-MeCl$_2$Si(ONO$^Q$) should be more favored relative to $\kappa^1$. The MeCl$_2$(DOPO$^Q$) analogue is an equilibrium mixture, therefore it is even more likely that the $\kappa^3$ form is the ground state for MeCl$_2$Si(ONO$^Q$).

The migration barriers for tin and silicon from $\kappa^3$ ground states can now be compared. The relative rates of methyl migration from MeCl$_2$M(DOPO$^Q$) (M = Si or Sn) are $k_{\text{rel}}$ Si/Sn $> 10^7$ ($\Delta\Delta G^\text{‡}_{\text{exp}} > 10.7$ kcal mol$^{-1}$); from MeCl$_2$M(ONO$^Q$) $k_{\text{rel}}$ Si/Sn $> 10^{10}$ ($\Delta\Delta G^\text{‡}_{\text{exp}} > 14$ kcal mol$^{-1}$). Evidently, migration from $\kappa^3$ silicon is faster than from $\kappa^3$ tin.
In cases where the $\kappa^1$ structures are the ground state (namely $\text{Me}_3\text{ML}^0$), migration is faster from tin. Stabilization of 6-coordinate $\kappa^3$-Sn or -Si species increases the barriers of methyl migration from them ($\Delta G^\ddagger_{\kappa^3\rightarrow TS}$) (Figure 6.24a). However, this stabilization of the $\kappa^3$ species decreases the net barrier of migration from $\kappa^1$ forms ($\Delta G^\ddagger_{\text{Mig}} = \Delta G^\ddagger_{\kappa^1\rightarrow TS}$), as stabilization of $\kappa^3$ structures is accompanied by stabilization of the transition state, but to a lower degree. The slopes of parallel lines for $\text{ONO}^Q$ and $\text{DOPO}^Q$ in Figure 6.24a show the relationship between $\Delta G^\circ$ and $\Delta G^\ddagger$: every 1 kcal of ground state stabilization results in approximately 0.65 kcal stabilization of the transition state. At $\Delta G^\circ = 0$, $\kappa^1$ and $\kappa^3$ species become equi-energetic. The continued stabilization of $\kappa^3$ species below the energy of $\kappa^1$ ($\Delta G^*_{\kappa^1\rightarrow \kappa^3} < 0$) changes the ground state to $\kappa^3$ and further stabilization results in an increase in the net migration barrier ($\Delta G^\ddagger_{\text{Mig}} = \Delta G^\ddagger_{\kappa^3\rightarrow TS}$), and slower migration.

The V shaped plot 6.24b shows experimentally derived migration barriers as a function of calculated $\Delta G^*_{\kappa^1\rightarrow \kappa^3}$ and confirms that migration slows as $\kappa^3$ is stabilized beyond the $\kappa^1$ energy ($\Delta G^*_{\kappa^1\rightarrow \kappa^3} < 0$). The theoretical and experimental studies reported here provide qualitatively consistent descriptions of the effect of induced hypervalency in silicon and tin intermediates. For both $\text{ONO}^Q$ and $\text{DOPO}^Q$ complexes, the substitution of methyl groups by electronegative chlorine substituents induces hypervalency and an increase in migration rates in comparison to tin ($k_{\text{Rel \ MeCl}_2[\text{Si/Sn}]}(L^0) > 10^7$ (DOPO$^Q$); $10^{10}$ (ONO$^Q$)). The vertical offset of ~16 kcal mol$^{-1}$ in Figure 6.24a between $\text{ONO}^Q$ and $\text{DOPO}^Q$ reflects that migrations are slower from the latter ligand though the difference is overestimated by theory ($k_{\text{Rel } [\text{ONO}^Q/\text{DOPO}^Q]} \text{ Si MeCl}_2 = .10^2$, calc $k_{\text{Rel}} = 10^{12}$).
The corollary of these results is that hypervalency in itself does not promote the increased reactivity of silicon over tin. In fact, both silicon and tin behave in the same predictable way dictated by the relative energies of $\kappa^1$ and $\kappa^3$ complexes. Ideally, the interplay between the relative energies of these $\kappa^1$ and $\kappa^3$ forms than can be fine tuned with ancillary groups to drive the desired increase in migration rates from silicon than from tin or vice versa.

6.4 Experimental Section

All procedures were carried out under an inert atmosphere in a nitrogen-filled glove box or on a vacuum line. Chlorinated solvents and acetonitrile were dried over 4 Å molecular sieves, followed by CaH₂. Benzene was dried over sodium. Deuterated solvents were obtained from Cambridge Isotope Laboratories, dried using the same procedures as their protio analogues, and stored in the drybox prior to use.
H(DOPO$_Q$)$_{125}$ was prepared in three steps. Iodobenzene dichloride was prepared by Jinlan Cui. Other reagents were commercially available and used without further purification. Unless otherwise noted, $^1$H and $^{13}$C($^1$H) NMR spectra were measured as CDCl$_3$ solutions on a Varian Inova 500 or Bruker Avance DPX 500 spectrometers. Chemical shifts for $^1$H and $^{13}$C($^1$H) spectra are reported in ppm downfield of TMS. Infrared spectra were recorded as neat solids (except as otherwise noted) on an ATR (Jasco FT/IR-6300). ESI mass spectra were obtained using a Bruker micrOTOF-II mass spectrometer, and peaks reported are the mass number of the most intense peak of isotope envelopes. Samples were injected as dichloromethane or acetonitrile solutions, preceded and followed by methanol. In all cases, the observed isotope patterns were in good agreement with calculated ones.

6.4.1 Pb(DOPO$_Q$)$_2$.\textsuperscript{123}$^a$

Into a 100 mL Erlenmeyer flask was weighed 1.45 g HDOPO$_Q$ (3.3 mmol), which was dissolved in 4 mL of CH$_2$Cl$_2$ to form a dark purple solution. Gooey lead(II) 2-ethylhexanoate (0.84 g, 1.69 mmol) was dissolved in 8 mL of CH$_2$Cl$_2$ and added to the HDOPO$_Q$ solution. After adding a stirbar to the mixed solution and stirring for 15 minutes, a deep sea blue color was observed. The reaction mixture was slurried with 15 mL of CH$_3$CN for an additional 15 minutes to induce precipitation of Pb(DOPO$_Q$)$_2$. The reaction mixture was suction filtered through a glass frit and the filtrate was washed with 2 × 5 mL CH$_3$CN and 2 × 3 mL MeOH and suction dried in air for 10 minutes to yield 1.35 g Pb(DOPO$_Q$)$_2$ (76%). $^1$H NMR: δ 1.19, 1.43 (s, 36H each, $^t$Bu), 7.45 (s, 2H, ArH).
6.4.2 2,4,6,8-Tetra-tert-butyl-9-(trimethylsiloxy)-1H-phenoxazin-1-one, \( \kappa^1 \)-Me\(_3\)Si(DOPO\(_Q\)).

To a solution of 0.077 g Pb(DOPO\(_Q\))\(_2\) (0.07 mmol) in 1 mL chloroform was added 27 \( \mu \)L chlorotrimethylsilane (0.22 mmol, 1.6 equiv) via syringe. The solution was mixed for 5 min at room temperature. The black reaction mixture was layered with 1 mL of CH\(_3\)CN in a screw cap NMR tube and kept in a refrigerator at 4 °C. A dark crystalline solid was isolated the following day by filtration and washed with 0.5 mL CH\(_3\)CN and air-dried for 10 min in the drybox to yield 20.3 mg of \( \kappa^1 \)-Me\(_3\)Si(DOPO\(_Q\)) (36%). The same product can also be prepared from a reaction of HDOPO\(_Q\) with Me\(_3\)SiCl and triethylamine.\(^1\)H NMR: \( \delta \) 0.55 (s, 9H, Si(CH\(_3\))\(_3\)), 1.41, 1.48, 1.54, 1.57 (s, 9H each, \( ^t\)Bu), 7.45, 7.57 (s, 1H each, ArH). \(^{13}\)C\({}^{1}\)H NMR: \( \delta \) 2.00 (SiCH\(_3\)), 29.43, 29.70, 30.06, 30.68 (C(CH\(_3\))\(_3\)), 34.08, 34.59, 35.07, 35.29 (C(CH\(_3\))\(_3\)), 120.35, 126.13, 126.33, 130.38, 134.14, 136.44, 139.12, 140.43, 142.46, 144.77, 152.63, 180.15. IR (evaporated film-cm\(^{-1}\)): 3154 (w), 2961 (s), 2871 (w), 1816 (w), 1793 (w), 1703 (w), 1633 (m), 1617 (w), 1588 (m), 1504 (s), 1470 (s), 1390 (m), 1365 (m), 1339 (m), 1324 (m), 1254 (m), 1217 (w), 1200 (w), 1174 (w), 1063 (m), 1033 (w), 1004 (w), 908 (s), 848 (m), 733 (s).

6.4.3 2,4,6,8-Tetra-tert-butyl-9a,9a\(^1\)-trimethyl-9a,9a\(^1\)-dihydro-1,5,9-trioxa-9a\(^1\)\( \lambda^4 \)-aza-9a\(^1\)\( \lambda^5 \)-silacyclopenta[mno]aceanthrylene, Me\(_2\)Si(DOPO-Me).

To a solution of 0.2210 g H(DOPO\(_Q\)) (0.506 mmol) in 2 mL chloroform was added 300 \( \mu \)L chlorotrimethylsilane (2.39 mmol, 4.7 equiv) and 300 \( \mu \)L triethylamine (2.15 mmol, 4.2 equiv) via syringe. The black reaction mixture was stirred in a sealed vial for 18 h at 62 °C in an oil bath. A color change to dark brown was observed the following
day and the reaction mixture was layered with 3 mL of CH₃CN. A light brown crystalline solid was isolated the following day by filtration, washed with 3 × 1 mL CH₃CN and air-dried with a bulb for 10 min in the drybox to yield 132.3 mg of Me₂Si(DOPO-Me) (51%).

¹H NMR: δ –0.10, 0.75 (s, 3H each, SiCH₃), 1.36, 1.51 (s, 18H each, ¹Bu), 2.89 (s, 3H, NCH₃), 7.12 (s, 2H, ArH). ¹³C{¹H} NMR: δ –0.06, 0.35 (SiCH₃), 29.60, 31.41 (C(CH₃)₃), 34.63, 34.85 (C(CH₃)₃), 46.95 (NC₃H₃), 118.02, 123.53, 126.94, 131.83, 145.92, 150.06 (C₆H₅). IR (cm⁻¹): 2954 (m), 2902 (w), 2868 (w), 1636 (m), 1568 (w), 1502 (m), 1482 (m), 1453 (m), 1417 (s), 1359 (m), 1294 (w), 1252 (s), 1221 (m), 1202 (m), 1179 (w), 1159 (w), 1133 (w), 1064 (s), 1051 (s), 1027 (m), 995 (s), 915 (m), 893 (m), 880 (m), 816 (s), 806 (s), 767 (s), 736 (m), 700 (m), 652 (s). Anal. Calcd for C₃₁H₄₉NO₂Si•CHCl₃: C, 61.09; H, 7.69; N, 2.23. Found: C, 61.05; H, 7.94; N, 2.34.

To a solution of 0.1080 g Pb(DOPOQ)₂ (0.100 mmol) in 2 mL methylene chloride was added 29 µL methyltrichlorosilane (0.27 mmol, 1.3 equiv). The reaction mixture immediately changed color from sea blue to violet and was stirred in a sealed vial in the drybox. After 15 min of stirring, PbCl₂ precipitated as a white solid and was filtered through a glass frit. The filtrate was layered with 3 mL CH₃CN and kept in the freezer overnight. A fine crystalline solid was isolated by filtration and washed with 2 × 1 mL CH₃CN. Upon drying in an N₂ atmosphere, 54.5 mg of a white amorphous solid, Cl₂Si(DOPO-Me), was isolated (49%). ¹H NMR (CD₂Cl₂): δ 1.37, 1.50 (s, 18H each, ¹Bu), 3.00 (s, 3H, NCH₃), 7.13 (s, 2H, ArH). ¹³C{¹H} NMR: δ 29.55, 31.21 (C(CH₃)₃), 34.57, 35.00
(C(CH₃)₃), 49.53 (NCH₃), 123.76, 124.13, 132.77, 132.84, 145.00, 149.61 (C₆O). IR (cm⁻¹): 2957 (m), 2909 (w), 2870 (w), 1627 (w), 1498 (m), 1479 (w), 1446 (m), 1405 (s), 1362 (w), 1311 (w), 1290 (w), 1248 (s), 1218 (m), 1181 (w), 1154 (m), 1134 (m), 1054 (s), 1041 (s), 987 (s), 921 (w), 915 (m), 893 (m), 851 (s), 820 (m), 800 (m), 779 (m), 763 (w), 739 (m), 691 (s), 617 (m). ESI-MS: 606.1809 (M-Cl, calcd 606.1809). Anal. Calcd for C₂₉H₄₁Cl₂NO₃Sn: C, 54.32; H, 6.44; N, 2.18. Found: C, 52.95; H, 6.66; N, 2.25.

6.4.5 2,4,6,8-Tetra-tert-butyl-9a,9a-dichloro-9a-methyl-9aH-1,5,9-trioxo-9a¹-aza-9aλ⁶-stannacyclopenta[mno]aceanthrylene, Cl(Me)(Cl)Sn(DOPO⁰).

A solution of 0.1050 g Pb(DOPO⁰)₂ (0.097 mmol) in 2 mL methylene chloride was added to 47 mg trichloromethylstannane (0.19 mmol, 1.0 equiv). The reaction mixture immediately changed color from sea blue to a vivid bottle green and was stirred in a sealed vial for 30 min. PbCl₂ precipitated as a white solid and was filtered through a plug of sand. The filtrate was layered with 3 mL CH₃CN and kept in the drybox. Large hexagonal crystals were isolated by decanting and washed with 1 × 1 ml CH₃CN to yield 35 mg of Cl(Me)(Cl)Sn(DOPO⁰) (29%). ¹H NMR (CD₂Cl₂): δ 1.46, 1.53 (s, 18H each, tBu), 1.79 (s, 3H, SnCH₃, J₃SnH = 19 Hz), 8.01 (s, 2H, ArH). ¹³C{¹H} NMR: δ 18.24 (SnCH₃), 29.06, 30.00 (C(CH₃)₃), 34.59, 35.49 (C(CH₃)₃), 122.18, 125.29, 137.73, 143.04, 144.96, 165.60 (C₆O). IR (cm⁻¹): 2960 (m), 2911 (w), 2869 (w), 1589 (s), 1545 (m), 1487 (w), 1444 (s), 1400 (m), 1376 (m), 1363 (s), 1347 (s), 1306 (s), 1288 (s), 1244 (s), 1194 (m), 1165 (s), 1089 (w), 1071 (s), 1011 (s), 1007 (s), 936 (w), 904 (m), 878 (m), 789 (m), 739 (m), 691 (s), 617 (m). ESI-MS: 606.1809 (M-Cl, calcd 606.1809). Anal. Calcd for C₂₉H₄₁Cl₂NO₃Sn: C, 54.32; H, 6.44; N, 2.18. Found: C, 52.95; H, 6.66; N, 2.25.
6.4.6 2,4,6,8-Tetra-tert-butyl-9a,9a{sup 1}-triphenyl-9a,9a{sup 1}-dihydro-1,5,9-trioxa-9a{sup 1}µ{sup 4}-aza-
9aλ{sup 5}-silacyclopenta[mno]aceanthrylene, Ph{sub 2}Si(DOPO-Ph).

A solution of 0.1523 g HDOPO{sup 1} (0.3480 mmol), 0.1542 g triphenylchlorosilane
(0.6960 mmol, 2.00 equiv), and 70 µL NEt{sub 3} (0.50 mmol, 1.4 equiv) in 2 mL CHCl{sub 3} in a 20
mL scintillation vial sealed with a Teflon-lined cap was stirred for 2 d at room
temperature. The solution was layered with 3 mL acetonitrile and allowed to stand for 4
d. Large colorless crystals of the product were filtered and used for crystallography. The
mother liquor was concentrated under vacuum and dissolved in 1 mL CHCl{sub 3}, filtered
through a plug of sand, and layered with 2 mL of CH{sub 3}CN. After 2 d standing, a bulk
crystalline sample was isolated by filtration and washed with 2 × 1 mL CH{sub 3}CN to give
0.0846 g Ph{sub 2}Si(DOPO-Ph) (35%). {sup 1}H NMR: δ 1.54, 1.60 (s, 18H each, {sup 4}Bu), 6.23 (d, 8 Hz,
2H, o-NPh), 6.74 (tt, 7, 1.5 Hz, 1H, p-NPh), 6.80 (t, 8 Hz, 2H, m-NPh), 6.99 (t, 7 Hz, 2H, m-
SiPh), 7.06 (tt, 8, 1.5 Hz, 1H, p-SiPh), 7.22 (s, 2H, ArH), 7.36 (m, 3H, m,p-SiPh), 7.46 (dd,
8, 1.5 Hz, 2H, o-SiPh), 7.86 (m, 2H, o-SiPh). {sup 13}C{sup {sup 1}H} NMR: δ 30.15, 31.62 (C(CH_{3})_{3}), 34.77,
34.87 (C(CH_{3})_{3}), 118.62, 122.06, 122.86, 125.25, 127.39, 127.44, 127.85, 128.48, 128.56,
131.96, 132.77, 133.12, 134.50, 134.53, 141.43, 149.24, 149.28, 153.24. IR (cm{sup -1}): 2956
(m), 2907 (w), 2866 (w), 1599 (w), 1489 (s), 1402 (s), 1358 (w), 1316 (w), 1286 (w), 1246
(s), 1197 (s), 1125 (m), 1117 (m) 1082 (w), 1045 (s), 1015 (m), 904 (m), 880 (w), 838 (s),
822 (s), 804 (w), 780 (w), 767 (m), 740 (w), 728 (w), 728 (s), 700 (s), 689 (s), 624 (w), 604
(m). ESI-MS: 696.3889 (M+H, calcd 696.3867). Anal. Calcd for C_{46}H_{53}NO_{3}Si: C, 79.38; H,
7.68; N, 2.01. Found: C, 79.11; H, 7.84; N, 2.21.
6.4.7 2,4,6,8-Tetra-tert-butyl-9a,9a,9a⁻¹-triphenyl-9a,9a⁻¹-dihydro-1,5,9-trioxa-9a⁻¹λ⁻⁴-aza-9a⁻¹λ⁻⁵-stannacyclopenta[mno]aceanthrylene, Ph₂Sn(DOPO-Ph).

Triphenyltin chloride (0.1900 g, 0.492 mmol, 1.5 equiv) was added to 2 mL of a chloroform solution of 0.1438 g H(DOPO⁻Q) (0.328 mmol) and 70 µL of triethylamine (0.502 mmol, 1.5 equiv). The dark purple solution changed color to a vibrant hue of deep blue upon stirring for two minutes. The reaction was allowed to stir overnight for 18 h, although the reaction is complete within 90 minutes. The solution was then layered with 3 mL CH₃CN to furnish colorless rod shaped crystals of Ph₂Sn(DOPO-Ph) (0.0758 g, 29%). The crystals were isolated by filtration and washed with 2 × 1 mL of CH₃CN. ¹H NMR: δ 1.56, 1.68 (s, 18H each, ¹Bu), 6.67 (d, 8 Hz, 2H, o-NPh), 6.93 (tt, 8 Hz, p-NPh), 7.02 (t, 8 Hz, 2H, m-NPh), 7.33 (m, 3H, m,p-SnPh), 7.34 (s, 2H, ArH), 7.37 (m, 3H, m,p-SnPh), 7.69 (dd, 8, 2 Hz, 2H, o-Ph), 7.86 (m, 2H, o-SnPh). ¹³C{¹H} NMR: δ 30.01, 31.48 (C(CH₃)₃), 34.80, 35.18 (C(CH₃)₃), 118.40, 119.84, 123.59, 125.53, 126.17, 128.47, 128.49, 129.03, 130.18, 130.30, 131.89, 136.06, 136.86, 138.24, 141.01, 146.43, 147.72, 154.04. IR (cm⁻¹): 2954 (m), 2907 (w), 2868 (w), 1618 (m), 1588 (w), 1549 (m), 1500 (m), 1431(w), 1405 (s), 1360 (m), 1305 (m), 1288 (w), 1253 (s), 1187 (w), 1134 (w), 1053 (s), 994 (w), 907 (w), 898 (w), 883 (w), 769 (s), 758 (m), 728 (s), 695 (s), 664 (m).

ESI-MS: 710.2628 (M-Ph, calcd 710.2659). Anal. Calcd for C₄₆H₅₃NO₃Sn: C, 70.24; H, 6.79; N, 1.78. Found: C, 69.98; H, 6.98; N, 1.74.
Methyltin trichloride (80.1 mg, 0.33 mmol, 2.0 equiv) was combined with a 3 mL chloroform solution containing 0.1648 g Pb(ONO$_2$)$_2$ (0.16 mmol). A dark green solution was formed and allowed to stir overnight. Lead chloride was removed by filtration through a glass frit and the solution was evaporated to dryness. The crude product was then recrystallized from a 1 mL solution in chloroform layered with 2 mL of acetonitrile at –35 °C. Green crystals were isolated by filtration to give 0.0983 g Cl(Me)(Cl)Sn(ONO$_2$) (50%).

$^1$H NMR: 1.30, 1.42 (s, 18H each, tBu), 1.54 (s, 3H, Sn-CH$_3$), 7.42, 7.55 (d, 2 Hz, 2H each, ArH). $^{13}$C($^1$H) NMR: δ 15.80 (SnCH$_3$), 29.40, 29.86 (C(CH$_3$)$_3$), 35.66, 35.93 (C(CH$_3$)$_3$), 116.34, 133.79, 139.00, 145.21, 149.92, 174.49. $^{117}$Sn($^1$H) NMR: δ –365.65. IR (cm$^{-1}$): 2990 (s), 2995 (s), 2903 (m), 2868 (m), 2851 (m), 1502 (s), 1450 (s), 1415 (s), 1362 (s), 1310 (s), 1269 (m), 1266 (m), 1240 (m), 1209 (w), 1187 (w), 1088 (m), 1041 (m), 1018 (m), 995 (w), 925 (m), 901 (m), 878 (w), 788 (w), 755 (m), 661 (w), 632 (w). ESI-MS: 592.2023 (M$^+$-Cl, calcd 592.1997). Anal. Calcd for C$_{29}$H$_{43}$Cl$_2$NO$_2$Sn: C, 55.53; H, 6.91; N, 2.23. Found: C, 55.28; H, 6.78; N, 2.19.

Kinetics of methyl migration from $\kappa^1$-Me$_3$Si(DOPO$^0$).

$\kappa^1$-Me$_3$Si(DOPO$^0$) was generated in situ from a reaction of 4.3 mg HDOPO$^0$ (0.01 mmol) with 15 µL Me$_3$SiCl (0.12 mmol, 12 equiv) and 15 µL NEt$_3$ (0.11 mmol, 11 equiv) in 1 mL CHCl$_3$ at room temperature. 20 µL of the stock solution was added to 2 mL of CHCl$_3$ in a 1.0 cm airtight quartz cuvette to yield $10^{-4}$ M solution of $\kappa^1$-Me$_3$Si(DOPO$^0$). Multiple rate measurements were made at 55.4 °C (measured using a thermocouple inserted into
a dummy cuvette) by preheating a multicell UV-vis holder with a recirculating heating bath and recording spectra every 5 min for 11 h. Absorbance data were collected (250-900 nm) and single wavelength kinetics data were analyzed at 575 and 675 nm.

6.4.10 Generation and VT NMR of κ1-Me3Sn(DOPO)Q, and the kinetics of its methyl migration.

H(DOPO)Q (8.7 mg, 0.02 mmol), 4 μL triethylamine (0.03 mmol, 1.5 equiv), and dimethylterephthalate (2.0 mg, standard) were dissolved in 600 μL CDCl3 in a screw cap NMR tube with a septum cap. The sample was inserted into the NMR probe and cooled to –45 °C. The sample was then briefly ejected and Me3Sn(DOPO)Q was generated in situ by the addition of 5 μL Me3SnI (0.02 mmol, 1 equiv) to the reaction mixture. The sample was shaken vigorously and the sample was reinserted and the probe was warmed to –30 °C. 1H NMR spectra were collected every 6 min for 2.5 h. The normalized integrals of methyl and aromatic peaks from product and intermediate were plotted as function of time and fit to 1st order kinetics. In a separate attempt, the same reaction was carried out at –40 °C and variable temperature 1H NMR spectra were collected from –95 °C to 10.0 °C. At room temperature the migration proceeds to completion in 15 min from reaction of stoichiometric amounts of Me3SnI and HDOPOQ with 3 eq. of base (NEt3). 1H NMR (CD2Cl2, –30 °C): δ 0.53 (s, 9H, Sn(CH3)3, JSnH = 60 Hz), 1.30, 1.41 (s, 18H each, tBu), 7.38 (s, 2H, ArH).
6.4.11 Generation and VT NMR of \( \kappa^1\text{-MeCl}_2\text{Si(DOPO}^0\text{)} \), and the kinetics of its methyl migration.

\[ \text{Pb(DOPO}^0\text{)}_2 \ (10.5 \text{ mg, 0.0097 mmol}) \text{ and dimethylterephthalate (1.0 mg, standard) were dissolved in 600 } \mu \text{L CDCl}_3 \text{ in a screw cap NMR tube with a septum cap and cooled to 0 } \degree \text{C in an ice bath. MeCl}_2\text{Si(DOPO}^0\text{)} \text{ was generated } \text{in situ} \text{ by the addition of 10 } \mu \text{L MeSiCl}_3 \ (0.096 \text{ mmol, 5 equiv}) \text{ at 0 } \degree \text{C. The tube was then inserted into the NMR probe which was precooled to 0 } \degree \text{C. } ^1\text{H NMR spectra were collected every 6 min for 4 h. Normalized integrals of methyl and aromatic peaks from migrated product and intermediate were plotted as function of time and fit to } 1^{\text{st}} \text{ order kinetics. In a separate attempt, the same reaction was carried out at -50 } \degree \text{C and variable temperature } ^1\text{H NMR spectra were collected from -80 } \degree \text{C to 22.5 } \degree \text{C.} \]

\[ ^1\text{H NMR (CD}_2\text{Cl}_2, 0 \degree \text{C): } \delta \ 1.35 \ (s, 3 \text{H, SiCH}_3), \ 1.39, 1.48 \ (s, 18 \text{H each, } \text{tBu}), \ 7.68 \ (s, 2 \text{H, ArH}). ^1\text{H NMR (CD}_2\text{Cl}_2, -80 \degree \text{C): } \delta \ 1.28 \ (s, 3 \text{H, SiCH}_3), \ 1.40, 1.46 \ (s, 18 \text{H each, } \text{tBu}), \ 8.12 \ (s, 2 \text{H, ArH}). \]

6.4.12 Kinetics of migration on reaction of MeSiCl\(_3\) and Pb(ONO\(^0\))\(_2\).

In a typical reaction run, Pb(ONO\(^0\))\(_2\) (10.5 mg, 0.010 mmol) and dimethylterephthalate (1.4 mg, standard) were dissolved in 600 \( \mu \)L CDCl\(_3\) in a screw cap NMR tube with a septum cap and cooled to -78 °C in an dry ice/acetone bath. The addition of 10.0 \( \mu \)L MeSiCl\(_3\) (0.096 mmol, 5 equiv.) was carried out at -78 °C and tube was shaken in the bath. The tube was then inserted into the NMR probe which was precooled to -50 °C, the inferred in situ generation of MeCl\(_2\)Si(ONO\(^0\)) occurs above -50 °C and the tube was gradually warmed to -30 °C. \(^1\)H NMR spectra were collected every 5
min for 2 h. Normalized integrals of the methyl peak of migrated product were plotted as function of time and fit to 1st order kinetics.

6.4.13 Computational Methods.

Geometry optimizations were performed on all complexes using 6-31G* basis set for all atoms except tin, for which LANL2DZ was utilized. A B3LYP functional with a PCM solvation model of dichloromethane for DOPO complexes was used in the Gaussian09 suite of programs.51 No solvation model was used for any ONO complexes. No symmetry constraints were applied during optimization and stationary points on the potential energy surface were identified as minima with no negative frequencies. Starting geometries of N-methylated five coordinate structures were obtained by importing the Cartesian coordinates of X-ray structures reported in Chapter 4 for the reduced ONO ligand and reported here for the reduced DOPO ligand into Gaussview and appending their ancillary groups as required. The tert-butyl groups on ONO and DOPO ligands were replaced with hydrogens to reduce computational costs. Starting geometries of tetrahedral intermediates were derived from the X-ray structure of κ1-Me3Si(DOPOO) reported here. Starting geometries for the octahedral intermediates were derived from the octahedral silane, Si(ONO)2 and stannane, Cl(Me)(Cl)SnL (L = ONOO, DOPOO). Geometry optimizations with constrained Si-O, Si-N, and Si-C distances were carried out to locate the vicinity of the saddle points, checking for the appropriate single negative frequencies. A transition state search with relaxed constraints was then performed to find the transition state. Geometries of each unique transition state that leads to stereoisomeric octahedral intermediates were computed. The transition state of
chelation for Me₃Sn(DOPO), 5-κ¹-TS-κ³, could not be located because the corresponding 5-κ³ complex of Me₃Sn(DOPO) is located on a very shallow potential energy surface and invariably relaxes to its κ¹ form. Optimization 5-κ³ with constraints on the Sn-N distance could only identify local minima, which were confirmed by the absence of negative frequencies. Similar difficulties were faced in finding κ¹-MeCl₂Sn(L⁰) structures because of the ease of relaxation into the corresponding κ³ complexes; however, global minima were eventually found upon altering the C-O-Sn-Cl dihedral angle close to 180°. Therefore, these transition states of chelation (not shown in Figure 6.20 and 6.22) could not be found on this shallow potential energy surface of ligand sets of MeCl₂Sn(L⁰) but lie very close in energy to their κ¹ form.

6.4.14 X-ray crystallography.

Crystals of κ¹-Me₃Si(DOPO)•CHCl₃ were grown from a concentrated solution of the complex in chloroform at –40 °C while the N-methylated Me₂Si(DOPO-Me) was grown by layering a chloroform solution with acetonitrile. N-phenylated products Ph₂Si(DOPO-Ph) and Ph₂Sn(DOPO-Ph)•CHCl₃ were grown from concentrated chloroform solutions layered with acetonitrile at room temperature and –40 °C, respectively.

Crystals of Cl(Me)(Cl)Sn(DOPO) were grown at room temperature from a concentrated solution of the compound in methylene chloride layered with acetonitrile. Crystals of Cl(Me)(Cl)Sn(NOQ)•CHCl₃ were grown at –35°C from a chloroform solution layered with acetonitrile. Crystals of radicals Me₂Sn(DOPO⁵) and Me₂Sn(DOP-CH₂-O) were grown from the reaction mixture of Me₃SnCl and Pb(DOPO)₂ in C₆D₆ after filtration of PbCl₂ and layering with acetonitrile.
All Crystals were placed in inert oil before transferring to the cold N\textsubscript{2} stream of a Bruker Apex II CCD diffractometer. Data were reduced, correcting for absorption, using the program SADABS. The structures were solved using direct methods. All non-hydrogen atoms not apparent from the initial solutions were found on difference Fourier maps, and all heavy atoms were refined anisotropically.

The migrated methylene C3 group and phenoxazine oxygen O3 in the radical Me\textsubscript{2}Sn(DOP-CH\textsubscript{2}-O) were compositionally disordered. Each atom was modeled as 50% carbon and 50% oxygen. Hydrogens on the disordered methylene group were placed in calculated positions, while all other hydrogen atoms were found on difference Fourier maps and refined isotropically. Calculations used SHELXTL (Bruker AXS),\textsuperscript{26} with scattering factors and anomalous dispersion terms taken from the literature.\textsuperscript{27} Further details about the individual structures are given in Tables 6.1-6.4.


(48) Budzelaar, P. H. M. gNMR, v. 3.5.6, Cherwell Scientific Publishing, 1996.


(60) Kopec, J. A.; Brown, S. N. Unpublished results.


(95) This compound has been generated in solution and characterized by EPR spectroscopy: Piskunov, A. V.; Sukhoshkina, O. Y.; Smolyaninov, I. V. *Russ. J. Gen. Chem.* 2010, 80, 790-799.


