Small Molecule Activation at Nickel and Platinum Centers Containing Bulky Tin and TEMPO Radical Ligands

Anjaneyulu Koppaka
University of Miami, anji361@gmail.com

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SMALL MOLECULE ACTIVATION AT NICKEL AND PLATINUM CENTERS CONTAINING BULKY TIN AND TEMPO RADICAL LIGANDS

By

Anjaneyulu Koppaka

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Coral Gables, Florida

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SMALL MOLECULE ACTIVATION AT NICKEL AND PLATINUM CENTERS CONTAINING BULKY TIN AND TEMPO RADICAL LIGANDS

Anjaneyulu Koppaka

Approved:

Burjor Captain, Ph.D.
Professor of Chemistry

Francisco M. Raymo, Ph.D.
Professor of Chemistry

Jamie D. Walls, Ph.D.
Professor of Chemistry

M. Brian Blake, Ph.D.
Dean of the Graduate School

Ali Ghahremaninezhad-M, Ph.D.
Professor of Civil, Architectural, and Environmental Engineering
Metal complexes have long been recognized as fundamental in activating simple small molecules, which provide low-barrier reaction pathways through binding. One way to make highly reactive metal complexes is by reacting metal precursors with sterically demanding ligands that can create electronic unsaturation on the metal center, where activation can occur. A series of sterically crowded metal complexes have been synthesized by reactions of Pt(COD)$_2$ with bulky tin ligands of the type HSnR$_3$ [ R = Bu$^t$, Ph and C$_6$H$_2$Me$_3$(mesitylene)]. These new complexes were studied for activation of small molecules like H$_2$, CO, C$_2$H$_2$, C$_2$H$_4$, and catalytic H$_2$ - D$_2$ exchange reactions at ambient conditions. The complex Pt(SnBu$_3$)$_2$(CNBu$^t$)$_2$ was found to activate H$_2$ and CO reversibly in solid state, as well as in solution. It also catalyzes the H$_2$-D$_2$ exchange at room temperature. Currently, the NHC carbene compounds as ligands are one of the most highly studied in organometallic chemistry. The role of NHC carbene ligands on the reactivity of Pt-Sn bimetallic complexes has also been studied. The Pt-Sn-NHC complex, [Pt(SnBu$_3$)(IBu$^t$)(H)]$_2$ was found to be highly reactive and efficient in the reversible activation of H$_2$, and C$_2$H$_4$ at room temperature. This compound also activates CO at room temperature.
The bimetallic complexes with inexpensive metals Ni & Sn were also synthesized and studied catalytically. The coordination chemistry of TEMPO radical with Ni metal was also explored. The 16 electron unsaturated ‘bow-tie’ complex, Ni(η^2-TEMPO)_2 was found to be highly efficient in activation of C-H bond of alkynes and also found to be highly reactive towards other small molecules such as H₂, CO, CO₂, and other coordinating solvents such as THF and CH₃CN. We were able to connect two Ni metal centers using an organic moiety in the complex Ni(η^2-TEMPO)(κ¹-TEMPO)[κ¹-κ¹-CC(C₆H₄)CC]Ni(η^2-TEMPO)(κ¹-TEMPO).
ACKNOWLEDGEMENTS

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Anjaneyulu Koppaka
Chemistry CANE
University of Miami
Coral Gables, Florida
USA
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Chapter 1: Unsaturated Transition Metal Complexes in Activation of Small Molecules: Role of Sterics Induced by Bulky Ligands and Metal-Ligand Synergistic Effects.

1.1. Introduction.

Highly abundant simple small molecules like \( \text{H}_2, \text{N}_2, \text{O}_2, \text{CO} \) and \( \text{CO}_2 \) are incredible sources of chemical energy. These can be used in many ways, for example, molecules like \( \text{H}_2, \text{N}_2 \) and \( \text{O}_2 \) can be used to fuel biological systems,\(^1\) and molecules like \( \text{CO} \) and \( \text{CO}_2 \) can be used as feed stocks of carbon for liquid fuels and synthesis of other useful organic compounds.\(^2,3\) Nature uses these simple molecules to construct highly systematic complex molecules for selective processes. Despite much understanding on how nature activates and uses these simple molecules, we are still underdeveloped in activating them to produce useful synthetic products at an industrial scale.

Today’s world is powered by the petroleum and natural gas industries, which generate ethylene and other products by ‘cracking’ the hydrocarbons; these in turn drive the chemical industry which is highly dependent on olefins and acetylenes. The understanding of the interactions of these chemicals with transition metal complexes is extremely important for the sustainability of these industries and also for the development of alternative routes for future energy sources in the wake of diminishing petroleum and natural gas resources. This is where a catalyst comes into picture and all the above mentioned issues can be addressed by well-developed catalyst industry with the understanding of the interaction of substrates, such as the above mentioned small molecules or the products of natural gas and petroleum and overcoming their significant energy barriers.
A catalyst is defined as a substance that accelerates the rates of chemical reactions without being consumed, enhances product selectivity with increased efficiency, reduces energy consumption and minimizes waste. This is the main reason why the majority of the chemical industry processes employ catalysts at certain stages during the manufacturing process. These catalysts are mainly classified into two categories i) Heterogeneous catalysts ii) Homogeneous catalysts. The majority of the catalysts at present are heterogeneous catalysts. These catalysts include finely divided metal particles, i.e., Raney nickel, platinum black etc. On the other hand, homogeneous catalysts are operated in solution state and are usually derived from well-defined precursors; the simplest example is $\text{H}^+$, generated in the acid catalyzed reactions, for example, acid catalyzed esterification of carboxylic acids. Some of the well-known metal complexes that are come across frequently in the literature as catalysts and non-catalysts are shown in the Figure 1.1.

![Catalyst Structures](https://via.placeholder.com/150)

**Figure 1.1.** Some of the well-known transition metal complexes.
Today, the majority of the catalytic process employs heterogeneous catalysts because of the advantage of ease of catalyst re-cyclization compared to homogeneous catalyst. But, homogeneous catalysts have other advantages which are not possible with heterogeneous catalysts; such as they can be operated at mild reaction conditions, high selectivity, less sensitivity to catalyst poison, insights into catalysis mechanisms and most importantly variability in terms of steric and electronic properties for selectivity; it is where the transition metal complexes aptly fit as homogeneous catalysts for a wide variety of industrial applications.  

1.2. Transition metal complexes in catalysis.

Metal complexes have long been recognized as fundamental in activation and catalysis chemistry, which provides low-barrier reaction pathways through binding. The first reported synthetic organometallic complex K[Pt(C₂H₄)Cl₃], synthesized by W.C. Zeise in 1827 was the activation of ethylene by PtCl₄. The nickel tetracarbonyl complex, Ni(CO)₄ reported by Mond in 1890 led to the development of industrial process called ‘Mond’s process’ for the purification of nickel ores.

Discovered in 1960s by J. W. DiLuzio and Lauri Vaska, the complex IrCl(CO)(PPh₃)₂ [trans-chlorocarbonyl]bis(triphenylphosphine)iridium(I)] (see Figure 1.1), inspired many inorganic chemists through its ability to activate a number of small molecules (see Scheme 1.1) and led to the synthesis of similar well-known complexes that revolutionized homogeneous catalysis. It was one of the first compounds discovered which mimics the action of hemoglobin, another organometallic complex of iron. Vaska’s complex reacts with O₂ and H₂ reversibly. The reaction with O₂ forms a η²- side on-bound complex unlike the case of hemoglobin, where O₂ is end-on bound. It is a 16
electron unsaturated square planar $d^8$ complex, and to satisfy 18 electron configuration it can oxidatively add (where the formal oxidation of metal center increases and reverse of it is reductive elimination where the oxidation state decreases) two one-electron donating ligands or one two-electron donating ligand, to become an octahedral complex (see Scheme 1.1).

Scheme 1.1. Reaction of Vaska’s complex with various small molecules.

The majority of the well-known industrially important processes use catalyst systems based on transition metals. For example, water-gas shift reaction employs
catalysts such as CuO, and ZnO for low temperature shift reaction (LTS), and Fe$_2$O$_3$ and Cr$_2$O$_3$ are used for high temperature shift reaction (HTS). The Fisher-Tropsch process, for the conversion of mixture of H$_2$ and CO into liquid hydrocarbons, uses a wide variety of transition metals, such as cobalt, iron, and ruthenium. Nickel is used to form methane. In the Haber Bosch process for making ammonia from N$_2$ and H$_2$, catalysts based on iron and ruthenium are used.

The water soluble vitamin B$_{12}$, known as coenzyme B$_{12}$, is the oldest known example of a naturally occurring transition metal complex which is known to aid the catalysis of 1-2 shifts in biochemical systems (see Scheme 1.2).$^9$

*Isomerization*

\[
\begin{array}{c}
\text{R} \\
\text{C} - \\
\text{H} \\
\text{H} \\
\text{H} \\
\hline
\end{array}
\xrightarrow{\text{B}_{12}}
\begin{array}{c}
\text{H} \\
\text{C} - \\
\text{H} \\
\text{R} \\
\text{H} \\
\hline
\end{array}
\]

*Isomerization and dehydration*

\[
\text{HO-CH$_2$-CH=CH$_3$} \xrightarrow{\text{B}_{12}} \text{HO-CH-CH$_2$-CH$_3$} \xrightarrow{\text{B}_{12}} \text{HC-CH$_2$-CH$_3$ + H$_2$O}
\]

**Scheme 1.2.** Catalytic reactions by coenzyme $B_{12}$.$^9$

In the homogeneous catalysis, some of the industrially important process such as hydroformylation (which involves activation of H$_2$ and CO),$^{10,11}$ transfer hydrogenation reactions (where dihydrogen is added to a molecule from a source other than gaseous H$_2$)$^{12}$, and Wacker process for the conversion of ethylene into acetaldehyde,$^{13}$ employ the transition metal organometallic complexes as catalysts. The basic principle in catalysis is activating the metal complex by creating an electronic deficiency or unsaturation on the
key central metal atom where the activation or catalysis happens. During this process, the ligands on the metal center play a key role in the form of dissociation-association from or to the metal center, migration to the other part of the complex to make way for the incoming molecule and provide stability to the molecule. Attempts were made to explain all these properties of the complexes in combination of the number of valence electrons on the metal center and molecular orbital theory.

1.3. The 18 electron rule, saturated and unsaturated transition metal complexes in activation of small molecules.

The 18 electron rule, similar to octect rule, was first proposed by Langmuir for relating the number of shared electrons or covalence ($V_c$) of a given atom in a compound to the number of valence electrons (e) and the number of electrons required to complete its valence shell (s), as shown in the equation 1.1.$^{14,15}$

$$V_c = s - e \text{ (or)} \quad V_c = 18 - e \quad (eq.1.1)$$

In the beginning, the 18 electron rule was used for counting the valence electrons of the carbonyl complexes of transition metal complexes. Later, it has been extended to transition metal complexes with other ligands as well.$^{15,16}$ The 18 electron rule has been used to rationalize the stoichiometries, structures, and stability of the metal complexes. Based on the fact that the complexes that obey 18 electron rule will attain the electronic configuration of the next group 18 rare gas, it has been postulated that those complexes that obey this rule are stable and that does not obey are unstable.$^{17}$ However, it has been found that the majority of transition metal complexes do not obey this rule; yet they are stable, and no satisfactory explanation was given by the 18 electron rule for this behavior.$^{18}$
The anomalies in stability of complexes that do not obey the rule have been explained in terms of molecular orbital theory. The Cr(0) complex, Cr(CO)$_6$, obeys the 18 electron rule (total electron count on Cr is 18, 12 electrons from 6 CO ligands and 6 electrons from Cr). If you look at the molecular orbital diagram (see Figure 1.2) of this complex, the $e_g$ orbitals are anti-bonding and addition of electrons destabilize the complex, similarly removing the electrons from the $t_{2g}$ bonding orbital, which are resulting from the strong $\pi$ acceptor ability of CO ligands will again destabilize the complex. Ligands that are both strong $\sigma$ donor and $\pi$ acceptor force the energy of molecular orbitals to appear as shown in the case of Cr(CO)$_6$ (see Figure 1.2), and force the molecule to obey the 18 electron rule.

**Figure 1.2.** Molecular orbital diagram of Cr(CO)$_6$.\(^\text{19}\)
The energy gap between the $e_g^*$ and $t_{2g}$ orbital varies depending up on the type of the ligand coordinating with the metal center. The ligands which do not have the above mentioned features, as in the case of CO, may or may not force their complexes to obey the rule. Most of the organic ligands do not have these capabilities and they form the complexes that may or may not obey the 18 electron rule and their MO diagrams resemble the one shown in Figure 1.3.

The 22 electron octahedral complex $[\text{Zn(en)}_3]^{2+}$ is a stable complex, though it has 4 electrons in the $e_g^*$ orbital. The en (ethylenediamine) ligand is not as good a $\sigma$ donor as CO ligand, as a result, the $e_g^*$ orbitals are not as strong anti-bonding as is the case of Cr(CO)$_6$, to destabilize the complex with electrons occupying $e_g^*$ anti-bonding orbital. The complex $[\text{Ti(F)}_6]^{2-}$ is an extreme example of octahedral complex, with just 12 electrons. In this case the F$^-$ ligand is a $\sigma$ donor as well as $\pi$ donor. As a result of $\pi$
donating ability, the $t_{2g}$ orbitals becomes slightly anti-bonding, which makes the complex to have 12 electrons in the bonding $6\sigma$ orbitals and no electrons in $t_{2g}$ orbitals.

These arguments are generally applicable to octahedral complexes and in some cases can be extended to other geometries as well, such as trigonal bipyramidal $\{[\text{Fe(CO)}_3]\}$ and tetrahedral complexes $[\text{Ni(CO)}_4]$. However, in the case of square planar complexes a different scenario arises where in most of the instances the 16 electron complexes are stable, particularly $d^8$ metal complexes. An example of MO diagram of $d^8$ square planar complex is shown in Figure 1.4.

Figure 1.4. Representative MO diagram of square planar complex.\textsuperscript{19}
As you see in the Figure 1.4, any additional electrons go into the anti-bonding orbital $b_{1g}^*$, which is derived from the anti-bonding interaction of $d_{x^2-y^2}$ orbital of metal with $\sigma$-donor orbitals of ligand. The $b_{1g}^*$, anti-bonding interactions are strongest as the $d_{x^2-y^2}$ orbital points directly towards the ligand, therefore resulting in square planar geometry; complexes that have both $\sigma$-donor and $\pi$-acceptor ligands are stable with 16 electrons. In some instances, these complexes can also accept one or two-electrons along the $z$-axis vacant co-ordination sites, and that is how the 16 electron complexes like Wilkinson’s catalyst and Vaska’s complexes react with small molecules.

Nevertheless, in general, complexes with less than 18 valence electrons, called unsaturated, are found to be more reactive than the complexes with 18 valence electrons (18 ve), saturated complexes. This generalization is still in use for predicting the reactivity and stoichiometries of transition metal complexes. The saturated complexes, also called coordinatively saturated complexes, are generally ‘exchange inert’ and they react with other compounds or ligands in different ways. Some well-known mechanisms include “Dissociation-Substitution (or association)”, where the formal oxidation state of the metal center remains same in the dissociative step (see Scheme 1.3), “Reductive elimination-Oxidative addition” fashion where the formal oxidation state of the metal center changes (see Scheme 1.4), and Insertion mechanism where an incoming ligand or molecule directly inserts in to the already existing metal-ligand bond (see Scheme 1.5). Other possible mechanisms are also reported for the insertion reactions. These insertion reactions have potential applications in synthetic organic chemistry. These complexes generally have octahedral or tetrahedral geometry.
Scheme 1.3. Dissociation-Substitution by a) tetrahedral Ni(CO)$_4$, $^{21}$ and by b) octahedral [Co(CN)$_5$(H$_2$O)]$^{2-}$ complex.$^{22}$

Scheme 1.4. Reductive elimination-Oxidative addition by octahedral iridium complex, [H$_2$Ir(CO)$_2$L$_2$].$^{23}$

The rate determining step is the dissociation step, $k_1$, which is slow, and no effect of $k_2$ on the overall rate of the reaction, was observed in these reactions (see Scheme 1.5).

Scheme 1.5. Rate determining steps in “Dissociation-Substitution” and “Reductive elimination -oxidative addition” reactions.
As mentioned earlier, the majority of transition metal complexes deviates from the 18 electron rule and are stable at ambient conditions. These complexes generally possess square planar geometry. Important examples of square-planar low-spin $d^8$ metal ions are Ni(II), Pd(II), and Pt(II). The well-known complexes include Vaska’s complex, $[\text{IrCl(CO)}(\text{PPh}_3)_2]$, Wilkinson’s complex, $[\text{RhCl(PPh}_3)_3]$, and Zeise’s salt, $[\text{PtCl}_3(\eta^2$-$\text{C}_2\text{H}_4)]^-$. The common feature with all these complexes is they are all square planar $d^8$ complexes with 16 valence electrons on the central metal atom. These complexes generally undergo reactions in a wide variety of ways, which include, a) Dissociation-Association, b) Oxidative addition, c) Reductive elimination, d) Nucleophilic displacement, e) Insertion, and f) Abstraction.

Many catalysts, during catalytic cycles, alternate between 16 and 14 or 18 and 16 or 14 valence electron intermediates with a series of above mentioned reactions connected in a cyclic fashion. Some well-known examples are Grubb’s catalyst in olefin metathesis. Olefin metathesis was first reported in 1950s, which involves the
formal exchange or redistribution of :CR₂ fragments (R= H or alkyl) between alkenes (see Scheme 1.7). Yves Chauvin, Robert H. Grubbs, and Richard R. Schrock were collectively awarded the 2005 Nobel Prize in Chemistry for the pioneering work done in this field. Robert H. Grubbs developed a series of transition metal-carbene complexes (see Figure 1.1), called Grubb’s catalysts, which catalyzes these reactions.\textsuperscript{25–28}

\begin{center}
\begin{tikzpicture}
\begin{scope}[every path/.style={thick}]
\begin{scope}[xshift=-2cm]

% Association
\node[draw,rectangle] (A) at (0,0) {Cl \quad \text{PCy}_3 \quad \text{Cl} \quad \text{PCy}_3 \quad \text{R}_1 \quad \text{H} \quad \text{Cl} \quad \text{PCy}_3 \quad \text{PCy}_3 \quad \text{R}_2}
\node[draw,rectangle] (B) at (2,0) {+ \quad \text{R} \quad \text{PCy}_3 \quad \text{Cl} \quad \text{PCy}_3 \quad \text{H} \quad \text{Cl} \quad \text{PCy}_3 \quad \text{PCy}_3 \quad \text{R}_1 \quad \text{R}_2}
\node[draw,rectangle] (C) at (4,0) {- \quad \text{R} \quad \text{PCy}_3 \quad \text{PCy}_3 \quad \text{R}_1 \quad \text{R}_2}
\node[draw,rectangle] (D) at (6,0) {16 \text{ e}^- \quad \text{Association}}
\end{scope}

\begin{scope}[xshift=2cm]

% Dissociation
\node[draw,rectangle] (E) at (0,0) {Cl \quad \text{PCy}_3 \quad \text{Cl} \quad \text{PCy}_3 \quad \text{R}_1 \quad \text{H} \quad \text{Cl} \quad \text{PCy}_3 \quad \text{PCy}_3 \quad \text{R}_1 \quad \text{R}_2}
\node[draw,rectangle] (F) at (2,0) {+ \quad \text{PCy}_3 \quad \text{Cl} \quad \text{PCy}_3 \quad \text{PCy}_3 \quad \text{R}_1 \quad \text{R}_2}
\node[draw,rectangle] (G) at (4,0) {- \quad \text{PCy}_3 \quad \text{PCy}_3 \quad \text{R}_1 \quad \text{R}_2}
\node[draw,rectangle] (H) at (6,0) {18 \text{ e}^- \quad \text{Dissociation}}
\end{scope}

\begin{scope}[xshift=4cm]

% Metallacycle formation
\node[draw,rectangle] (I) at (0,0) {Cl \quad \text{PCy}_3 \quad \text{Cl} \quad \text{PCy}_3 \quad \text{H} \quad \text{Cl} \quad \text{PCy}_3 \quad \text{PCy}_3 \quad \text{R}_1 \quad \text{R}_2}
\node[draw,rectangle] (J) at (2,0) {+ \quad \text{PCy}_3 \quad \text{PCy}_3 \quad \text{R}_1 \quad \text{R}_2}
\node[draw,rectangle] (K) at (4,0) {16 \text{ e}^- \quad \text{Metallacycle formation} \quad (\text{C-C bond formation})}
\end{scope}

\begin{scope}[xshift=6cm]

% Products
\node[draw,rectangle] (L) at (0,0) {Cl \quad \text{PCy}_3 \quad \text{Cl} \quad \text{PCy}_3 \quad \text{H} \quad \text{Cl} \quad \text{PCy}_3 \quad \text{PCy}_3 \quad \text{R}_1 \quad \text{R}_2}
\node[draw,rectangle] (M) at (2,0) {- \quad \text{CH}_2=\text{CHR}_1 \quad \text{PCy}_3 \quad \text{PCy}_3 \quad \text{R}_1 \quad \text{R}_2}
\node[draw,rectangle] (N) at (4,0) {+ \quad \text{PCy}_3 \quad \text{PCy}_3 \quad \text{R}_1 \quad \text{R}_2}
\node[draw,rectangle] (O) at (6,0) {14 \text{ e}^- \quad \text{Products}}
\end{scope}
\end{scope}
\end{tikzpicture}
\end{center}

\textbf{Scheme 1.7}: Olefin metathesis by Grubb’s catalyst.\textsuperscript{28}

In Monsanto Acetic acid process, for the synthesis of acetic acid by catalytic carbonylation of ethanol, involves a 16 electron rhodium complex, [Rh(CO)₂(I)₂] (see Scheme 1.8).\textsuperscript{29}
Similarly in the catalytic hydrogenation of alkenes using Wilkinson’s catalyst RhCl(PPh_3)_3, the catalytic cycle involves the transition of complex between 16 valence electrons to 18 valence electrons. This catalyst is also known to selectively hydrogenate the alkenes. This is possibly due to the bulky phosphine ligands on the metal Rh (see next section). The industrial process, Wacker (or Smidt) process for the synthesis of acetaldehyde from ethylene, involves the 16 electron unsaturated palladium complex, [PdCl_4]^{2-}.

Scheme 1.8. Monsanto process of Acetic acid synthesis from methanol and CO.²⁹
1.4. The role of steric s induced by ligands in catalysis.

Ligands play a vital role in stabilizing transition metal complexes. The stability, as well as the reactivity of a metal in its complex form, depends upon the number, size, and the type of ligands it is bound to. Sterics imparted by the size of the ligand are found to be as equally important as electronic factors and plays a significant role in creation of unsaturation on the metal center. Sterics greatly influence the structures, spectroscopic properties, and chemical behavior of the metal complexes. By increasing the size of the ligand, one can alter the bond angle, increase the bond lengths, and favor lower coordination numbers (unsaturation) and coordination of smaller ligands. The Tolman cone angle, a concept introduced by Chadwick A. Tolman, to define the size of the ligand is highly used in homogeneous catalysis such as hydroformylation and hydrogenation reactions, to design a catalyst of specific interest to achieve selectivity.

Tolman reported the influence of ligand size on the rate of hydrocyanation of butadiene by the nickel complex, Ni(CO)$_3$L (see Scheme 1.9). By increasing the size of ligand, he was able to achieve greater reaction rates by increasing the rate of formation of the intermediate HNi(CO)$_3$(CN).

\[
\text{HCN} + \text{Ni(CO)}_3\text{L} \xrightarrow{K} \text{HNIr(CO)}_3\text{CN} + \text{L}
\]

L = P(OEt)$_3$, PPh(OEt)$_2$, P(O-o-Tolyl)

\[K = 0.005 \text{ [P(OEt)$_3$]} < 0.03 \text{ [PPh(OEt)$_2$]} < 10^4 \text{ [P(O-o-Tolyl)$_3$]}\]

Scheme 1.9. Effect of size of ligand on rate of hydrocyanation of butadiene.
The best example for the effect of steric on the catalysis is the Wilkinson’s catalyst in the hydrogenation of alkenes. This catalyst has three bulky phosphine ligands on the Rh catalyst, which stabilizes this complex. During hydrogenation catalysis, these ligands restrict the approach of bulky centers of the molecule being reduced towards the Rh metal center where the reduction happens. When a molecule with a large number of double bonds is catalyzed, it selectively hydrogenates the double bonds which are sterically less hindered. Among a mixture of alkenes, the one which is less hindered gets reduced faster compared to the other alkenes (see the equation 1.2 and Table 1.1).

\[
\text{C} = \text{C} + \text{H}_2 \xrightarrow{\text{Ph}_3\text{P} \text{Rh} \text{Cl} \text{PPh}_3} \text{C} - \text{C} \quad (\text{eq. 1.2})
\]

<table>
<thead>
<tr>
<th>Compound hydrogenated</th>
<th>Rate constant x 100 (L/mols)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_2\text{H}_4 )</td>
<td>31.6</td>
</tr>
<tr>
<td>( \text{H}_3\text{C} = \text{C} = \text{C} )</td>
<td>9.9</td>
</tr>
<tr>
<td>( \text{H}_3\text{C} = \text{C} )</td>
<td>1.8</td>
</tr>
<tr>
<td>( \text{CH}_3 )</td>
<td>0.6</td>
</tr>
<tr>
<td>( \text{H}_3\text{C} = \text{C} = \text{CH}_3 )</td>
<td>&lt; 0.1</td>
</tr>
</tbody>
</table>

*Table 1.1. Relative rates of hydrogenation using Wilkinson’s catalyst at 25 °C.*
1.5. Bi metallic complexes with promising results in catalysis.

Superior synthetic methods and catalysts always evolve over time; chemists have long been interested in catalyzing reactions by using bimetallic complexes that contain two or more different metal centers rather than monometallic compounds, because of the superior catalytic performance of bimetallic compounds over monometallic compounds.\textsuperscript{37,38} Again, the inspiration for the development of this field of inorganic chemistry is drawn from nature. Nature uses a variety of bimetallic complexes, particularly enzymes, for various functions.\textsuperscript{39} The advantage with bimetallic complexes is that they offer a variety of reactions happening at the same time on two different active metal centers.\textsuperscript{40} Thus, one could imagine progress of different types of oxidative-addition, reductive-elimination patterns, and the stabilization of unusual oxidation states and of ligand-bonding modes happening at same time which are not possible in monometallic complexes.

Takayuki Komatsu and co-workers used bimetallic compounds of Ni-Sn to catalyze de-hydrogenation of cyclohexane to benzene and methane.\textsuperscript{41} Piscina, J. and co-workers found that silica supported Ni-Sn compounds catalyzes CO oxidation reaction.\textsuperscript{42} In another example, Yuriy Román-Leshkov and co-workers found that bimetallic carbon supported copper-ruthenium (CuRu/C) catalysts are more superior than monometallic compounds, copper chromite (CuCrO\textsubscript{4}) in converting 5-hydroxymethylfurfural (HMF) to 2,5-dimethylfuran (DMF), a potential liquid transportation biofuel.\textsuperscript{43} In this reaction, Ru acts as a chloride resistant, which they introduce to purify the synthesized DMF from intermediates and other impurities. Recent work from our lab on bimetallic complex of Fe-Sn shows successful selective activation of benzylic C-H bond, and importance of the
bimetallic complexes.\textsuperscript{44} One of the highly studied bimetallic complex systems is transition metal-tin (TM-Sn) chemistry. Tin ligands have shown versatile properties in coordination chemistry. They are used in catalytic and non-catalytic reactions. They are found to have a strong labilizing effect on their \textit{trans} ligands, and by themselves they are also labile and thus can provide necessary vacant coordination sites in the catalysis and also can promote the migratory insertions reactions.\textsuperscript{45,46} These ligands are also found to accomplish oxidative addition and subsequent reductive elimination processes with ease. Most importantly a variety of organo-tin compounds are available for catalysis with the flexibility of varying bulkiness on the tin center. Various transition metal–tin heterobimetallic catalysts were synthesized and studied effectively in the catalytic and non-catalytic fields of hydrogenation, isomerization of olefins, polymerization, hydroformylation, and coupling reactions. A review by Marks S. Holt, William L. Wilson, and John H. Nelson efficiently summarized the application of TM-Sn bimetallic complexes for various applications in chemistry.\textsuperscript{47}

1.6. Statement of purpose.

The aim of the work that has been presented here is to synthesize electronically unsaturated, inexpensive bimetallic complexes aided by sterically demanding ligands that can exclusively activate the small molecules. The above detailed Schemes and reactions represent the underlying principles in successful synthesis of the reactive unsaturated transition metal (TM) complexes stabilized by bulky ligands. As discussed above tin has been found to display a variety of properties that can aid in the activation of small molecules. By using tin as both ligand and hetero metal, we wanted to probe the cooperative reactivity between two metals in the resulting TM-Sn bimetallic complexes.
Interestingly, these complexes were found to successfully activate small molecules, and, do so in some instances, catalytically. The initial work reported here comprises of Pt-Sn bimetallic complexes. Though Pt is an expensive metal, we employed this metal to test its ability to activate small molecules in homogenous catalysis, because of its superior catalytic properties. We also used other bulky ligands such as carbenes in combination with tin to test their reactivity towards small molecules. Later we tried to replace the Pt metal with inexpensive Ni metal to mimic the reactivity of Pt-Sn bimetallic complexes. The Ni-Sn complexes were found to be photo sensitive and indicated the formation of radicals in the presence of light they also displayed some interesting catalytic properties in polymerization.

The stable radical TEMPO is a well-known radical trap and its applications as a coordinating ligand are very few. It is known to coordinate to metal centers in different modes. Here, in the last chapter, the unexpected complexes of this seemingly bulky TEMPO radical as ligand and its unexpected Ni-TEMPO complexes and their synergistic reactivity to activate carbon-hydrogen bond of small organic molecules have been discussed.

2.1 Background.

Transition metal – tin chemistry has been quite well known for some time now, and one way to prepare transition metal – tin complexes is by using triaryl and trialkyl stannanes (R₃SnH). R₃SnH reacts readily with transition metals via oxidative addition of the Sn-H bond to the metal atom. Tin compounds have been used extensively as modifiers of the platinum group metals, and platinum-tin bimetallic heterogeneous catalysts have been shown to be highly efficient for use by the petroleum industry for a number of processes vital to petroleum reforming, catalytic hydrogenations⁴⁸⁻⁵¹ and dehydrogenations.⁵²,⁵³ Under homogeneous conditions, tin complexes have also been shown to catalyze many important reactions such as hydrogenation and isomerization of olefins, the water gas shift reaction, and also to improve the product selectivities of the reactions⁴⁷,⁵⁴⁻⁵⁶. Recently, it was reported that the trimetallic tin containing catalyst PtRu₃Sn, exhibited the highest selectivity for formation of unsaturated alcohols in the hydrogenation of citral.⁵⁷

We have been interested in investigating bulky tin compounds as a reagent in organometallic chemistry. The sterically encumbered stannane, tri-tert-butyltinhydride, Bu₃SnH, has great potential, however, there isn’t much chemistry associated with this compound in the literature. To demonstrate the versatility of this new ligand, we have already prepared a few metal complexes from reactions of Bu₃SnH with metal carbonyl compounds. For example, the reaction of Bu₃SnH with Pt₂Ru₄(CO)₁₈ yields the new trimetallic Pt/Ru/Sn mixed metal cluster Pt₂Ru₂(CO)₆(SnBu₃)₂(µ-H)₂, which was shown
to be a hydrogenation catalyst when supported on mesoporous silica. In addition to our work with precious metals, preliminary investigations of the coordination chemistry of bulky tin ligands with less expensive metals such as cobalt, nickel and iron have begun. We recently communicated the facile reversible activation of hydrogen by the bimetallic Pt-Sn complex Pt(SnBu\textsubscript{3})\textsubscript{2}(CNBu\textsubscript{3})\textsubscript{2}, that occurs both in solution and in the solid state.

The Pt(0) compound, Pt(COD)\textsubscript{2} (COD= cyclooctadiene), is a highly reactive compound. It is moisture sensitive, air sensitive, and temperature sensitive in solution state and is highly efficient in activation of the Sn-H bond at room temperature. The bulky stannane ligand Bu\textsubscript{3}SnH is also a reactive compound sensitive to moisture and air. The complexes synthesized from the reaction of these two reagents are unsaturated and stabilized by the steric imparted by the bulky tert-butyl groups.

Here this chapter reported the synthesis and characterization of a series of heterobimetallic complexes that were obtained by reacting Pt(COD)\textsubscript{2} with bulky tri-tert- butyl stannane (Bu\textsubscript{3}SnH), trimesityl stannane \{(2,4,6-Me\textsubscript{3}C\textsubscript{6}H\textsubscript{2})\textsubscript{3}SnH or Mes\textsubscript{3}SnH\} and triphenyl stannane, (Ph\textsubscript{3}SnH) reagents. Here is also presented the reactivity of these complexes towards small molecules such as H\textsubscript{2}, CO and catalyzation of H\textsubscript{2}-D\textsubscript{2} exchange reaction at room temperature and at depressed temperatures of -78 °C.

2.2 Results and discussion.

**Reaction of Pt(COD)\textsubscript{2} with one equivalent of Bu\textsubscript{3}SnH:** When one equivalent of Bu\textsubscript{3}SnH was added drop wise to hexane solution of Pt(COD)\textsubscript{2} at room temperature under argon atmosphere, the solution immediately changed color to dark reddish-brown to yield
a mononuclear 16-electron Pt(II) complex Pt(COD)(SnBu$_3$)(H), 2.1. Structure of 2.1 is shown in Figure 2.1 (further crystallographic data can be found in Appendix A, Table A.1).

Figure 2.1. An ORTEP of the molecular structure of Pt(COD)(SnBu$_3$)(H), 2.1, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows: Pt(1)-Sn(1) = 2.5984(2); Pt(1)-H(11) = 1.45(3); Pt(1)-C(1) = 2.289(2); Pt(1)-C(2) = 2.324(2); Pt(1)-C(5) = 2.245(2); Pt(1)-C(6) = 2.266(2); Sn(1)-Pt(1)-H(11) = 74(1); Sn(1)-Pt(1)-C(1) = 160.11(6); Sn(1)-Pt(1)-C(5) = 101.70(5).

It is evident from the structure that compound 2.1 is formed by the elimination of one COD ligand and oxidative addition of Sn-H bond to the Pt metal center as shown in equation 2.1.

$$\text{Pt(COD)}_2 + \text{Bu}_3\text{SnH}, \text{rt} \rightarrow \text{PtBu}_3\text{SnH} \text{ COD} \text{- COD} \quad (\text{eq. 2.1})$$
The complex 2.1 was characterized by the combination of $^1$H NMR and single crystal X-ray crystallography. The COD ligand is slightly bent away from the Pt center to accommodate the terminal hydride ligand. The isolation of 2.1 is tedious, as it is always associated with some unidentified oily products. The Pt-Sn bond length in compound 2.1 is 2.598(18) Å, and Pt-H bond length is 1.45(3) Å, which is consistent with reported Pt-Sn single bond in Pt(II) complexes.\textsuperscript{10,62} The hydride ligand is located and refined during crystallographic data collected at 100 K. The presence of the hydride ligand was also confirmed by $^1$H NMR spectroscopy, where it shows up at -3.74 ppm in C$_6$D$_6$ solvent with appropriate one-bond coupling to Pt ($^1J_{\text{Pt-H}}$ =1223.2 Hz) and two-bond coupling to Sn ($^2J_{\text{Sn-H}}$ = 48.2 Hz). Compound 2.1 is a 16 electron highly reactive unsaturated Pt-Sn bimetallic complex, it is sensitive to air, moisture and temperature. It can be used as a precursor to synthesize a variety of complexes by the substitution of easily replaceable COD ligand with another Bu$_3$SnH group.

**Addition of one more equivalent of Bu$_3$SnH to compound 2.1:** The aim here was to isolate a 14 electron unsaturated Pt(IV) complex with two terminal Bu$_3$Sn ligands and two hydride ligands, Pt(Bu$_3$Sn)$_2$(H)$_2$, 2.2 (see equation 2.2) by replacing the COD ligand. Very few 14 electron neutral Pt complexes are characterized and reported in literature.\textsuperscript{63–65} These complexes are highly unsaturated, unstable, and highly reactive. They also have the tendency to form dimers to gain stability.

![Equation 2.2](equation2.2.png)
When the reaction was carried out by adding an equivalent of Bu$_3$SnH to compound 2.1 in C$_6$D$_6$ solvent, new peaks were observed in $^1$HNMR spectroscopy in the hydride region at -7.8 ppm. However, these complexes were not identified and were not able to be isolated. Interestingly, when the reaction mixture was dissolved in dichloromethane and plated on TLC to collect a yellow band, gave an unexpected new Pt-Sn cluster complex [Pt(SnBu$_3^\prime$)(μ-SnBu$_2^\prime$)(H)$_2$)$_2$. 2.3, upon crystallization in hexane solvent at -20 °C. The molecular structure of 2.3 is shown in Figure 2.2 (further crystallographic data can be found in Appendix A, Table A.1). The compound 2.3 is characterized by the combination of $^1$H NMR, single crystal X-ray crystallography and mass spectrometry. The yield was low due to decomposition on the TLC plate. Compound 2.3 can also be prepared by reacting excess Bu$_3$SnH with Pt(COD)$_2$ as discussed below.

**Figure 2.2.** An ORTEP of the molecular structure of [Pt(SnBu$_3^\prime$)(μ-SnBu$_2^\prime$)(H)$_2$)$_2$. 2.3, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows: Pt(1)-Sn(1)=2.6550(4), Pt(1)-Sn(2)=2.6353(4), Sn(1)-Pt(1)-Sn(2)=126.19(1); Sn(1)-Pt(1)-Pt(1*)=178.04(1); Sn(2)-Pt(1)-Pt(1*)=54.09(1); Pt(1)-Sn(2)-Pt(1*)=71.78(1).
Extensive research has been done in the activation of group 14 Element-H bonds using late transition metal complexes with emphasis on activation of Sn-H and Ge-H bonds. Pt-Sn and Pt-Ge complexes similar to complex 2.3 were reported in the literature. The Pt-Sn complex [(Ph₃P)₂(H)Pt(µ-SnPh₂) (µ-η²-H-SnPh₂)Pt(PPh₃)] (see Scheme 2.1) reported is the first example of unsymmetrical diplatinum complex with bridging (µ-η²-H-SnPh₂) ligand.

**Scheme 2.1.** Sn bridged dinuclear Pt complex [(Ph₃P)₂(H)Pt(µ-SnPh₂) (µ-η²-H-SnPh₂)Pt(PPh₃)].

**Reaction of Pt(COD)₂ with excess of Bu₁³SnH:** The reaction of Pt(COD)₂ with Bu₁³SnH is further explored to make new unsaturated Pt-Sn complexes like compound 2.3. Drop wise addition of benzene solution of excess Bu₁³SnH to Pt(COD)₂ at room temperature in a glove box, followed by slow evaporation of solvent, afforded light yellow crystals covered with brown oily residue. Crystals were washed with dichloromethane several times to yield pure crystals of compound 2.3, (crystal structure shown in Figure 2.2 and line drawing shown in Figure 2.3), which was previously obtained by reacting Pt(COD)₂ with two equivalents of Bu₁³SnH, but this time the yields are decent but still very low, about 5%. These low yields can be attributed to the
formation of unidentified oily bi-products. Apart from compound 2.3, no new Pt-Sn complexes were isolated from this reaction.

Compound 2.3 is an unsaturated symmetrical dinuclear Pt complex, with a Pt-Pt bond that is bridged by two SnBu′2 groups. There is a terminal SnBu′3 ligand on each Pt atom. The complex also contains four hydride ligands, (see Figure 2.3), two on each Pt, that were confirmed by ¹H NMR spectroscopy.

The presences of hydrides in 2.3 were confirmed by ¹H NMR taken in toluene-d₈ solvent. The hydride peaks resonance appears at -3.45 ppm with appropriate one-bond coupling to Pt (¹J_{Pt-H} = 905 Hz) and two-bond coupling to Sn (²J_{Sn-H} = 32 Hz). The Pt-Pt bond length in compound 2.3 is 3.0877 Å, longer than the average Pt-Pt single bond distance of 2.70 Å. In the analogous Pt-Ge dinuclear complex [(GePh₃)(CO)Pt(µ-GePh₂)]₂, a Pt-Pt bond distance of 2.8394 (3) Å was reported. The longer bond length in 2.3 can be attributed to the steric induced by bulky SnBu′₂ ligands which are even bigger than GePh₂ ligands.

The Pt(IV) tetrahydride complex 2.3 is stable towards moisture and air in the solid state, and poorly soluble in most organic solvents. Solubility can be increased by heating.
the solution and is stable in solution up to 100 °C for four hours but on prolonged heating the tert-butyl groups cleave off from the tin, producing isobutane gas and other unidentified tin bi-products.

**Proposed reaction mechanism for the formation of compound 2.3:** Based on the experimental observations, the following reaction mechanism (Scheme 2.2) has been proposed for the formation of compound 2.3. The first step is the oxidative addition of two equivalents of Bu$_3$SnH to the Pt center, followed by reductive elimination of the COD ligand to yield the unstable, highly reactive intermediate compound 2.2. The second step is the cleavage of one tert-butyl group from the Bu$_3$Sn group to yield the proposed intermediate compound I accompanied by the abstraction of a hydride by the cleaved tert-butyl group to produce isobutane gas. Peaks corresponding to free isobutane in the $^1$H NMR spectrum were observed when the reaction was performed in toluene-$d_8$ solution in the NMR tube. Cleavage of an alkyl group from organotin ligands bonded to transition metals has been previously observed.$^{71,72}$ Intermediate I dimerizes at room temperature to afford another unsaturated intermediate [(H)Pt(µ-SnBu$_2$)(SnBu$_3$)]$_2$, II, a 28 electron unsaturated dinuclear Pt-Sn bimetallic complex. The unusual electronic unsaturation at the platinum metal center in intermediate II initiates the abstraction of hydride from excess Bu$_3$SnH to yield compound 2.3. The activation of Si-H and C-H bonds is a common feature of unsaturated Pt complexes.$^{73,74}$ An increase in the product yield in the presence of excess Bu$_3$SnH also supports this reaction mechanism as the excess Bu$_3$SnH provides the necessary proton for the formation of compound 2.3. We have not been able to isolate any of the above proposed intermediates.
Scheme 2.2. Proposed mechanism for the formation of compound 2.3.

**Reaction of [Pt(µ-SnBu'2)(SnBu'3)(H)]2, 2.3, with CO:** The dinuclear Pt-Sn complex 2.3 reacts with CO gas reversibly at room temperature both in solid state as well as in solution state, to give corresponding CO added product [Pt(SnBu'3)(µ-SnBu'2)(CO)(H)]2, 2.4, see Figure 2.4, (further crystallographic data can be found in Appendix A, Table A.1). When CO gas is purged through the hexane solution of 2.3 at room temperature, the solution turns to dark yellow instantaneously to afford 2.4. Compound 2.4 is moderately stable. Removal of the CO atmosphere by applying vacuum or introducing argon gas results in regeneration of the starting compound 2.3 in quantitative yield (see
equation 2.3). The solubility of dinuclear Pt-Sn carbonyl complex 2.4 is better than that of compound 2.3, but it decomposes rapidly when exposed to air while in solution.

![Molecular structure](image)

**Figure 2.4.** The molecular structure for \([\text{Pt}(\text{SnBu}_3)(\mu-\text{SnBu}_2)(\text{CO})(\text{H})_2]_2, 2.4.\)

Compound 2.4 is a 34 electron dinuclear Pt-Sn cluster complex. Its structure is similar to compound 2.3 except that the CO ligands are added in trans-positions to each other. The Pt-Pt bond distance is 3.1894 (6) Å, slightly longer than that observed in compound 2.3 (3.0149 Å). The Pt1-C11(1.929 Å) bond distance is consistent with the known Pt-C distance in Pt-carbonyl complexes (1.888 Å). The CO groups lie perpendicular to the plane of Pt$_2$Sn$_2$ square to avoid steric repulsion from tin ligands.
Compound 2.4 was also characterized by the combination of $^1$H NMR, single crystal X-ray crystallography, and IR spectroscopy.

The hydride ligands were identified by the $^1$H NMR where they show up at -12.77 ppm with appropriate one bond coupling to Pt ($^1J_{Pt-H} = 702$ Hz), and their number was identified by appropriate integration with respect to other proton resonances. Interestingly, with the addition of CO to the compound 2.3, there is a dramatic shift in the hydride resonance of hydride ligands in the $^1$H NMR. In toluene-$d_8$ solution, for compound 2.3 the hydride resonance appears at -3.71 ppm ($^1J_{Pt-H} = 905$ Hz), and for compound 2.4 the resonance appears at -12.77 ppm ($^1J_{Pt-H} = 702$ Hz) (Figure 2.5).

\[
\text{Figure 2.5. } ^1\text{H NMR spectrum in hydride region for compound 2.3 and compound 2.4.}
\]

The more-up field appearance of hydrides resonance could be due to the increased electron density around platinum metal center by the back donation of electrons from the
CO ligands which in turn increases the electron density around hydride ligands, which causes the hydrides to resonate more up-field compared to the hydrides resonance in compound 2.3.

**Reaction of Pt(COD)\(_2\) with Bu\(_3\)SnH in the presence of CNBu\(^t\):** The reaction of Pt(COD)\(_2\) with one equivalent of Bu\(_3\)SnH and two equivalents of tert-butylisocyanide, CNBu\(^t\), at room temperature afforded the dihydrido Pt-Sn complex Pt(SnBu\(_3\))\(_2\)(CNBu\(^t\))\(_2\)(H)\(_2\), 2.5, in 32 % yield. High yields can be obtained by performing the reaction at -78 °C. Compound 2.5 was characterized by the combination of \(^1\)H NMR, mass spectrometry, and single crystal x-ray diffraction analyses and IR spectroscopy. An ORTEP showing the molecular structure of 2.5 is shown in Figure 2.6, (further crystallographic data can be found in Appendix A, Table A.2).

![An ORTEP of the molecular structure of Pt(SnBu\(_3\))\(_2\)(CNBu\(^t\))\(_2\)(H)\(_2\), 2.5, showing 30% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows: Pt(1) – Sn(1) = 2.6718(5); Pt(1) – C(1) = 2.014(8); Pt(1)-H(1) = 1.65(9); Sn(1)-Pt(1)-Sn(1*) = 161.35(3); C(1)-Pt(1)-C(1*) = 102.5(4); C(1)-Pt(1)-Sn(1) = 95.82(3); Sn(1)-Pt(1)-H(1) = 84.2(4).](image)
For the formation of compound 2.5, it is proposed that the addition of 2 equivalents of Bu₃SnH to Pt(COD)₂ first gives the highly reactive 14 electron complex Pt(SnBu₃)₂(H)₂, 2.2, via oxidative addition of the Sn-H bond (see Scheme 2.3). This unsaturated complex then adds 2 equivalents of CNBu' to afford the 18 electron complex 2.5.

**Scheme 2.3.** Proposed pathway for the formation of Pt(SnBu₃)₂(CNBu')₂(H)₂, 2.5.

Compound 2.5 is an 18 electron mono nuclear platinum complex with distorted octahedral geometry and over all possesses a C₂ᵥ symmetry. The hydride ligands are located and refined in the structural analysis performed at 100 K. Their presence was further confirmed by ¹H NMR, which shows one resonance for both the hydrides at -13.52 ppm in C₆D₆ with appropriate one bond coupling to Pt (¹Jₚt-H = 697 Hz) and two bond coupling to Sn (²Jₚt-H = 34 Hz). The Pt-Sn bond distance in 2.5 is 2.6718(5) Å and the Pt-H bond distance is 1.65(9) Å. The Pt-Sn bond length is consistent with the
literature value for mononuclear octahedral Pt(IV) complexes {2.554 Å for Pt-stannaborate isocyanide complex}.

**Compound 2.5 reversibly loses both the hydrides in solution and solid state:** Both the hydride ligands in 2.5 can be displaced at room temperature. When argon gas is purged through the compound 2.5 both in the solution state and in solid state, it loses both the hydrides to furnish the complex Pt(SnBu₃)₂(CNBu')₂, 2.6, in very high yields. Compound 2.6 activates hydrogen gas both in solid state and in solution state. Compound 2.6 was also characterized crystallographically and its structure in the solid state is shown in Figure 2.7, (further crystallographic data can be found in Appendix A, Table A.2).

![ORTEP of the molecular structure of Pt(SnBu₃)₂(CNBu')₂, 2.6, showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows: Pt(1)-Sn(1) = 2.6765(3); Pt(1)-Sn(2) = 2.6851(3); Pt(1)-C(1) = 1.932(3); Pt(1)-C(2) = 1.929(3); Sn(1)-Pt(1)-Sn(2) = 159.539(8); C(1)-Pt(1)-C(2) = 158.69(13).](image)

The loss of the hydride ligands gives a 16 electron configuration around the Pt atom in 2.6 with a formal oxidation state of +2. The complex as seen in Figure 2.7 is...
not planar, as expected for Pt(II) $d^8$ complexes, and could be considered as more of a “saw-horse” type structure, due to the steric impediments imparted by the bulky $Bu^t$ groups.

Analysis of the X-ray crystal structures reveals how the ligands in 2.6 rearrange to accommodate hydride ligands upon addition of hydrogen. The C2-Pt1-C1 bond angle in compound 2.6 is 158.69(13)$^\circ$, whereas the C1-Pt1-C1$^*$ bond angle in compound 2.5 is squeezed significantly to 102.5(4)$^\circ$ to accommodate the two hydride ligands (see Figure 2.8).$^{61}$ Such a rearrangement of coordination geometry of ligands is common in the addition of hydrogen or CO to the transition metal carbonyl clusters.$^{75-77}$ There is no considerable change in the Sn-Pt-Sn bond angle upon addition of H$_2$ to compound 2.6. Similarly, the Pt-Sn bond lengths also remain essentially the same after addition of H$_2$.

![Figure 2.8. Change in coordination geometry of ligands after addition of H$_2$ to 2.6.](image)

Compounds 2.5 and 2.6 also display a marked difference in the IR resonances of CN stretches. The $\nu_{CN}$ stretching frequency for 2.6 in hexane solution shows a sharp peak
around 2112 cm\(^{-1}\), slightly out of the literature reported range of 2225-2170 cm\(^{-1}\), common for Pt(II)-bound isocyanide complexes.\(^{78}\) The IR spectrum of compound Pt(SnBu\(_3\))\(_2\)(CNBu\(_3\))\(_2\)(H)\(_2\), \(2.5\) in hexane solution shows two peaks, one weak intensity peak at 2112 cm\(^{-1}\) corresponding to the two terminal hydrides (\(\nu_{\text{Pt-H}}\) stretching frequency) and one sharp peak at 2139 cm\(^{-1}\) corresponding to \(\nu_{\text{CN}}\) stretching of the CNBu\(_3\) ligands. Upon addition of hydride ligands to Pt(II) isocyanide complex \(2.6\), there is a slight shift in \(\nu_{\text{CN}}\) stretching frequency (2112 cm\(^{-1}\), \(2.5\)) this might be due to increase in electron density around the Pt-metal center in \(2.5\). The absorption peak of \(\nu_{\text{Pt-H}}\) for Pt(IV)hydride complex \([\text{PtH}_2(\text{SnPh}_3)_2(\text{PMe}_2\text{Ph})_2]\) synthesized by Eaborn et al. several years ago also has \(\nu_{\text{Pt-H}}\) values in the same range (2085, and 2115 cm\(^{-1}\)).\(^{86}\)

**Activation of H\(_2\) by compound Pt(SnBu\(_3\))\(_2\)(CNBu\(_3\))\(_2\), \(2.6\) in solid state:** As mentioned earlier compound \(2.6\) activates hydrogen not only in the solution state but also in the solid state at room temperature and also at -78 °C. Upon exposing the purple-colored crystals of compound \(2.6\) to H\(_2\) atmosphere, the colorless crystals of compound \(2.5\) formed over a period of 10 minutes in almost quantitative yield, consistent with the solid state structure of \(2.5\) for two hydride ligands. Removing the hydrogen gas and placing the colorless crystals of compound \(2.5\) in vacuum for 12 hours regenerates purple crystals of compound \(2.6\). A similar phenomena of crystal to crystal transformation during the activation of small molecules (H\(_2\), CO, and C\(_2\)H\(_4\), NH\(_3\)) by [Ir]-N\(_2\) pincer complex (see Figure 2.9) was reported by the Brookhart group.\(^{79}\) Here the crystal structure remains intact during the ligand exchange reactions, without decaying to microcrystalline powder form.
**Figure 2.9.** Line drawing for crystal to crystal transformations of [Ir]-pincer complexes of N₂, H₂ and C₂H₄, reported by Brookhart group.⁷⁹

**Nature of hydride ligands of 2.5, reaction of compound Pt(SnBuᵗ疏通)₂(CNBuᵗ疏通)₂, 2.6 with HD gas:** Compound 2.5-d₁ was prepared by the reaction of 2.6 with HD gas to test for the existence of direct H-H interactions in 2.5, i.e., to know whether it is a molecular hydrogen H-H or two terminal hydrides attached to Pt metal center. The ¹H NMR spectrum of 2.5-d₁ did not show any H-D coupling, suggesting that there is no significant H-D interaction, which is consistent with the crystal structure analysis of 2.5. In addition to the resonance of 2.5-d₁, the hydride resonance for 2.5 was also present in the ¹H NMR spectrum (see Figure 2.10). The small shift difference in the spectrum in Figure 2.10 (top) is due to isotope shift effects.
Figure 2.10. Overlay of $^1$H NMR spectra of the hydride region (bottom) for 2.5 from the addition of H$_2$ to 2.6 and (top) for the addition of HD to 2.6. Pt-H one-bond couplings are not shown.

**Compound Pt(SnBu$_3^t$)$_2$(CNBu$_2^t$)$_2$, 2.6 catalyzes H$_2$-D$_2$ exchange:** In solution, compound 2.6 catalyzes the H$_2$-D$_2$ exchange to give HD gas at room temperature (see Figure 2.11), which was monitored by $^1$H NMR (see Figure 2.12). Also the three possible isotopomers of 2.5 are also observed in the $^1$H NMR. Unlike activation of H$_2$ in solid state, compound 2.6 catalyzes the H$_2$-D$_2$ exchange only in the solution state and not in the solid state.
Figure 2.11. Catalytic H$_2$-D$_2$ exchange by Pt(SnBu$_3$)$_2$(CNBu)$_2$, 2.6.

The catalysis of H$_2$-D$_2$ exchange is not uncommon with transition metal complexes. Several years ago, HD gas was reported to be formed both from [CpRu(PPh$_3$)(Bu'NC)(H$_2$)]$^+$ and D$_2$ in dichloromethane, and in thermal H$_2$-D$_2$ exchange reactions of Cr(CO)$_4$(H$_2$)$_2$ in liquid xenon. Kubas et al. also observed H$_2$-D$_2$ exchange over their M(CO)$_3$(PR$_3$)$_2$(H)$_2$ complex to produce HD gas both in solution and in solid state.

The catalytic H$_2$-D$_2$ exchange reaction with 2.6 is monitored in C$_6$D$_6$ solvent at room temperature by $^1$H NMR. Mixture of H$_2$-D$_2$ gas is purged through the solution of 2.6 using syringe, followed by vigorous shaking for 15 minutes, the $^1$H NMR indicated the formation of HD gas. The $^1$H NMR of a 1:1 molar ratio of H$_2$-D$_2$ mixture without catalyst 2.6 shows a single peak for free hydrogen (see Figure 2.12). The $^1$H NMR
spectrum also indicates that the $\text{H}_2 + \text{D}_2 \rightleftharpoons \text{2HD}$ equilibrium has been reached (as there was no change in the integration ratio of the peaks even after 5 days) and appropriately integration of the peaks is consistent with $K_{\text{eq}} \sim 3.6$.\textsuperscript{83}

![Figure 2.12. $^1$H NMR spectra in C$_6$D$_6$ for catalytic H$_2$-D$_2$ scrambling by Pt(SnBu$_3$)$_2$(CNBu)$_2$, 2.6.](image)

**Mechanism of H$_2$-D$_2$ exchange:** The fact that compound Pt(SnBu$_3$)$_2$(CNBu)$_2$, 2.6 catalyzes H$_2$-D$_2$ exchange, and that its reaction with H-D gas afforded a mixture of isotopomers of Pt(SnBu$_3$)$_2$(CNBu)$_2$(H)$_2$, 2.5, prompted us to understand this exchange mechanism on the Pt center. Addition of H$_2$ to 2.6 gives 2.5 which is an 18 electron, formally Pt(IV) complex in an octahedral geometry. Thus addition of D$_2$ to an intact 2.5 would increase the oxidation state from IV to VI and the coordination number on
platinum to 20 electrons which is highly unlikely, so the H₂-D₂ exchange process should be accompanied by ligand loss in 2.5. An alternate could be that once complex 2.5 is formed by addition of H₂, reductive elimination of Bu₃SnH could occur providing intermediate I with vacant coordination sites (see equation 2.4) for the addition of D₂. With both hydride and deuteride coordinated to platinum, reductive elimination of HD could then proceed.

\[
\text{Bu}^\text{t}_3\text{NC} \quad \text{(eq. 2.4)}
\]

<table>
<thead>
<tr>
<th>Bu\textsuperscript{t}3\text{NC}</th>
<th>SnBu\textsuperscript{t}3</th>
<th>+ H₂</th>
<th>\text{rt}</th>
<th>Bu\textsuperscript{t}3\text{NC}</th>
<th>H</th>
<th>SnBu\textsuperscript{t}3</th>
<th>\text{rt}</th>
<th>Bu\textsuperscript{t}3\text{NC}</th>
<th>SnBu\textsuperscript{t}3</th>
<th>Bu\textsuperscript{t}3\text{SnH}</th>
</tr>
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<tbody>
<tr>
<td>\text{Pt} \quad \text{Bu}^\text{t}3\text{NC}</td>
<td>\text{Bu}^\text{t}3\text{NC}</td>
<td>\text{H}</td>
<td>\text{SnBu}^\text{t}3</td>
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<td>\text{Bu}^\text{t}3\text{SnH}</td>
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To test if the rate of H₂ addition to 2.6 is affected by the presence of free Bu₃SnH, there was no detectable decrease in the rate of H₂ addition in the presence of a 32-fold excess of Bu₃SnH at room temperature. Since the H₂ addition reaction is instantaneous at room temperature, the addition of H₂ to 2.6 in the presence of excess Bu₃SnH was carried out at lower temperatures. Even at -78 °C, no detectable decrease in the rate was observed, perhaps suggesting that H₂ addition could proceed without ligand dissociation. To further dwell on the possibility of Bu₃SnH elimination from 2.5, the reaction was carried out in the presence of another R₃SnH reagent, namely Ph₃SnH, to see if the complex Pt(SnBu₃)(SnPh₃)(CNBu₃)(H)₂, could be isolated, where one of the SnBu₃ groups in 2.5 is replaced by a SnPh₃ group. If the SnBu₃ group is replaced by the other SnR₃ group in the presence of H₂ gas with the formation of free HSnBu₃, then the proposed mechanism in equation 2.4 is pretty much proved. The mechanistic pathway of
loss of CNBu in the presence of H2/D2 has been ruled out as a new rose colored product Pt(SnBu3)2(CNBu3), 2.7 (see Figure A.1 in Appendix A) has been isolated in the presence of excess CNBu and H2/D2 indicating the strong binding capability of CNBu with Pt metal center. A similar compound with Ni metal has also been synthesized in our lab.84

Exchange of SnBu3 group in Pt(SnBu3)2(CNBu3), 2.6 with Ph3Sn group: When 3 fold excess Ph3SnH, which is less bulky than SnBu3H, is added to the hexane solution of 2.6 in the presence of H2 gas (where compound 2.5 will be formed immediately), an immediate white colored precipitate was observed in the reaction mixture. Residue was filtered in the glove box and recrystallized in CH2Cl2/Hexane solvent mixture at -30 °C to give colorless crystals of Pt(SnPh3)3(CNBu3)2(H), 2.8 in 90% yield. Wherein both the Bu3Sn ligands in 2.5 were replaced by two Ph3Sn ligands, a third Ph3Sn ligand is also coordinated the Pt metal center and there is also a hydride ligand on the Pt metal center to form an 18 electron Pt(IV) complex in an octahedral geometry. Compound 2.8 can also be prepared even in the absence of H2 gas. We believe it is a highly strained structure given the steric crowdedness around the Pt metal center. Very few literature examples were reported with three or more tin ligands on the same Pt metal center but there are only two examples with three bulky tin ligands on the same Pt metal center in an octahedral symmetry.85,86 Compound 2.8 can also be prepared by reacting Pt(COD)2 with two equivalents of CNBu and 3 equivalents of Ph3SnH at -78 °C in the presence of inert atmosphere. An ORTEP showing the molecular structure of 2.8 is shown in Figure 2.13, (further crystallographic data can be found in Appendix A, Table A.2). Compound 2.8 is
characterized by the combination of IR, $^1$H NMR, elemental and single crystal x-ray diffraction analyses.

**Figure 2.13.** An ORTEP of the molecular structure of Pt(SnPh$_3)_3$(CNBu't)$_2$(H), 2.8 showing 30% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows: Pt(1)-Sn(1) = 2.6761(8), Pt(1)-Sn(3) = 2.6140(7), Pt(1)-C(1) = 2.03(1), Pt(1)-H(1) = 1.65(6) Sn(1)-Pt(1)-Sn(2) = 171.07(3), Sn(2)-Pt(1)-Sn(3)=93.32(2), C(1)-Pt(1)-Sn(3) = 94.1(3), C(1)-Pt(1)-C(6) = 102.8(4), Sn(2)-Pt(1)-C(1) = 89.2(3), Sn(1)-Pt(1)-(C6) = 85.0(3), C(6)-Pt(1)-H(1) = 66(2), Sn(3)-Pt(1)-H(1) = 97(2).

The $^1$H NMR of Pt(SnPh$_3)_3$(CNBu't)$_2$(H), 2.8 displayed some interesting temperature dependent dynamics in solution (see Figure 2.14). The $^1$H NMR in toluene showed two broad resonances in the hydride region at 25 °C ($\delta = -6.42$, and -11.91). As the temperature was decreased to -20 °C, two distinct hydride resonances were observed showing coupling to both platinum and tin ($\delta = -6.62$, $J_{^{119}Sn-H} = 679$ Hz, $J_{^{117}Sn-H} = 647$Hz, $J_{Pt-H} = 775$ Hz, and $\delta = -11.90$, $J_{Pt-H} = 665$ Hz, $J_{^{119}Sn-H} = 26.68$ Hz, $J_{^{117}Sn-H} = 13.95$ Hz) which is consistent with the presence of isomers in solution. As the temperature is
raised from -20 °C, the two hydride signals start to broaden and coalesce; however, the averaged fast exchange limit could not be obtained as the complex decomposes above 30°C.

![Diagram of VT ¹HNMR overlay of Pt(SnPh₃)₃(CNBu^t)₂(H), 2.8.](image)

As shown in Figure 2.14, both the hydride resonances show one bond coupling to platinum. The hydride resonance at -11.90 ppm has a Sn coupling of 27Hz (¹¹⁹Sn) which is consistent with the two bond coupling value, indicating this resonance could be due to the structure 2.8 (compound 2.8), where the H1 atom is cis to the Sn3 atom (Figure 2.13). The resonance at -6.62 ppm also shows coupling to Sn, with J₁¹⁹Sn-H = 679 Hz, which we are not sure about the order of coupling, as this value is far off from the one bond ¹¹⁹Sn-H
coupling (as the $^{1}J_{^{119}\text{Sn-H}}$ in Ph$_3$SnH is 1936 Hz) and also far higher to be a two bond coupling. But there is a possibility that this unusual Sn coupling could be due to a resonance structure where the hydride bridges a Sn and Pt metal centers (see Scheme 2.4a). However subsequent literature searches lead to the belief that this could indeed be due to two bond Sn coupling as suggested by Prof. Richard Adams, where hydride is two bond trans to the Sn$_{87-90}$ (see Scheme 2.4b).

Efforts to identify the hydride bridging isomer by $^{119}$Sn NMR spectroscopy failed as the proton coupled spectra was too broad and did not show any possible doublets due to

\[
\begin{align*}
J_{^{119}\text{Sn-H}}^{a} &= 679 \text{ Hz (complex 2.8)} & (\text{vs}) & J_{^{119}\text{Sn-H}}^{1} &= 1936 \text{ Hz (Ph}_3\text{SnH)} \\
J_{^{119}\text{Sn-H}}^{b} &= 679 \text{ Hz (complex 2.8)} & (\text{vs}) & J_{^{119}\text{Sn-H}}^{2} &\approx 800 \text{ to } 1000 \text{ Hz (trans)}
\end{align*}
\]

Scheme 2.4: a) Proposed resonance structures with bridging hydride. b) Proposed cis/trans isomers.
to hydride couplings. The only possible solution to this is to crystallize the isomers and study them using single crystal x-ray spectroscopy. At this point it is unclear about the existence of type of isomerism/isomer in the solution of 2.8, and further research is underway to identify the isomer at -6.62 ppm.

As expected, compound Pt(SnPh$_3)_3$(CNBu')$_2$(H), 2.8 is unstable in air and loses hydride as H$_2$ and Ph$_3$Sn ligand as Ph$_3$SnSnPh$_3$ and (Ph$_3$)$_4$Sn and forms a stable yellow colored compound Pt(SnPh$_3)_2$(CNBu')$_2$, 2.9. An ORTEP diagram of the molecular structure of 2.9 is shown in Figure 2.15, (further crystallographic data can be found in Appendix A Table A.3).

![Figure 2.15](image)

**Figure 2.15.** An ORTEP of the molecular structure of Pt(SnPh$_3)_2$(CNBu')$_2$, 2.9 showing 30% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows: Pt(1)-Sn(1) = 2.6231(3), Pt(1)-C(1) = 1.936(5). Sn(1)-Pt(1)-Sn(1') = 180.00, Sn(1)-Pt(1)-C(1) = 87.5(1), Sn(1)-Pt(1)-C(1') = 92.5(1), C(1)-Pt(1)-C(1') = 180.0(2).

Compound Pt(SnPh$_3)_2$(CNBu')$_2$, 2.9 is a $d^8$ square planar, 16 electron Pt(II) compound. Compound 2.9 is characterized by the combination of IR, $^1$H NMR, elemental
and single crystal x-ray diffraction analyses. Compound 2.9 can also be prepared by reacting Pt(COD)_2 with two equivalents each of Ph_3SnH and CNBu^t at -78°C. Interestingly, compound 2.9 is stable towards H_2 or CO addition, but reacts with Ph_3SnH under inert atmosphere to generate back compound Pt(SnPh)_3(CNBu^t)_2(H), 2.8.

**Exchange of SnBu^t_3 group with Mes_3Sn group:** Reaction of compound 2.6 with Ph_3SnH didn’t give much insight into the mechanism of H_2-D_2 exchange as it reacts by itself even in the absence of H_2 gas to give the compound 2.8. So the exchange reaction was carried with other Sn ligand Mes_3SnH, trimesityl stannane {(2,4,6- Me_3C_6H_2)_3SnH or Mes_3SnH} which is bulkier than Bu^t_3SnH. There was essentially no reaction of compound 2.6 with a 3 fold excess of Mes_3SnH at room temperature (^1H NMR of the reaction mixture shows only very trace amounts of product and reaction takes 7 days for completion at room temperature). However when H_2 gas is introduced to the reaction system (which first forms compound 2.5), the reaction proceeds faster to afford Pt(SnBu^t_3)(SnMe_3)(CNBu^t)_2, 2.10 (see Scheme 2.5). This is imaginable as in case of 2.5 there is a readily available hydride on Pt, which can be bonded to SnBu^t_3 group to be removed as Bu^t_3SnH. But in the case of 2.6, in the absence of H_2 gas the hydride has to come from Mes_3SnH which is a time consuming process with relatively high energy barrier compared to previous route.
Crystal structure for **2.10** is shown in Figure 2.16 (further crystallographic data can be found in Appendix Table A.3). In the absence of H₂ gas, the formation of Pt(SnBuᵅ₃)(SnMes₃)(CNBuᵅ)/₂, **2.10** from **2.6** in fact proceeds through complex **2.5**, where complex **2.5** forms first and then the reductive elimination of Buᵅ₃SnH takes place (which is evident from ¹HNMR where peaks corresponding to both compound **2.5** and Buᵅ₃SnH were observed) to facilitate the oxidative addition of Mes₃SnH. A variety of exchange reactions at the Pt metal center are reported in the literature,⁹¹–⁹⁵ but to our knowledge this is the first example of an exchange reaction where we have successfully replaced a single tin ligand with a different tin ligand to furnish a stable complex that has two different terminal tin ligands coordinated to a Pt metal center.
Figure 2.16. An ORTEP of the molecular structure of \( \text{Pt(SnMes}_3\text{)(SnBu}_3\text{t})(CNBu}_3\text{t)}_2 \), 2.10 showing 30% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows: Sn(1)-Pt(1)=2.6797(5), Sn(2)-Pt(1)=2.6775(5), C(1)-Pt(1) =1.947(6), C(6)-Pt(1)=1.945(6), Sn(1)-Pt(1)-Sn(2)=171.50(2), C(1)-Pt(1)-C(6) = 167.1(3), C(6)-Pt(1)-Sn(1) =92.1(2), C(1)-Pt(1)-Sn(1)=93.3(2), C(1)-Pt(1)-Sn(2)=89.3(2), C(6)-Pt(1)-Sn(2)=87.0(2).

Compound 2.10 is similar in structure to 2.6 where in place of one of the SnBu\textsubscript{3t} there is a SnMes\textsubscript{3} group. The complex is not square planar but at the same time not as distorted to a “sawhorse” type structure as in 2.6, \([C(1)-Pt(1)-C(6) = 167.1(3) \degree, \text{Sn}(1)-\text{Pt}(1)-\text{Sn}(2)=171.50(2)\text{]}\). Complex 2.10 does not contain any hydride ligands, but it can be assumed that the dihydride complex \( \text{Pt(SnBu}_3\text{t)(SnMes}_3\text{)(CNBu}_3\text{t)}_2(H}_2 \) first forms, which in turn loses H\textsubscript{2} to give 2.10. Considering how labile the hydride ligands are in 2.5, it is not surprising that \( \text{Pt(SnBu}_3\text{t)(SnMes}_3\text{)(CNBu}_3\text{t)}_2(H}_2 \), could not be detected. Furthermore, addition of H\textsubscript{2} or CO to 2.10 does not occur as in the case with 2.5 at room temperature and is highly stable to exchange other Bu\textsubscript{3t}Sn even with excess Mes\textsubscript{3}SnH.
Efforts to exchange the other SnBu$_3^t$ ligand from compound Pt(SnMes$_3$)(SnBu$_3^t$)(CNBu$_t^t$)$_2$, 2.10 with the excess of Mes$_3$SnH to form the compound Pt(SnMes$_3$)$_2$(CNBu$_t^t$)$_2$, 2.11 were unsuccessful at room temperature. However, we were able to make the Pt(SnMes$_3$)$_2$(CNBu$_t^t$)$_2$, 2.11 directly from the reaction of Pt(COD)$_2$ with two equivalents of each CNBu$_t^t$ and Mes$_3$SnH at -78 °C in 80% yield. A crystal structure of 2.11 is shown in Figure 2.17, (further crystallographic data can be found in Appendix Table A.3). Compound 2.11 is highly stable and similar in structure to compound 2.10, except compound 2.11 is highly sterically encumbered and it is also unreactive towards H$_2$ or CO at room temperature as in the case of Pt(SnBu$_3^t$)(SnMes$_3$)(CNBu$_t^t$)$_2$, 2.10.

![Molecular structure of Pt(SnMes$_3$)$_2$(CNBu$_t^t$)$_2$, 2.11.](image)

**Figure 2.17.** An ORTEP of the molecular structure of Pt(SnMes$_3$)$_2$(CNBu$_t^t$)$_2$, 2.11, showing 30% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows: Sn(1)-Pt(1) = 2.6615(6), C(1)-Pt(1) = 1.92(1), Sn(1)-Pt(1)-Sn(1*) = 175.74(3), Sn(1)-Pt(1)-C(1) = 89.0(3), C(1)-Pt(1)-C(1*)= 164.2(4).
Exchange between Pt(SnBu$_3$)$_2$(CNBu$_3$)$_2$(D)$_2$, 2.5-$d_2$ and free Bu$_3$SnH: While the experiment conducted with Mes$_3$SnH and 2.6, shows exchange of the tin groups, it can be assumed that reductive elimination of Bu$_3$SnH should occur from 2.5. To further prove this, we performed the reaction of the dideuteride complex Pt(SnBu$_3$)$_2$(CNBu$_3$)$_2$(D)$_2$, 2.5-$d_2$ and free Bu$_3$SnH. When an equimolar mixture of 2.5-$d_2$ and Bu$_3$SnH was carried out in an NMR tube with C$_6$D$_6$ solvent, $^2$H$^1$H NMR revealed formation of Bu$_3$SnD showing appropriate one bond coupling to both $^{119}$Sn and $^{117}$Sn, ($\delta = 5.62$, $^1J_{119\text{Sn-D}} = 213$ Hz and $^1J_{117\text{Sn-D}} = 203$ Hz). The deuteride region showed a peak at $\delta = -13.48$, $^1J_{\text{Pt-H}} = 106$ Hz due to 2.5-$d_2$ and 2.5-$d_1$, and appropriately $^1$H NMR showed a resonance at ($\delta =$ -13.49 for 2.5-$d_1$ and -13.52 for 2.5) (see Figure 2.18).

![Reaction Diagram](image)

**Figure 2.18:** $^2$H$^1$H NMR of Bu$_3$SnD in the reaction mixture of Pt(SnBu$_3$)$_2$(CNBu$_3$)$_2$(D)$_2$, 2.5-$d_2$, and Bu$_3$SnH.
These exchange experiments further support the proposed mechanism in equation 2.4, for reductive elimination of SnBu\textsubscript{3}H in the presence of H\textsubscript{2}/D\textsubscript{2} gas to facilitate the exchange to form HD gas. Based upon these experimental results the following mechanism (see Scheme 2.6) has been proposed for the catalytic formation of HD gas from H\textsubscript{2}-D\textsubscript{2} in the presence of compound 2.5.

Scheme 2.6. Proposed mechanism for the catalytic formation of HD gas from H\textsubscript{2}-D\textsubscript{2} in the presence of compound 2.5.

The catalysis begins with the formation of 2.5, followed by the reductive elimination of free Bu\textsubscript{3}SnH from 2.5, to form intermediate A with two vacant coordination sites. Step I is believed to be the rate determination step. Then H\textsubscript{2}/D\textsubscript{2} adds to the intermediate A in oxidative addition fashion to form another intermediate B. It is where H\textsubscript{2}-D\textsubscript{2} exchange happens to form HD gas and the intermediate A. The catalytic steps II and III keep on going until there reaches equilibrium between HD/H\textsubscript{2}/D\textsubscript{2}. Once equilibrium is attained the catalysis stops and the cycles proceeds to step IV where the
free $\text{Bu}_3\text{SnH}$ formed during step I, adds to intermediate $A$ in an oxidative addition fashion to form back the compound 2.5.

**Reaction of CO gas with reaction mixture of Pt(COD)$_2$ and $\text{Bu}_3\text{SnH}$:** The hydride ligands in the compound 2.5 are labile and can be eliminated under mild conditions. We were fortunate to isolate complex 2.5 in pure form and obtain its crystal structure. However, we were unable to isolate the analogous carbonyl complex $\text{Pt}($SnBu$^t_3$)$_2$(CO)$_2$(H)$_2$ when the reaction of one equivalent of Pt(COD)$_2$ with two equivalents of $\text{Bu}_3\text{SnH}$ was carried out at room under an atmosphere of carbon monoxide gas (in place of CNBu$^t$). Instead, new compound Pt(CO)$_2$(SnBu$^t_3$)$_2$, 2.12, was isolated from the reaction mixture. When CO gas is purged at room temperature through the brownish-red colored reaction mixture of two equivalents of $\text{Bu}_3\text{SnH}$ and one equivalent of Pt(COD)$_2$ in hexane solution, the color of the solution turned to green within 10 minutes. The IR spectra showed new peaks corresponding to the CO stretching. The reaction mixture was filtered through silica plug to yield a green colored 16 electron Pt(II) compound Pt(CO)$_2$(SnBu$^t_3$)$_2$, 2.12, in 91% yield which does not contain any hydride ligands. The structure of 2.12 is shown in Figure 2.18, (further crystallographic data can be found in Appendix Table A.4). As expected for platinum complexes in $d^8$ configuration the molecular geometry is square planar. The ligands are *trans* to each other and that the structure of 2.12 deviates considerably from planarity is due to the steric of the CNBu$^t$ ligands versus the CO ligands as seen in Figure 2.19. The Pt-Sn bond length is 2.7317 Å, slightly longer than that observed in compound 2.5. The Pt1-C1 bond length (1.894 Å) is in the same range as reported for similar Pt-carbonyl complexes.$^{68}$ The complex 2.12 is stable in solid state at room temperature for few hours,
but decomposes upon prolonged exposure to air. Compound 2.12 was characterized by the combination of $^1$H NMR, single crystal X-ray crystallography, and IR spectroscopy.

**Figure 2.19.** An ORTEP of the molecular structure of Pt(SnBu$_3$)$_2$(CO)$_2$, 2.12, showing 40% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows: Pt(1)–Sn(1) = 2.7317(4); Pt(1)–Sn(1*) = 2.7317(4); Pt(1)–C(1) = 1.847(1); Pt(1)–C(2) = 1.894(1); Sn(1)–Pt(1)–Sn(1*) = 176.08(2); C(1)–Pt(1)–C(2) = 180.0(6); Sn(1)–Pt(1)–C(1) = 88.0(5); Sn(1)–Pt(1)–C(2) = 92.0(4).

Compound 2.12 is electronically similar to compound Pt(SnBu$_3$)$_2$(CNBu)$_2$, 2.6, except the bulky isocyanides force geometrical distortion from square planarity as evidenced by the “X” shape in 2.12, and the steric in 2.6 force the molecule to adopt a see-saw type geometry. Compound 2.12 is also analogous to the hypothesized compound 2.2, and can be assumed that it is formed by the replacement of both the hydride ligands in Pt(SnBu$_3$)$_2$(H)$_2$, 2.2 by two CO ligands (Scheme 2.7). Adams et al. recently reported a similar Pt(II) carbonyl complex with GePh$_3$ ligands, Pt(CO)$_2$(GePh$_3$)$_2$, and Braunschweig group prepared an analogous Pt(0) carbonyl complex with phosphine ligands Pt(Cy$_3$P)$_2$(CO)$_2$.96
Scheme 2.7. Proposed pathway for the formation of Pt(SnBu$_3$)$_2$(CO)$_2$, 2.12.

The IR spectrum of 2.12 in hexane solution shows a single strong absorption peak corresponding to a $\nu_{CO}$ stretching frequency at 2007 cm$^{-1}$ in agreement with a trans-conformation. The CO ligands on Pt(SnBu$_3$)$_2$(CO)$_2$, 2.12 are found to be labile and they can be substituted with other ligands.

**Reaction of compound Pt(SnBu$_3$)$_2$(CO)$_2$, 2.12 with CNBu$^t$:** The carbonyl ligands in 2.12 can be replaced with CNBu$^t$ groups to give compound 2.6, however *en route* to 2.6, we obtained the complex Pt(SnBu$_3$)$_2$(CNBu$^t$)$_2$(CO), 2.13, in 96 % yield at room temperature. Addition of two equivalents of CNBu$^t$ to the green-colored solution of the Pt(SnBu$_3$)$_2$(CO)$_2$, 2.12, in hexane resulted in evolution of the CO gas from the reaction mixture and formed a colorless precipitate of the intermediate Pt(II)-monocarbonyl complex, Pt(SnBu$_3$)$_2$(CNBu$^t$)$_2$(CO), 2.13, The structure of 2.13 is shown in Figure 2.20, (further crystallographic data can be found in Appendix Table A.4). Compound 2.13 is
characterized by the combination of $^1$H NMR, and single crystal X-ray crystallography and, IR spectroscopy.

**Figure 2.20.** An ORTEP of the molecular structure of Pt(SnBu$_3$)$_2$(CNBu$'$)$_2$(CO), 2.13, showing 30% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows: Pt(1)–Sn(1) = 2.7147(6); Pt(1)-C(1) = 2.02(1); Pt(1)–C(12) = 1.89 (2); Sn(1)-Pt(1)-Sn(1*) = 170.66(3); C(1)-Pt(1)-C(12) = 128.2(6); Sn(1)-Pt(1)-C(1) =92.9(3); Sn(1)-Pt(1)-C(12)=85.3(5); C(1)-Pt(1)-C(1*) = 103.7(4).

The molecular geometry of complex 2.13 is trigonal bipyramidal, in which the two SnBu$_3$ groups occupy both of the axial positions, while the two CNBu$'$ and one CO ligand lie in the in the equatorial plane. The geometry around the Pt(II) metal center in 2.13 is slightly distorted from trigonal bipyramidal geometry due to steric effects induced by SnBu$_3$ ligands. The Pt-Sn and Pt-CO bond lengths remain almost the same as observed in precursor complex 2.12. The Pt-Sn bond length in complex 2.13 is 2.714 (8) Å,
slightly longer than Pt-Sn bond length in complex 2.5. The C1-Pt-C1\* bond angle in 2.13 is the same as in compound 2.5.

**Reversible activation of CO by compound 2.6:** Compound 2.13 is stable in the solid state for approximately 24 hours. In hexane solution, compound 2.13 rearranges to 2.6 over a period of 12 hours at room temperature even under argon atmosphere with the elimination of a CO ligand. Compound 2.6 in hexane solution activates the CO molecule at room temperature to afford Pt(CO)(SnBu\textit{t}_3)\textit{2}(CNBu\textit{t})\textit{2}, 2.13 in quantitative yield (see equation 2.6).

![Equation 2.6](image_url)

The addition of CO gas to compound 2.6 is reversible in the solid state as well; as observed in the addition of H\textsubscript{2}. The purple crystals of 2.6 turn colorless upon exposure to CO atmosphere in 15 minutes at room temperature to yield 2.13 quantitatively. Similarly, colorless crystals of 2.13 turn purple under argon flow after 24 hours, yielding quantitative amounts of 2.6. Interestingly, the CO ligand in 2.13 can also be exchanged with the hydride ligands. Addition of H\textsubscript{2} to compound 2.13 affords Pt(IV) isocyanide complex 2.5 at room temperature. A similar phenomenon of inter conversion between CO complex to (H)\textsubscript{2} complex was observed by M. J. Mays and co. in their iridium complex. The reversible activation of H\textsubscript{2} and CO molecules by the 16 electron Pt(II) isocyanide complex 2.6 are summarized in Scheme 2.8.
Scheme 2.8. Interconversion between compounds 2.6, 2.5 and 2.13.

2.3 Summary and conclusions.

Scheme 2.9 presents the summary of synthesis of various saturated and unsaturated Pt-Sn bimetallic complexes discussed in this chapter. This project has been started with the aim of synthesizing sterically crowded Pt-Sn unsaturated complexes to activate small molecules. Reaction of Pt(COD)2 with one equivalent Bu3SnH yielded highly reactive unsaturated compound 2.1. Efforts to synthesize compound 2.2 with two equivalents of Bu3SnH were unsuccessful. However the reaction of Pt(COD)2 with presence of excess Bu3SnH yielded the compound 2.3 believed to be formed from 2.2. When Pt(COD)2 was reacted with Bu3SnH in the presence of CNBu1, it formed dihydride Pt(IV) compound 2.5, which reversibly loses both the hydrides to furnish Pt(II) compound 2.6. Compound 2.6 activates hydrogen reversibly even at -78 °C and it also catalyzes H2-D2 exchange. Compounds 2.6 and 2.5 are inter-convertible even in the solid
state. The SnBu$_3$ group from 2.5 can be replaceable with Ph$_3$Sn to give Pt(IV) compound 2.8 and with Mes$_3$Sn to give compound 2.10. The proposed mechanism for the H$_2$-D$_2$ exchange involves the reductive elimination of a free Bu$_3$SnH to create vacant sites on the Pt metal center, which in turn are attacked by H$_2$/D$_2$ for the exchange to happen.

Compound 2.8 displays fluxional behavior in the solution, which was attributed to the cis-trans isomerization in the solution, and we were not able to isolate the trans isomer of compound 2.8. Compound 2.8 is highly strained and loses a Ph$_3$Sn ligand and the hydride to form stable Pt(II) compound 2.9. Compound 2.10 is stable towards exchanging the Bu$_3$Sn ligand to form compound 2.11, even in the presence of excess Mes$_3$SnH under refluxing conditions. However, compound 2.11 was directly synthesized from the reaction of Pt(COD)$_2$ with two equivalents of Mes$_3$SnH. The reaction of Pt(COD)$_2$ with Bu$_3$SnH in the presence of CO gas yielded Pt(II) compound 2.12. Compound 2.12 in the presence of CNBu$_3$ loses a CO ligand and forms compound 2.13. Compound 2.13 reversibly loses the CO ligand to from compound 2.6 both in solid state and solution state.
Scheme 2.9. Summary of reactions discussed in chapter 2.
2.4 Experimental section.

**General Data:** Unless indicated otherwise, all reactions were performed under an atmosphere of Argon. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Nicolet 380 FT-IR spectrophotometer. $^1$H NMR were recorded on a Bruker 300 and 400 spectrometer operating at 300.13 MHz and 399.99 MHz respectively. Elemental analyses were performed by Columbia Analytical Services (Tuscon, AZ). Mass spectrometric measurements performed by a direct–exposure probe using electron impact ionization (EI) were made on a VG 70S instrument at the University of South Carolina, Columbia, SC. Tertiary butylisocyanide, CNBu\textsubscript{t}, was purchased from Sigma-Aldrich and used without further purification. Triphenyltin hydride was purchased from Alfa Aesar and used without further purification. Bis(1,5-cyclooctadiene)platinum, Pt(COD)$_2$,\textsuperscript{t} tri-tert-butylstannane, Bu\textsubscript{t}$_3$SnH,\textsuperscript{t} Mes$_3$SnH\textsuperscript{t} were prepared according to the published procedures. Silica gel (60-200 µm, 70-230 mesh) used for chromatographic separations was purchased from Silicycle.

**Synthesis of Pt(SnBu\textsubscript{t}$_3$)(COD)(H), 2.1:** In a glove box, under an atmosphere of argon, 25mg of Bu\textsubscript{t}$_3$SnH (0.086 mmol) dissolved in 3mL of freshly distilled hexane was added to 30.0 mg of Pt(COD)$_2$ (0.073 mmol). The reaction mixture immediately turned dark brown. The reaction mixture stirred at room temperature for an additional 10 min and was filtered through kimwipe and the solvent was evaporated completely dry under argon gas flow. The yellowish-brown solid residue was redissolved in diethylether and placed in -20 °C freezer overnight which gave crystalline Pt(SnBu\textsubscript{t}$_3$)(COD)(H), 2.1, covered with black oily residue. After washing the crystalline product with isopropyl alcohol (3 x
0.3 mL), 13.2 mg (30 % yield) of 2.1 was obtained. Spectral data for 2.1: $^1$H NMR (C$_6$D$_6$, rt, in ppm): δ = 5.80 (m, $^2$J$_{Pt-H}$ = 51.4 Hz, $^3$J$_{Sn-H}$ = 5.0 Hz, 2H; CH- cod), 5.45 (m, $^2$J$_{Pt-H}$ = 44.7 Hz, $^3$J$_{Sn-H}$ = 6.5 Hz, 2H; CH- cod), 1.82-1.51 (broad m, 8H; CH$_2$-cod); 1.53 (s, $^3$J$_{Sn-H}$ = 52.5 Hz, 27H, SnBu$_t^3$); -3.74 (s, $^1$J$_{Pt-H}$ = 1223.2 Hz, $^2$J$_{Sn-H}$ = 48.2 Hz, 1H, hydride).

**Synthesis of [Pt(SnBu$_t^3$)(µ-SnBu$_t^2$)(H)]$_2$, 2.3:** In a glove box, under an atmosphere of argon, 583 mg of Bu$_t^3$SnH (2.000 mmol) dissolved in 1mL of freshly distilled toluene was added slowly drop wise to 103 mg of Pt(COD)$_2$ (0.250 mmol) over a period of 20 min at room temperature with continuous stirring. The solvent was allowed to evaporate in dry box overnight. The black oily residue was washed with dichloromethane solvent several times until the solution was colorless, yielding 34 mg of 7 (19 % yield). Yield is low because of unidentified side products. Spectral data for 2.3: $^1$H NMR (C$_7$D$_8$, rt, in ppm): δ = 1.58(s, 36 H, SnBu$_t^2$, $^2$J$_{Sn-H}$ = 64 Hz), 1.50 (s, 54H, SnBu$_t^3$, $^3$J$_{Sn-H}$ = 60 Hz), -3.71(s, 4H, hydride, $^1$J$_{Pt-H}$ = 905 Hz, $^2$J$_{Sn-H}$ = 32 Hz). Mass Spec. EI/MS m/z. 1383 (M$^+$-Bu$^t$), 1326(M$^+$-2Bu$^t$). The isotope pattern is consistent with the presence of two platinum and four tin atoms.

**Synthesis of [Pt(SnBu$_t^3$)(µ-SnBu$_t^2$)(CO)(H)]$_2$, 2.4:** In a 10 ml schlenk tube, under atmosphere of argon, 25 mg (0.017 mmol) of 2.3 dissolved in 3 ml of hexane/dichloromethane (1:1 mixture) was transferred. The reaction mixture was colorless and turbid. With the purging of CO gas through solution at room temperature for 10 min, solution color turned to dark yellow and solution became clear. The reaction mixture filtered through Kim wipe and crystallized in ice bath (0 °C) under CO gas stream to obtain 20 mg (78% yield) of yellow crystals of 2.4 (after washing 2 times with
small portions of hexane). ¹H NMR (C₇D₈, rt, in ppm): δ = 1.69 (s, 36 H, SnBu₄₂, ²Jₜₜ-H = 72 Hz), 1.45 (s, 54 H, SnBu₄₃, ³Jₜₜ-H = 61 Hz), -12.77 (s, 4H, hydride, ¹Jₚt-H = 702 Hz, ²Jₜₜ-H = 28 Hz). IR v CO (cm⁻¹ in hexane): 2163 (w), 2027 (vs), 2008 (m). Elemental Anal, calc.: C, 33.72; H, 6.33 % Found: C, 34.18; H, 5.92 %.

**Conversion of** [Pt(SnBu₄₃)(µ-SnBu₄₂)(CO)(H)]₂, **2.4 to** [Pt(SnBu₄₃)(µ-SnBu₄₂)(H)]₂, **2.3 in solution:** In a 10 mL schlenk tube, 10.0 mg of 2.4 (0.0067 mmol) was dissolved in 2 mL of hexane. The solvent was removed overnight in glove box during which time the color of the solution changed from yellow to colorless. This yielded 9.0 mg (94 % yield) of crystalline 2.3.

**Synthesis of** Pt(SnBu₄₃)(CNBu₄₁)₂, **2.5:** In a glove box, under an atmosphere of argon, 49.5 mg of Bu₄₃SnH (0.170 mmol) dissolved in 5 mL of freshly distilled hexane was added to 35.0 mg of Pt(COD)₂ (0.085 mmol). The reaction mixture was stirred at room temperature for 5 min after which time 14.0 mg of CNBu₁ (0.170 mmol) was added and the reaction mixture was stirred at room temperature for an additional 10 min. The solution was then filtered, and the filtrate was placed in a -20 °C freezer overnight which gave crystalline Pt(SnBu₄₃)(CNBu₄₁)₂, **2.5.** After washing the crystalline product with approx. 2 mL of acetonitrile, 26 mg (32 % yield) of 2.5 was obtained. Spectral data for 2.5: ¹H NMR (C₆D₆, rt, in ppm): δ = 1.57 (s, 54 H, SnBu₄₃, ³Jₜₜ-H = 51 Hz), 0.96 (s, 18H, Bu₄₁); -13.52 (s, 2H, hydride, ¹Jₚt-H = 697 Hz, ²Jₜₜ-H = 34 Hz). ¹¹⁹Sn NMR (C₆D₆, rt, in ppm): δ = 81.50 (s, 2 Sn, ¹Jₚt-Sn = 3604 Hz). IR (cm⁻¹ in Hexane): vCN 2139 (s), vPt-H 2112 (m). Mass Spec. El/MS m/z. 942 (M⁺), 883 (M⁺-H₂-Bu¹). Mass Spec. El/MS m/z. 942 (M⁺), 883 (M⁺-H₂-Bu¹). The isotope pattern is consistent with the presence of one platinum and two tin atoms.
Conversion of Pt(SnBu₃)₂(CNBu)₂(H)₂, 2.5 to Pt(SnBu₃)₂(CNBu)₂, 2.6 in solution:
A 15.0 mg amount of 2.5 (0.016 mmol) was dissolved in 50 mL of distilled hexane. With stirring, argon was then allowed to purge through the solution at 25 °C for approximately 20 h. Within minutes the colorless solution starts to turn violet. ¹H NMR of the reaction mixture showed complete conversion of the starting 2.5 to 2.6. The solvent was removed in vacuo, and the purple color residue was crystallized by evaporation of a benzene/acetonitrile solvent mixture under a stream of argon at room temperature to yield 13.2 mg (88 %) of crystalline 2.6. Spectral data for 2.6: ¹H NMR (C₆D₆, rt, in ppm): δ = 1.60 (s, 54 H, SnBu₃, 3JSn-H = 49 Hz), 1.15 (s, 18 H, Bu'). IR (cm⁻¹ in Hexane): νCN 2112(s). Mass Spec. EI/MS m/z. 940 (M⁺), 883 (M⁺-Bu'). The isotope pattern is consistent with the presence of one platinum and two tin atoms.

Conversion of Pt(SnBu₃)₂(CNBu)₂, 2.6 to Pt(SnBu₃)₂(CNBu)₂(H)₂, 2.5 in solution:
In a 10 mL schlenk tube, 28.0 mg of 2.6 (0.030 mmol) was dissolved in 5 mL of hexane. The solvent was removed under a slow stream of hydrogen gas (approx. 3 h) during which time the color of the solution changed from violet to colorless. This yielded 26.2 mg (93 % yield) of crystalline 2.5.

Conversion of Pt(SnBu₃)₂(CNBu)₂(H)₂, 2.5 to Pt(SnBu₃)₂(CNBu)₂, 2.6 in the solid state: In a 10 mL schlenk tube containing 10.0 mg of colorless crystalline 2.5 (0.011 mmol), argon gas was purged through the system for 24 h in the dark at room temperature, at which time the color of the crystalline 2.5 turned to violet. ¹H NMR indicated complete consumption of starting 2.5 in quantitative yield to Pt(SnBu₃)₂(CNBu)₂, 2.6.
Conversion of Pt(SnBu$_3$)$_2$(CNBu')$_2$, 2.6 to Pt(SnBu$_3$)$_2$(CNBu')$_2$(H)$_2$, 2.5 in the solid state: In a 10 mL schlenk tube containing 12.0 mg of violet crystalline 2.6 (0.013 mmol), hydrogen gas was purged through the system for 15 min in the dark at room temperature, at which time the color of the crystalline 2.6 turned to colorless. $^1$H NMR indicated complete consumption of starting 2.6 in quantitative yield to 2.5.

Synthesis of Pt(SnPh$_3$)$_3$(CNBu')$_2$(H), 2.8: A 20 mg (0.049mmol) amount of Pt(COD)$_2$ was transferred into 50 ml schlenk tube and the flask was evacuated and refilled with argon several times. To this, 10 mL of distilled hexane was added under argon at -78°C. While maintaining -78°C, a mixture of 51.2 mg of Ph$_3$SnH (0.146 mmol, 3 equ) and 8.08 mg of BuNC (0.097 mmol, 2equ) dissolved in 15 mL of distilled hexane solvent was added drop wise to Pt(COD)$_2$ solution under argon. The reaction mixture was stirred at -78°C for 10 min, after which slowly allowed to warm to the room temperature, during which time a white insoluble precipitate was observed. The reaction mixture was stirred at RT for an additional 1 hr. The solution was filtered through glass frit in glove box. The white colored residue was washed three times with 2 mL portions of distilled hexane. The residue was dissolved CH$_2$Cl$_2$/hexane mixture, filtered through Kim wipe and crystallized at -30°C in the glove box to obtain 60mg (86 % yield) of color less crystals. Spectral data for Pt(SnPh$_3$)$_3$(CNBu')$_2$(H), 2.8: Note: Compound exhibits fluxional behaviour in solution. $^1$H NMR (Toluene-$_d$$_8$, -20 °C, in ppm): δ = 7.8 – 6.9 (m, Ph), 0.83 (s, CNBu'), 0.51 (s, CNBu'), 0.44 (s, CNBu'), 0.44 (s, CNBu'), -6.63 (s, hydride, $^1$J$_{119}$Sn-H = 679 Hz, $^1$J$_{117}$Sn-H = 647Hz, $^1$J$_{Pt}$-H = 775 Hz, $^1$J$_{Pt}$-H = -11.91 (s, hydride, $^1$J$_{Pt}$-H = 665 Hz, $^2$J$_{119}$Sn-H = 26.68 Hz, $^2$J$_{117}$Sn-H = 13.95Hz)). IR v$_{CN}$ (cm$^{-1}$ in CH$_2$Cl$_2$): 2190(vs). Elemental Anal, calc.: C, 54.42; H, 4.57; N, 1.98 %. Found: C, 53.94; H, 4.88; N, 1.82 %.
Conversion of Pt(SnBu$_3$)$_2$(CNBu)$_2$, 2.6 to Pt(SnPh$_3$)$_3$(CNBu)$_2$(H), 2.8 in solution in glove box: In a 10 mL schlenk tube, 10 mg of 2.6 (0.011 mmol) was dissolved in 3 mL of freshly distilled hexane. To which 13.52 mg of Ph$_3$SnH (0.039 mmol, 3.5 equ) dissolved in 3 mL of hexane solvent was added drop wise over a period of 10 minutes while stirring the reaction mixture, during which time violet colored solution turned color less and a white colored precipitate was observed at the bottom of the schlenk tube. The precipitate was washed three times with 2 mL portions of distilled cold hexane. The residue was dissolved in mixture of CH$_2$Cl$_2$/hexane solvent, filtered through Kim wipe and crystallized at -30°C in the glove box to obtain 14 mg (90 % yield) of Pt(SnPh$_3$)$_3$(CNBu)$_2$(H), 2.8.

Synthesis of Pt(SnPh$_3$)$_2$(CNBu)$_2$, 2.9: A 20 mg (0.049 mmol) amount of Pt(COD)$_2$ was transferred into 50 mL schlenk tube and flask was evacuated and refilled with argon several times. To this, 10 mL of distilled hexane was added under argon at -78°C. While maintaining -78°C, a mixture of 34.12 mg of Ph$_3$SnH (0.097 mmol, 2 equ) and 8.08 mg of Bu'NC (0.097 mmol, 2 equ) dissolved in 15 mL of distilled hexane solvent was added drop wise to Pt(COD)$_2$ solution under argon while maintaining the reaction mixture at -78°C. The reaction mixture was stirred at -78°C for 10 min, after which was slowly allowed to warm to the room temperature, during which time solution color changed to cloudy yellow. The reaction mixture was stirred at RT for an additional 12 hrs. The solvent was removed in vacuo, and the residue was dissolved in CH$_2$Cl$_2$/Hexane solvent mixture, filtered through Kim wipe and crystallized at -30°C in the glove box to obtain 44 mg (84 % yield) of yellow colored crystals. Spectral data for [Pt(SnPh$_3$)$_2$(CNBu)$_2$], 2.9: $^1$H NMR (CD$_2$Cl$_2$, rt, in ppm): δ = 0.883 (s, 18 H, 2 CNBu'), δ = 7.22-7.7 (m, 30 H,
2 Ph3Sn). IR νCN (cm$^{-1}$ in CH2Cl2): 2165 (vs). Elemental Anal, calc.: C, 52.05; H, 4.56; N, 2.64 %. Found: C, 52.10; H, 4.74; N, 2.61 %.

**Conversion of Pt(SnPh3)$_2$(CNBu')$_2$, 2.9 to Pt(SnPh3)$_3$(CNBu')$_2$(H), 2.8 to in solution:** In glove box, 20 mg of Pt(SnPh3)$_2$(CNBu')$_2$, 2.9 (0.019 mmol) was transferred in to a 10 mL schlenk tube containing 3 mL of hexane. To which, Ph3SnH (7 mg, 0.02 mmol) dissolved in minimum amount of hexane solvent was added drop wise while stirring the contents. The solution became color less over a period of 5 minutes and a white insoluble precipitate of compound 2.8 was obtained at the bottom of the schlenk tube. The precipitate was washed three times with 2 mL portions of cold hexane. The residue was dissolved in a mixture of CH2Cl2/hexane solvent, filtered through Kim wipe and crystallized at -30°C in the glove box to obtain 18 mg (90 % yield) of Pt(SnPh3)$_3$(CNBu')$_2$(H), 2.8.

**Conversion of Pt(SnPh3)$_3$(CNBu')$_2$(H), 2.8 to Pt(SnPh3)$_2$(CNBu')$_2$(CNBu')$_2$, 2.9 in solution:** In a 10 mL vial, 20 mg of Pt(SnPh3)$_3$(CNBu')$_2$(H), 2.8 (0.014 mmol) was dissolved in 3 mL of CH2Cl2/octane solvent mixture and crystallized at RT while exposing it to the air to obtain 9 mg (60 % yield) of the yellow crystals of Pt(SnPh3)$_2$(CNBu')$_2$, 2.9.

**Synthesis of Pt(SnMes3)(SnBu')$_3$(CNBu')$_2$, 2.10:** In a 50 mL schlenk flask, 80 mg of Pt(SnBu')$_3$(CNBu')$_2$, 2.6 (0.085 mmol) was dissolved in 20 mL of distilled hexane. To which, 40.6 mg of Mes3SnH (0.085 mmol) dissolved in 10 mL of distilled hexane solvent was added drop wise over a period of 10 minutes while stirring the reaction mixture. Then, the reaction mixture was stirred for another 1 hr at RT under a slow stream of H2 gas purge through the solution to give an orange colored solution. After which H2 gas flow was stopped, and the reaction flask was sealed under H2 gas and stirred for an
additional 12 hrs at RT. After which the solvent was removed in vacuo, to give an orange colored residue. The residue was washed three times with 2 mL portions of cold pentane. Then the residue was re dissolved in a mixture of CH₂Cl₂/ hexane solvent, filtered through Kim wipe and crystallized at -30°C in the glove box to obtain 53 mg (55% yield). Spectral data for Pt(SnMes₃)(SnBu₃)(CNBu'), 2.10: ¹H NMR (C₆D₆, rt, in ppm): δ = 0.80 (s, 18 H, 2 CNBu'), δ = 1.61 (s, 27H, Bu¹'Sn), δ = 2.16 (s, 9H, 3-pCH₃, Mes₃Sn), δ = 2.60 (s, 18H, 6-oCH₃, Mes₃Sn), δ = 6.78 (s, 6CH, Mes₃Sn). IR νCN (cm⁻¹ in CH₂Cl₂): 2138(vs). Mass spectroscopy: EI/MS m/z. 1071 (M⁺-Bu'), 837 (M⁺. Bu¹'Sn).

**Synthesis of Pt(SnMes₃)₂(CNBu')₂, 2.11:** A 20 mg (0.049mmol) amount of Pt(COD)₂ was transferred into 50 mL schlenk tube and the flask was evacuated and refilled with argon several times. To this, 10 mL of distilled hexane was added under argon at -78°C. To this, a mixture of 46.4 mg of Mes₃SnH (0.097 mmol, 2equ) and 8.08 mg of Bu¹NC (0.097 mmol, 2equ) dissolved in 15 mL of distilled hexane solvent was added drop wise under argon while maintaining the reaction mixture at -78°C. The reaction mixture was stirred at -78°C for an additional 10 min, after which was slowly allowed to warm to the room temperature, during which time solution color changed to orange. Reaction mixture was stirred at RT for 1 hr. The solvent was removed in vacuo, and the residue was dissolved in CH₂Cl₂ and plated on a TLC silica gel in hexane solvent and the top yellow colored product band was collected and crystallized in hexane solvent at -30°C to obtain 52 mg (80% yield) of crystalline yellow colored product. Spectral data for Pt(SnMes₃)₂(CNBu')₂, 2.11: ¹H NMR (C₆D₆, rt, in ppm): δ = 0.53 (s, 18 H, 2 CNBu'), δ = 2.17 (s, 18H, 6-pCH₃, 2Mes₃Sn), δ = 2.67 (s, 36H, 12-oCH₃, 2Mes₃Sn), δ = 6.82 (s, 12CH, 2Mes₃Sn). IR νCN (cm⁻¹ in CH₂Cl₂): 2154(vs). Mass spectroscopy ES⁺/MS
calculated for [M⁺] = 1313; found 1313. The isotope distribution is consistent with the presence of one Pt atom.

**Synthesis of Pt(SnBu₃)₂(CO)₂, 2.12:** A 53 mg (0.129 mmol) amount of Pt(COD)₂ was transferred into 10 ml schlenk tube and the flask was evacuated and refilled with argon several times. A 80 mg of Bu₃SnH (0.274 mmol) dissolved in 8 mL of distilled hexane solvent was added to Pt(COD)₂ under argon. The brown color reaction mixture was stirred at room temperature for 5 min after which time CO gas was bubbled through the solution for additional 30 min. The solution was filtered through silica plug to give a green color solution. The solvent was removed in vacuo to obtain 98 mg (91 % yield) of green solid. Spectral data for 2.12: ¹H NMR (CDCl₃, rt, in ppm): δ = 1.38 (s, 54 H, SnBu₃, 3Jₘₖ-Sn-H = 59 Hz. ¹H NMR (C₆D₆, rt, in ppm): δ = 1.44 (s, 54 H, SnBu₃, 3Jₘₖ-Sn-H = 59 Hz IR ν₃CO (cm⁻¹ in hexane): 2007(vs). Elemental Anal, calc.: C, 37.57; H, 6.55 % Found: C, 37.77; H, 6.42 %.

**Synthesis of Pt(SnBu₃)₂(CNBu')₂(CO), 2.13:** In a glove box, under an atmosphere of argon, a 40.0 mg (0.480 mmol) amount of CNBu' was added to 195 mg of Pt(SnBu₃)₂(CO)₂, 2.12 (0.235 mmol) dissolved in 2 mL of freshly distilled hexane at room temperature. With the addition of CNBu' the CO gas evolves from the reaction mixture (gas bubbles can be seen), and the green color solution slowly turns into colorless solution, and the colorless crystals crashes out of the solution. The solution is then placed in -20 °C freezer overnight to obtain more crystals. The solvent is removed and colorless crystals were washed with 0.2 ml of hexane to afford 219 mg (96 % yield). The crystals turn to violet color on prolonged exposure to air. Spectral data for 2.13: ¹H NMR (C₆D₆, rt, in ppm): δ = 1.57 (s, 54 H, SnBu₃, 3Jₘₖ-Sn-H = 51 Hz), 0.96 (s, 18H, Bu').
Note: NMR spectra recorded under a CO atmosphere. IR $\nu_{\text{CO}}$ (cm$^{-1}$ in hexane): 2144(w), 2112 (vs), 1966 (s).

**Conversion of Pt(SnBu$_3^\prime$)$_2$(CNBu)$_2$(CO), 2.13 to Pt(SnBu$_3^\prime$)$_2$(CNBu)$_2$, 2.6 in solution:** A 17.0 mg amount of 2.13 (0.0175 mmol) was dissolved in 10 mL of distilled hexane. With stirring, argon gas was then allowed to purge through the solution at 25 °C for approximately 10 min. Within minutes the colorless solution starts to turn violet. IR of the reaction mixture showed complete conversion of the starting 2.13 to 2.6. The solvent was removed *in vacuo*, and the purple color residue was crystallized by evaporation of a benzene/acetonitrile solvent mixture under a stream of argon gas at room temperature to yield 15.0 mg (91 %) of crystalline 2.6.

**Conversion of Pt(SnBu$_3^\prime$)$_2$(CNBu)$_2$, 2.6 to Pt(SnBu$_3^\prime$)$_2$(CNBu)$_2$(CO), 2.13 in solution:** A 17.0 mg amount of 2.6 (0.0181 mmol) was dissolved in 25 mL of distilled hexane. With stirring, CO gas was then allowed to purge through the solution at 25 °C for approximately 10 min. Within minutes the purple solution starts to turn colorless. IR of the reaction mixture showed complete conversion of the starting 2.6 to 2.13. The solvent was removed *in vacuo*, and the purple color residue was crystallized by evaporation of a benzene/acetonitrile solvent mixture under a stream of CO gas at room temperature to yield 15.0 mg (85 %) of crystalline 2.13.

**Conversion of Pt(SnBu$_3^\prime$)$_2$(CNBu)$_2$, 2.6 to Pt(SnBu$_3^\prime$)$_2$(CNBu)$_2$(CO), 2.13 in the solid state:** In a 10 mL schlenk tube containing 10.0 mg of purple crystalline 2.6, CO gas was purged through the system for 1 hr in the dark at room temperature, at which time the color of the crystalline 2.13 turned to colorless. $^1$H NMR indicated complete consumption of starting 2.6 in quantitative yield to Pt(SnBu$_3^\prime$)$_2$(CNBu)$_2$(CO), 2.13.
Conversion of Pt(SnBu$_3^\text{t}$)$_2$(CNBu$_\text{t}$)$_2$(CO), 2.13 to Pt(SnBu$_3^\text{t}$)$_2$(CNBu$_\text{t}$)$_2$, 2.6 in solid state: In a 10 mL schlenk tube containing 10.0 mg of colorless crystalline 2.13, argon gas was purged through the system for 16 hr in the dark at room temperature, at which time the color of the crystalline 2.13 turned to violet. $^1$H NMR indicated complete consumption of starting 2.13 in quantitative yield to Pt(SnBu$_3^\text{t}$)$_2$(CNBu$_\text{t}$)$_2$, 2.6.

2.5 Crystallographic analysis.

Colorless crystals of Pt(SnBu$_3^\text{t}$)(COD)(H), 2.1 suitable for diffraction analysis were grown by slow evaporation of a solution of 2.1 in hexane solvent under a slow stream of argon gas at 0 °C (ice-water bath). Colorless crystals of [Pt(SnBu$_3^\text{t}$) (µ-SnBu$_2^\text{t}$)(H)$_2$]$_2$, 2.3 suitable for diffraction analysis were grown by slow evaporation of a solution of 2.3 in hexane solvent under a slow stream of argon gas at 0 °C (ice-water bath). Light yellow color crystals of [Pt(SnBu$_3^\text{t}$)(µ-SnBu$_2^\text{t}$)(CO)(H)$_2$]$_2$, 2.4 suitable for diffraction analysis were grown by slow evaporation of a solution of 2.4 in dichloromethane/hexane solvent mixture under a slow stream of CO gas at room temperature.

Colorless crystals of Pt(SnBu$_3^\text{t}$)$_2$(CNBu$_\text{t}$)$_2$(H)$_2$, 2.5 suitable for diffraction analysis were grown by slow evaporation of a solution of Pt(SnBu$_3^\text{t}$)$_2$(CNBu$_\text{t}$)$_2$, 2.6 in diethyl ether solvent under a slow stream of hydrogen gas at 0 °C (ice-water bath). Violet colored crystals of Pt(SnBu$_3^\text{t}$)$_2$(CNBu$_\text{t}$)$_2$, 2.6 suitable for diffraction analysis were grown by slow evaporation of solvent from a hexane solution at −20 °C in a glove box.

Colorless colored crystals of Pt(Ph$_3$)(CNBu$_\text{t}$)$_2$(H)$_2$, 2.8, suitable for diffraction analysis were grown by slow evaporation of a solution of 2.8 in a mixture of CH$_2$Cl$_2$/
hexane solvent at -30 °C in glove box. Yellow colored crystals of Pt(Ph₃Sn)₂(CNBuᵗ)₂, 2.9, suitable for diffraction analysis were grown by slow evaporation of a solution of 2.9 in a mixture of CH₂Cl₂/ hexane solvent at -30 °C in glove box.

Orange colored crystals of Pt(Mes₃Sn)(Bu³Sn)(CNBuᵗ)₂, 2.10, suitable for diffraction analysis were grown by slow evaporation of a solution of 2.10 in a mixture of CH₂Cl₂/ hexane solvent at -30 °C in glove box. Yellow colored crystals of Pt(Mes₃Sn)₂(CNBuᵗ)₂, 2.11, suitable for diffraction analysis were grown by slow evaporation of a solution of 2.11 in hexane solvent at -30 °C in glove box.

Green colored crystals of Pt(SnBuᵗ₃)(CO)₂, 2.12 suitable for diffraction analysis were grown by slow evaporation of solvent from a hexane solution in -80 °C freezer. Colorless crystals of Pt(SnBuᵗ₃)₂(CNBuᵗ)₂(CO), 2.13 suitable for diffraction analysis were grown by slow evaporation of solvent from a hexane solution at -20 °C in a glove box.

The data crystal for Pt(SnBuᵗ₃)(COD)(H), 2.1, [Pt(SnBuᵗ₃)(µ-SnBuᵗ₂)(CO)(H)₂]₂, 2.4, Pt(SnBuᵗ₃)₂(CNBuᵗ)₂(H)₂, 2.5 and Pt(SnBuᵗ₃)₂(CNBuᵗ)₂, 2.6 was mounted onto the end of a thin glass fiber using Paratone-N.

The data crystal for [Pt(SnBuᵗ₃)(µ-SnBuᵗ₂)(H)₂]₂, 2.3, Pt(SnPh₃)₂(CNBuᵗ)₂(H), 2.8, Pt(SnPh₃)₂(CNBuᵗ)₂, 2.9 Pt(Mes₃Sn)(Bu³Sn)(CNBuᵗ), 2.10, Pt(Mes₃Sn)₂(CNBuᵗ)₂, 2.11, Pt(SnBuᵗ₃)₂(CO)₂, 2.12 and Pt(SnBuᵗ₃)₂(CNBuᵗ)₂(CO), 2.13, was glued onto the end of a thin glass fiber. X-ray intensity data were measured by using a Bruker SMART APEX2 CCD-based diffractometer using Mo Kα radiation (λ = 0.71073 Å). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm. Corrections for Lorentz and polarization effects were also applied with
SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS. Both structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares on $F^2$, by using the SHELXTL software package.\textsuperscript{100,101}

Crystal data, data collection parameters, and results of the analyses are listed in Appendix A Tables A.1-A.4 in the supporting information.

Compound Pt(COD)(SnBu\textsubscript{3})(H), \textbf{2.1} crystallized in the monoclinic crystal system. The systematic absences in the intensity data identified the unique space group $P2_1/n$. The hydride ligand was located from the difference map but refined on its positional parameters with a fixed isotropic thermal parameter.

Compound [Pt(SnBu\textsubscript{3})(\mu-SnBu\textsubscript{2})(H)\textsubscript{2}]\textsubscript{2}, \textbf{2.3} crystallized in the monoclinic crystal system. The systematic absences in the intensity data identified the unique space group $P2_1/n$. With $Z = 4$, there is half a formula equivalent of the molecule present in the asymmetric unit that has crystallographic center of inversion symmetry.

Compound [Pt(SnBu\textsubscript{3})(\mu-SnBu\textsubscript{2})(CO)(H)\textsubscript{2}]\textsubscript{2}, \textbf{2.4} crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful refinement and solution of the structure. The CO-Pt-Pt-CO core in the molecule is disordered over two orientations which were refined with fixed site-occupancy factors in the ratio 50/50. The two orientations are mirror images of each other and the CO-Pt-Pt-CO core as seen in Figure 1 are offset by an angle of $12.07^\circ$. Atoms Pt1 and Pt1* lie above and below the Sn1-Sn2-Sn1*-Sn2* plane at a distance of 0.4411(4) \textgreek{Å}, while atoms Pt2 and Pt2* lie above and below the Sn1-Sn2-Sn1*-Sn2* plane at a distance of 1.0020(4) \textgreek{Å}. The carbon atoms of the two Bu\textsubscript{i} groups attached to atom Sn2 are also...
disordered. The disorder components in the Bu\textsuperscript{1} groups were located from the difference map and refined with fixed site-occupancy factors in the ratio 50/50. The hydride ligand was not located and included in the refinement. There is still minor disorder present in the structure which was not accounted for due to satisfactory low R values (R1 = 3.91\%) during the final stages of the refinement cycles.

![Image](image.jpg)

**Figure 2.21.** An ORTEP of the disordered CO-Pt-Pt-CO core in 2.4.

Compound Pt(SnBu\textsuperscript{1})\textsubscript{2}(CNBu\textsuperscript{1})\textsubscript{2}(H)\textsubscript{2}, 2.5 crystallized in the orthorhombic crystal system. The systematic absences in the intensity data were consistent with either of the space groups $Pmn2_1$ or $Pmmn$. The centrosymmetric space group $Pmmn$ was assumed and confirmed by the successful solution and refinement of the structure. With $Z = 2$ there is half a formula equivalent of the molecule in the asymmetric crystal unit about a site of $mm2$ symmetry. Half a molecule of diethyl ether from the crystallization solvent,
co-crystallized with the complex on a crystallographic $mm2$ symmetry cite. The hydride ligand was located and refined with an isotropic thermal parameter. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements.

Compound $\text{Pt(SnBu}^3\text{)}_2(\text{CNBu}^\text{t})_2$, 2.6 crystallized in the monoclinic crystal system. The space group $P2_1/n$ was confirmed on the basis of the systematic absences in the data. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements.

Compound $\text{Pt(SnPh}^3\text{)}_2(\text{CNBu}^\text{t})_2(\text{H})$, 2.8 crystallized in the orthorhombic crystal system. The space group $P2_12_12_1$ was confirmed on the basis of the systematic absences in the data for compound 12. The hydride ligand was located and refined with geometric restraints.

Compound $\text{Pt(SnPh}^3\text{)}_2(\text{CNBu}^\text{t})_2$, 2.9 crystallized in the Triclinic crystal system. The space group $P \bar{1}$ was assumed and confirmed by the successful refinement and solution of the structure. The molecule is crystallographically centrosymmetric. Two C atoms (C37 and C38) of one the phenyl rings are disordered. The disorder was modelled and refined in a 50:50 ratio.

Compound $\text{Pt(SnMes}^3\text{)(SnBu}^3\text{)}(\text{CNBu}^\text{t})_2$, 2.10 crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the space groups $P2_1/n$. 
Compound Pt(SnMes$_3$)$_2$(CNBu$_t^t$)$_2$, 2.11 crystallized in the trigonal crystal system. The systematic absences in the intensity data were consistent with either of the space groups $P3c1$ or $P\overline{3}c1$. The latter space group was chosen and confirmed by the successful refinement and solution of the structure. Only half a molecule of the complex is present in the asymmetric crystal unit which lies about a 2-fold rotation site.

Compound Pt(SnBu$_t^t$)$_2$(CO)$_2$, 2.12 crystallized in the monoclinic crystal system. The systematic absences in the intensity data identified the unique space group $C2/c$. With $Z = 4$, there is half a formula equivalent of the molecule present in the asymmetric unit that has crystallographic center of inversion symmetry.

Compounds Pt(SnBu$_t^t$)$_2$(CNBu$_t^t$)(CO), 2.13 crystallized in the orthorhombic crystal system. The systematic absences in the intensity data were consistent with either of the space groups $Pmn2_1$ or $Pmmm$. The centrosymmetric space group $Pmmm$ was assumed and confirmed by the successful solution and refinement of the structure. With $Z = 2$ there is half a formula equivalent of the molecule in the asymmetric crystal unit about a site of $mm2$ symmetry.

3.1 Background.

Carbene is a molecule with two unshared valence electrons and N-Heterocyclic carbene (NHC) is a cyclic carbene with at least one α-amino substituent as shown in the Figure 3.1.

![Structures of some of the highly encountered N-Heterocyclic Carbene subclasses. The Suffix “ylidene” should be added to obtain the generic name of each NHC subclass.](image)

**Figure 3.1.** Structures of some of the highly encountered N-Heterocyclic Carbene subclasses. The Suffix “ylidene” should be added to obtain the generic name of each NHC subclass.\(^{102}\)

Though Öfele\(^{103}\) and Wanzlick\(^{104}\) first reported the TM-NHC (TM = transition metal) complexes in 1968, followed by significant contributions from Lappert,\(^{105}\) the chemistry of TM-NHC exploded only after the synthesis of first stable “bottle-able” carbene by Arduengo et al.,\(^{106}\) in 1991. Since then a wide variety of TM-NHC complexes have been reported and studied as catalysts.\(^{107-109}\) The Hermann group extensively researched on use of NHC ligands for synthesis of low coordinate transitional metal
complexes and also as potential substitute for electron rich organophosphanes. The ever increasing applications of these NHCs as supporting ligands in catalysis is attributed to the strong $\sigma$-electron-donating properties, which helps form a strong NHC-metal bond, where a carbon atom with unshared electrons bonds to the metal atom, and thus prevents the decomposition of the metal complex - an essential property of a successful catalyst. As it can be seen in the Figure 3.1, NHCs are also flexible to varying bulkiness on the heteroatom (N) by modifying the ‘R’ group substituents. This is an added advantage for synthesizing highly unsaturated and reactive TM-NHC complexes.

These TM-NHC complexes have been successfully studied in catalytic activation of C-H bond and in formation of C-H, C-C, C-N, and C-O bonds. Palladium complexes of NHC ligand have been extensively studied in catalysis. In fact, the initial reports of catalytically active TM-NHC complexes involved Pd metal, in Heck coupling of aryl bromides and aryl halides, followed by Suzuki and Sonogashira coupling reactions. Grubbs, Nolan extensively studied the field of olefin metathesis using NHC substituted metal complexes, and Organ also made significant contributions in cross coupling reactions using these Pd-NHC complexes. Later TM-NHC chemistry had been extended to other metals as well.

The past decade has seen extensive research in the field of organic syntheses using these TM-NHC complexes. More recently focus is laid on the activation of small molecules using electronically unsaturated TM-NHC complexes (TM = Ir, Rh, Pd, Ni) which is also our field of interest. Nolan group activated H$_2$ using the complex Pd(IPr)(PCy3), a 14 electron mononuclear Pd-NHC complex and Hazari group activated the CO$_2$ using Ni-NHC complex. The NHC complexes of Co, Rh, Ir, Pd, and
Au are all well studied, and their catalytic activity is known to be superior to corresponding phosphine complexes.\textsuperscript{11,102,130–132} The Co-NHC complex reported by Llewellyn and coworkers not only activates both CO and H\textsubscript{2} it also gave promising results in the hydroformylation of 1-octene as shown in the Scheme 3.1.\textsuperscript{133}

\begin{center}
\textbf{Scheme 3.1}. Activation of CO and H\textsubscript{2} by Co-NHC complex, [Co(IMes)(CO)\textsubscript{3}(Me)], A and hydroformylation of 1-octene by hydrido Co-NHC complex ‘C’.
\end{center}
A significant number of Pt-NHC complexes were synthesized and studied catalytically. Much emphasis was laid on mono nuclear Pt-NHC complexes which were shown as outstanding in the catalytic hydrosilylation of olefins with high selectivity and efficiency,\(^\text{134}\) and also in reductive cyclization of diynes.\(^\text{135}\)

Though mononuclear Pt-NHC complexes are studied well, much less work was done on Pt-NHC complexes coupled to a hetero metal, particularly group 14 metals. Only two Pt-Sn-NHC complexes with established crystal structure were reported in the literature.\(^\text{135,136}\) It is worth to examining the effect of NHC ligands on the reactivity of Pt-Sn complexes in homogeneous catalysis. The bimetallic synergetic effect in Pt-Sn-NHC complexes has to be explored further to identify efficient homogeneous catalysts for hydroformylation and small molecule activation. The synthesis of bimetallic NHC carbene complexes will sure aid us in understanding the role of electronic and steric effects exerted by an additional metal on the Pt-NHC complexes.

In the previous chapter a series of sterically crowded unsaturated Pt-Sn bimetallic complexes in the activation of small molecules have been discussed. The driving force there is the unsaturation created by the bulky tert-butyl groups. As the literature suggests, these NHCs not only make a stable bond with the metals, but also aid in the synthesis of highly reactive unsaturated complexes which can be engineered to exclusively activate small molecules. This prompted us to synthesize Pt-Sn-NHC complexes to activate a variety of small molecules. In this chapter, a bulky two-electron donating N,N’-di-tert-butylimidazol-2-ylidene (IBu\(^t\) carbene) ligand has been used to study the effect of NHC on the reactivity of Pt-Sn complexes for potential catalytic application in the fields of small molecule activation, hydro-formylation and hydrogenation catalysis.
3.2. Results and discussion.

**Reaction of compound (H)Pt(COD)(SnBu$_t^3$)$_2$, 2.1 with IBu$^t$ carbene:** In the previous chapter, synthesis of highly reactive unsaturated compound (H)Pt(COD)(SnBu$_t^3$)$_2$, 2.1 was discussed, which was shown to react readily by losing the four electron donating COD ligand. When a toluene solution of bulky NHC carbene ligand, N, N’-di-tert-butylimidazol-2-ylidene (IBu$^t$) was added at room temperature in a drybox to a hexane solution of Pt(COD)(SnBu$_t^3$)(H)$_2$, a red solid precipitate was observed at the bottom of the reaction flask. Precipitate was separated and washed with cold hexane to give Pt-Sn carbene complex, [Pt(SnBu$_t^3$)(IBu$^t$)(H)]$_2$, 3.1, in 75% yield. This compound can also be prepared directly by reacting Pt(COD)$_2$, Bu$_t^3$SnH and IBu$^t$ at room temperature. However, clean product and higher yield can be achieved when the reaction was performed at -78 °C. The possible pathway for the formation of compound 3.1 is shown in Scheme 3.2. The aim here was to synthesize the 14 electron Pt(II)-NHC complex Pt(SnBu$_t^3$)(IBu$^t$)(H), 3.2, by replacing the COD ligand in compound 2.1 with IBu$^t$ carbene. But we were unable to isolate compound 3.2, instead we ended up making dinuclear Pt complex 3.1, which we believe is formed by the dimerization of complex 3.2 which is highly unsaturated and highly reactive. This work has been done in collaboration with Prof. Carl. D. Hoff at the University of Miami.
Scheme 3.2. Proposed pathway for the formation of compound 3.1.

The complex [Pt(SnBu\textsubscript{3})(IBu\textsuperscript{i})(H)]\textsubscript{2}, 3.1, is stable in air in the solid state, but decomposes slowly in solution state at room temperature on prolonged exposure to air. The molecular structure of 3.1 is shown in Figure 3.2 (further crystallographic data is provide in Appendix Table B.2). Compound 3.1 has two terminal SnBu\textsubscript{3} groups and two IBu\textsuperscript{i} groups positioned \textit{trans} to each other. The Pt-Pt metal bond is bridged by two hydride ligands which are equivalent. Presence of both the hydride ligands was confirmed by \textsuperscript{1}H NMR where they show up at -5.61 ppm (in THF-\textit{d}\textsubscript{8}) with appropriate one and two bond couplings to Pt (\textsuperscript{1}J\textsubscript{Pt-H} = 652 Hz, \textsuperscript{2}J\textsubscript{Pt-H} = 205 Hz), and two-bond coupling to Sn (\textsuperscript{2}J\textsubscript{Sn-H} = 55.0 Hz) (see Figure 3.5).
Figure 3.2. The molecular structure of [Pt(SnBu\textsubscript{3})(IBu\textsuperscript{t})(H)]\textsubscript{2}, 3.1. Showing 30% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows: Pt(1)-Pt(1)\textsuperscript{*} = 2.6715(1), Pt(1)-H(1) \textsuperscript{*} =1.75(3), Pt(1)-H(1)\textsuperscript{*} = 1.87(3), Pt(1)-Sn(1)=2.5933(2), Pt(1)-C(1) = 2.021(2). C(1)-Pt(1)-Sn(1)=97.61(6), C(1)-Pt(1)-H(1)\textsuperscript{*} = 96.5(8), C(1)-Pt(1)-H(1)\textsuperscript{*} = 95(1), H(1)-Pt(1)-H(1)\textsuperscript{*} = 85(1).

As is evident from the structure, the Pt1 –H1 and Pt1\textsuperscript{*} - H1 bond lengths are not same (same applies to H1\textsuperscript{*}) and one would expect two different sets of one bond coupled Pt satellites for the resonance at -5.61 ppm. But that was not the case as we see only one set of one bond coupled Pt satellites, indicating some sort of fluxional process between these two bonds, which also explains why the satellites are a bit broader. The Pt-Pt bond length in compound 3.1 is 2.6715 Å and is consistent with Pt-Pt single bond reported by Stone and co., for a similar complex [Pt(\textmu-H)(SiR\textsubscript{3})PR\textsubscript{3}]\textsubscript{2}, with a Pt-Pt bond distance of 2.692 Å.\textsuperscript{137}
Compound 3.1 is an unsaturated 28 electron dinuclear Pt complex. We performed Fenske-Hall molecular orbital calculations on compound 3.1 to obtain a clear picture of its unsaturation. These molecular orbital calculations revealed the presence of a low lying unoccupied molecular orbital, LUMO, which could accommodate two valence bonding electrons to bring the electron count to 30, making the cluster saturated. The contours of the LUMO orbital, shown in Figure 3.3, are predominantly concentrated on the platinum atoms. Based on these observations, we believe that the addition or activation of small molecules will occur at the Pt metal center. Experimental results also suggested the same, where the compound 3.1 reacts with small molecules by breaking the cluster into two monomers to accommodate the incoming molecule, indicating the high reactivity of the Pt-Pt metal bond.

![Figure 3.3. The LUMO orbital for [Pt(SnBu\textsubscript{3})(IBu\textsuperscript{t})(H)]\textsubscript{2}, 3.1.](image)

**Reaction of complex** [Pt(SnBu\textsubscript{3})(IBu\textsuperscript{t})(H)]\textsubscript{2} 3.1, with CO: When compound 3.1 was exposed to CO atmosphere at room temperature, the orange-red colored solution of 3.1 in toluene solvent turned to light yellow instantaneously to yield mono nuclear Pt-NHC compound Pt(SnBu\textsubscript{3})(IBut\textsubscript{2})(CO)(H), 3.3, in a quantitative yield (90%) as shown in
equation 3.1. The molecular structure of 3.3 is shown in Figure 3.4 (further crystallographic data is provided in the Appendix Table B.2). It is evident from the structure that the Pt-Pt bond in the starting dinuclear complex breaks with the addition of CO to afford the mononuclear Pt(II)-carbonyl compound Pt(SnBu$_3$)(IBut$_2$)(CO)(H), 3.3, as shown in equation 3.1.

![Equation 3.1]

**Figure 3.4.** The molecular structure of Pt(SnBu$_3$)(IBut$_2$)(CO)(H), 3.3. Showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows: Sn(1)-Pt(1)=2.6112(3), H(1)-Pt(1)=1.37(6), C(1)-Pt(1)=1.885(5), C(2)-Pt(1)=2.091(4), Sn(1)-Pt(1)-C(2)=160.0(1), Sn(1)-Pt(1)-H(1)=78(3), Sn(1)-Pt(1)-C(1)=94.8(2), C(1)-Pt(1)-H(1)=170(3), C(1)-Pt(1)-C(2)=105.1(2).
Compound 3.3 is characterized by the combination of $^1$H NMR spectroscopy, single crystal X-ray diffraction technique, and IR spectroscopy. Compound 3.3 is a 16 electron mononuclear Pt (II) complex with the CO and hydride ligands positioned $trans$ to each other. The position of the hydride ligand was determined and refined crystallographically, and its presence was further confirmed by $^1$H NMR where its resonance shows up at -2.48 ppm with appropriate one bond coupling to Pt with $^1J_{Pt-H} = 891.8$ Hz, and two bond coupling to Sn with $^2J_{Sn-H} = 18.4$ Hz. The C(1)-Pt(1)-Sn(1) bond angle in compound 3.3 is 94.79° and the C(1)-Pt(1)-C(2) bond angle is 105.06°. As is evident from these bond angles, compound 3.3 is distorted from square planar geometry which can be attributed to the small unbalanced steric of the hydride compared to the larger steric of $trans$ CO ligand with bulky Bu$^1$ groups.

Compound 3.3 is stable at room temperature in the solid state, and can be handled in air. Addition of CO to compound 3.1 is irreversible. The IR spectrum of 3.3 in hexane solution shows a medium intensity peak at 2104 cm$^{-1}$ for $\nu_{Pt-H}$ stretching frequency and a very strong peak for the Pt-bound carbonyl group at 1979 cm$^{-1}$. Pt complexes with terminal hydride ligands are known to have a $\nu_{Pt-H}$ stretching frequency in the range of 2050-2120 cm$^{-1}$.

Reversible activation of H$_2$ by complex 3.1 to form Pt- tri hydride complex: When H$_2$ gas is purged through the solution of compound 3.1 (3.1 is highly soluble in THF and CH$_2$Cl$_2$, moderately soluble in benzene, toluene and insoluble in hexane), a slight change in color of the solution was observed (from red to red orange). Attempts to isolate and crystallize the product were unsuccessful as we were able to isolate only the starting complex 3.1, indicating the high instability of the product.
Reaction was also monitored by $^1$H NMR. After purging H$_2$ gas through the anhydrous THF-$d_8$ solution of complex 3.1 in a sealed NMR tube followed by vigorous shaking for 5 minutes, $^1$H NMR was recorded. Which indicated the disappearance of the hydride resonance peaks corresponding to complex 3.1, and appearance of a new hydride resonances showing one-bond coupling to Pt and two-bond coupling to Sn (see Figure 3.5). Appropriate integration of the proton peaks, lead us to postulate the structure Pt(SnBu$_3^t$)(IBu$_2^t$)(H)$_3$, 3.4, as shown in the equation 3.2.

Figure 3.5. $^1$H NMR spectrum showing the hydride region of compounds 3.1 and 3.3 in THF-$d_8$. 

\[ [\text{H}_{\text{Pt}(\text{SnBu}_3^t)(\text{IBu}_2^t)}](\text{H})]_2 + \text{H}_2 \]
It is evident from Figure 3.5 that both the hydrides of the compound [Pt(SnBu$_3$)(IBu$_2$)(H)]$_2$, 3.1 show up at -5.59 ppm with a set of one bond coupled $^{195}$Pt satellites ($^1J^{195}_{\text{Pt-H}} = 652$ Hz), one set each of two bond coupled $^{119}$Sn and $^{117}$Sn satellites ($^2J^{119}_{\text{Sn-H}} = 205$ Hz, $^2J^{117}_{\text{Sn-H}} = 199$ Hz) and one set of two bond coupled $^{195}$Pt satellites ($^2J^{195}_{\text{Pt-H}} = 55$ Hz) (at the base of the hydride) consistent with the structure 3.1. But when H$_2$ gas is purged through the solution of compound 3.1, a shift in the hydride resonances was observed. The new resonances now show up at -2.75 ppm with one set of one bond coupled $^{195}$Pt satellites ($^1J^{195}_{\text{Pt-H}} = 671$ Hz), one set each of two bond coupled $^{119}$Sn and $^{117}$Sn satellites ($^2J^{119}_{\text{Sn-H}} = 136$ Hz, $^2J^{117}_{\text{Sn-H}} = 130$ Hz). Interestingly, now the two bond coupled $^{195}$Pt satellites are missing, indicating that the structure could be a mononuclear Pt complex, as was expected.

To further confirm the nuclearity and the number of hydrides on the Pt metal center, $^{195}$Pt NMR and $^{119}$Sn NMR experiments haves been carried out on the reaction mixture of [Pt(SnBu$_3$)(IBu$_2$)(H)]$_2$ + H$_2$ (see Figure 3.6).
Figure 3.6. Overlay of $^{195}$Pt and $^{119}$Sn NMR spectra of [Pt(SnBu$_3^\prime$)(IBu$_2^\prime$)(H)]$_2$ + H$_2$ in THF-$d_8$.

The proton decoupled $^{195}$Pt NMR showed one peak corresponding to $^{195}$Pt at -6216.70 ppm with both one bond coupled $^{119}$Sn and $^{117}$Sn satellites ($^{1}J_{Sn-Pt} = 4737$ Hz, $^{2}J_{Sn-Pt} = 4524$ Hz). Similarly, the proton decoupled $^{119}$Sn NMR showed one peak corresponding to $^{119}$Sn at 145.84 ppm with one bond coupled $^{195}$Pt satellites ($^{1}J_{Pt-Sn} = 4737$ Hz). The second order or other multi order couplings are not observed, consistent with the presence of one Pt and one Sn in the new product.

As predicted, the proton coupled spectra of $^{195}$Pt NMR showed a quartet for the Pt resonance at -6216.70 ppm with $^{1}J_{H-Pt} = 671$ Hz, (see Figure 3.7, tin satellites are shown as Sn) exactly matching the one bond coupled $^{195}$Pt $J$ value from $^1$H NMR, see Figure 3.5. This indicates that we are looking at the same proton-Pt couple in both $^1$H and
$^{195}$Pt NMR spectra. However, the proton coupled $^{119}$Sn NMR did not show any distinct resonances due to two bond coupling to proton as the resonances, due to the fact that one bond coupling to $^{13}$C were prominent and broad (in SnBu$_3^1$, Sn is one bond coupled to three ‘C’ atoms of three Bu$_i^1$ groups).

![Proton coupled $^{195}$Pt NMR spectra of $[\text{Pt(SnBu}_3^1)\text{(IBu}_2^1\text{)(H)})_2^+\text{H}_2$](image)

**Figure 3.7.** Proton coupled $^{195}$Pt NMR spectra of $[\text{Pt(SnBu}_3^1)\text{(IBu}_2^1\text{)(H)})_2^+\text{H}_2$ in THF-$d_8$.

Similar to addition of CO to compound 3.1, addition of H$_2$ also proceeds through the breaking of Pt-Pt bond in dinuclear Pt(II)-NHC complex 3.1 to afford the proposed mononuclear complex Pt(SnBu$_3^1$)(IBu$_2^1$)(H)$_3$, 3.4. Apart from the NMR data which was consistent with the structure 3.4, and visual color change upon purging H$_2$ gas through the solution of complex 3.1, we don’t have any other experimental evidence to prove the existence of structure 3.4 in solution, as isolation of products from the reaction mixture of compound 3.1 + H$_2$ is extremely sensitive to moisture, temperature, air and also to H$_2$ atmosphere. Upon removal of H$_2$ atmosphere we observed regeneration of compound 3.1 in solution as shown in equation 3.2, and the reaction mixture showed a large number of
unidentified hydride peaks when either wet solvents or oxygenated solvents were used. To our knowledge, Pt-carbene complexes with three hydrides are unknown; no precedent examples exist for comparison. However, Pt-NHC complexes with dihydrides are known. Recently, Nolan et al. prepared an analogous 14 electron Pd(0) dihydride complex Pd(Ipr)(H)2(PCy3) with IPr NHC ligand.128 Crabtree et al. also reported a similar dihydride Ir-NHC carbene complex.142 We were unable to isolate and characterize the compound 3.4 crystallographically, but it’s presence has been proved in the solution through combination of 195Pt, 119Sn and 1H NMR.

Activation of ethylene by Pt-Sn NHC complex 3.1: In a similar fashion to the addition of CO to compound 3.1, ethylene addition also yields a mononuclear Pt-carbene complex. Ethylene is bound to Pt metal center in an $\eta^2$ mode through C=C $\pi$-bond to yield a 16 electron Pt-NHC-ethylene complex, Pt(SnBu$_3$)(IBu)(C$_2$H$_4$)(H), 3.5. The addition of ethylene to 3.1 is also reversible both in the solid state and in solution state at room temperature. Replacing the ethylene atmosphere with argon gas or by applying vacuum, compound 3.5 regenerates compound 3.1. Crystals suitable for X-ray diffraction were also grown under ethylene atmosphere. Compound 3.5 was characterized by the combination of 1H NMR and single crystal X-ray diffraction techniques. The molecular structure of compound 3.5 is shown in Figure 3.8 (further crystallographic data is given in the Appendix B Table B.2).
Figure 3.8. Molecular structure of Pt(SnBu$_3^t$)(IBu$_t^t$)(C$_2$H$_4$)(H), 3.5. Showing 30% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows: Pt(1)-Sn(1) = 2.6293(4), Pt(1)-H(1) = 1.60(5), Pt(1)-C(1)=2.078(4), Pt(1)-C(12)=2.163(6), Pt(1)-C(12)=2.161(6), C(13)-C(12)= 1.410(8). C(1)-Pt(1)-Sn(1) =146.6(2), C(1)-Pt(1)-H(1) = 81(2), Sn(1)-Pt(1)-H(1) = 67(2).

Interestingly, the position of ethylene in 3.5, is similar to that of CO in 3.3, both are added in the trans position to the hydride ligand. The position of the hydride ligand in 3.5 was determined and refined crystallographically using the data collected at 100 K. The presence of the hydride ligand was also confirmed by $^1$H NMR spectroscopy, where the proton resonance of the hydride ligand appears at -3.57 ppm with appropriate one bond coupling to Pt (s, $^1J_{Pt-H} = 891.8$ Hz) and two-bond coupling to Sn ($^2J_{Sn-H} = 18.4$ Hz). The C12-C13(ethylene) bond distance in compound 3.5 is 1.410 Å (in free ethylene it is 1.339 Å), which is close to the reported C=C bond distance of 1.434 Å in a similar ethylene-bound mononuclear Pt-complex Pt(PPh$_3$)$_2$(C$_2$H$_4$)$_2$.\textsuperscript{143}

Attempted catalytic hydroformylation of ethylene with compound 3.1: As shown above, we have successfully activated CO, H$_2$, and ethylene using compound 3.1 which is
an essential requirement of a hydroformylation catalyst in homogeneous catalysis. This led us to attempt the hydroformylation of ethylene using compound 3.1. We carried out this experiment in a small Parr-reactor. Initially, reactor was loaded with toluene solution of compound 3.1. Then, the reactor was pressurized with ethylene gas to yield compound 3.5. Then an equimolar mixture of H$_2$ and CO gas (1:1 ratio) was introduced at room temperature and the reactor was sealed. Reactions were carried out from a total pressure of 75 psi to 150 psi with varying amounts of ethylene and H$_2$+CO mixture. The progresses of the reactions were monitored by $^1$H NMR spectroscopy. After 24 hours we observed the disappearance of peaks corresponding to ethylene compound 3.5 and complete conversion of compound 3.5 into Pt-carbonyl compound 3.3. Unfortunately, we were unable to identify peaks corresponding to any products resulting from hydroformylation in the $^1$H NMR spectra of the reaction mixture. Even at the refluxing temperatures of toluene we have not observed any products of hydroformylation. Probably varying experimental conditions or modification of substituents on the nitrogen atom of the NHC ligand may promote hydroformylation of olefins. Further studies on hydroformylation of other alkenes in the presence of compound 3.1 are underway.

3.3. **Summary and conclusions.**

Reaction of IBu$^t$ carbene with compound Pt(COD)(SnBu$^t$)(H), 2.1, gave a stable but highly reactive dinuclear Pt compound [Pt(SnBu$^t$)(IBu$^t$)(H)]$_2$, 3.1. Efforts to synthesize the proposed intermediate Pt(SnBu$^t$)(IBu$^t$)(H), 3.2 were unsuccessful with IBu$^t$ carbene. Probably it is possible with more sterically demanding carbenes. Compound 3.1 successfully activated CO, ethylene and H$_2$ molecules at room temperature. The reactions with ethylene and H$_2$ are reversible. However, the reaction of
compound 3.1 with H₂ is highly sensitive to air, moisture, and temperature, and we could not isolate the proposed trihydride-Pt product 3.4. Its presence in solution has been proven by NMR spectroscopy. Summary of the complexes is given in Scheme 3.3.

Compound 3.1 has all the required properties of a hydroformylation catalyst as it successfully activated CO, C₂H₄ (alkene), and H₂; but the efforts to hydroformylate C₂H₄ were unsuccessful, indicating the need to alter the reaction conditions. It might also work on a different alkene. More research has been planned along these lines. Efforts to activate other small molecules such as N₂ and CO₂ were unsuccessful and further research is required in synthesizing the Pt-NHC complexes that can activate these molecules.

Scheme 3.3. Summary of NHC complexes synthesized.
3.4. Experimental section.

**General Data:** Unless otherwise indicated, all reactions were performed under an atmosphere of Argon. Reagent grade solvents were dried by standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Nicolet 380 FT-IR spectrophotometer. $^1$H NMR were recorded on Bruker 300 and 400 spectrometer operating at 300.13 MHz and 399.99 MHz respectively. Elemental analyses were performed by Columbia Analytical Services (Tuscon, AZ). Mass spectrometric measurements performed by a direct-exposure probe using electron impact ionization (EI) were made on a VG 70S instrument at the University of South Carolina, Columbia, SC. The NHC carbenes IBu$^t$ and IPr were purchased from Strem chemicals and used without further purification. Ethylene, CO, and CO$_2$, H$_2$ gases of 99.9% purity were purchased from Air gas south and used without further purification. Tertiary butylisocyanide, CNBu$^t$, was purchased from Sigma-Aldrich and used without further purification. Bis(1,5-cyclooctadiene)platinum, Pt(COD)$_2$, and tri-tert-butylstannane (Bu$^t$_3SnH), were prepared according to the published procedures. Silica gel (60-200 µm, 70-230 mesh) used for chromatographic separations was purchased from Silicycle.

**Synthesis of [Pt(SnBu$^t$_3)(IBu$^t$)(H)]$_2$, 3.1:** In a glove box, under an atmosphere of argon, 30.0 mg of Bu$^t$_3SnH (0.103 mmol) dissolved in 3mL of freshly distilled hexane was added to 40.0 mg of Pt(COD)$_2$ (0.097 mmol). The reaction mixture immediately turned dark brown. The reaction mixture was stirred at room temperature for an additional 10 minutes then 17.0 mg of IBu$^t$ dissolved in 0.5 ml of toluene solution was added to dark brown reaction mixture. The reaction mixture immediately turned red. The reaction was stirred for 30 minutes, after which solvent was reduced to c.a. 1 mL. The solid was
filtered and washed with 3x 3.0 mL of pentane to yield 48 mg (yield 75%) of cherry red powder. Spectral data for 3.1: $^1$H NMR (THF-$d_8$, rt, in ppm): $\delta = 7.33$ (s, 4H; imid), 2.03 (s, 36H; C(CH$_3$)$_3$), 1.09 (s, 54H; $^2$J$_{Sn-H} = 49.3$ Hz, C(CH$_3$)$_3$); -5.61 (s, $^1$J$_{Pt-H} = 652$ Hz, $^2$J$_{Sn-H} = 205$ Hz, $^2$J$_{Pt-H} = 55.0$ Hz, 2H, hydride). $^1$H NMR (C$_6$D$_6$, rt, in ppm): $\delta = 6.60$ (s, 4H; imid), 1.94 (s, 36H; C(CH$_3$)$_3$), 1.42 (s, 54H; $^2$J$_{Sn-H} = 49.3$ Hz, C(CH$_3$)$_3$); -5.61 (s, $^1$J$_{Pt-H} = 652$ Hz, $^2$J$_{Sn-H} = 205$ Hz, $^2$J$_{Pt-H} = 55.0$ Hz, 2H, hydride). $^{195}$Pt NMR (THF-$d_8$, rt, in ppm): $\delta = -3789.16$ (s, proton decoupler on), proton decoupler off, $\delta = -3789$ [triplet (1:2:1), $^1$J$_{Pt-Pt} = 650.84$ Hz]. $^{119}$Sn NMR Spectral data for 3.1: (THF-C$_6$D$_6$, rt, in ppm): -17.85 (s, $^1$J$_{Pt-Sn} = 12815$ Hz, $^2$J$_{Pt-Sn} = 5714$ Hz). Elemental analysis, Calc: C, 41.45; H, 7.26; N, 4.20 %, Found: C, 41.47; H, 7.41; N, 4.09 %.

**Synthesis of Pt(SnBu$_t^3$)(IBu$_t^3$)(CO)(H), 3.3:** A 25 mL schlenk tube was charged with 30 mg of 3.1 (0.023 mmol) which was subsequently dissolved in 4.0 mL of toluene. The red solution was under an atmosphere of c.a. 10 psi CO and shaken vigorously. The resultant solution turned light orange immediately. The solvent was removed under reduced pressure. The solid was then washed with 3x 0.25 mL heptane and yielded 28.6 mg (90% yield) of a khaki-colored powder. Spectral data for 3.3: $^1$H NMR (C$_6$D$_6$, rt, in ppm): $\delta = 6.60$ (s, $^4$J$_{Pt-H} = 8.8$ Hz, 2H; imid), 1.67 (s, 27 H, SnBu$_t^3$), $^3$J$_{Sn-H} = 51.8$ Hz, 1.37 (s, 18 H, C(CH$_3$)$_3$); -2.48 (s, $^1$J$_{Pt-H} = 891.8$ Hz, $^2$J$_{Sn-H} = 18.4$ Hz, 1H, hydride). IR $\nu_{CO}$ (cm$^{-1}$ in hexane): 1979(vs), 2104(m).

**Reaction of 3.1 with H$_2$ gas, compound 3.4:** $^1$H NMR; A 5 mL NMR tube was charged with 10.0 mg of 3.1 which was subsequently dissolved in 0.5 mL of toluene-$d_8$. The NMR tube was sealed under argon, and the red solution was exposed to an atmosphere of c.a. 1 atm H$_2$ and shaken vigorously. The resultant solution turned light orange
immediately to yield mononuclear Pt-Sn carbene complex with the three hydride ligands. Spectral data for 3.4: $^1$H NMR ($C_6D_6$, rt, in ppm): $\delta = 6.60$ (s, $^4J_{Pt-H} = 8.8$ Hz, 2H; imid), 1.56 (s, 27 H, SnBu$_3$, $^3J_{Sn-H} = 62.1$ Hz), 1.41 (s, 18 H, C(CH$_3$)$_3$); -4.36 (s, $^1J_{Pt-H} = 726.5$ Hz, $^2J_{Sn-H} = 127.5$ Hz, 3H, hydride). $^1$H NMR (THF-$d_8$, rt, in ppm): $\delta = -2.75$ (s, $^1J_{Pt-H} = 671$ Hz, 3H, hydride, $^1J^{119}_{Sn-H} = 136$ Hz, $^1J^{117}_{Sn-H} = 130$ Hz),

$^{195}$Pt NMR: A 5 mL NMR tube was charged with 40 mg of 3.1 which was subsequently dissolved in 0.5 mL of THF-$d_8$. The NMR tube was sealed under argon, and the red solution was exposed to an atmosphere of c.a. 1 atm H$_2$ and shaken vigorously. The resultant solution turned light orange immediately to yield mononuclear Pt-Sn carbene complex with the three hydride ligands. $^{195}$Pt NMR spectral data for 3.4: (THF-$d_8$, rt, in ppm): -6216.70 (s, decoupler on, $^1J^{119}_{Sn-Pt} = 4736$ Hz, $^1J^{117}_{Sn-Pt} = 4524$ Hz), decoupler off, quartet (1:3:3:1), -6216.70 ( $^1J_{Pt-Pt} = 667$ Hz). $^{119}$Sn NMR: (THF-$d_8$, rt, in ppm): 145.83 (s, $^1J^{95}_{Pt-Sn} = 4737$ Hz).

**Synthesis of Pt(SnBu$_3$)(IBu)$_5$(C$_2$H$_4$)(H), 3.5:** A 25 mL schlenk tube was charged with 30.0 mg (0.023 mmol) of 3.1 which was subsequently dissolved in 4.0 mL of toluene. The red solution was under an atmosphere of c.a. 10 psi ethylene and shaken vigorously. The resultant solution turned light yellow immediately. The solvent was removed under slow flow of ethylene gas to yield 26.6 mg (85% yield) of a light yellow-colored powder.

Spectral data for 3.5: $^1$H NMR (toluene-$d_8$, rt, in ppm): $\delta = 6.60$ (s, $^4J_{Pt-H} = 8.8$ Hz, 2H; imid), 2.45 (s, 4H, ethylene), 1.88 (s, 27 H, SnBu$_3$, $^3J_{Sn-H} = 51.8$ Hz), 1.63 (s, 18 H, C(CH$_3$)$_3$); -3.57 (s, $^1J_{Pt-H} = 891.8$ Hz, $^2J_{Sn-H} = 18.4$ Hz, 1H, hydride).

**Reaction of 3.1 with a mixture of H$_2$ and CO (1:1 mole ratio):** In a typical reaction, a 3 mg of compound 3.1, 1 mL of anhydrous toluene or toluene-$d_8$ and a magnetic stir bar
were sealed in a Parr reactor under ethylene atmosphere of 25psi. The Parr reactor was pressurized with 25 psi of H₂ and 25 psi of CO gas at room temperature. The reaction was monitored by ¹H NMR at different time intervals. Every time experiment was setup with fresh sample and fresh gases. The reaction was monitored at room temperature and at refluxing temperature of toluene from 75psi to 150psi pressures. After 24 hours the ¹H NMR of reaction mixture showed peaks corresponding to compound 3.3 and free ethylene. No peaks were observed corresponding to acetaldehyde. The Parr reactor was then placed in an oil bath with a stir bar that was pre-heated to 120 °C. The reaction was monitored by ¹H NMR at different time intervals. After two days, the ¹H NMR of reaction mixture showed peaks corresponding to compound 3.3 and free ethylene. There was no product observed resulting from hydroformylation of ethylene.

3.5. Crystallographic analyses.

Red-colored crystals of 3.1 suitable for diffraction were grown by slow evaporation of toluene solution at room temperature in a glove box. Yellow crystals of 3.3 were grown by evaporation of hexane solution of 3.1 at 0 °C under the slow stream of the CO gas. Light yellow crystals of 3.5 of suitable quality for diffraction were grown by slow evaporation of hexane solution under a stream of ethylene gas in an ice bath (0 °C). Orange-colored crystals of 3.6 were grown by evaporation of hexane solution in glove box at room temperature.

Each data crystal was mounted onto the end of a thin glass fiber using Paratone-N. X-ray intensity data were measured by using a Bruker SMART APEX2 CCD-based diffractometer using Mo Kα radiation (λ = 0.71073 Å). The raw data frames were
integrated with the SAINT+ program by using a narrow-frame integration algorithm. Corrections for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS. Both structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares on $F^2$, by using the SHELXTL software package. Crystal data, data collection parameters, and results of the analyses are listed in Tables B.2- B.4 in Appendix B.

The compound 3.1 crystallized in triclinic system. The space group $P \bar{1}$ was assumed and confirmed by the successful refinement and solution of the structure. The hydride ligand was located from the difference map but refined on its positional parameters with a fixed isotropic thermal parameter. Compound 3.3 crystallized in monoclinic system. The space group $P21/c$ was confirmed on the basis of the systematic absences in the data. With $Z= 8$, there were two molecules in the structure and the hydride ligand was located from the difference map but refined on its positional parameters with a fixed isotropic thermal parameter.

Compound 3.5 crystallized in triclinic system. The space group $P \bar{1}$ was confirmed on the basis of the systematic absences in the data. The ether solvent molecule co-crystallized with the compound 3.5. The hydride ligand was located from the difference map but refined on its positional parameters with a fixed isotropic thermal parameter.

4.1. Background.

The complexes of precious transition metals such as platinum group metals (PGM) are used as catalysts for a wide variety of industrial processes, such as in hydrogenation reactions. Though platinum is one of the highly used metals in various catalytic processes, it is one of the rarest metals available in the earth’s crust and highly expensive. There is a need for cost effective alternatives to make an industrial process sustainable amid frequent financial meltdowns. This can be achieved by replacing expensive methods with economical ones, and this represents the incredible opportunity to develop processes which involve non-precious metals. It is where the inexpensive organometallic complexes of Ni fit aptly with the catalytic applications competitive to those of PGM.

Nickel is one of the most highly abundant transition metals in the earth’s crust, and it is also an inexpensive (at present, Ni is 2555 times cheaper than Pt) metal compared to platinum. Nickel is used as hydrogenation catalyst in many important industrial reactions. It also plays an important role biologically.

The organometallic chemistry of Ni had been started in 1890 with the dramatic discovery of Ni(CO)₄ by Mond, Langer, and Quincke. This had been later employed in industry to purify Ni metal, called Mond’s process. It is the first carbonyl of a zerovalent metal to be made. Nickel also forms zero-valent and stable complexes with other strong π- acceptors such as isocyanides and carbenes. This had led to use these complexes as catalysts in organic synthesis as carbonylation (see Scheme 4.1), hydrocyanation and hydrosilylation reagents. Nickel also has a strong tendency to form complexes
with alkenes and alkynes, and this leads to the development of catalytically active Ni complexes that can perform oligomerization of alkenes, hydrogenation of alkenes, alkene isomerization, and also alkyl-aryl cross coupling reactions. It was also found that Ni oxidatively couples carbon dioxide to unsaturated compounds such as alkenes, alkenes, dienes, conjugated dienes, cumulenes, imines or aldehydes and converts carbon dioxide into a variety of useful organic products.\textsuperscript{158–161}

![Scheme 4.1. Reppe carbonylation (addition of CO and HX to alkyne or alkene) of acetylene to produce acrylate ester using Ni complex (X= halide).](image)

Organometallic compounds of nickel are also found to be photolytically active. The cluster complex Ni\(_3\) (µ\(_3\)-I)\(_2\)(dppm)\(_3\), was shown to reduce CO\(_2\) photochemically,\textsuperscript{162} yielding the radical anion CO\(_2\)\. This reaction selectively produces the industrial feed stock chemical 1, 2-cyclohexanedicarboxylic acid. Such reactions of photochemical activation and transformation of abundant atmospheric gasses like CO\(_2\), O\(_2\), and N\(_2\) into useful chemical products may dominate the future technologies.

As mentioned earlier, tin is extensively used as a modifier of the platinum group metals, to increase the catalytic efficiency. Similarly, Ni–Sn bimetallic complexes are
also shown to display promising results in catalysis. Ni-Sn complexes, supported on silica were shown to catalyze CO oxidation reactions,\textsuperscript{42} as well as the dehydrogenation of cyclohexene\textsuperscript{41} compared to mono Ni complexes. Recently, Raney Ni-Sn catalyst has been used very efficiently for the production of H\textsubscript{2} from biomass derived hydrocarbons.\textsuperscript{52}

Ni(COD)\textsubscript{2} is a highly reactive yellow crystalline solid. It is extremely sensitive to air, moisture and temperature. The COD ligands on Ni metal center are highly labile and can be easily replaced by the isocyanide ligands at ambient conditions. This chapter presets the efforts that have been placed to synthesize the Ni-Sn analogues of Pt-Sn complexes and the reactivity of resultant complexes.

4.2. Results and discussion.

In the previous two chapters, synthesis of Pt-Sn complexes and their reactivity towards small molecules have been discussed. As mentioned earlier, this project has been started with the aim of replacing the expensive Pt metal with Ni and carryout the activation of mall molecules. The initiation for this chapter comes from chapter 2, where a series of exciting Pt-Sn complexes and the reaction of these complexes with small molecules have been discussed. Emphasis was laid on the synthesis of the Ni analogues of complexes Pt(SnBu\textsubscript{3})\textsubscript{2}(H)\textsubscript{2}, 2.2, Pt(SnBu\textsubscript{3})\textsubscript{2}(Bu\textsuperscript{t}NC)\textsubscript{2}(H)\textsubscript{2}, 2.5 and Pt(SnBu\textsubscript{3})\textsubscript{2}(Bu\textsuperscript{t}NC)(CO), 2.13 for carrying out the reversible activation of H\textsubscript{2} and CO.

**Reaction of Ni(COD)\textsubscript{2} with Bu\textsuperscript{t}\textsubscript{3}SnH and CNBu\textsuperscript{t}:** From the reaction of Pt(COD)\textsubscript{2} with Bu\textsuperscript{t}\textsubscript{3}SnH and CNBu\textsuperscript{t}, a simple unsaturated Pt-Sn complexe Pt(SnBu\textsubscript{3})\textsubscript{2}(CNBu\textsuperscript{t})(H)\textsubscript{2}, 2.5 was made,\textsuperscript{84} and the proposed pathway for the formation was shown in the equation 4.1.
Nevertheless, the nickel analogue of this platinum-ditin-dihydride compound was not made and attempts to synthesize the intermediate were also unsuccessful.

$$\text{Pt(COD)}_2 + \text{Bu}_3^1\text{SnH} + 2\text{CNBu}^1 \rightarrow \begin{array}{c} \text{Bu}^1\text{NC} \text{Pt} \text{Bu}^1\text{NC} \\ \text{H} \text{H} \text{SnBu}_3^1 \text{SnBu}_3^1 \end{array} (\text{eq. 4.1})$$

However, when one equivalent of Ni(COD)$_2$ was reacted with two equivalents of $^1\text{Bu}_3\text{SnH}$ and two equivalents of $\text{CNBu}^1$ under argon atmosphere in hexane solution, a red dark solution was formed. The FTIR spectra of this solution showed new broad stretches in the isocyanide region with no appreciable decrease in the amount of free tin hydride but complete consumption of free CNBu$^1$, and when the reaction mixture was brought to 68 °C the solution quickly changed color from dark red to gold, and the volatiles were removed in vacuo. The residues were re-dissolved in a methylene chloride/hexane mixture and filtered through silica gel. Slow evaporation of solvent yielded orange block crystals which were determined by X-ray crystallographic analysis to be Ni(SnBu$_3^1$)$_2$(CNBu$^1$)$_3$, 4.1 (see Figure 1.1). Further crystallographic data is listed in Appendix C Table C.1. The compound Ni(SnBu$_3^1$)$_2$(CNBu$^1$)$_3$, 4.1 was characterized by a combination of $^1$H NMR, FTIR, UV-Vis, elemental analysis, mass spectrometry, and single crystal X-ray diffraction.
Figure 4.1. An ORTEP showing the molecular structure of Ni(SnBu\textsubscript{3})\textsubscript{2}(CNBu\textsuperscript{t})\textsubscript{3}, 4.1 at 30 % thermal ellipsoid probability. Selected interatomic distances (Å) and angles (deg) are as follows: Ni1-C1= 1.862, Ni1-Sn1=2.6108; Sn1-Ni1-Sn1* = 179.24, C2-Ni1-C1= 120.9, Sn1-Ni1-C1=90.3.

Compound 4.1 is an 18\textsuperscript{e} saturated complex. The FTIR spectrum of Ni(Sn'Bu\textsubscript{3})\textsubscript{2}(BuNC)\textsubscript{3}, 4.1 shows two distinct isocyanide resonances, as opposed to the theoretical one $\nu_{CN}$ for trigonal bipyramidal M(L)\textsubscript{2}(L )\textsubscript{3} with axial L. It is still unknown why there is an extra FTIR active stretch, but evidence for sterically induced symmetry distortion in solution is provided below. The FTIR disagreement with normal symmetry theory is the first of many unusual pieces of information found in this work. The platinum analogue Pt(Sn'Bu\textsubscript{3})\textsubscript{2}(BuNC)\textsubscript{3} (see chapter 5) and the palladium analogue Pd(Sn'Bu\textsubscript{3})\textsubscript{2}(BuNC)\textsubscript{3} are also synthesized in our lab.\textsuperscript{163}

The pathway for the formation of complex 4.1 is shown in Scheme 4.2. Complex Ni(CNBu\textsuperscript{t})\textsubscript{4} will be formed first then it releases a CNBu\textsuperscript{t} ligand to react with two Bu\textsuperscript{t}\textsubscript{3}SnH to form complex Ni(SnBu\textsubscript{3})\textsubscript{2}(CNBu\textsuperscript{t})\textsubscript{3}, 4.1. Indeed this analogy was proved
later where Ni(SnBu\textsubscript{3})\textsubscript{2}(CNBu\textsuperscript{i})\textsubscript{3} is readily formed from the reaction of Ni(CNBu\textsuperscript{i})\textsubscript{4} with two equivalents of Bu\textsuperscript{i}\textsubscript{3}SnH in refluxing hexane, as shown in equation 4.1, with the release of H\textsubscript{2} gas and CNBu\textsuperscript{i}.

The reaction proceeds at room temperature as well but much more slowly.

The proposed mechanism for the formation of Ni(SnBu\textsubscript{3})\textsubscript{2}(CNBu\textsuperscript{i})\textsubscript{3}, \textit{4.1} involves the formation of intermediate Ni(RNC)\textsubscript{3} first, as the reactivity of the complexes of the type Ni(RNC)\textsubscript{4} proceed via ligand dissociation yielding reactive trigonal planar Ni(RNC)\textsubscript{3} intermediates.\textsuperscript{164} After the formation of Ni(RNC)\textsubscript{3} intermediate, the Bu\textsuperscript{i}\textsubscript{3}SnH ligand adds to it stepwise, as shown in Scheme 4.2. A concerted mechanism to produce Ni(SnBu\textsubscript{3})\textsubscript{2}(CNBu\textsuperscript{i})\textsubscript{3}, \textit{4.1} with release of H\textsubscript{2} has been ruled out due to steric restraints.

\textbf{Scheme 4.2.} Line drawing of proposed formation for Ni(SnBu\textsubscript{3})\textsubscript{2}(CNBu\textsuperscript{i})\textsubscript{3}, \textit{4.1}.

Slow and drop wise addition of one equivalent of diluted Bu\textsuperscript{i}\textsubscript{3}SnH to a solution of Ni(CNBu\textsuperscript{i})\textsubscript{4} at any temperature will afford only a mixture of Ni(SnBu\textsubscript{3})\textsubscript{2}(CNBu\textsuperscript{i})\textsubscript{3}, \textit{4.1} and Ni(CNBu\textsuperscript{i})\textsubscript{4}. Unsuccessful detection of any hydride in the reaction mixture suggests a rapid reaction to form the product \textit{4.1}, once initiated by the first tin binding. The initial reaction conditions described earlier used only 2eq of CNBu\textsuperscript{i} and formed a dark red
intermediate. A literature search determined that this afforded the nickel cluster Ni₄(CNBuᵗ)₇ which also apparently reacts with Buᵗ₃SnH to give the same product Ni(SnBuᵗ)₂(CNBuᵗ)₃ but in understandably lower yield due to deficiency of isocyanide.¹⁶⁵

**Reaction of Ni(SnBuᵗ)₂(CNBuᵗ)₃, 4.1 with Carbon Monoxide, CO:** When CO gas is purged through the room temperature gold colored hexane solution of Ni(SnBuᵗ)₂(CNBuᵗ)₃, 4.1 a color change to light-yellow was observed. FTIR spectroscopy analysis of the reaction mixture confirmed the presence of a free CNBuᵗ and resonances of a new compound displaying both CN and CO stretches. Solvent was removed under vacuo and the residue was crystallized in a mixture of CH₂Cl₂/Hexane solvent at -25 °C. Analyzing the resultant crystals using X-ray crystallography yielded a molecular structure of Ni(SnBuᵗ)₂(CNBuᵗ)(CO), 4.2 shown in Figure 4.2. Further crystallographic data is found in Appendix C Table C.1. The complex Ni(SnBuᵗ)₂(CNBuᵗ)(CO), 4.2 was characterized by a combination of ¹H NMR, ¹³C-CO NMR, FTIR, UV-Vis, mass spectrometry, and single crystal X-ray diffraction.
Figure 4.2. An ORTEP showing the molecular structure of Ni(SnBu$_3$)$_2$(CNBu)$_2$(CO), 4.2 at 30% thermal ellipsoid probability. Selected interatomic distances (Å) and angles (deg) are as follows: Ni1-C1 = 1.736, Ni1-Sn1 = 2.6087, Ni1-C2 = 1.875; Sn1-Ni1-Sn1* = 164.33, C2-Ni1-C1 = 123.6, Sn1-Ni1-C1 = 82.2, Sn1-Ni1-C2 = 94.3, C2-Ni1-C2* = 112.9.

The symmetry distortion due to steric repulsion between the bulky Bu$_3^t$ groups is clearly evident from the crystal structure shown in Figure 4.2. The structure of Ni(SnBu$_3$)$_2$(CNBu)$_2$(CO), 4.2 is very similar to the mono CO platinum complex Pt(SnBu$_3$)$_2$(CNBu)$_2$(CO), 2.13 discussed in the chapter 2, which reversibly loses CO to regenerate complex Pt(SnBu$_3$)$_2$(CNBu)$_2$, 2.6. The axial tin groups seen in 4.2 bend away from the bulky equatorial isocyanides in an attempt to relieve steric strain. The tert-butyl groups even arrange themselves appropriately anti to further reduce any molecular tension. Both the compounds Ni(SnBu$_3$)$_2$(CNBu)$_3$, 4.1 and Ni(SnBu$_3$)$_2$(CNBu)$_2$(CO), 4.2 are stable in air in solid state and in solution state for extended periods of time.

When CO gas is purged through either Ni(SnBu$_3$)$_2$(CNBu)$_3$, 4.1 or Ni(SnBu$_3$)$_2$(CNBu)$_2$(CO), 4.2 in refluxing hexane or THF, formation of an almost 50:50
mixture of Ni(SnBu\textsubscript{3})\textsubscript{2}(CNBu\textsubscript{i})\textsubscript{2}(CO), 4.2 and Ni(SnBu\textsubscript{3})\textsubscript{2}(CNBu\textsubscript{i})\textsubscript{2}(CO)\textsubscript{2}, 4.3 was observed (see Scheme 4.3). These two compounds are extremely similar, and their separation requires large amounts of time and resources. Compound, 4.3 is characterized by FTIR, \textsuperscript{1}H NMR, and X-ray crystallographic analysis, but we did not pursue further its reactivity or photochemical properties due to difficulty involved in isolation and purification. The synthesis and characterization of 4.3 can be found here.\textsuperscript{84}

Scheme 4.3. Formation of compounds 4.2 and 4.3 from 4.1.

**Compound Ni(SnBu\textsubscript{3})\textsubscript{2}(CNBu\textsubscript{i})\textsubscript{2}(CO), 4.2, is photo active:** The compound Ni(SnBu\textsubscript{3})\textsubscript{2}(CNBu\textsubscript{i})\textsubscript{2}(CO), 4.2, was found to be highly light sensitive. When an oxygen-free yellow colored hexane solution of 4.2 was exposed to incandescent light, a quick color change to metallic purple occurred, as shown in Figure 4.3.
Figure 4.3. Photographs showing the color change of Ni(SnBu\textsubscript{3})\textsubscript{2}(CNBu\textsubscript{1})\textsubscript{2}(CO), 4.2, before photolysis (left), after photolysis (right).

As mentioned, compound 4.2 is very sensitive to light. Exposure to sunlight or even under normal tube light it changes the color to purple. That was how Dr. Derek Isrow discovered the photolytic activity of this compound when he was walking in the sunlight with a solution of this compound in an NMR tube, and the compound became purple from yellow and this led to a series of experiments to characterize its photolytic activity.

Initially, the photolytic activity was thought to be due to the induced elimination of CO producing Ni(SnBu\textsubscript{3})\textsubscript{2}(CNBu\textsubscript{1})\textsubscript{2}, the Ni analogue of the platinum-tin complex Pt(SnBu\textsubscript{3})\textsubscript{2}(CNBu\textsubscript{1})\textsubscript{2}, 2.6 from chapter 2. As the CO dissociation is a very common mechanism in metal-carbonyl photochemical reactions,\textsuperscript{166} carbon monoxide gas is purged through the purple colored solution to check for regeneration of the starting material, however, the purple solution was relatively stable to CO, as well as hydrogen gas. We
were unable to produce either the complex Ni(SnBu\textsuperscript{t}3)\textsubscript{2}(CNBu\textsuperscript{t})\textsubscript{2} or its di-hydride product Ni(SnBu\textsuperscript{t}3)\textsubscript{2}(CNBu\textsuperscript{t})\textsubscript{2}(H)\textsubscript{2} as shown in equation 4.2.

The purple colored product is highly sensitive to air and moisture. It was also found that lower temperatures increases the rate of formation of this purple colored product. Crystallization of this purple colored product is very difficult, and after repeated attempts, product was finally crystallized as dichroic purple/green colored crystals by slow evaporation of concentrated diethyl ether solutions at -20 °C under argon atmosphere. Crystallographic analysis yielded the dimeric structure of [Ni(SnBu\textsuperscript{t}3)(CNBu\textsuperscript{t})\textsubscript{2}(CO)]\textsubscript{2}, \textbf{4.4} as shown in Figure 4.4. Further crystallographic data is provided in Appendix C Table C.1. The compound [Ni(SnBu\textsuperscript{t}3)(CNBu\textsuperscript{t})\textsubscript{2}(CO)]\textsubscript{2}, \textbf{4.4}, was characterized by the combination of \textsuperscript{1}H NMR, \textsuperscript{13}C-CO NMR, FTIR, UV-Vis, ESR, elemental and single crystal X-ray diffraction analyses. It is stable in the solid state in air for an extended period of time, but will quickly decolorize to yellow in both oxygenated and oxygen free room temperature solution state even under argon atmosphere. As it is evident from the structure the Sn-Ni-Ni-Sn back bone adopted a zigzag pattern with \textit{anti}-configuration to relieve equatorial strain between bulky \textit{tert}-butyl groups.
Figure 4.4. An ORTEP showing the molecular structure of [Ni(SnBu$_3^t$)(CNBu$_3^t$)$_2$(CO)$_2$], 4.4, at 30 % thermal ellipsoid probability. Selected interatomic distances (Å) and angles (deg) are as follows: Sn1-Ni1=2.5639(4), Ni1-Ni1*=2.6515(4), Ni1-C1=1.747(3), Ni1-C2= 1.858(3), Ni1-C3= 1.863(3); Sn1-Ni1-Ni1*=166.26(2), Sn1-Ni1-C1= 89.0(1), Sn1-Ni1-C2= 94.29(9), Ni1*-Ni1-C1= 77.3(1), Ni1*-Ni1-C2= 91.87 (9).

Radical mechanism for the formation of [Ni(SnBu$_3^t$)(CNBu$_3^t$)$_2$(CO)$_2$], 4.4: As it can be seen in the Figure 4.4, the crystal structure of compound 4.4 still displays CO ligands which were not lost as proposed in the equation 4.3, but rather Ni-Sn bonds were cleaved and a new Ni-Ni bond was formed. The $^1$H NMR analysis of the Ni(SnBu$_3^t$)$_2$(CNBu$_3^t$)$_2$(CO), 4.2 solution after photolysis indicated the presence of hexa-tert-butyl-di-stannane, Bu$_3^t$Sn-SnBu$_3^t$, a known compound and later it has been isolated from the crystallization of the photolysis product. Which was believed to be formed by combining two Bu$_3^t$Sn moieties and these di-stannanes are known to produce tri-alkyl tin radicals by thermolysis at elevated temperatures. If extreme care is not taken to eliminate as much oxygen from the reaction mixture as possible, another known compound, Bu$_3^t$Sn-O-SnBu$_3^t$ is detected and isolated as colorless plates.
Based on these experimental evidences a radical mechanism has been proposed (see Scheme 4.4) for the formation of product $[\text{Ni(SnBu}\text{'}_3\text{)(CNBu}\text{'}_2\text{(CO)}]]_2$, 4.4, with photolytic generation of the elusive and paramagnetic tetrahedral Ni$^1$ radical$^{170}$ $\bullet$ Ni(SnBu$^{13}$)(CNBu$^{13}$)$_2$(CO) and the planar $\bullet$ Sn$^{13}$Bu$_3$ radical.

Scheme 4.4. Proposed mechanism for photolysis of Ni(SnBu$^{13}$)$_2$(CNBu$^{13}$)$_2$(CO), 4.2 to [Ni(SnBu$^{13}$)(CNBu$^{13}$)$_2$(CO)]$_2$, 4.4 with generation of Bu$^{13}$Sn-SnBu$^{13}$.

The proposed tetrahedral Ni$^1$ species $\bullet$Ni(SnBu$^{13}$)(CNBu$^{13}$)$_2$(CO) is unsaturated by one electron and apparently dimerizes forming the compound [Ni(SnBu$^{13}$)(CNBu$^{13}$)$_2$(CO)]$_2$, 4.4. Though the existence and stability of the radical $\bullet$Ni(SnBu$^{13}$)(CNBu$^{13}$)$_2$(CO) in solution is still mostly unclear to us presently.

ESR studies on [Ni(SnBu$^{13}$)(CNBu$^{13}$)$_2$(CO)]$_2$, 4.4: After proposing the radical mechanism for the formation of [Ni(SnBu$^{13}$)(CNBu$^{13}$)$_2$(CO)]$_2$, 4.4 we set out to prove the
existence of radicals in solution. When ESR studies were performed on toluene solution of 4.4 at 134 K, an ESR signal with g = 2.059 was observed which is in good agreement with the literature reported g value for the NiI centered radicals.\(^{171}\) Typical g-values for Sn-centered radicals range from 1.988 to 2.027.\(^{172}\) The \(^{13}\)CO-[Ni(SnBu\(_3\))(CNBu\(_3\))\(_2\)(CO)]\(_2\) spectrum is shown below in Figure 4.5 and the \(^{12}\)CO spectrum is shown in Appendix C Figure C.3.

\[\text{Figure 4.5. ESR spectra of } ^{13}\text{CO-[Ni(SnBu}_3\text{)(CNBu}_3\text{)]}_2\text{ at 134 K. } g = 2.059.\]

**Efforts to trap proposed radical species:** After learning from ESR experiments that the complex 4.2 is generating paramagnetic species in solutions when exposed to the light, we carried out few more experiments to further confirm the generation of radicals in solution. In the first experiment we wanted to capture the radicals using a well known radical trap (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl, TEMPO (see Figure 4.6).\(^{173,174}\) This
widely used radical trap has many other industrial application such as polymerization
initiation, catalytic oxidation, etc., which will be discussed in the next chapter.

Figure 4.6. Line structure of (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl, TEMPO, radical.

When the yellow colored solution of the compound Ni(SnBu\textsubscript{t}\textsubscript{3})\textsubscript{2}(CNBu\textsubscript{t})\textsubscript{2}(CO), 4.2 was exposed to the light in the presence of three equivalents of TEMPO radical, the solution did not change to the characteristic purple color of the dimer, but rather darkened slightly to a brownish yellow. Similar color change was observed with Ni(SnBu\textsubscript{t}\textsubscript{3})\textsubscript{2}(CNBu\textsubscript{t}), 4.2 as well. Evacuation of volatiles and recrystallization of the solid residue from diethyl ether at -25 °C yielded brown yellow crystalline blocks of Ni(\texteta\textsuperscript{2}-TEMPO)(SnBu\textsubscript{t}),(CNBu\textsubscript{t}), 4.5 (see Figure 4.7) in 54 % yield. It was characterized by a combination of \textsuperscript{1}H NMR, FTIR, and single crystal X-ray diffraction. Further crystallographic data is found in Appendix C Table C.1.
Figure 4.7. An ORTEP showing the molecular structure of Ni(η^2-TEMPO)(SnBu^t_3)(CNBu'), 4.5 at 30% thermal ellipsoid probability. Selected interatomic distances (Å) and angles (deg) are as follows: Ni1-Sn1=2.4964(3), Ni1-N1=1.957(2), Ni1-O1=1.825(2), Ni1-C1=1.760(2), N1-O1=1.409(3); Sn1-Ni1-C1=94.00(8), Sn1-Ni1-O1=101.70(7), Ni1-O1-N1=73.2(1), Ni1-N1-O1=63.2(1), N1-Ni1-O1=43.57(9), N1-Ni1-C1=120.7(1)

It is evident from the Figure 4.7 that a CO ligand and a CNBu\(^t\) are missing from the Ni metal center. After careful consideration and study of the molecule and reaction the following mechanism (see Scheme 4.5) has been proposed for the formation of Ni(η^2-TEMPO)(SnBu^t_3)(CNBu'), 4.5. TEMPO is known to bind to metal centers through η^1 and η^2 modes (further discussed in the next chapter 5). Here, we believe TEMPO initially binds to the Ni\(^{\text{I}}\) radical center through oxygen atom in η^1 mode to form the intermediate I, which results in 1e\(^-\) reduction of TEMPO to its monoanion and oxidation of Ni\(^{\text{I}}\) back to Ni\(^{\text{II}}\). This is followed by repulsive elimination of isocyanide to form the tetrahedral 16e\(^-\) intermediate Ni(η\(^1\)-TEMPO)(SnBu^t_3)(CNBu')(CO), II. Then TEMPO transforms to its 3e\(^-\) η\(^2\) binding mode, displacing a CO ligand (or a second isocyanide for
Ni(SnBu\textsubscript{t}3)(CNBu\textsubscript{t}3) due to steric interactions and favorable heats of formation, forcing a 16e\textsuperscript{-} distorted square planar final product. The N1-O1 bond distance of 1.409(1) Å is longer than that found in free TEMPO which is 1.283(9) Å. The geometry around the N1 atom is pyramidal [O1-N1-C22 = 117.75(4) °, O1-N1-C26 = 111.16(7) °, C26-N1-C22 = 119.25(1) °] and the Ni1-N1 and Ni1-O1 bond distances are short [Ni1-N1 = 1.958(2) Å, Ni1-O1 = 1.825(4) Å]. All of these structural parameters are consistent with a bidentate $\eta^2$-TEMPO coordination mode and formulation of a reduced TEMPO radical as a monoanionic TEMPO ligand according to the literature.\textsuperscript{175}

\begin{itemize}
\item[Ni(SnBu\textsubscript{t}3)(CNBu\textsubscript{t}3)]
\end{itemize}

\textbf{Scheme 4.5.} Proposed mechanism for the formation of Ni($\eta^2$-TEMPO)(SnBu\textsubscript{t}3)(CNBu\textsubscript{t}), 4.5.
TEMPO also reacts with non-radical metal centers in a similar fashion to form $\eta^1$ and $\eta^2$ TEMPO bound products$^{170,176-178}$ that will be discussed in detail in the next chapter. In this case it is also possible that TEMPO is reacting with a non-radical Ni compound, but ESR studies, peak broadening at low temperature in $^1$H NMR and isolation of Bu'Sn-O-SnBu' product from the photolyzed reaction mixture in the presence of oxygen, where oxygen is known to react with radicals, supports the radical mechanism shown in Scheme 4.4, and also the formation of Ni($\eta^2$-TEMPO)(SnBu',3)(CNBu'), shown in Scheme 4.5. Further study on the reactivity of complex 4.5 is currently underway in our lab.

In the Scheme 4.4, dimer dissociation of [Ni(SnBu',3)(CNBu')$_2$(CO)]$_2$, 4.4 into two $\bullet$Ni(SnBu',3)(CNBu')$_2$(CO) radicals has also been proposed. To test this mechanism two equivalents of TEMPO radical was added to the pure crystalline 4.4 dissolved in C$_6$D$_6$. Solution quickly decolorized to brownish yellow in ambient light. $^1$H NMR spectroscopy of the reaction mixture confirmed the presence of mixture of Ni($\eta^2$-TEMPO)(SnBu',3)(CNBu'), 4.3 and free isocyanide. The formation of Ni($\eta^2$-TEMPO)(SnBu',3)(CNBu'), 4.5 compound indicates that TEMPO is reacting with the same compound that is being generated in the solution of [Ni(SnBu',3)(CNBu')$_2$(CO)]$_2$, 4.4, which is also present in the photolysed solution of Ni(SnBu',3)$_2$(CNBu')$_2$(CO), 4.2. This seems to support the dissociation of 4.4 into the radical monomers, which then reacts with the TEMPO radical to form compound Ni($\eta^2$-TEMPO)(SnBu',3)(CNBu'), 4.5.

Though we haven’t successfully captured the proposed $\bullet$Ni(SnBu',3)(CNBu')$_2$(CO) radical as such using TEMPO radical we have got some evidence for the existence of the radicals in the solution in the form of radical polymerization catalysis.
Attempt to capture the other proposed radical $\bullet\text{SnBu}_3^i$ were partially successful. These radical are known to exist in planar geometry\textsuperscript{179} and Dr. Derek was able to isolate them as a polymer $[(\text{tBu}_3\text{Sn})(\text{PF}_4)]_\infty$ with trapped planar SnBu\textsuperscript{i3} in between PF\textsubscript{4}⁻ moiety.\textsuperscript{84} Efforts are still under way to capture both the proposed radicals of Ni and Sn from the photolyzed reaction mixture of compound 4.2.

**Sunlight triggered photo polymerization catalysis with Ni(SnBu\textsuperscript{i3})\textsubscript{2}(CNBu\textsuperscript{i})\textsubscript{2}(CO):**

Photo polymerization using transition metal complexes is well known in the literature.\textsuperscript{180–183} Ni complexes are also shown to catalyze photo polymerization.\textsuperscript{184–186} After being learned that compound 4.2 forms radical species photolytically, we performed some polymerization reactions. When 1% (w/w) solution of compound 4.2 in trimethyl propane ethoxylate triacrylate in the presence of triethanolamine, a cointitiator\textsuperscript{187} was exposed to either flood light lamp or sunlight, it rapidly, almost instantaneously polymerized to give the polytrimethyl propane ethoxylate triacrylate (TPET) (see Scheme 4.6). The presence of co-initiator is required as when we tried to perform the reaction without co-initiator we were not able to trigger the polymerization process. But, the polymerization of methylmethacrylate (MMA) with compound 4.2 is not as rapid as in the case of TPET monomer polymerization. Interestingly there was no characteristic purple coloration, that we observe when compound 4.2 undergoes photolysis. Probably there was no sufficient time to form dimeric compound 4.4. We are still in the process of understanding the mechanistics of the polymerization processes.
Scheme 4.6. Polymerization reactions with compound 4.2 in the presence of visible light.

When, benzophenone (BP), a well-known photo initiator of the polymerization reactions, was used in place of compound 4.3, the same monomer was polymerized in 30 minutes. This indicates the efficiency of compound 4.3 in polymerization of TPET. The process involved in the polymerization of monomer MMA using benzophenone and triethanol amine is reported in the literature by Merlin André and co. (see Scheme 4.7).\textsuperscript{187}
Based on the above shown mechanism we believe compound 4.2 is also playing a similar role as that of benzophenone. As mentioned before we did not observe the characteristic purple color of the dimer, this indicates that dimerization is not happening in the polymerization reaction. In such case there is a good chance of isolating the radical moiety as such. More research is required to understand the exact role of compound 4.2 in the above discussed polymerization reactions.

4.3. Summary and conclusions.

We have reported the successful synthesis of new heterobimetallic Ni-Sn compounds containing the sterically encumbered SnBu$_3^\prime$ ligand: Ni(SnBu$_3^\prime$)$_2$(CNBu$^\prime$)$_2$, 4.1, Ni(SnBu$_3^\prime$)$_2$(CNBu$^\prime$)$_2$(CO)$_2$, 4.2, Ni(SnBu$_3^\prime$)$_2$(CNBu$^\prime$)(CO)$_2$, 4.3, [Ni(SnBu$_3^\prime$)(CNBu$^\prime$)$_2$(CO)]$_2$, 4.4 and Ni($\eta^2$-TEMPO)(SnBu$^\prime$$_3$$^\prime$)(CNBu$^\prime$), 4.5. Compound Ni(SnBu$_3^\prime$)$_2$(CNBu$^\prime$)$_2$(CO), 4.2 is found to be photo active. Compound [Ni(SnBu$^\prime$$_3$$^\prime$)(CNBu$^\prime$)$_2$(CO)]$_2$, 4.4 has been isolated from the photolysis reaction of
Ni(SnBu\textsubscript{3})\textsubscript{2}(CNBu\textsubscript{3})\textsubscript{2}(CO), \textbf{4.2}. A radical mechanism has been proposed for the formation of compound \textbf{4.5}. ESR, NMR and polymerization studies support the formation of both nickel and tin centered radicals due to initial bond photolysis generating \( \textbullet \text{Ni(SnBu}_3\text{)}\textsubscript{2}(CNBu}_3\text{)}\textsubscript{2}(CO) \) and \( \textbullet \text{Sn}^\text{I}_3\text{Bu} \) as well as dissociation of the Ni-Ni bond in \([\text{Ni(SnBu}_3\text{)}(CNBu}_3\text{)}\textsubscript{2}(CO)]_2\), \textbf{4.5} yielding two \( \textbullet \text{Ni(SnBu}_3\text{)}(CNBu}_3\text{)}\textsubscript{2}(CO) \). Attempted trapping of \( \textbullet \text{Ni(SnBu}_3\text{)}(CNBu}_3\text{)}\textsubscript{2}(CO) \) or \( \textbullet \text{Ni(SnBu}_3\text{)}(CNBu}_3\text{)}\textsubscript{3} \) with the stable TEMPO radical afforded the 16e\textsuperscript{-} square planar Ni(\texteta\textsuperscript{2}-TEMPO)(SnBu\textsubscript{3})(CNBu\textsuperscript{3}), \textbf{4.5}.

Compound \textbf{4.2}, has shown some extraordinary catalytic activity. It catalyzed the monomer polytrimethyl propane ethoxylate triacrylate (TPET) just under 1 minute in the presence of visible light. This reaction also supports the proposed radical formation by compound \textbf{4.2} in the presence of light. Pd(Sn\textsuperscript{I}_3Bu\textsubscript{3})(\textsuperscript{t}BuNC)\textsubscript{3} and Pt(Sn\textsuperscript{I}_3Bu\textsubscript{3})(\textsuperscript{t}BuNC)\textsubscript{3} have also been synthesized in our laboratory, however neither of these precious metal analogues showed any signs of photo sensitivity, this displays the unusual reactivity of Ni-Sn complexes. Indeed, Ni-Sn bimetallic compounds do exhibit useful functionality and may yield future complexes which reduce the need for platinum, palladium and other precious metals. Further study of all reported compounds is under way.

\textbf{4.4. Experimental section.}

\textbf{General Data:} Unless otherwise stated, all reactions were carried out under an argon atmosphere in Schlenk flasks or an MBraun Unilab inert atmosphere glovebox. Reagent grade solvents were dried according to standard procedures and freshly distilled before use. Infrared spectra were recorded on a Nicolet 380 FT-IR spectrophotometer. Single crystal FTIR spectra were recorded on a Perkin Elmer Spectrum 400 using a Perkin
Elmer Universal ATR Sampling Accessory. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker 400 spectrometer operating at 399.993 MHz. UV-Vis spectra were recorded on a Varian Cary 100 Bio Spectrophotometer using screw-cap quartz cuvettes with 1 cm path lengths. Mass spectrometric measurements performed by direct–exposure probe using electron impact ionization (EI) were made on a VG 70S instrument at the University of South Carolina, Columbia, SC, and electrospray mass spectrometric measurements were obtained on a Bruker microTOF-Q II at the University of Miami. ESR spectra were recorded on a Bruker EMX ESR Spectrometer. Elemental analyses were performed by Columbia Analytical Services (Tucson, AZ). Photolysis was accomplished with a 150 W Sylvania flood lamp. Bis(1,5-cyclo-octadiene) nickel, Ni(COD)$_2$, was purchased from Strem Chemicals and used without further purification. Tri-iron dodecacarbonyl, Fe$_3$(CO)$_{12}$, was purchased from Aldrich and used without further purification. Tert-butyl isocyanide, CNBu$^t$, trityl hexafluorophosphate, Ph$_3$C$^+$PF$_6^-$, and TEMPO radical were purchased from Alfa Aesar and used without further purification. Argon, carbon monoxide, hydrogen, and carbon dioxide gasses were purchased from AirGas Supplies. $^{13}$CO was kindly provided to us by Dr. Carl Hoff and his group. Triethanolamine and Methylmethacrylate were provided by Dr. Francisco Raymo and his group. Tri-tert-butyl tin hydride, Bu$^t$$_3$SnH, was synthesized according to the published procedure. For the synthesis of compounds 4.3, see the reference.$^{84}$

**Synthesis of Ni(SnBu$^t$$_3$)$_2$(CNBu$^t$)$_3$, 4.1:** A 100 mg (0.36 mmol) sample of Ni(COD)$_2$ and 215 mg (0.74 mmol) of Bu$^t$$_3$SnH were loaded into a sidearm Schlenk flask equipped with a water cooled condenser. Under flow of argon, 50 mL of hexane was added by cannula and the mixture was stirred to dissolve all solids. 100 mg (1.25 mmol) of CNBu$^t$ was
added resulting in an immediate color change to pale yellow. The solution was stirred for 10 minutes and heated to a brief reflux, resulting in a color change to gold, before removing the volatiles in vacuo. The solid residue was redissolved in methylene chloride and passed down a column of silica gel. The solution was evacuated to dryness, redissolved in 4ml of a 1:1 methylene chloride/hexane solution, filtered into a glass vial, and placed in a -25 °C freezer in the drybox. Slow evaporation of solvent resulted in 239 mg (74% yield) of orange blocks of Ni(SnBu$_3$)$_2$(CNBu$_3$)$_3$. A similar yield can be obtained by room temperature reaction after approximately 12 hours. Spectral data for Ni(SnBu$_3$)$_2$(CNBu$_3$)$_3$, 4.1: $^1$H NMR (C$_6$D$_6$ in ppm): δ= 1.676 (s, $^3$J$_{Sn-H}$ = 47 Hz, 54 H, Sn-Bu$^t$), 1.191 (s, 27 H, CN-Bu$^t$). FTIR in hexane- $\nu_{CN}$ cm$^{-1}$: 2034 (s), 2062 (w). UV-Vis= 392 nm. Elemental analysis: Found = C 51.98 %, H 9.12 %, N 4.46 %; Calculated = C 52.75 %, H 9.19 %, N 4.73 %. EI Mass Spec shows major peak at 598 m/z which is Ni(SnBu$_3$)$_2$(CNBu$_3$)$_3$ - (SnBu$_3$)= 888 - 290= 598. Spectral pattern is consistent with the presence of 1 Ni and 1 Sn atom.

**Synthesis of Ni(SnBu$_3$)$_2$(CNBu$_3$)$_2$(CO), 4.2:** A 50 mg (0.0056 mmol) sample of Ni(SnBu$_3$)$_2$(CNBu$_3$)$_3$, 4.1, was loaded into a sidearm Schlenk flask. Under flow of argon, 30 mL of hexane was added by cannula and the mixture was stirred to dissolve all solids. The argon atmosphere was evacuated and replaced by carbon monoxide, CO. The stirred solution changed color from dark gold to light yellow over a period of several minutes. The solution was evacuated to dryness and the solid residue was redissolved in 2ml of a 1:1 methylene chloride/hexane solution, filtered into a glass vial, and placed in a -25 °C freezer in a drybox. Slow evaporation of solvent resulted in 38 mg (82% yield) of yellow blocks of Ni(SnBu$_3$)$_2$(CNBu$_3$)$_2$(CO), 4.2. A sample of $^{13}$CO- Ni(SnBu$_3$)$_2$(CNBu$_3$)$_2$(CO)
was prepared for $^{13}$C NMR by using $^{13}$CO in the same procedure. Spectral data for Ni(SnBu$_3^t$)$_2$(CNBu$_t^i$)$_2$(CO): $^1$H NMR (C$_6$D$_6$ in ppm): $\delta$ = 1.642 (s, 54H, Sn-Bu$_t^i$, $^3$J$_{Sn-H}$= 52 Hz), 1.037 (s, 18H, CN-Bu$^i$). $^{13}$C-CO NMR (toluene-$d_8$) = 197.27 ppm (s, 1C, $^2$J$_{Sn-C}$= 127 Hz at 25°C) and 197.40 ppm (s, 1C, $^2$J$_{Sn-H}$= 127 Hz at -80°C). FTIR in hexane- $\nu_{CN}$ cm$^{-1}$: 2092 (s), 2114 (m). $\nu_{CO}$ cm$^{-1}$: 1935 (s). Single Crystal FTIR- $\nu_{CN}$ cm$^{-1}$: 2094 (s), 2118 (m). $\nu_{CO}$ cm$^{-1}$: 1920 (s). UV-Vis= 375 nm. EI Mass Spec shows major peaks at 832, 775 and 747 m/z which are Ni(SnBu$_3^t$)$_2$(CNBu$_t^i$)$_2$(CO), Ni(SnBu$_3^t$)$_2$(CNBu$_t^i$)$_2$(CO) – Bu$^i$ = 832 – 57 = 775 and Ni(SnBu$_3^t$)$_2$(CNBu$_t^i$)$_2$(CO) – Bu$^i$ – CO = 832 – 57 – 28 = 747, respectively. Spectral pattern is consistent with the presence of 1 Ni and 2 Sn atoms.

**Synthesis of [Ni(SnBu$_3^t$)(CNBu$_t^i$)$_2$(CO)]$_2$, 4.4:** A 30 mg (0.0036 mmol) sample of compound Ni(Sn$^t$Bu$_3$)$_2$(tBuNC)$_2$(CO), 4.2 was loaded into a sidearm Schlenk flask. Under flow of argon, 30ml of hexane was added by cannula and the mixture was stirred to dissolve all solids. The flask was placed under slight vacuum and then irradiated with a 150W Sylvania flood lamp. The solution began to change color from light yellow to pink to deep purple over the period of one minute. The light was extinguished and the mixture was evacuated to dryness. The purple solid residue was redissolved in 2ml of diethyl ether, filtered into a glass vial, and placed in a -25 °C freezer in a drybox. Slow evaporation of solvent resulted in 6.25 mg (32 % yield) of purple blocks of [Ni(SnBu$_3^t$)(CNBu$_t^i$)$_2$(CO)]$_2$, 4.5. A sample of $^{13}$CO-[Ni(SnBu$_3^t$)(CNBu$_t^i$)$_2$(CO)]$_2$, 4.4 was prepared for $^{13}$C NMR by using $^{13}$CO-Ni(SnBu$_3^t$)$_2$(CNBu$_t^i$)$_2$(CO) in the same procedure. Spectral data for [Ni(SnBu$_3^t$)(CNBu$_t^i$)$_2$(CO)]$_2$: $^{13}$C-CO NMR (toluene-$d_8$ in ppm)= 205 (s, 1C, -80°C). Single Crystal FTIR- $\nu_{CN}$ cm$^{-1}$: 2096 (s), 2063 (m). $\nu_{CO}$ cm$^{-1}$: 1906 (s).
UV-Vis = 564 nm. Elemental analysis: Found = C 50.12 %, H 8.40 %, N 4.87 %; Calculated = C 50.81 %, H 8.35 %, N 5.15 %.

Synthesis of Ni(η²-TEMPO)(SnBu₃)(CNBu₄), **4.5**: A 30 mg (0.0036 mmol) sample of Ni(SnBu₃)₂(CNBu₄)₂(CO), **4.2** and 17 mg (0.0108 mmol) of TEMPO were loaded into a sidearm Schlenk flask. Under flow of argon, 30 ml of hexane was added by cannula and the mixture was stirred to dissolve all solids. The flask was placed under slight vacuum and then irradiated with a 150 W Sylvania flood lamp. The solution began to change color from light yellow to brownish yellow over the period of one minute. The light was extinguished and the volatiles were removed in vacuo. The brownish yellow solid residue was redissolved in 2 ml of diethyl ether, filtered into a glass vial, and placed in a -20 °C freezer in a drybox. Slow evaporation of solvent resulted in 11.5 mg (54 % yield) of brownish yellow blocks of Ni(η²-TEMPO)(SnBu₃)(CNBu₄), **4.5**. Spectral data for compound **4.5**: ¹H NMR (C₆D₆ in ppm): δ = 1.639 (s, ⁴J_Sn-H = 49 Hz, 27H, Sn-Bu), 0.954 (s, 9H, CN-Bu), 1.784 (s, 6H, (CH₃)₂-TEMPO), 1.213 (s, 6H, (CH₃)₂-TEMPO). FTIR in hexane- νCN cm⁻¹: 2086 (s).

**4.5. Crystallographic analysis.**

Single crystals of Ni(SnBu₃)₂(CNBu₄)₂(CO), **4.2**, [Ni(SnBu₃)(CNBu₄)₂(CO)]₂, **4.4**, and Ni(η²-TEMPO)(SnBu₃)(CNBu₄), **4.5**, suitable for diffraction analysis were grown by slow evaporation of concentrated diethyl ether solutions at –20 °C. The data crystal for Ni(SnBu₃)₂(CNBu₄)₃, **4.1** was grown by slow evaporation of a concentrated benzene solution at 5 °C. All data crystals were glued onto the end of a thin glass fiber and collected under ambient atmosphere at room temperature.
X-ray intensity data were measured using a Bruker SMART APEX2 CCD-based diffractometer using Mo Kα radiation (λ = 0.71073 Å). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm. Corrections for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares on F², by using the SHELXTL software package. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located from the difference map and refined with isotropic thermal parameters. Crystal data, data collection parameters, and results of the analyses are listed in Appendix C Tables C.1.

The compound Ni(SnBu₃)₂(CNBu)₃, 4.1 crystallized in the orthorhombic crystal system. The systematic absences in the intensity data were consistent with the unique space group Cmca. Ni(Sn'Bu₃)₂(BuNC)₃ crystallized with a molecule of benzene solvent in the unit cell.

The compound Ni(SnBu'₃)₂(CNBu')₂(CO), 4.2 crystallized in the orthorhombic crystal system. The systematic absences in the intensity data were consistent with the unique space group Pmmn. Ni(SnBu'₃)₂(CNBu')₂(CO) crystallized with a molecule of diethyl ether in the unit cell.

The compound [Ni(SnBu'₃)(CNBu')₂(CO)]₂, 4.4 crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the unique space group P2₁/n.
The compound Ni(η²-TEMPO)(SnBu³)(CNBu¹), 4.5 crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the unique space group $P2_1/c$. 

5.1 Background.

The stable tetraalkynitroxyl radical TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) is a well-known oxidation catalyst first synthesized by Lebedev and Kazarnowskii in 1960. Since then it has been not only used in a wide variety of industrial applications but also gained constant attention in academia as well. This solid, red-orange, sublimable heterocyclic radical is prepared by oxidation of the 2,2,6,6-tetramethylpiperidine, as shown in equation 5.1. Oxidation generally involves the use of hydrogen peroxide and tungsten based catalyst such as sodium-tungstate or phosphotungstic acid.

\[
\begin{align*}
\text{N} & \text{H} \\
\text{H}_2\text{O}_2, \text{Tungsten catalyst} \\
\text{2,2,6,6-tetramethylpiperidine} & \xrightarrow{\text{Oxidation}} \text{(2,2,6,6-tetramethylpiperin-1-yl)oxyl TEMPO}} \\
\end{align*}
\]

TEMPO is a stable persistent free radical. Stability of this radical is attributed to the steric crowding imparted by the four methyl groups around the oxygen radical center. It is commonly used as radical trap and also widely used in the fields of controlled radical polymerization initiation reactions, oxidation reactions, catalysis as well as a spin-probe/label in ESR studies to understand the environment of complex chemical and biochemical systems. TEMPO radical is a mild oxidation reagent and is a
widely used catalyst in selective oxidation of primary alcohols to aldehydes and carboxylic acid.\(^{216}\)

Though the chemistry of TEMPO as a reagent in the fields of catalysis, oxidation and in ESR studies is well investigated, its coordination chemistry is less studied. The coordination chemistry of this paramagnetic species with metal complexes is found to be interesting as it has been shown that the TEMPO ligand is able to coordinate through both \(\eta^1\) and \(\eta^2\) bonding motifs.\(^{170,175-177,195,196,217-225}\)

Recently a few attention-grabbing metal-TEMPO complexes exhibiting catalytic and non-catalytic reactions have been reported.\(^{193,194,226-230}\) Hayton and co-workers reported the 1e- oxidative homolysis of the Ni−NO bond and subsequent evolution of NO gas from the reaction of TEMPO with \([\text{Ni(NO)(bipy)}][\text{PF}_6]\) to form \([(\text{bipy})\text{Ni}(\eta^2\text{-TEMPO})][\text{PF}_6]\) complex.\(^{194}\) In this complex TEMPO makes a \(\eta^2\) coordination with Ni center. This is one of the few reported examples of NO dissociation upon oxidation of a metal nitrosyl complex. The transition metal /TEMPO catalytic systems are currently receiving increased attention for oxidation of alcohols. The \(\eta^1\) coordinated TEMPO to Lewis acids such as \(\text{FeCl}_3\) reported by Hayton and co-workers\(^{193}\) was shown to oxidize 9, 10-dihydroanthraquinone and also primary and secondary alcohols via a mechanism involving concerted proton-coupled electron transfer (CPET) in which proton from C-H bond of the substrate transfers to the nitrogen atom of the \(\eta^1\) coordinated TEMPO, much like the systems that we recently reported\(^{231}\) wherein a proton from the substrate transfers to the nitrogen atom of the \(\eta^2\) coordinated TEMPO ligand, subsequently forming \(\eta^1\) coordinated TEMPO containing N-H bond. Stahl and co-workers recently reported a (bpy) Cu\(^{1+}\) / TEMPO catalyst system with NMI (bpy =2,2′-bipyridine, TEMPO = 2,2,6,6-
tetramethylpiperidine-N-oxyl, NMI = N-methylimidazole) for the aerobic oxidation of alcohols to aldehydes and ketones.\textsuperscript{226,232} This catalyst system was shown to overcome nearly all the limitations of using Pd(II) as catalyst for the aerobic oxidation of alcohols and also found to be superior in catalytic activity at least an order of magnitude than the homogeneous Pd(II) catalysts upon which much attention has been focused. In another example, an Fe-TEMPO complex has been investigated for the oxidation of 9, 10-dihydroanthraquinone and also primary and secondary alcohols, with a mechanism involving H atom transfer from the organic substrate to the nitrogen atom of the $\eta^1$ coordinated TEMPO ligand.\textsuperscript{193} A recent report also shows the oxygen atom transfer capability of an Fe-TEMPO complex, which leads to formation of an Fe(III) oxo intermediate.\textsuperscript{230}

Very few metal-TEMPO compounds have been synthesized and studied among them there is only one literature reported example of an organometallic complex possessing exclusively TEMPO ligands, and this dinuclear lanthanide complex, [($\eta^1$-ONC$_5$H$_6$Me$_4$)$_2$Sm($\mu$-$\eta^1$-$\eta^2$-ONC$_5$H$_6$Me$_4$)]$_2$, contains $\eta^1$, $\eta^2$, and $\mu_2$-TEMPO ligands.\textsuperscript{149} Very few examples of Group 10 metal-TEMPO compounds with Ni and Pd were reported in the literature but there are no reported platinum-TEMPO compounds.

The inspiration for all the work that has been presented in this chapter comes from the unsuccessful attempt to trap the proposed photolytically generated Ni radical • Ni(SnBu$_3$)(CNBu$_3$)$_2$(CO) with TEMPO radical, that was discussed in chapter 4. There we isolated the 16$\epsilon^-$ square planar complex Ni($\eta^2$-TEMPO)(SnBu$_3$)(CNBu$^\prime$), \textit{4.5} with a distorted square planar structure, as shown in Figure 5.1.
**Figure 5.1.** An ORTEP showing the molecular structure of \( \text{Ni}(\eta^2\text{-TEMPO})(\text{SnBu}^t_3)(\text{CNBu}^t) \), 4.5 at 30 % thermal ellipsoid probability.

As it can be seen in Figure 5.1, the TEMPO ligand is coordinated to Ni center in an \( \eta^2 \) mode by inducing the elimination of both an isocyanide and CO ligand from tetrahedral \( \bullet \text{Ni(\text{SnBu}^t_3)(\text{NCBu}^t)_2(\text{CO})} \) to form \( \text{Ni}(\eta^2\text{-TEMPO})(\text{SnBu}^t_3)(\text{CNBu}^t) \), 4.5. This Ni-O-N metallacycle is remarkably stable to subsequent reactions with tert-butyl isocyanide, \( \text{Bu}^t\text{SnH} \), or carbon monoxide, even in great excess. The preferential binding of TEMPO radical with Ni center as 3e\(^-\) donating \( \eta^2 \)-TEMPO to form a 16e\(^-\) square planar geometry as opposed to the \( \eta^1 \)-O-TEMPO may be due to some thermodynamic preference as suggested in literature.\(^{233}\) All of the published Ni or Pd-TEMPO compounds are square planar and possess this \( \eta^2 \)-TEMPO ligand.\(^{170,177,194,195,234-236}\) As mentioned before the interesting complex 4.5 (see Figure 5.1) led us to start an excited chemistry exclusively with the TEMPO radical as ligand. Reported in this chapter is the synthesis and characterization of \( \text{Ni}(\eta^2\text{-TEMPO})_2 \), the first example of 16 e\(^-\) unsaturated mononuclear transition metal complex supported exclusively by the TEMPO ligand.
system and detailed reactivity study of Ni($\eta^2$-TEMPO)$_2$ with a wide variety of chemical reagents as depicted in Scheme 5.1, where the reactivity of the complex Ni($\eta^2$-TEMPO)$_2$ is assisted by the TEMPO ligand to transform from an $\eta2$ binding mode to an $\eta1$ binding mode. Here is also reported detailed computational mechanistic studies on the reactivity of Ni($\eta^2$-TEMPO)$_2$.

**Note:** All complex designations were suffixed with a $t$ or $c$ to distinguish between the two isomeric possibilities, *trans* and *cis* of Ni($\eta^2$-TEMPO)$_2$ and its complexes with various reagents.

**Scheme 5.1.** Products of Ni($\eta^2$-TEMPO)$_2$, 5.1$t$ with various reagents.
5.2 Computational methods.

Computational studies on all the compounds discussed in this chapter were performed in collaboration with Charles Edwin Webster, Department of Chemistry, University of Memphis. All computations were performed using the Gaussian09 software package.\textsuperscript{237} Gas-phase energies, optimized geometries, and unscaled harmonic vibrational frequencies were obtained using density functional theory (DFT).\textsuperscript{238} The hybrid B3LYP\textsuperscript{239,240} and pure PBEPBE\textsuperscript{241} functionals were used with default grid parameters (the PBEPBE functional will be referred to as PBE throughout the article, default pruned fine grids (75 radial shells, 302 angular points) for energies and default pruned course grids for gradients and Hessians (35 radial shells, 110 angular points). There are few qualitative differences between the structural and energetic PBE and B3LYP results. Therefore, all discussion in the text will refer to the PBE functional, and B3LYP data will be presented as Supporting Information. The basis set for nickel was the Hay and Wadt basis set and effective core potential (ECP) combination (LANL2DZ),\textsuperscript{242,243} as modified by Couty and Hall (Ni: 341/341/41),\textsuperscript{244} where the two outermost p functions have been replaced by a split of the optimized Ni 4p function, respectively. All C, N, O, and H atoms utilized the 6-31G(d') basis set,\textsuperscript{245,246} \{The 6-31G(d') basis set has the d polarization functions for C,N, and O taken from the 6-311G(d) basis set, instead of the original arbitrarily assigned value of 0.8 used in the 6-31G(d) basis set\}. Spherical harmonic d-functions were used throughout; i.e., there are five angular basis functions per d-function. The Hessian of the energy was computed at all stationary points to designate them as either minima or transition states (first-order saddle points). Zero-point energies (ZPE) and thermal enthalpy/free energy corrections
were computed at 1 atm and 298.15 K. Aqueous solvation energies were computed using the SMD model with standard cavity parameters for n-hexane. For the major reactants and products investigated, the computed singlet energies were generally lower by 8–10 kcal mol⁻¹ than corresponding geometry-optimized triplet states. Therefore, all reported mechanisms and relative energies refer to closed-shell singlet species (except for the free TEMPO radical).

Note: Mechanistic pathways of addition reactions of the various adducts (tert-butyl isocyanide, phenylacetylene, pyridine, acetylene, 1, 4-diacetylenebenzene, and trimethylsilyl acetylene, respectively) are discussed in the section: Kinetics, Thermodynamics, and Possible Isomerization Mechanisms.

5.3. Results and discussion.

Reaction of Ni(COD)₂ with TEMPO radical: When two equivalents of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl, TEMPO, radical were added to the hexane solution of one equivalent of (1,5-biscyclooctadiene) nickel, Ni(COD)₂, under argon atmosphere at room temperature, a color change from light orange to deep purple occurred over a period of approximately 10 minutes. The reaction was found to be almost instantaneous at 68 °C. Removal of volatiles in vacuo and crystallization of the solid residue from diethyl ether yielded purple colored block crystals of Ni(η²-TEMPO)₂, 5.1t in 78 % yield. The ORTEP diagram of complex 5.1t is shown in Figure 5.2. Complex 5.1t was characterized by ¹H NMR, mass spectroscopy, and X-ray diffraction analysis. Further crystallographic data can be found in Appendix D Table D.1. Complex 5.1t is highly air and moisture sensitive and crystallographic analysis data was collected at 100 K under flow of N₂ to avoid fast crystal decomposition.
Figure 5.2 An ORTEP of the molecular structure of Ni(η²-TEMPO)$_2$, 5.1t showing 50 % thermal ellipsoid probability. Selected bond distances (Å) and angles (°) are: Ni1-O1=1.8404(11), Ni1-N1=1.9360(10), N1-O1=1.4136(12), N1-C5=1.5240(16), N1-C5=1.5240(16), O1-Ni1-O1*=180.0, N1-Ni1-N1*=180.0, N1-Ni1-O1=43.88(4), N1-Ni1-O1*=136.12(4), N1-O1-Ni1=71.66(6), O1-N1-Ni1=64.47(6), C5-N1-O1=110.83(9), C5-N1-Ni1=119.99(8).

As you see in Figure 5.2 the nickel, nitrogen, and oxygen atoms all lie in the same plane creating a “bow-tie” type rectangular planar structure. In the solid state, the molecule lies about an inversion center and can be viewed to overall possess approximately $C_{2h}$ symmetry. The N-O bond distance is 1.4136(12) Å, which is longer than that found in free TEMPO [1.283(9) Å]. The N-Ni-O angle is 43.88(4)°. The geometry around the nitrogen atom is pyramidal [O1-N1-C5 = 110.83(9)°, O1-N1-C9 = 110.97(9)°, C5-N1-C9 = 116.59(9)°], and the Ni-N and Ni-O bond distances are short [Ni1-N1= 1.9360(10) Å, Ni1-O1=1.8404(11) Å]. These structural parameters are consistent with the bidentate monoanionic reduced TEMPO radical, which are known to act as neutral 3e$^-$ or anionic 4e$^-$ donors.$^{231,233}$ These observations conclude that the complex 5.1t is a 16e$^-$ unsaturated complex with a formal oxidation of $+2$ on the Ni metal center.
The DFT optimized structure of 5.1t was also found to possess $C_{2h}$ symmetry with structural parameters in reasonable agreement with those of the X-ray crystal structure (Table 5.1). The metal-ligand bond distances are slightly longer than experimental results (0.020 Å for $r_{\text{e-Ni-O}}$ and 0.044 Å for $r_{\text{e-Ni-N}}$). Typical of DFT results, intraligand bond distances ($\text{C-C}$, $\text{N-O TEMPO}$ bonds) are shorter than the X-ray crystal structure parameters of 5.1t.

<table>
<thead>
<tr>
<th>Ni($\eta^2$-TEMPO)$_2$</th>
<th>Theory 5.1t</th>
<th>Expt. 5.1t</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-O $r_e$</td>
<td>1.8870 Å</td>
<td>1.8404 Å</td>
</tr>
<tr>
<td>Ni-N $r_e$</td>
<td>1.9733 Å</td>
<td>1.9360 Å</td>
</tr>
<tr>
<td>N-O TEMPO $r_e$</td>
<td>1.3882 Å</td>
<td>1.4136 Å</td>
</tr>
<tr>
<td>N-Ni-O angle</td>
<td>41.89°</td>
<td>43.88°</td>
</tr>
<tr>
<td>O-N-C angle</td>
<td>112.13°</td>
<td>110.83°</td>
</tr>
<tr>
<td>C-N-C angle</td>
<td>116.46°</td>
<td>116.59°</td>
</tr>
<tr>
<td>free TEMPO ligand N-O $r_e$</td>
<td>1.2798 Å</td>
<td>1.283$^a$</td>
</tr>
<tr>
<td>free TEMPO anion N-O $r_e$</td>
<td>1.3966 Å</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.1. Geometric parameters of compound 5.1t using the PBE level of theory. $^a$ see the reference for the data.

The “cis” complex with C2 point group symmetry has also been theoretically determined which we are not able to isolate experimentally (5.1c; see Scheme 5.2). Scheme 5.3 also shows 2D illustrations and a simplified interpretation of the 2D structural skeleton of 5.1 that will be used throughout further schemes. In the cis structure, the Ni–O bond is shortened, while the Ni–N bond is elongated. For all substituted complexes (vide infra) as well as complex 5.1, only a single isomer has been isolated and characterized experimentally.
Scheme 5.2. Structures of 5.1t and 5.1c. (a) Hydrogen atoms omitted for clarity.

Two monoanionic $\eta^2$-TEMPO ligands can each serve as 4 e$^-$ donors giving the Ni atom a 16 electron configuration and a formal oxidation state of 2+ ($d^8$). Proton NMR study of this purple compound confirmed that the solid state $\eta^2$ binding mode persists in solution, displaying magnetically inequivalent methyl groups of the TEMPO as two distinct sets exist on differing sides of the N-O bonds. Even at extreme temperatures these acute Ni-O-N metallacycles appear to be stable as little change was found in the variable temperature $^1$H NMR spectrum from -80 °C to 90 °C in toluene-$d_8$. However, as stated earlier, 5.1t is extremely air and moisture sensitive and exposure to either one results in rapid decomposition to colorless products which are insoluble in all the tested solvents.
Reaction of \(\text{Ni}(\eta^2\text{-TEMPO})_2\), \(5.1t\), with \(\text{tert-Butyl Isocyanide, Bu}^t\text{NC}\): When one equivalent of \(\text{CNBu}^t\) was added to the hexane solution of \(5.1t\), a very quick color change from purple to dark red was observed. After which, the reaction mixture was stirred for 10 minutes and the volatiles were removed in vacuo. Crystallization of the solid residue from diethyl ether gave red colored blocks of \(\text{Ni}(\eta^2\text{-TEMPO})(\eta^1\text{-TEMPO})(\kappa^1\text{-CNBu}^t)\), \(5.2c\), in 90 % yield. X-ray crystallographic analysis of these crystals yielded the distorted square planar structure for \(5.2c\) shown in Figure 5.3. Further crystallographic information is provided in Appendix D, Table D.1.

![Figure 5.3](image)

**Figure 5.3.** An ORTEP showing the molecular structure of \(\text{Ni}(\eta^2\text{-TEMPO})(\eta^1\text{-TEMPO})(\kappa^1\text{-CNBu}^t)\), \(5.2c\) at 50 % thermal ellipsoid probability. Selected bond distances (Å) and angles (°) are: Ni1-O1=1.8796(7), Ni1-N1=1.8801(8), Ni1-O2=1.8378(7), Ni1-C1=1.8210(10), N1-O1=1.3851(10), N2-O2=1.4354(10), C1-N3=1.1544(13), N1-Ni1-O1=43.23(3), O1-Ni1-C1=153.50(4), C1-Ni1-O2=100.59(4), N1-Ni1-C1=110.27(4), O1-Ni1-O2=105.90(3), N2-O2-Ni1=115.02(5), Ni1-N1-O1=68.37(4), Ni1-O1-N1=68.40(4).

Compound \(5.2c\) was characterized by the combination of \(^1\text{H NMR, FTIR, mass spectroscopy, and X-ray crystallographic analysis. Compound}\ 5.2c\ is also highly air and moisture sensitive like \(5.1t\) and to avoid rapid crystal decomposition, crystallographic data was collected at 100 K under flow of \(\text{N}_2\) gas.
As is evident from Figure 5.3, compound 5.2c has a distorted square planar structure, but more importantly the complex has isomerized to a cis form and one of the \( \eta^2 \)-TEMPO ligands in the starting complex 5.1f has now become an \( \eta^1 \)-bonding ligand. The electron count around nickel remains at 16 with the CNBu\(^t\) and \( \eta^1 \)-TEMPO groups each, acting as two electron donors. The two TEMPO ligands remain reduced to their monoanionic TEMPO forms in 5.2c, giving a formal oxidation state of 2+ on the nickel metal center. The computed geometric parameters of cis-Ni(\( \eta^2 \)-TEMPO)(k\(^1\)-TEMPO)(\( \kappa^1 \)-CNBu\(^t\)), 5.2c are also in reasonable agreement with those of the X-ray crystal structure (Table 5.2).

<table>
<thead>
<tr>
<th>Ni(( \eta^2 )-TEMPO)(k(^1)-TEMPO)(( \kappa^1 )-CNBu(^t))</th>
<th>Theory 5.2c</th>
<th>Expt. 5.2c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-O ( \eta^1 )-TEMPO ( r_e )</td>
<td>1.8613 Å</td>
<td>1.8378 Å</td>
</tr>
<tr>
<td>Ni-O ( \eta^2 )-TEMPO ( r_e )</td>
<td>1.9423 Å</td>
<td>1.8796 Å</td>
</tr>
<tr>
<td>N-O ( \eta^1 )-TEMPO ( r_e )</td>
<td>1.3769 Å</td>
<td>1.4354 Å</td>
</tr>
<tr>
<td>N-O ( \eta^2 )-TEMPO ( r_e )</td>
<td>1.3648 Å</td>
<td>1.3851 Å</td>
</tr>
<tr>
<td>Ni-C ( \kappa^1 )-CNBu(^t) ( r_e )</td>
<td>1.7780 Å</td>
<td>1.8210 Å</td>
</tr>
</tbody>
</table>

**Table 5.2.** Geometric parameters of compound 5.2c using the PBE level of theory.

The companion trans structure (5.2t) has not been isolated. No square pyramidal Ni(\( \eta^2 \)-TEMPO)(k\(^1\)-TEMPO)(\( \kappa^1 \)-CNBu\(^t\)) complexes were located, which corresponds to the hypothesis of steric crowding from the incoming CNBu\(^t\) ligand,\(^{231}\) and all the computations were collapsed to either 5.2c or 5.2t. To better understand these steric, space filling models are also prepared (see Figure 5.4). As is evident from the Figure 5.4 the axial sites above and below the N1-O1-N1*-O1* square plane are simply not accessible as the bulky methyl groups are shielding the Ni atom (shown in green) completely. However, the Ni atom can be accessible from equatorial position as the shielding from methyl groups is not that effective in the equatorial position. The
mechanistic pathway for the formation of \textbf{5.2c} is discussed in the section: Kinetics, Thermodynamics, and Selectivity of Substituted Species.

![Diagram of Ni(\text{\(\eta^2\)-TEMPO})\textsubscript{2}, 5.1t seen from (a) down the \(C_2\) (Z) axis above the square plane and (b) down the XY plane perpendicular to the \(C_2\) (Z) axis. Atomic dimensions are the van der Waals radii. Nickel is shown in green, oxygen in red, nitrogen in blue, carbon in gray, and hydrogen in white.](image)

**Figure 5.4.** Space-filling model of Ni(\text{\(\eta^2\)-TEMPO})\textsubscript{2}, 5.1t seen from (a) down the \(C_2\) (Z) axis above the square plane and (b) down the XY plane perpendicular to the \(C_2\) (Z) axis. Atomic dimensions are the van der Waals radii. Nickel is shown in green, oxygen in red, nitrogen in blue, carbon in gray, and hydrogen in white.

The \(^1\text{H}\) NMR spectrum of complex \textbf{5.2c} at room temperature consists of a series of broad overlapping peaks indicative of some dynamical processes occurring in solution. Variable temperature \(^1\text{H}\) NMR spectra in the range of 25\(^\circ\) to 90 \(^\circ\)C resulted in some sharpening of the peaks, however, as shown in Appendix D Figure D.1, peak broadening stayed even at the high temperature of 90 \(^\circ\)C. Above 90 \(^\circ\)C the complex decomposes.
Similar fluxional processes were observed in the $^1\text{H}$ NMR spectra of complex 5.9t, a complex of 5.1t with pyridine, that will be discussed later in this chapter. These fluxional processes appear to be due to equilibrium formation in solution due to weak bonding interactions between the reagents. Though it is clear that some exchange occurs within this molecule, the exact nature of the fluxional process remains unresolved presently.

**Reaction of Ni($\eta^2$-TEMPO)$_2$, 5.1t with Phenylacetylene, HC≡CPh:** Nickel complexes are known to catalytically activate C≡C bonds.$^{248,249}$ Keeping this in mind, we wanted to see how complex 5.1t reacts with the alkynes, as alkynes are well known to coordinate with the metal centers in two different ways, “side-on” $\eta^2$ or “end-on” $k^1(\eta^1)$. When 1 eq of phenylacetylene was added to a hexane solution of Ni($\eta^2$-TEMPO)$_2$, 5.1t a color change from purple to red occurred over a period of less than 1 hour. The reaction is almost instantaneous at 68 °C reflux. Removal of volatiles in vacuo and crystallization from diethyl ether resulted in light red bars of Ni($\eta^2$-TEMPO)(κ$^1$-TEMPOH)(κ$^1$-CCPh), 5.3c in 73 % yield. X-ray crystallographic analysis generated distorted square planar structure for 5.3c, as shown in Figure 5.5. Further crystallographic information is provided in Appendix D Table D.2. This complex was characterized by the combination of $^1\text{H}$ NMR, FTIR, mass spectroscopy, and X-ray crystallographic analysis. Complex 5.3c is moderately air and moisture sensitive and crystallographic data was collected at 100 K under flow of N$_2$ to avoid crystal decomposition.
Figure 5.5. An ORTEP showing the molecular of Ni(η²-TEMPO)(κ¹-TEMPOH)(κ¹-CCPh), 5.3c at 50% thermal ellipsoid probability. Selected bond distances (Å) and angles (°) are: Ni1-O1=1.8868(7), Ni1-N1=1.8608(8), Ni1-O2=1.8927(7), Ni1-C1=1.8648(10), N1-O1=1.3869(10), N2-O2=1.4048(10), C1-C2=1.2205(14), N1-Ni1-O1=43.43(3), O1-N1-C22=112.57(7), O1-N1-C26=112.92(7), C22-N1-C26=118.21(7), O2-N2-C13=110.87(7), O2-N2-C17=110.52(7), C13-N2-C17=118.06(7).

As evident from Figure 5.5, the phenylacetylene reagent did not bind to the Ni atom in side-on, η² mode but has rather been transformed into an “end-on” phenylacetylide group, k¹-C≡CPh. This reaction is an unusual example of sp hybridized C-H bond activation (~130 kcal/mol)²⁵⁰,²⁵¹ by a group 10 organometallic complex which is somewhat uncommon for that group. Very few complexes of the type Ni(k¹-CCPh) were reported in the literature and nearly all of them were synthesized using salt metathesis or other intricate procedures.²⁵²–²⁵⁶ Even most of the published Pt and Pd phenylacetylides require several step syntheses or intense UV photolysis.²⁵⁶,²⁵⁶–²⁶¹ The facile room temperature activation of a sp hybridized C-H bond and formation of an η¹-CCPh phenylacetylide was unusual, surprising, and shows unexpected chemical reactivity of the non-precious nickel metal.
Based on the X-ray crystal structure data collected at 100 K, the position of the H atom on the atom N2 that was coming from PhCC-H was located and refined satisfactorily. Further, it was also monitored by $^1$H NMR which showed a peak at 7.62 ppm with an appropriate integration of one H. The location of the H atom on nitrogen was further established by 2D [$^1$H, $^{15}$N] HSQC NMR which showed a direct correlation between atoms N2 and H1 with an observed $^1J(^{15}$N-H) coupling constant of 78 Hz, see Appendix D Figure D.2.

When the complex 5.1t was reacted with phenylacetylene-$d_1$ (99 %), it gave the complex 5.3c-$d_1$ and its $^1$H NMR spectrum showed all the appropriate resonances for 5.3c, with the exception of the peak at 7.62 ppm which was almost totally absent (see Appendix D Figure D.3). Compound 5.3c remains a 16 electron Ni(II) complex, with the $\kappa^1$-TEMPOH ligand acting as a 2 electron donor neutral ligand. The $\kappa^1$-TEMPOH ligand is now protonated at nitrogen and can be viewed as a monoanionic TEMPO, as in the tautomeric form of free TEMPOH (where H is bonded to O). This type of bonding mode for $\kappa^1$-TEMPOH is rather rare in transition metal complexes and there are only few other crystallographically characterized examples. Interestingly, the structure of 5.3c is also cis-disposed compared to the unsubstituted complex 5.1t. Computed geometries of 5.3c (see Table 5.3) show excellent structural agreement with the experimental crystal structure due to an elongated Ni–O $\eta^2$- TEMPO bond and a much shorter Ni–N $\eta^2$-TEMPO optimized bond length. In free TEMPO, the N–O bond length is 1.283(9) Å,19 while, once coordinated, the N–O bond length is elongated (by more than ~0.1 Å), which is expected for a reduced monoanionic ligand with a pyramidal geometry about the nitroxy N atom. Interestingly, in the compounds 5.2c and 5.3c (along with the other
following complexes), the side-bound $\eta^2$-TEMPO always has a shorter N–O bond than the end-bound $k^1$-TEMPO. These results suggest the $k^1$-TEMPO ligand is more anionic than the $\eta^2$-TEMPO ligand, possibly depopulating a N–O antibonding orbital in the $\eta^2$ case, with the net result that the Ni center donates more electrons to $\eta^1$-TEMPO.

<table>
<thead>
<tr>
<th>Ni(\eta^2\text{-TEMPO})(\kappa^1\text{-TEMPOH})(\kappa^1\text{-CCPh})</th>
<th>Theory</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-O $\kappa^1$-TEMPOH $r_e$ (Å)</td>
<td>1.9242</td>
<td>1.8927</td>
</tr>
<tr>
<td>Ni-O $\eta^2$-TEMPO $r_e$ (Å)</td>
<td>1.9402</td>
<td>1.8868</td>
</tr>
<tr>
<td>Ni-N $\eta^2$-TEMPO $r_e$ (Å)</td>
<td>1.8914</td>
<td>1.8608</td>
</tr>
<tr>
<td>N-O $\kappa^1$-TEMPOH $r_e$ (Å)</td>
<td>1.3888</td>
<td>1.4048</td>
</tr>
<tr>
<td>N-O $\eta^2$-TEMPO $r_e$ (Å)</td>
<td>1.3567</td>
<td>1.3869</td>
</tr>
<tr>
<td>N-H $\kappa^1$-TEMPOH $r_e$ (Å)</td>
<td>1.0557</td>
<td>n.d.</td>
</tr>
<tr>
<td>Ni-C CCPh $r_e$ (Å)</td>
<td>1.8385</td>
<td>1.8648</td>
</tr>
<tr>
<td>C-C CCPh $r_e$ (Å)</td>
<td>1.2535</td>
<td>1.2205</td>
</tr>
</tbody>
</table>

**Table 5.3.** Geometric parameters of compound 5.3c using the PBE level of theory.

In order to find out any observable differences in the reaction of 5.1t in the abstraction of H/D, a 1:1 mixture of PhCCH and PhCCD in toluene-$d_8$ solvent was prepared and the reaction was monitored by $^1$H NMR at room temperature. Integration of the resonances of the product showed approximately a 50:50 ratio for the formation of products 5.3c and 5.3c-$d_1$, indicating that there was no noticeable difference between the rates of formation of the products 5.3c and 5.3c-$d_1$. The reaction was also monitored by $^2$H{$^1$H} NMR using toluene solvent, and the appropriate integration of the singlet deuterium resonances in the starting PhCCD verses the product N-D resonances in 5.3c-$d_1$ also showed approximately a 50:50 ratio. This reaction was also monitored using a 6:6 mixture of PhCCH and PhCCD, to give the same product ratio (see Appendix D Figure D.4 and D.5). This result is interpreted as being consistent with an addition mechanism that does not involve deprotonation of the C–H or C–D bond as the rate determining step,
in keeping with the computational results discussed in the section ‘Kinetics Thermodynamics, and Selectivity of Substituted Species’.

**Reaction of 5.1t with Trimethylsilyl acetylene, Me₃SiC≡CH and Triisopropylsilyl acetylene, ¹Pr₃SiC≡CH:** Reactivity study of 5.1t with alkynes was further extended to Me₃SiCCH and ¹Pr₃SiCCH. These two silyl acetylenes are similar in structure with the only difference of steric crowdedness around the Si atom imparted by Me₃ groups in Me₃SiCCH (less bulky) and ¹Pr₃ in ¹Pr₃SiCCH (more bulky).

When one equivalent of Me₃SiCCH was added to a room temperature hexane solution of 5.1t, a color change from purple to light red occurred over a period of less than one hour. The reaction was almost instantaneous at 68 °C. The volatiles were removed in vacuo and the crystallization of solid residue in diethyl ether afforded bright red blocks of Ni(η²-TEMPO)(κ¹-TEPOH)(κ¹-CSiMe₃), 5.4c in 79 % yield. X-ray crystallographic analysis yielded the distorted square planar structure of shown in Figure 5.6. Further crystallographic information is provided in Appendix D Table D.2. This complex was characterized by ¹H NMR, FTIR, mass spectroscopy, and X-ray crystallographic analysis. Complex 5.4c is stable in air compared to the previous compounds, and X-ray crystallographic data was collected successfully at ambient conditions with no apparent decomposition in the crystal.
Figure 5.6. An ORTEP showing the molecular structure of Ni(η²-TEMPO)(κ¹-TEMPOH)(κ¹-CCSiMe₃), **5.4c** at 30 % thermal ellipsoid probability. Selected bond distances and angles are as follows: Ni1−C1 = 1.860(3) Å, Ni1−N1 = 1.862(2) Å, Ni1−O1 =1.8701(17) Å, Ni1−O2 = 1.8871(15) Å, C1−C2 = 1.223(4) Å, N1−O1 = 1.388(2) Å, N2−O2 = 1.402(2) Å, and Si1−C2 = 1.806(3) Å;C1−Ni1−N1 = 111.84(9)°, C1−Ni1−O1 = 155.47(9)°, N1−Ni1−O1 = 43.66(7)°, C1−Ni1−O2 = 99.95(9)°, N1−Ni1−O2 =148.21(7)°, O1−Ni1−O2 = 104.56(7)°, N1−O1−Ni1 = 67.86(11)°,N2−O2−Ni1 = 117.07(12)°, O1−N1−Ni1 = 68.49(11)°.

As seen in Figure 5.6, the crystal structure of the compound **5.4c** is similar to compound **5.3c**. The alkyne hydrogen from C-H of Me₃SiCCH was again abstracted and bonded to N2. Its position was identified and refined using X-ray crystallographic analysis and further confirmed by ¹H NMR. The FTIR spectrum shows a single C≡C stretch at lower frequency 2009 cm⁻¹ in hexane, compared to other Ni-TEMPO-acetylene derivatives which can be attributed to the electropositive silicon atom donating electron density into the triple bond and weakening it.
Though Me$_3$SiCCH reacts with 5.1t, $^3$Pr$_3$SiCCH does not react with 5.1t at all even under refluxing conditions to yield the expected product Ni($\eta^2$-TEMPO)(κ$^1$-TEMPOH)(κ$^1$-CCSi$^3$Pr$_3$) similar to 5.4c.

**Reaction with symmetrical alkynes and dimerization reactions:** After exploring the reaction of Ni($\eta^2$-TEMPO)$_2$, 5.1t with substituted alkynes where sp hybridized C-H bond was successfully activated to generate monomeric Ni-TEMPO products, the reactivity of 5.1t has been extended to symmetrical alkynes with two sp hybridized C-H bonds to check the possibility of synthesizing bridged Ni-TEMPO products where two Ni metal atoms will be bridged with the carbon-carbon bonds; these type of compounds can be used for charge transfer reactions and also have the potential to further develop into molecular wires. The first symmetrical alkyne that has been tried is acetylene.

**Reaction of Ni($\eta^2$-TEMPO)$_2$ with Acetylene Gas, HC≡CH:** When acetylene gas was purged through a hexane solution of 5.1t, a color change from purple to light red occurred over the period of one hour. The reaction was found to be almost instantaneous at 68 °C reflux. Removal of volatiles in vacuo followed by crystallization from diethyl ether afforded bright red blocks of Ni($\eta^2$-TEMPO)(κ$^1$-TEMPOH)(κ$^1$-CCH), 5.5c in 74 % yield. X-ray crystallographic analysis yielded the distorted square planar structure for the complex, 5.5c, shown in Figure 5.7. Further crystallographic information is provided in Appendix D Table D.2.
Figure 5.7. An ORTEP showing the molecular structure of Ni(η²-TEMPO)(κ¹-TEMPOH)(κ¹-CCH). 5.5c at 30 % thermal ellipsoid probability. Selected bond distances and angles are as follows: Ni1–O1 = 1.8614(12) Å, Ni1–C1 = 1.8708(15) Å, Ni1–N1 = 1.8750(12) Å, Ni1–O2 = 1.8878(10) Å, N1–O1 = 1.3877(15) Å, N2–O2 = 1.4011(14) Å, and C1–C2 = 1.195(2) Å; O1–Ni1–C1 = 157.23(5)°, O1–Ni1–N1 = 43.60(5)°, C1–Ni1–N1 = 113.66(6)°, O1–Ni1–O2 = 103.17(4)°, C1–Ni1–O2 = 99.59(5), N1–Ni1–O2 = 146.73(5)°, N1–O1–Ni1 = 68.72(7)°, N2–O2–Ni1 = 117.22(8)°, N2–O2–Ni1 = 117.22(8)°, and O1–N1–Ni1 = 67.68(7)°.

Compound 5.5c was characterized by ¹H NMR, FTIR, mass spectroscopy, and X-ray crystallographic analysis. The structure of compound is similar to 5.3c. Interestingly, only one C-H bond of HC≡CH was activated and again the position of hydrogen on N2 was successfully identified and refined using X-ray crystallographic analysis and its presence was further confirmed by ¹H NMR which showed the usual N-H resonance at 7.64 ppm. A crystallographic database search provided very few examples of “end-on” group 10 metal-CCH compounds, all of which were synthesized by salt elimination.²⁵⁶,²⁶⁷–²⁶⁹ We believe 5.5c to be the first structurally characterized example of acetylene C-H bond activation to yield a Ni-(k¹-CCH) compound. The FTIR stretch for the C≡C bond is now found at 1933 cm⁻¹ in hexane, significantly lower in energy than
any of the other Ni-acetylene compounds above. Literature values for these terminal acetyldes are also around 1930 cm$^{-1}$.\textsuperscript{270}

As seen in Figure 5.8, there is another terminal alkyne C-H bond available, and it could be considered that the reaction of \textbf{5.1t} with acetylene gas would also yield a product, where another molecule of \textbf{5.1t} reacts with \textbf{5.5c}, to give compound \textbf{5.6cc} as shown in Scheme 5.4. However, we did not obtain this product. This is explainable in terms of steric crowding and repulsion between the approaching TEMPO moieties that is limiting the accessibility to the already coordinated acetylide ligand. Another possibility could be that the pKa for the second proton in acetylene is much higher (more basic). Though \textbf{5.6cc} could not be synthesized, we were able to obtain and study the computational structures (Scheme 5.3).

Scheme 5.3. Structures of \textbf{5.6cc}. a) Computational structure (hydrogens omitted for clarity), b) Line drawing.

Unlike compound \textbf{5.8cc} (discussed below), one of the Ni(TEMPO)(TEMPOH) moieties in \textbf{5.6cc} is twisted 90 degrees (see computational structure) from the other to
relieve the pronounced steric repulsion. Compound \textbf{5.6cc} is not thermodynamically favored over its constituent monomers. The dimerization thermodynamics can be computed in two ways, via addition of two equivalents of \textbf{5.1t} and HCCH, or via the reaction of \textbf{5.1t} and \textbf{5.5c}. The computed solution-phase free energy of reaction is quite large and positive for both cases: +5.4 and +9.2 kcal mol\(^{-1}\) (see Table 5.4 and Table D.4 in Appendix D).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(\Delta G_{\text{soln}}) (kcal mol(^{-1}))</th>
<th>(\Delta \Delta G_{\text{soln}}) (kcal mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 equiv \textbf{5.1t} + HCCH (\rightarrow) \textbf{5.6cc}</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>\textbf{5.5c} + \textbf{5.1t} (\rightarrow) \textbf{5.6cc}</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td>\textbf{5.8cc} ({}^{a})</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>\textbf{5.8ct}</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>\textbf{5.8tt}</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td>2 equiv \textbf{5.1t} + HCCPhCCH (\rightarrow) \textbf{5.8cc}</td>
<td>-5.2</td>
<td></td>
</tr>
<tr>
<td>\textbf{5.7c} + \textbf{5.1t} (\rightarrow) \textbf{5.8cc}</td>
<td>-0.8</td>
<td></td>
</tr>
</tbody>
</table>

\({}^{a}\)Isomer \textbf{5.8cc} is arbitrarily set to 0.0 kcal mol\(^{-1}\).

\textbf{Table 5.4.} Solution-Phase reaction free energies (\(\Delta G_{\text{soln}}\) in kcal mol\(^{-1}\)) of bimetallic complexes and the relative free energies (\(\Delta \Delta G_{\text{soln}}\) in kcal mol\(^{-1}\)) of Isomers of \textbf{5.8cc}.

\textbf{Reaction of 5.1t with 1, 4-Diethynylbenzene, HC\(\equiv\)C(C\(_6\)H\(_4\))C\(\equiv\)CH:} After learning that \textbf{5.1t} activates only one C-H bond of small acetylene molecule work has been extended to other interesting aromatic alkyne 1, 4-diethynylbenzene to further explore the efforts to link two Ni(TEMPO)\(_2\) molecules. The alkyne, 1, 4-diethynylbenzene is an interesting
aromatic compound consisting of a benzene ring substituted with two acetylene groups positioned *para* to each other, shown in Figure 5.8.

![Figure 5.8](image)

**Figure 5.8.** Line drawing of 1,4-diethynylbenzene.

When 1 eq of 1,4-diethynylbenzene was added to a hexane solution of 5.1t, a color change from purple to auburn red occurred over a period of 1 hour. The reaction is nearly instantaneous at 68 °C. Removal of volatiles in *vacuo* and crystallization of solid residues from diethyl ether resulted in cherry red bars of Ni(η^2^-TEMPO)(κ^1^-TEMPOH)(κ^1^-CC[C₆H₄]CCH), 5.7c in 71% yield. X-ray crystallographic analysis yielded the anticipated distorted square planar structure as shown in Figure 5.10. Further crystallographic information is provided in Appendix D Table D.2. Compound 5.7c was characterized by ^1^H NMR, FTIR, mass spectroscopy, and X-ray crystallographic analysis. Complex 5.7c is remarkably stable in air compared to the preceding compounds.

Similar to the compounds 5.3c, 5.4c and 5.5c, there is only one acetylide group bonded to the Ni center in 5.7c (see Figure 5.9). Again, the position of the H atom bonded to N2 atom was located and refined satisfactorily from the data collected using X-ray crystallographic analysis. ^1^H NMR spectroscopy again shows evidence for the N-H at 7.65 ppm with exact integration of one H, as well as also showing the second acetylene
hydrogen intact at 3.26 ppm in C₆D₆. FTIR spectroscopy gives the broad hump suggestive of a N-H stretch around 3200 cm⁻¹.

**Figure 5.9.** An ORTEP showing the molecular structure of Ni(η²-TEMPO)(κ¹-TEMPOH)(κ¹-CC[C₆H₄]CCH), 5.7c at 30 % thermal ellipsoid probability. Selected bond distances (Å) and angles (°) are: Ni1-N1=1.8605(9), Ni1-C1=1.8748(12), Ni1-O2=1.8890(8), Ni1-O1=1.8909(8), N1-O1=1.3840(11), N2-O2=1.4027(12), C1-C2=1.2146(17), N1-Ni1-C1=111.22(4), N1-Ni1-O2=149.15(4), C1-Ni1-O2=99.43(4), N1-Ni1-O1=43.29(3), C1-Ni1-O1=154.51(4), O2-Ni1-O1=106.02(3), O1-N1-Ni1=69.52(5), N1-O1-Ni1=67.19(5), N2-O2-Ni1=116.72(6).

The crystal structure of 5.7c is similar to that of 5.3c, except now there is a free dangling alkyne hydrogen available for further reaction with another molecule of 5.1t. Assuming there is enough steric space to allow approach of 5.1t, this reaction should yield the dimeric product Ni(η²-TEMPO)(κ¹-TEMPOH)[κ¹-κ¹-CC(C₆H₄)CC]Ni(η²-TE
MPO)(κ¹-TEMPOH), where two molecules of Ni(η²-TEMPO)₂, 5.1t are bridged by the dialkyne HC≡C(C₆H₄)C≡CH.
As expected, when the reaction was carried out with two equivalents of \textbf{5.1t} and one equivalent of 1,4-diethynylbenzne we did indeed obtain the complex \( \text{Ni}(\eta^2\text{-TEMPO})(\kappa^1\text{-TEMPOH})(\kappa^1\text{-CC(C}_6\text{H}_4\text{CC})\text{Ni}(\eta^2\text{-TEMPO})(\kappa^1\text{-TEMPOH}), \textbf{5.8cc} \) in 80 \% yield where now two \( \text{Ni}(\eta^2\text{-TEMPO})(\kappa^1\text{-TEMPOH}) \) groups are linked by a diacetylidebenzene group, see Figure 5.10. Consequently compound \textbf{5.8cc} is also synthesized by the reaction of compound \textbf{5.7c} with one equivalent of \textbf{5.1t} at room temperature.

**Figure 5.10.** An ORTEP of the molecular structure of \( \text{Ni}(\eta^2\text{-TEMPO})(\kappa^1\text{-TEMPOH})(\kappa^1\text{-CC(C}_6\text{H}_4\text{CC})\text{Ni}(\eta^2\text{-TEMPO})(\kappa^1\text{-TEMPOH}), \textbf{5.8cc} \), showing 50 \% thermal ellipsoid probability. Selected bond distances (Å) and angles (°) are: Ni1-N1=1.8685(16), Ni1-C1=1.8582(19), Ni1-O2=1.8918(13), Ni1-O1=1.8795(13), N1-O1=1.3912(19), N2-O2=1.4114(19), C1-C2=1.217(3), N1-Ni1-C1=112.20(7), N1-Ni1-O2=149.13(6), C1-Ni1-O2=98.67(7), N1-Ni1-O1=43.58(6), C1-Ni1-O1=155.76(7), O2-Ni1-O1=105.56(5), O1-N1-Ni1=68.63(8), N1-O1-Ni1=67.79(8), N2-O2-Ni1=117.19(10).
Compound 5.8cc is characterized by the combination of \(^1\)H NMR, FTIR, mass spectroscopy, and X-ray crystallographic analysis. Compound 5.8cc is highly stable and can be handled in air unlike previous compounds. Again positions of both the protons bonded to N2 and N2* as shown in Figure 5.10 were identified and refined satisfactorily using X-ray crystallographic analysis. Their presence was further confirmed by the \(^1\)H NMR, which showed a peak at 7.66 ppm in C\(_6\)D\(_6\) solvent with an appropriate integration of two H. As you see in Figure 5.10, the compound 5.8cc is bridged by an aromatic link and these types of compounds are known to exhibit charge transfer in the near IR region.\(^{271}\) Further experiments on this compound to study its charge transfer capabilities are underway in our lab.

While we have not attempted to model dimerization reaction kinetics or mechanisms, the various isomeric possibilities of 5.8 have been explored. Three possibilities arise, the cis-cis, cis-trans, or trans-trans isomers, which are labeled 5.8cc, 5.8ct, and 5.8tt, respectively (Scheme 5.4).

![Diagram](image)

**Scheme 5.4.** Possible isomers of compound 5.8.
From Table 5.4, the **5.8cc** isomer is lowest in solution phase free energy by 4.1 and 9.1 kcal mol\(^{-1}\) compared to the **5.8ct** and **5.8tt** isomers, respectively, which is in agreement with the experimental characterization of **5.8cc**. The results from Table 5.4 also confirm that both experimental procedures for producing complex **5.8cc**, addition of two equivalents of compound **5.1t** to HCC(C\(_6\)H\(_4\))CCH as well as addition of compound **5.7c** to compound **5.1t**, have thermochemically favorable reaction free energies.

**Reaction of Ni(\(\eta^2\)-TEMPO)\(_2\), 5.1t with Pyridine:** Except the compound **5.2c**, all the products discussed so far are the result of reaction between **5.1t** and 1e\(^{-}\) donating reagents. Study has been extended to 2e\(^{-}\) donating ligands to further explore the reactivity of **5.1t**. At room temperature when 2e\(^{-}\) donating ligand, pyridine, was added to the hexane solution of compound **5.1t**, an immediate color change from purple to dark brown/yellow occurred. During removal of volatiles in *vacuo* a partial regeneration of purple color on the Schlenk flask walls was observed. Recrystallization of solid residues from diethyl ether with a drop of pyridine afforded dark brown blocks of Ni(\(\eta^2\)-TEMPO)(\(k^1\)-TEMPO)(\(\kappa^1\)-NC\(_5\)H\(_5\)), **5.9t** in 95 % yield. X-ray crystallographic analysis yielded the expected distorted square planar structure as shown in Figure 5.11. Further crystallographic information is provided in Appendix D Table D.3. Compound **5.9t** was characterized by \(^1\)H NMR, mass spectroscopy, and X-ray crystallographic analysis. Compound **5.9t** is highly air, moisture and temperature sensitive, and X-ray crystallographic data was collected at 100K under flow of N\(_2\) to avoid crystal decomposition.
Figure 5.11. An ORTEP of the molecular structure of \( \text{Ni}(\eta^2\text{-TEMPO})(k^1\text{-TEMPO})(\kappa^1\text{-NC}_5\text{H}_5) \), 5.9\text{t} showing 50 % thermal ellipsoid probability. Selected bond distances (Å) and angles (°) are: Ni1-O2=1.8407(10), Ni1-N1=1.9063(12), Ni1-O1=1.8690(10), Ni1-N3=1.9032(12), N1-O1=1.3946(15), N2-O2 =1.4308(15), O2-Ni1-O1=148.36(4), O2-Ni1-N3=108.55(5), O1-Ni1-N3=103.08(5), O2-Ni1-N1=105.04(5), O1-Ni1-N1=43.34(5), N3-Ni1-N1=146.23(5), O1-Ni1-N1=66.91(6), O1-N1-C14 =112.02(11), O1-N1-C10=112.71(11), O2-N2-C23=107.48(10).

A close look at the structure of compound 5.9\text{t} reveals the unusual orientation of the TEMPO ligands. As you can see in the Figure 5.12, the oxygen atoms are not cis but rather trans as in the starting compound 5.1\text{t}. This kind of orientation had been expected for all the products, with the simple opening of one metallacycle and addition of a new ligand without flipping to yield cis oxygen atoms. Compound 5.9\text{t} also contains an \( k^1\)-TEMPO ligand, and the orientation of the pyridine ring is coplanar with the distorted square planar geometry around nickel. Unlike the previous substituted complexes, the pyridine adduct is the only one observed in this study that retains the trans-disposition of the original complex.
As indicated earlier, compound 5.9t appears to exist in equilibrium between starting material 5.1t and its pyridine adduct. Removal of the solvent from the reaction mixture under reduced pressure always resulted in regeneration of some starting material 5.1t. In fact even crystallization at atmospheric pressure at room temperature results in regeneration of some starting material. Analysis by mass spectroscopy required addition of a drop of pyridine to the solution of compound 5.9t to get the parent peak of 450 m/z which is a minor peak. Major peak corresponds to the mass of 370 m/z which is due to the starting material 5.1t.

The 1H NMR analysis of 5.9t was also difficult due to the reasons stated above. When pure crystal of compound 5.9t were dissolved in any non-coordinating solvent such as toluene or benzene, it was immediately converted back to 5.1t, liberating free pyridine. The 1H NMR spectrum of 5.9t in pyridine-d5 solvent did not show the resonance of the pyridine ligand, because it was rapidly exchanged with pyridine-d5 from the solvent. In order to find out the binding strength of pyridine, a series of experiments for the addition of excess amounts of pyridine (49–294 equiv) to 5.1t, were monitored by 1H NMR (see Figure D.6 in Appendix D), which did not show complete conversion of starting material 5.1t to 5.9t. Using a rough estimate of ~80% conversion to 5.9t in pure pyridine solvent, a $K_{eq}$ value of 0.33 was estimated. This result suggests that binding of pyridine is very poor (in agreement with the computational results, vida infra). Furthermore, the 1H NMR spectrum at room temperature showed broad, overlapping peaks indicative of fluxional processes associated with the TEMPO ligand. Variable-temperature 1H NMR spectra in the range of ~40° to 105 °C (see Figure D.7 in Appendix D) did not reveal a static spectrum that is consistent with the solid state structure of 5.9t. This fluxional process
**Scheme 5.5.** Proposed line structures of products of 5.1 with a) THF, b) CO, c) H₂CCH₂, was also observed in the ¹H NMR spectrum of compound 5.2c at room temperature. Variable-temperature ¹H NMR spectra in the range of 25°–90 °C resulted in some sharpening of the peaks. However, as shown in Figure D.7 in the Appendix D, some broadening remained, even at high temperature. At temperatures above 90 °C, 5.9t decomposes. It is clear that some broadening and exchange occurs at higher temperatures as well. The exact nature of the fluxional processes in 5.2c and 5.9t remains unresolved at this point. While we are unable to unambiguously assign the dynamical process, work is underway to theoretically determine whether these processes occur due to η¹ (k¹) to η² exchange of the TEMPO ligands in solution or from conformational distortion of TEMPO.
**Reaction of 5.1t with other small molecules and coordinating solvents:** Based on the reaction of 5.1t with Bu^tNC and acetylene gas to afford 5.2c and 5.5c, work has been extended to activate other small molecules such as CO, C_2H_4, H_2 and coordinating solvents such as CH_3CN and THF. Scheme 5.5 depicts the conceivable (other possible isomers are not shown here) product types with these small molecules.

d) H_2, e) CH3CN.

**Reaction with CO, H_2 and H_2C=CH_2:** When Carbon monoxide gas was purged through a room-temperature hexane solution of 5.1t an immediate color change to a dark reddish purple was observed, but within minutes, the solution becomes clear and a colorless solid precipitates at the bottom of the flask. Even at the depressed temperature of -78 °C, the same result was observed with no apparent signs of stabilization in the reaction mixture. This precipitate is not soluble in any of the tested solvents such as hexane, toluene, diethyl ether, tetrahydrofuran, dimethyl sulphoxide, methylene chloride, or water. The colorless product is yet be identified and efforts are underway in our lab to characterize it. Similarly when either H_2 or C_2H_2 gas is purged through the solution of 5.1t, even at depressed temperatures, there was rapid decolorization with precipitation of insoluble colorless solids. Again, there was no isolation of any new products.

It is possible that the proposed products with CO, H_2 and C_2H_2, lacks the sufficient steric volume to prevent further access to the unsaturated nickel center by the presence of excess amount of the reacting gasses but even the addition of equimolar amounts of gasses to the compound 5.1t to get the above proposed products were unsuccessful. At
this time we are unsure as to why this product is so prone to decomposition, but as stated below, unstable reaction with small molecules is common for 5.1t.

**Reaction of 5.1t with tetrahydrofuran (THF) and acetonitrile (CH$_3$CN) solvents:** It has been observed that compound 5.1t is stable in non-coordinating solvents such as hexane, benzene, toluene, methylene chloride and diethyl ether. However, after dissolving purple crystals of 5.1t in either THF or CH$_3$CN solvent, the solution quickly becomes colorless and a colorless solid precipitates at the bottom of the reaction flask in a similar fashion to the reaction with CO gas, even at -78 °C. Again, no products were isolated from the reaction mixture. These observations of a strong reaction with coordinating solvents even at depressed temperature suggest that these reactions can be used for the synthesis of useful organic products in the presence of other reagents.

**Exchange reactions between the acetylide products of compound 5.1t:** It is evident from compounds 5.3c, 5.4c and 5.5c, that 5.1t activates sp hybridized bond of symmetric and unsymmetric terminal alkynes. This is an essential step in the Sonogashira coupling reaction where a C-C bond is made. It is possible that the activated acetylides present on the Ni center can be coupled with other organic compounds to make new C-C, C-N, or C-O bonds and thus can be used to synthesize various useful organic products. Based on this idea, some interesting catalytic reactions were attempted to make new organic products with PhCCH and C$_2$H$_2$. Though, so far, the efforts to form new C-C bonds are unsuccessful, these attempts lead us to identify some interesting exchange reactions, occurring on the Ni center of these complexes as shown in equations 5.2 to 5.4.
Phenyl acetylene and Bu^1NC replaces acetylene from 5.5c: When PhCCH and 5.5c were reacted in 1:1 ratio, it was observed that PhCCH replaces the acetylene from 5.5c and forms phenyl acetylide product 5.3c within 30 minutes. These reactions were monitored by both IR and \(^1\)H NMR which showed the resonances corresponding to both the products. This exchange reaction happens at RT and under refluxing conditions. A similar exchange phenomenon was observed with Bu^1NC, where it replaces acetylene and forms compound 5.2c. Unfortunately, these reactions do not go to the completion and stops after reaching some sort of equilibrium between the products. During this process unidentified black colored oily products were also observed.

Acetylene replaces phenyl acetylene from compound 5.3c. In this exchange reaction, acetylene gas is purged through the hexane solution of compound 5.3c. Interestingly,
acetylene gas replaces the phenyl acetylene from the compound 5.3c only at refluxing temperature to form compound 5.5c. In this case, CNBu^1 does not replace Phenyl acetylide even under refluxing conditions. Again this reaction too does not go to the completion and stops after reaching some sort of equilibrium between both the products. Also, a black colored oily product was observed during the reaction.

### 5.4. Kinetics, thermodynamics, and selectivity of substituted species.

Mechanistic pathways of addition reactions of the various adducts (tert-butyl isocyanide, phenylacetylene, pyridine, acetylene, 1,4-diacetylenebenzene, and trimethylsilyl acetylene, respectively) are mapped out and discussed in the following section. First, transition states corresponding to the addition of the CN^iBu ligand to the cis and trans form of 5.1 have been computed and proceed via a simple association reaction. Both the cis and trans transition states (TS-5.2c and TS-5.2t, respectively) possess an imaginary mode with Ni-N-O ring opening coupled to ligand addition. The PBE TS of the trans structure (Scheme 5.6) has a Ni-N bond distance of 2.427 Å versus 2.807 Å for the cis.
Scheme 5.6. Addition of CNBu to compound 5.1t.

From Scheme 5.7, it is evident that 5.2c and 5.2t are nearly isoenergetic. In the solution phase computations, the experimentally observed 5.2c isomer is only 0.1 kcal mol$^{-1}$ lower in free energy. Theory shows the experimentally observed isomer being slightly favored thermodynamically, but disfavored kinetically (the $\Delta G$ of TS-5.2c is 15.1 kcal mol$^{-1}$ versus TS-5.2t with a $\Delta G$ of 13.8 kcal mol$^{-1}$). Among the complexes discussed in this paper, the 5.2c/5.2t pair shows the closest relative free energies in terms of both kinetics and thermodynamics. However, attempts to force crystallization of the 5.2t isomer under a variety of experimental conditions (variation of temperature and solvents) were unsuccessful and only resulted in formation of 5.2c crystals.
In Scheme 5.7, the mechanism of phenylacetylene (PhCCH) addition to trans-Ni(\(\eta^2\)-TEMPO)\(_2\) to form the trans-Ni(\(\eta^2\)-TEMPO)(k\(^1\)-TEMPOH)(\(\eta^1\)-CCPh) complex (5.3t) is proposed. Note that intermediates in the addition reaction mechanism Schemes (both in the manuscript and in Appendix D) will be incrementally numbered starting after the first experimentally synthesized compound, i.e. starting with 10.

Scheme 5.7. Formation of 5.3t from compound 5.1t.

In Scheme 5.7 beginning with 5.1t + PhCCH, a dipole-dipole intermediate (10) is obtained that is 8.1 kcal mol\(^{-1}\) higher in free energy than the infinitely separated trans-Ni(\(\eta^2\)-TEMPO)\(_2\) and PhCCH. In this complex, a hydrogen atom from the phenyl ring is oriented towards one of the TEMPO oxygen atoms. The alkyl hydrogen of 10 is away from the complex at a distance of 5.811 Å from the Ni center. The phenyl of PhCCH
reorients significantly during **TS-10-11**, which has a $\Delta G$ of 20.5 kcal mol$^{-1}$ compared to the separated species. The imaginary vibrational mode of **TS-10-11** corresponds to concerted ring opening of the Ni-O-N bond and formation of a single Ni-C bond with the terminal alkyl carbon. The subsequent intermediate (11) has the plane of the phenyl ring oriented parallel to the O-Ni-O plane (the out of plane angle is 17.5°). The intermediate 11 then undergoes a facile shift of the phenyl ring through the plane created by the Ni-O-N of the ($k^1$-TEMPO), **TS-11-12**, with $\Delta G = 8.3$ kcal mol$^{-1}$. Finally, proton transfer of the alkyl hydrogen to the nitrogen atom on the ($k^1$-TEMPO) ligand occurs in **TS-12-5.3t** ($\Delta G = 13.8$ kcal mol$^{-1}$) to give the final $\text{trans-Ni}(\eta^2$-TEMPO)($k^1$-TEMPOH)(\eta$^1$-CCPh) product, **5.3t**, with a $\Delta G$ of 1.2 kcal mol$^{-1}$.

In Scheme 5.8, the mechanism of PhCCH ligand addition to the $\text{cis-Ni}(\eta^2$-TEMPO)$_2$.5.1c complex is described. Upon association of the ligand, an interesting dipole-dipole species (13) is obtained where the hydrogen atom of the alkyne is oriented directly at the Ni-complex center, at a distance of 2.64 Å. This intermediate is 5.8 kcal mol$^{-1}$ higher in free energy than the infinitely separated reactants (5.1c and PhCCH), and 12.4 kcal mol$^{-1}$ higher in free energy than 5.1t + PhCCH. The Ni-N bond of the TEMPO ligand opens and the Ni-C$_\text{alkyl}$ bond forms in concert (**TS-13-14**). This transition state has a slightly higher free energy of activation than the equivalent $\text{trans}$ TS (**TS-10-11**), with a $\Delta G_{(\text{soln})}$ of 21.8 kcal mol$^{-1}$. The reaction pathway of 5.3c has one less step when compared to 5.3t, as there is no reorientation of the alkyl bond needed to perform proton transfer (akin to **TS-11-12**). The intermediate 14 can directly transfer the proton to the TEMPO nitrogen atom (**TS-14-5.3c**). This transition state has a lower free energy of activation (14.6 kcal mol$^{-1}$) and is quite early with a CH bond distance of 1.144 Å. The final product
**5.3c** has $C_s$ point group symmetry and very closely resembles the X-ray crystal structure of the *cis*-Ni($\eta^2$-TEMPO)($k^1$-TEMPOH)($\eta^1$-CCPh) complex (5.3c).

**Scheme 5.8.** Formation of 5.3c from 5.1c.

Addition of acetylene to complex 5.1t and addition of HCCH to 5.1c is mechanistically very similar to the addition of PhCCH (see Appendix D, Schemes D.5 and D.6). The proposed mechanisms for the formation of 5.4c, 5.4t, 5.7c, and 5.7t occur similarly to those described above, and are briefly discussed in Appendix Schemes D.1–D.4.

In Scheme 5.9, the thermodynamics of pyridine addition to complexes 5.1t and 5.1c to form complex 5.9t and 5.9c, respectively, is shown. It is the least
thermodynamically stable of the product species, as it is the only one where the experimentally characterized structure has a computed positive binding energy (+2.1 kcal mol\(^{-1}\)). It is also the only adduct where the trans isomer has been isolated experimentally.

![Diagram](image)

**Scheme 5.9.** Formation of 5.9\(t\) from 5.1\(t\).

**Kinetics, thermodynamics, and possible isomerization mechanisms:** Table 5.5 shows the theoretical ligand binding energies for the addition of all substituents to complex 5.1 as well as solution phase activation free energies for the computed rate-limiting steps of the various addition reactions.
Table 5.5. Theoretical PBE Solution-Phase Reaction Free Energies ($\Delta G_{\text{soln}}$) for the Addition of All Ligands to Complex 5.1t. Further computational results for the gas-phase thermodynamics and gas-phase and solution-phase kinetics are included in the Appendix Table D.5. Included in the first rows are the relative energies of the trans and cis isomers of complex 5.1t. The reaction free energy of the experimentally observed isomer is shown in bold text. The relative free energy of 5.1c refers to the lowest energy conformer. The conformer that directly reacts to form the various addition products is slightly higher in free energy ($\Delta G_{\text{soln}} = 6.6$ kcal mol$^{-1}$); and this relative free energy is used along the reaction mechanisms shown in Schemes 5.7, 5.9, 5.11, 5.12, D.2 and D.4.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction free energy $\Delta G_{\text{soln}}$ (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1t</td>
<td>0</td>
</tr>
<tr>
<td>5.1c</td>
<td>4.0$^b$</td>
</tr>
<tr>
<td>5.1t + CNBu$^1$ $\rightarrow$ 5.2t</td>
<td>$-13.0$</td>
</tr>
<tr>
<td>5.1t + CNBu$^1$ $\rightarrow$ 5.2c</td>
<td>$-13.1$</td>
</tr>
<tr>
<td>5.1t + PhCCH $\rightarrow$ 5.3t</td>
<td>1.2</td>
</tr>
<tr>
<td>5.1t + PhCCH $\rightarrow$ 5.3c</td>
<td>$-3.3$</td>
</tr>
<tr>
<td>5.1t + HCCSi(CH$_3$)$_3$ $\rightarrow$ 5.4t</td>
<td>$-0.1$</td>
</tr>
<tr>
<td>5.1t + HCCSi(CH$_3$)$_3$ $\rightarrow$ 5.4c</td>
<td>$-4.2$</td>
</tr>
<tr>
<td>5.1t + HCCH $\rightarrow$ 5.5t</td>
<td>$-2.5$</td>
</tr>
<tr>
<td>5.1t + HCCH $\rightarrow$ 5.5c</td>
<td>$-3.8$</td>
</tr>
<tr>
<td>5.1t + HCCPhCCH $\rightarrow$ 5.7t</td>
<td>$-0.8$</td>
</tr>
<tr>
<td>5.1t + HCCPhCCH $\rightarrow$ 5.7c</td>
<td>$-4.4$</td>
</tr>
<tr>
<td>5.1t + py $\rightarrow$ 5.9t</td>
<td>2.1</td>
</tr>
<tr>
<td>5.1t + py $\rightarrow$ 5.9c</td>
<td>5.6</td>
</tr>
</tbody>
</table>

There are a few unexpected trends that have occurred in the reactions of the donor ligands with Ni(TEMPO)$_2$. First is that the trans-Ni(TEMPO)$_2$ complex (5.1t) was isolated, but all adducts except for 5.9t were crystallized in the cis form. The formation of 5.9t is also unique because both cis and trans isomers are endergonic in the
solution phase computed pathways ($\Delta G = +5.6$ and $+2.1$ kcal mol$^{-1}$, respectively). This corresponds well to the comparatively short lifetime, as well as the careful synthetic conditions necessary to isolate complex 5.9t. The second related phenomenon is that in all cases [again except for the addition of pyridine to the Ni(TEMPO)$_2$ complex (Scheme 5.10)] the PBE computations suggest that the experimentally observed product isomer is thermodynamically, but not kinetically controlled. In order to progress from the trans disposition of the reactant (5.1t) versus the cis disposition of the various adducts (5.2, 5.3, 5.4, 5.5, 5.7), an isomerization must take place. There are three possibilities for an isomerization pathway, shown in Scheme 5.10.

Scheme 5.10. Isomerization possibilities.

When does this isomerization occur? The first possibility is that isomerization takes place in the initial complex 5.1t, and then 5.1c undergoes the addition reaction with
the alkyne substituent. The second possibility is that the isomerization occurs when the
adduct is bound to the complex, but before the hydrogen transfer to the \( \eta_1 \)-TEMPO
ligand, (i.e., a pathway connecting 11/12 to 14, 16 to 18, 20 to 22, or 24 to 26, shown in
Schemes 5.8, 5.9 and in Schemes D.1 to D.6 in the Appendix D). Finally, there is the
possibility that \( \text{trans-cis} \) isomerization can occur after the hydrogen transfer takes place
(in a mechanism between 5.3c and 5.3t, for example). All of this discussion of \( \text{trans-to-cis} \)
isomerization is complicated by two factors: (1) the relative energy of the lowest
energy 5.1c isomer is 4.0 kcal mol\(^{-1}\) higher than the lowest energy isomer of 5.1t and (2)
astonishingly, the computed NMR spectrum of 5.1c is very similar to the computed NMR
spectrum of 5.1t (which is in relatively good agreement with the experimentally observed
NMR spectrum of 1t). Therefore, the very small amount of cis isomer produced from
raising the temperature would only slightly alter the peak integrations. (See the
Supporting Information for further discussion of these points).

5.5. Conclusions.

Synthesis and characterization of Ni(\( \eta_2 \)-TEMPO)\(_2\), 5.1t, the first literature
example of an unsaturated transition metal complex with exclusively of TEMPO radicals
as ligands, has been reported in this chapter. Complex 5.1t is a 16electron unsaturated
molecule with “bow-tie” type rectangular planar structure with oxygen atoms \( \text{trans} \) to
each other. Complex 5.1t is highly air and moisture sensitive. This simple molecule
demonstrated a complex reactivity with a wide variety of small molecules (see Scheme
5.2) by displaying bifunctional cooperativity between the hemilabile TEMPO ligand and
the Ni center in its reactivity with organic substrates at room temperature.
The reaction of 5.1t with tert-butyl isocyanide to afford Ni(η^2-TEMPO)(κ^1-CNBU)', 5.2c, demonstrates one of several possible modes of reactivity. This reaction displays the ability of 5.1t to transform one of the coordinated TEMPO ligand from η^2 to η^1 mode to yield a 16e-planar product, where now the oxygen atoms are cis to each other. This compound exhibited broadened ^1H NMR resonances suggestive of dynamical processes in solution suggestive of a fluxional equilibrium in solution. A similar dynamical process in solution was observed in case of reaction of 5.1t, with pyridine, though, here the mode of reactivity is completely different. Addition of pyridine to 5.1t produces the dark brown product Ni(η^2-TEMPO)(k^1-TEMPO)(κ^1-NC_5H_5), 5.9t. This is the only product synthesized which shows trans oxygen atoms as opposed to cis unlike other products of 5.1t.

Compound 5.1t reacts with terminal alkynes and activates sp hybridized C-H bond to yield acetylide products 5.3c, 5.4c, 5.5c, and 5.7c, which is rare, with the N atom on the TEMPO ligand acting as a base to deprotonate the alkyne. All these products contain cis-disposed oxygen atoms. Complex 5.8cc, is a good example where two terminal alkynes of same molecule are activated to link two Ni(η^2-TEMPO)(κ^1-TEMPOH) groups to form a bridging dinuclear complex.

Attempts to activate other small molecules such as H_2, C_2H_2, CO, CO_2, N_2 etc., by 5.1t are unsuccessful. Compound 5.1t is highly unstable in coordinating solvents such as tetrahydrofuran, acetonitrile, methanol etc., and forms unidentified products which are insoluble in all the tested solvents. These observations indicate a strong reaction of 5.1t with above mentioned small molecules and solvents with the possibility to synthesize useful compounds by tweaking reaction conditions.
Density functional theory (DFT) has been employed to study the structural and thermochemical properties of the molecules shown in Scheme 5.2. Computed solution-phase relative free energies of the various characterized Ni-centered complexes are in agreement with the experimentally observed isomers. However, rate-limiting transition states of the addition reactions suggest that, in all cases except for the initial complex Ni(η²-TEMPO)$_2$, $5.1t$ and the product formed via the addition of pyridine ($5.9t$), the experimentally observed isomer is always kinetically disfavored. The mechanism by which the trans complex $5.1t$ isomerizes to the various cis product complexes upon substrate addition is still not completely understood. Further experimental and computational work will be performed in tandem to explore the fascinating conformational complexity of the isomerization reactions. Both theory and experiment also validate the formation of the bimetallic complex $5.8cc$ (two C–H bond activations of 1,4-diethynylbenzene) and are correspondingly in agreement that the proposed bimetallic complex $5.6cc$ (two C–H bond activations of acetylene) will be too sterically crowded to exist under the same experimental conditions used to isolate complex $5.8cc$.

The reactions presented in this report are facile under mild conditions. The brief survey of contained reactions present a good start, in the wake of exchange reactions between dissimilar acetylide complexes of $5.1t$, studies are planned in carbon–carbon bond coupling. Studies are also planned in the fields of homogeneous catalysis, targeting small molecules and C–H bond activation and oxygen atom transfer.

5.6. Experimental section.

General Data. Unless indicated otherwise, all reactions were performed under an atmosphere of argon. Reagent-grade solvents were dried by the standard procedures and
were freshly distilled prior to use. Solution-phase infrared spectra were recorded on a Nicolet 380 FT-IR spectrophotometer. Single-crystal FTIR spectra were obtained on a Perkin–Elmer Spectrum 400 using a Perkin–Elmer Universal ATR Sampling Accessory. 1H NMR spectra were recorded on a Bruker 400 spectrometer operating at 399.993 MHz. 2D [1H, 15N] HSQC NMR were collected on a Bruker Avance-IIIHD 500 NMR spectrometer operating at 500.21 MHz for 1H and 50.69 MHz for 15N at the University of South Carolina. Elemental analyses were performed by Columbia Analytical Services (Tucson, AZ). Electrospray mass spectrometric measurements were obtained on a Bruker microTOF-Q II. Bis(1,5-cyclooctadiene)nickel, Ni(COD)2, was purchased from Strem Chemicals, used without further purification, and stored and handled in a drybox. TEMPO (2,2,6,6-tetramethylpiperidine-N-oxide), tert-butyl isocyanide, and phenylacetylene were purchased from Alfa Aesar and used without further purification. 1,4-Diethynylbenzene was purchased from TCI and used without further purification. Atomic-absorption-grade acetylene and argon (UHP grade) were purchased from AirGas and used without further purification. Phenylacetylene-d1 (99%), pyridine, and trimethylsilyl acetylene were purchased from Sigma–Aldrich and used without further purification.

**Synthesis of Ni(η2-TEMPO)2.5t:** A 100 mg (0.36 mmol) amount of Ni(COD)2 and 115 mg (0.72 mmol) of TEMPO were loaded into a Schlenk flask. 30 mL of hexane solvent was then added to the flask using a cannula. The stirred solution changed color from light orange to deep purple as it was heated to reflux, for approximately 5 min. The solvent was then removed in vacuo and the residue was dissolved in 4 mL of diethyl ether, filtered into a glass vial, and placed in a -25 °C freezer in a drybox. Evaporation of
Spectral data for 5.1t: $^1$H NMR (C$_6$D$_6$ in ppm): $\delta = 2.39$ (s, 12 H, 4 CH$_3$), 1.36 (s, 12 H, 4 CH$_3$), 1.40 – 1.25 (m, broad, 12 H, 6 CH$_2$). Mass Spec. ES$^+$/MS calcd for [M + CH$_3$CN], 412; found 412. The isotope distribution is consistent with the presence of one nickel atom.

**Synthesis of Ni($\eta^2$-TEMPO)($k^1$-TEMPO)($\kappa^1$-CNBu$t$), 5.2c:** A 40 mg (0.108 mmol) amount of Ni($\eta^2$-TEMPO)$_2$ was loaded into a sidearm Schlenk flask and dissolved in 20 mL of hexane after which 10 mg (0.125 mmol) of Bu$t$NC was added, resulting in an immediate color change from purple to dark red. The reaction mixture was stirred at room temperature for 10 min. The volatiles were removed in vacuo and the residue was dissolved in 2 mL of diethyl ether, filtered into a glass vial, and placed in a -25 °C freezer in a dry box. Evaporation of solvent afforded 44 mg (90% yield) of red crystalline blocks of Ni($\eta^2$-TEMPO)($k^1$-TEMPO)($\kappa^1$-CNBu$t$), 5.2c, Spectral data for 5.2c: IR $\nu_{CN}$ (cm$^{-1}$, in hexane) 2169. $^1$H NMR (toluene-$d_8$ in ppm): $\delta = 2.46$ (s), 2.43-1.00 (broad), 1.55 (s), 1.50-1.20 (broad), 1.19 – 1.02 (broad multiplet), 0.95 (s). Note: The $^1$H NMR spectrum at room temperature indicates some dynamical processes in solution, see text and supporting information. Mass Spec. EI/MS: m/z calcd for M$^+$= 453; found 453; calcd (M$^+$- tBuNC)= 370 (= Ni[$\eta^2$-TEMPO]$_2$); found 370. The isotope distribution is consistent with the presence of one nickel atom.

**Synthesis of Ni($\eta^2$-TEMPO)($\kappa^1$-TEMPOH)($\kappa^1$-CCPh), 5.3c:** A 40 mg (0.108 mmol) amount of Ni($\eta^2$-TEMPO)$_2$ was loaded into a sidearm Schlenk flask and dissolved in 20 mL of hexane. 12 mg (0.117 mmol) of phenylacetylene was added and the reaction mixture was stirred at room temperature for 1 hour, during which time the color changed
from purple to light red. The volatiles were then removed in **vacuo** and the residue dissolved in 2 mL of diethyl ether, filtered into a glass vial, and placed in a -25 °C freezer in a dry box. Evaporation of solvent afforded 37 mg (73% yield) of red crystalline blocks of Ni(η²-TEMPO)(κ¹-TEMPOH)(κ¹-CCPh), 5.3c. Spectral data for 5.3c: FTIR (single crystal) \( \nu_{(C\equiv C)} \) : 2079(s) cm\(^{-1}\), \( \nu_{(N-H)} \) : 3675-3100 (broad) cm\(^{-1}\). FTIR \( \nu_{(C\equiv C)} \) (cm\(^{-1}\) in hexane): 2074(s). \(^1\)H NMR (C\(_6\)D\(_6\) in ppm): \( \delta = 7.62 \) (s, 1 H, N-H), 7.50 (d, 2 H, Ph), 7.10 (t, 2 H, Ph), 6.96 (t, 1 H, Ph), 3.10 (s, 6 H, 2 CH\(_3\)), 2.11 (s, 6 H, 2 CH\(_3\)), 1.76 (br, 2 H, CH\(_2\)), 1.29 (s, 8 H, 2 CH\(_3\) and 1 CH\(_2\)), 1.08 (m, 6 H, 3 CH\(_2\)), 0.90 (s, 8 H, 2 CH\(_3\) and 1 CH\(_2\)). Mass Spec. ES\(^+\)/MS calced for [M + H]\(^+\) = 473; found 473. The isotope distribution is consistent with the presence of one nickel atom.

**Synthesis of Ni(η²-TEMPO)(κ¹-TEMPOH)(κ¹-CCSiMe\(_3\)), 5.4c:** A 40 mg (0.108 mmol) amount of Ni(η²-TEMPO)\(_2\) was loaded into a sidearm Schlenk flask and dissolved in 20 mL of hexane. 12 mg (0.122 mmol) of trimethylsilyl acetylene was added and the reaction mixture was stirred at room temperature for 1 h, during which time the color changed from purple to light red. The volatiles were then removed in **vacuo** and the residue dissolved in 2 mL of diethyl ether, filtered into a glass vial, and placed in a -25 °C freezer in a dry box. Evaporation of solvent afforded 40 mg (79 % yield) of red crystalline blocks of Ni(η²-TEMPO)(κ¹-TEMPOH)(κ¹-CCSiMe\(_3\)), 5.4c. Spectral data for 5.4c: FTIR \( \nu_{(C\equiv C)} \) (cm\(^{-1}\) in hexane): 2009(s). \(^1\)H NMR (C\(_6\)D\(_6\) in ppm): \( \delta = 7.69 \) (s, 1 H, N-H), 2.99 (s, 6 H, 2 CH\(_3\)), 2.09 (s, 6 H, 2 CH\(_3\)), 1.76 (m, 2 H, CH\(_2\)), 1.26 (s, 6 H, 2 CH\(_3\)), 0.91 (s, 6 H, 2 CH\(_3\)), 1.5-0.9 (m, broad, 10 H, 5 CH\(_2\)), 0.29 (s, 9 H, SiMe\(_3\)). Mass Spec. ES\(^+\)/MS calculated for [M + H]\(^+\) = 470 m/z; found 470 m/z. The isotope distribution is consistent with the presence of one nickel atom.
Synthesis of Ni(η²-TEMPO)(κ¹-TEMPOH)(κ¹-CCH), 5.5c: A 40 mg (0.108 mmol) amount of Ni(η²-TEMPO)₂ was loaded into a sidearm Schlenk flask and dissolved in 20 mL of hexane. Acetylene gas was purged through the reaction mixture and stirred at room temperature for 1 h, during which time the color changed from purple to light red. The volatiles were then removed in *vacuo* and the solid residue dissolved in 2 mL of diethyl ether, filtered into a glass vial, and placed in a -25 °C freezer in a dry box. Evaporation of solvent afforded 32 mg (74 % yield) of red crystalline blocks of Ni(η²-TEMPO)(κ¹-TEMPOH)(κ¹-CCH), 5.5c. Spectral data for 5.5c: FTIR ν(C≡C) (cm⁻¹ in hexane): 1933(s). ¹H NMR (C₆D₆ in ppm): δ= 7.64 (s, 1 H, N-H), 3.10 (s, 6 H, 2 CH₃), 2.08 (s, 6 H, 2 CH₃), 2.06 (s, 1 H, CCH), 1.78 (m, 2 H, CH₂), 1.26 (s, 6 H, 2 CH₃), 0.90 (s, 6 H, 2 CH₃), 1.4-0.8 (m, broad, 10 H, 5 CH₂). Mass Spec. ES⁺/MS calculated for [M + H]⁺ = 397 m/z; found 397 m/z. The isotope distribution is consistent with the presence of one nickel atom.

Synthesis of Ni(η²-TEMPO) (κ¹-TEMPOH)(κ¹-CC[CH₆H₄]CCH), 5.7c: A 40 mg (0.108 mmol) amount of Ni(η²-TEMPO)₂ was loaded into a sidearm Schlenk flask and dissolved in 20 mL of hexane. 15 mg (0.119 mmol) of 1,4-diethynylbenzene was added and the reaction mixture was stirred at room temperature for 1 h, during which time the color changed from purple to auburn red. The volatiles were then removed in *vacuo* and the residue dissolved in 2 mL of diethyl ether, filtered into a glass vial, and placed in a -25 °C freezer in a dry box. Evaporation of solvent afforded 38 mg (71 % yield) of red crystalline blocks of Ni(η²-TEMPO) (κ¹-TEMPOH)(κ¹-CC[CH₆H₄]CCH), 5.7c. Spectral data for 5.7c: FTIR ν(C≡C) (cm⁻¹ in hexane): 2071(s). ¹H NMR (C₆D₆ in ppm): δ= 7.65 (s, 1 H, N-H), 7.44-7.31 (d, 4 H, C₆H₄), 3.26 (s, 1 H, C≡CH), 3.08 (s, 6 H, 2 CH₃), 2.10 (s, 6
H, 2 CH₃), 1.76 (m, 2 H, CH₂), 1.28 (s, 6 H, 2 CH₃), 0.90 (s, 6 H, 2 CH₃), 1.5-0.8 (m, broad, 10 H, 5 CH₂). Mass Spec. ES⁺/MS calculated for [M + H]⁺ = 497; found 497. The isotope distribution is consistent with the presence of one nickel atom.

**Synthesis of Ni(η²-TEMPO)(κ¹-TEMPO)(κ¹-CC(C₆H₄)CC)Ni(η²-TEMPO)(κ¹-TEMPO), 5.8cc:** To 48 mg (0.129 mmol) of Ni(η²- TEMPO)₂ and 8 mg (0.063 mmol) of 1,4-diacetylenebenzene in a sidearm Schlenk flask, 20 mL of hexane was added. The reaction mixture was stirred at room temperature for 3 h, during which time the color changed from purple to auburn red. The volatiles were then removed in vacuo and the residue dissolved in approximately 2 mL of benzene, filtered into a glass vial, and placed in a dry box. Evaporation of solvent at room temperature afforded 44 mg (80 % yield) of pure red crystalline blocks of Ni(η²-TEMPO)(κ¹-TEMPOH)[ κ¹-CC(C₆H₄)CC]Ni(η²-TEMPO)(κ¹-TEMPO)(η¹-TEMPOH). Spectral data for 9: FTIR ν(C≡C) (cm⁻¹ in hexane): 2073(s). ¹H NMR (C₆D₆): δ = 7.66 (s, 2 H, N-H), 7.43 (s, 4 H, C₆H₄), 3.09 (s, 12 H, 4 CH₃), 2.10 (s, 12 H, 4CH₃), 1.73 (t, 4 H, 2 CH₂), 1.29 (s, 12 H, 4 CH₃), 1.20 – 1.36 (br, 8 H, 4 CH₂), 1.00 – 1.15 (br, 12 H, 6 CH₂), 0.90 (s, 12 H, 4 CH₃). Mass Spec. ES⁺/MS calculated for [M + H]⁺ = 868; found 868. The isotope distribution is consistent with the presence of two nickel atoms.

**Synthesis of Ni(η²-TEMPO)(κ¹-TEMPO)(κ¹-NC₅H₅), 5.9r:** A 40 mg (0.108 mmol) amount of Ni(η²-TEMPO)₂ was loaded into a sidearm Schlenk flask and dissolved in 20 mL of hexane. Excess pyridine (0.1 mL) was added and the reaction mixture immediately changed color from purple to dark brown. The volatiles were then removed in vacuo and the residue dissolved in 2 mL of diethyl ether with a drop of pyridine, filtered into a glass vial, and placed in a -25 °C freezer in a dry box. Evaporation of
solvent afforded 46 mg (95 % yield) of brown blocks of Ni(η²-TEMPO)(k¹-TEMPO)(κ¹-NC₅H₅), 5.9t. Spectral data for 5.9t: ¹H NMR (C₆D₆ in ppm, pyridine peaks and integrations not listed due to dynamical processes):  δ= 2.96 (s), 2.35 (s), 3.0-1.8 (broad), 1.54 (s), 1.35 (s). ¹H NMR (NC₅D₅ in ppm, pyridine peaks and integrations not listed due to dynamical processes): δ= 3.03 (s), 2.38 (s), 3.0-1.8 (broad), 1.55 (s), 1.36 (s), 1.19 (s) (see Figure D.7 in Appendix D). Mass Spec. ES⁺/MS calculated for [M]⁺= 450 m/z; found 450 m/z. The isotope distribution is consistent with the presence of one nickel atom. NOTE: It should be noted that additional peaks with higher molecular weights were also present in the mass spectrum, presumably because of decomposition in the spectrometer. Similarly, reliable elemental analysis results were not obtained for this relatively unstable compound. Placing solid 5.9t under vacuum, results in partial decomposition and regeneration of 5.1t. Dissolving 5.9t in hexane or benzene appears to create equilibrium between starting 5.1t and product 5.9t.

Conversion of 5.7c to 5.8cc: To 20 mg (0.040 mmol) of 5.7c and 15 mg (0.040 mmol) of 5.1t in a sidearm Schlenk flask, 20 mL of hexane was added. The reaction mixture was stirred at room temperature for 2 h. The volatiles were then removed in vacuo and the residue dissolved in approximately 2 mL of benzene, filtered into a glass vial, and placed in a dry box. Evaporation of solvent at room temperature afforded 22 mg (63 % yield) of pure red crystalline blocks of 5.8cc.

Addition of 1 equivalent each of PhCCH and PhCCD to 5.1t: To an equimolar mixture of PhCCH and PhCCD (7.5 µL, 0.069 mmol) dissolved in 0.5 mL of toluene-d₈ in a 5 mm NMR tube, 25.0 mg (0.068 mmol) of 5.1t was added. ¹H NMR after approximately 10 min showed peaks corresponding to the product. Integration of the
resonances indicated approximately a 1:1 ratio for products 5.3c and 5.3c-d1. Similarly when the reaction was carried out in non-deuterated toluene solvent, 2H{1H} NMR showed two singlet resonances for the starting PhCCD and product 5.3c-d1 with relative intensities of approximately 1:1.

**Reaction of 5.1t with 6 equiv PhCCH and 6 equiv PhCCD:** To an equimolar mixture of PhCCH and PhCCD (44.4 µL, 0.404 mmol) dissolved in 0.6 mL of toluene-d8 in a 5 mm NMR tube, 12.5 mg (0.034 mmol) of 5.1t was added. 1H NMR after ~10 min showed peaks corresponding to the product. Integration of the resonances indicated an ~1:1 ratio for products 5.3c and 5.3c-d1. Similarly, when the reaction was carried out in nondeuterated toluene solvent, 2H{1H} NMR showed two singlet resonances for the starting PhCCD and product 5.3c-d1 with relative intensities of ~1:11 (see Figures D.4 and D.5 in Appendix D).

**Reaction of 5.1t with Excess Pyridine:** A stock solution of 5.1t in C6D6 was prepared by dissolving 80.5 mg of 5.1t in 5 mL of C6D6. In an NMR tube, to 0.5 mL of this solution (0.022 mmol), 87 µL of pyridine (1.06 mmol) was added, followed by the addition of C6D6, such that the total volume was 1.023 mL. Similarly, in a series of experiments, to 0.5 mL solution of 5.1t, pyridine in the amounts of 174, 349, and 523 µL, was added. 1H NMR spectra are shown in Figure D.6 in Appendix D.

**5.7. Crystallographic analysis.**

Single crystals of 5.1t, 5.2c, 5.3c, 5.4c, 5.5c, and 5.7c suitable for X-ray diffraction (XRD) analysis were grown by evaporation of diethyl ether solutions at −25 °C. Single crystals of 5.9t suitable for XRD analysis were grown by evaporation of a
diethyl ether solution with a drop of pyridine. Single crystals of 5.8cc suitable for XRD analysis were grown by evaporation of a benzene solution. Single crystals of 5.10t suitable for XRD analysis were grown by evaporation of mixture of CH₂Cl and hexane solution. Data crystals for 5.4c, 5.5c, and 5.7c were glued to the end of a thin glass fiber for data collection under ambient conditions. Data crystals for 5.1t, 5.2c, 5.3c, 5.8cc, and 5.9t were mounted onto the end of a thin glass fiber using Paratone-N for data collection at 100 K under flow of N₂. X-ray intensity data were measured using a Bruker SMART APEX2 CCD-based diffractometer using Mo Kα radiation (λ = 0.71073 Å). The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm. Corrections for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares on F², by using the SHELXTL software package. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located from the difference map and refined with isotropic thermal parameters. Crystal data, data collection parameters, and results of the analyses are listed in Tables D1 and D2 in Appendix D.

The compound Ni(η²-TEMPO)₂, 5.1t, crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the unique space group P2₁/n. With Z = 2 the molecule is crystallographically centrosymmetrical and thus contains only one-half of the formula equivalent of the molecule in the asymmetric crystal unit.
The compound Ni(η²-TEMPO)(κ¹-TEMPO)(κ¹-CNBu³), 5.2c, crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the unique space group P2₁/n.

Compound Ni(η²-TEMPO)(κ¹-TEMPOH)(κ¹-CCPh), 5.3c, crystallized in the triclinic crystal system. The space group P1̅ was assumed and confirmed by the successful solution and refinement of the structure.

The compound Ni(η²-TEMPO)(κ¹-TEMPOH)(κ¹-CCSiMe₃), 5.4c, crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the unique space group P2₁/c.

The compound Ni(η²-TEMPO)(κ¹-TEMPOH)(κ¹-CCH), 5.5c crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the unique space group P2₁/c.

The compound and Ni(η²-TEMPO) (κ¹-TEMPOH)(κ¹-CC[C₆H₄]CCH), 5.7c crystallized in the triclinic crystal system. The space group P1̅ was assumed and confirmed by the successful solution and refinement of the structure.

The compound Ni(η²-TEMPO)(k¹-TEMPOH)[k¹CC(C₆H₄)CC]Ni(η²-TEMPO)(k¹-TEMPOH), 5.8cc crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the unique space group P2₁/c. The molecule is also crystallographically centrosymmetrical, and, moreover, the asymmetric unit contains two molecules of benzene from the crystallization solvent that co-crystallized with the complex.
The compound Ni(η²-TEMPO)(k¹-TEMPO)(κ¹-NC₅H₅), \textbf{5.9t}, crystallized in the orthorhombic crystal system. The systematic absences in the intensity data were consistent with the unique space group Pbca.

Compounds Ni(η²-TEMPO)\textsubscript{2}, \textbf{5.1t}, Ni(η²-TEMPO)(k¹-TEMPO)(κ¹-CNBu\textsuperscript{t}), \textbf{5.2c}, Ni(η²-TEMPO)(κ¹-TEMPOH)(κ¹-CCPh), \textbf{5.3c}, and Ni(η²-TEMPO)(k¹-TEMPO)(κ¹-NC₅H₅), \textbf{5.9t}, decompose rapidly in air and thus their X-ray data collections were performed at 100 K under flow of N₂.
References.


<table>
<thead>
<tr>
<th>Number</th>
<th>Reference</th>
</tr>
</thead>
</table>


130. Praetorius, J. M.; Crudden, C. M. *Dalton. Trans.* **2008**, 4057–4180.


237. Frisch, M. J. *Frisch, M. J. Gaussian 09, Rev. B.01; Gaussian, Inc.: Wallingford, CT, 2009.*


Appendix A: Supporting Information for Chapter 2.

Table A.1. Crystallographic data for compounds 2.1, 2.3 and 2.4.

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<th>Compound</th>
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<th>2.4</th>
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<td>Pt&lt;sub&gt;2&lt;/sub&gt;Sn&lt;sub&gt;4&lt;/sub&gt;C&lt;sub&gt;40&lt;/sub&gt;H&lt;sub&gt;94&lt;/sub&gt;</td>
<td>Pt&lt;sub&gt;2&lt;/sub&gt;Sn&lt;sub&gt;4&lt;/sub&gt;C&lt;sub&gt;42&lt;/sub&gt;H&lt;sub&gt;94&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>Lattice parameters</td>
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<td>c (Å)</td>
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<td>P&lt;sub&gt;2&lt;/sub&gt;1&lt;sub&gt;n&lt;/sub&gt; (# 14)</td>
<td>P ̅&lt;sub&gt;T&lt;/sub&gt; (# 2)</td>
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<td>0.0391; 0.0974</td>
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<td>Multi-scan</td>
<td>Multi-scan</td>
</tr>
<tr>
<td>Largest peak in Final Diff. Map (e&lt;sup&gt;−&lt;/sup&gt;/ Å&lt;sup&gt;3&lt;/sup&gt;)</td>
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<td>0.994</td>
<td>0.995</td>
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*R = Σ<sub>hkl</sub>(|F<sub>obs</sub> - |F<sub>calc</sub>|)/Σ<sub>hkl</sub>|F<sub>obs</sub>|; R<sub>w</sub> = [Σ<sub>hkl</sub>W(|F<sub>obs</sub> - |F<sub>calc</sub>|)²/Σ<sub>hkl</sub>W<sup>2</sup>]<sup>1/2</sup>,

w = 1/σ<sup>2</sup>(F<sub>obs</sub>); GOF = [Σ<sub>hkl</sub>W(|F<sub>obs</sub> - |F<sub>calc</sub>|)²/(n<sub>data</sub> − n<sub>var</sub>)]<sup>1/2</sup>.
Table A.2. Crystallographic data for compounds 2.5, 2.6 and 2.8.

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<td>PtSn$<em>3$N$<em>2$C$</em>{64}$H$</em>{64}$</td>
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<td>Lattice parameters</td>
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<td>13.2568(6)</td>
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<td>$b$ (Å)</td>
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<td>$c$ (Å)</td>
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*GOF = $\sum_{hkl}w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2/\sum_{hkl}wF_{\text{obs}}^2$; Residuals* = $R_1 = \frac{\sum_{hkl}(|F_{\text{obs}}| - |F_{\text{calc}}|)^2}{\sum_{hkl}wF_{\text{obs}}^2}$; R$_w$ = $\frac{\sum_{hkl}w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2}{\sum_{hkl}wF_{\text{obs}}^2}^{1/2}$, w = $1/\sigma^2(F_{\text{obs}})$. 

$R = \sum_{hkl}(|F_{\text{obs}}| - |F_{\text{calc}}|)/\sum_{hkl}|F_{\text{calc}}|$. 

$w = 1/\sigma^2(F_{\text{obs}}); \text{GOF} = (\sum_{hkl}w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2)/n_{\text{data}}/n_{\text{vari}}$. 

$\sigma^2(F_{\text{obs}})$.
Table A.3. Crystallographic data for compounds 2.9, 2.10 and 2.11.

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<td><strong>γ</strong> (deg)</td>
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*R = Σ<sub>hkl</sub>(|F<sub>obs</sub>| - |F<sub>calc</sub>|) / Σ<sub>hkl</sub>|F<sub>obs</sub>|; w = 1/σ²(F<sub>obs</sub>); GOF = [Σ<sub>hkl</sub>w(|F<sub>obs</sub>| - |F<sub>calc</sub>|)²/Σ<sub>hkl</sub>w|F<sub>obs</sub>|²]¹/², w = 1/σ²(F<sub>obs</sub>); GOF = [Σ<sub>hkl</sub>w(|F<sub>obs</sub>| - |F<sub>calc</sub>|)²/(n<sub>data</sub> - n<sub>vari</sub>)]¹/².
Table A.4. Crystallographic data for compounds 2.12 and 2.13.

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<td>b (Å)</td>
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<td>c (Å)</td>
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<td>γ (deg)</td>
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<td>90.00</td>
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<td>2499.0(3)</td>
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<td>Pmmn (# 59)</td>
</tr>
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<td>Z value</td>
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<td>2</td>
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<td>0.001</td>
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<td>0.0442; 0.1369</td>
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<tr>
<td>Absorption Correction, Max/min</td>
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<td>Multi-scan</td>
</tr>
<tr>
<td>Largest peak in Final Diff. Map (e$^-$/Å$^3$)</td>
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*R = Σ$_{hkl}$ (|F$^{obs}$| - |F$^{calc}$|)/Σ$_{hkl}$ |F$^{obs}$|; R$_{w}$ = [Σ$_{hkl}$w(|F$^{obs}$| - |F$^{calc}$|)$^2$/Σ$_{hkl}$wF$_{obs}^2$]$^{1/2}$; w = 1/σ$^2$(F$^{obs}$); GOF = [Σ$_{hkl}$w(|F$^{obs}$| - |F$^{calc}$|)$^2$/n$_{data}$ - n$_{var}$]$^{1/2}$. 
Figure A.1. An ORTEP of the molecular structure of Pt(SnBu$_3$)(CNBu), 2.7 showing 30% thermal ellipsoid probability.
**Appendix B: Supporting Information for Chapter 3**

**Table B.1. Crystallographic data for compounds 3.1 and 3.3.**

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<tr>
<th>Compound</th>
<th>3.1</th>
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</tr>
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<tr>
<td>Empirical formula</td>
<td>Pt$<em>2$Sn$<em>2$C$</em>{46}$H$</em>{96}$N$_4$</td>
<td>PtSnC$<em>{24}$H$</em>{48}$N$_2$O</td>
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<tr>
<td>Formula weight</td>
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<td>694</td>
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<td>Crystal system</td>
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**Lattice parameters**

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<td>$b$ (Å)</td>
<td>11.76800(10)</td>
<td>27.5135(7)</td>
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<tr>
<td>$c$ (Å)</td>
<td>13.5031(2)</td>
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<td>102.1810(10)</td>
<td>90.00</td>
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<td>$\beta$ (deg)</td>
<td>106.6930(10)</td>
<td>104.69</td>
</tr>
<tr>
<td>$\gamma$ (deg)</td>
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<td>90.00</td>
</tr>
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<td>$V$ (Å$^3$)</td>
<td>1324.02(3)</td>
<td>5936.3(2)</td>
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<td>$P \bar{1}$ (# 2)</td>
<td>$P2_1/c$ (# 14)</td>
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<tr>
<td>Z value</td>
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<td>8</td>
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<td>54.0</td>
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<td>No. Parameters</td>
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<td>9939</td>
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<td>Goodness of fit GOF*</td>
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<td>Max. shift in cycle</td>
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<td>0.005</td>
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<td>Residuals*: R1; wR2</td>
<td>0.0145; 0.0366</td>
<td>0.0279; 0.0562</td>
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<tr>
<td>Absorption Correction,</td>
<td>Multi-Scan</td>
<td>Multi-scan</td>
</tr>
<tr>
<td>Max/min</td>
<td>0.7062/0.3163</td>
<td>0.8969/0.2690</td>
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<tr>
<td>Largest peak in Final Diff. Map (e$^-$/Å$^3$)</td>
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<td>1.000</td>
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*R = \Sigma_{hkl}[(F_{\text{obs}} - |F_{\text{calc}}|)/\Sigma_{hkl}|F_{\text{obs}}|; R_w = [\Sigma_{hkl}w(F_{\text{obs}} - |F_{\text{calc}}|)^2/\Sigma_{hkl}wF_{\text{obs}}^2]^{1/2}; w = 1/\sigma^2(F_{\text{obs}}); \text{GOF} = [\Sigma_{hkl}w(F_{\text{obs}} - |F_{\text{calc}}|)^2/(n_{\text{data}} - n_{\text{vari}})]^{1/2}.
Table B.2. Crystallographic data for compounds 3.5 and 3.7.

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<th>3.6</th>
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<td>PtSnC_{24}H_{74}N_{2}O</td>
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<td>Formula weight</td>
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<td>Crystal system</td>
<td>Triclinic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Lattice parameters</td>
<td></td>
<td></td>
</tr>
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<td>$a$ (Å)</td>
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<td>11.9259(5)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>12.3233(5)</td>
<td>13.9050(6)</td>
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<td>$c$ (Å)</td>
<td>14.8142(6)</td>
<td>26.0856(10)</td>
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<td>96.2210(10)</td>
<td>90.00</td>
</tr>
<tr>
<td>$\beta$ (deg)</td>
<td>93.0120(10)</td>
<td>90.00</td>
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<td>$\gamma$ (deg)</td>
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<td>90.00</td>
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<td>$V$ (Å$^3$)</td>
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<td>4325.8(3)</td>
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<td>$P\bar{1}$ (# 2)</td>
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<td>4</td>
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<td>$\rho_{\text{calc}}$ (g / cm$^3$)</td>
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<td>0.002</td>
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<td>Multi-scan</td>
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<td>Absorption Correction, Max/min</td>
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<td>0.0330; 0.0665</td>
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<td>Largest peak in Final Diff. Map (e$^-$/Å$^3$)</td>
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<td>1.262</td>
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*R = Σ$_{hk}$|F$_{obs}$ - F$_{calc}$|/Σ$_{hk}$|F$_{obs}$|; R$_{w}$ = [Σ$_{hk}$w(|F$_{obs}$| - |F$_{calc}$|)$^2$/Σ$_{hk}$wF$_{obs}^2$]$^{1/2}$, w = 1/$\sigma^2$(F$_{obs}$); GOF = [Σ$_{hk}$w(|F$_{obs}$| - |F$_{calc}$|)$^2$/n$_{data}$ - n$_{vari}$]$.1/2$. 
Appendix C: Supporting Information for Chapter 4.

Table C.1. Crystallographic data for compounds Ni(SnBu<sub>3</sub>)<sub>2</sub>(CNBu<sub>3</sub>)<sub>3</sub>, 4.1 and Ni(SnBu<sub>3</sub>)<sub>2</sub>(CNBu<sub>3</sub>)<sub>2</sub>(CO), 4.2.

<table>
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<tr>
<th>Compound</th>
<th>4.1•C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</th>
<th>4.2•Et&lt;sub&gt;2&lt;/sub&gt;O</th>
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</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>NiSn&lt;sub&gt;2&lt;/sub&gt;N&lt;sub&gt;3&lt;/sub&gt;C&lt;sub&gt;45&lt;/sub&gt;H&lt;sub&gt;87&lt;/sub&gt;</td>
<td>NiSn&lt;sub&gt;2&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;39&lt;/sub&gt;H&lt;sub&gt;82&lt;/sub&gt;</td>
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<td>Formula weight</td>
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<td>Orthorhombic</td>
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<td>b (Å)</td>
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<td>c (Å)</td>
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<td>9.2939(4)</td>
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<td>90.00</td>
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<tr>
<td>β (deg)</td>
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<td>90.00</td>
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<td>γ (deg)</td>
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<td>90.00</td>
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<td>V (Å&lt;sup&gt;3&lt;/sup&gt;)</td>
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<td>Multi-scan</td>
<td>Multi-scan</td>
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<tr>
<td>Largest peak in Final Diff. Map (e&lt;sup&gt;-&lt;/sup&gt;/Å&lt;sup&gt;3&lt;/sup&gt;)</td>
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<td>0.569</td>
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*R = Σ<sub>hkl</sub>|F<sub>obs</sub>| - |F<sub>calc</sub>| / |Σ<sub>hkl</sub>|F<sub>obs</sub>| ; R<sub>w</sub> = [Σ<sub>hkl</sub>W(|F<sub>obs</sub>|- |F<sub>calc</sub>|)<sup>2</sup>]<sup>1/2</sup>/Σ<sub>hkl</sub>W|F<sub>obs</sub>|<sup>2</sup>; w = 1/σ<sup>2</sup>(F<sub>obs</sub>) ; GOF = [Σ<sub>hkl</sub>W(|F<sub>obs</sub>|- |F<sub>calc</sub>|)<sup>2</sup>]<sup>1/2</sup>/n<sub>data</sub> - n<sub>vari</sub>).
Table C.2  Crystallographic data for compounds [Ni(Sn\text{Bu}t)\text{BuNC}\text{(CO)}_2]_4.4 and Ni(\eta^2\text{-TEMPO})(\text{SnBu}_3^\text{t})(\text{CNBu}^\text{t}), 4.5.

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<td>NiSnON$<em>2$C$</em>{26}$H$_{54}$</td>
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<td>Monoclinic</td>
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<td></td>
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<td>$b$ (Å)</td>
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<td>11.3442(4)</td>
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<td>$c$ (Å)</td>
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<td>17.5158(7)</td>
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<td>90.00</td>
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<td>$\beta$ (deg)</td>
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<td>$\gamma$ (deg)</td>
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<td>90.00</td>
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<td>$V$ (Å$^3$)</td>
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<td>3224.5(2)</td>
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<td>$\rho_{\text{calc}}$ (g / cm$^3$)</td>
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<td>56.00</td>
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<td>Goodness of fit</td>
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<td>Max. shift in cycle</td>
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<td>0.004</td>
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<tr>
<td>Residuals*:R1; wR2</td>
<td>0.0317; 0.0782</td>
<td>0.0292; 0.0750</td>
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<tr>
<td>Absorption Correction,</td>
<td>Multi-scan</td>
<td>Multi-scan</td>
</tr>
<tr>
<td>Max/min</td>
<td>0.7465, 0.6127</td>
<td>0.7457, 0.5671</td>
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<td>Largest peak in Final Diff. Map (e$^-$/Å$^3$)</td>
<td>0.438</td>
<td>0.857</td>
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</table>

$^R = \sum_{hkl} (|F_{\text{obs}}| - |F_{\text{calc}}|) / \sum_{hkl} F_{\text{obs}}^2$; $R_w = (\sum_{hkl} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / \sum_{hkl} w F_{\text{obs}}^2)^{1/2}$, $w = 1/\sigma^2(F_{\text{obs}})$; GOF = $[\sum_{hkl} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / (n_{\text{data}} - n_{\text{vari}})]^{1/2}$. 

*
Figure C.1. Single crystal FTIR spectrum of Ni(SnBu$_3$)$_2$(CNBu)$_2$(CO) (purple) vs $^{13}$CO-Ni(SnBu$_3$)$_2$(CNBu)$_2$(CO) (black).

Figure C.2. Single crystal FTIR spectrum of [Ni(SnBu$_3$)(CNBu)$_2$(CO)]$_2$ (green) vs $^{13}$CO-[Ni(SnBu$_3$)(CNBu)$_2$(CO)]$_2$ (black).
Figure C.3. ESR spectrum of $^{12}$CO-[$\text{Ni(SnBu}_3\text{)(CNBu}_3\text{)}_2\text{(CO)}_2$] in toluene at 134 K.

Figure C.4. ESR spectrum of proposed $\text{Ni(SnBu}_3\text{)(tBuNC)}_3$ in toluene at 170 K.
Appendix D: Supporting Information for Chapter 5.

**Figure D.1.** $^1$H NMR spectra at 400 MHz of Ni($\eta^2$-TEMPO)(κ$^1$-TEMPO)(CN$^t$Bu), 5.2c at various temperatures in toluene-$d_8$ solvent. * denotes the methyl peak from toluene-$d_8$ solvent.
Figure D.2. 2D [$^1$H, $^{15}$N] HSQC NMR spectra of Ni($^{\eta^2}$-TEMPO)($^{\kappa^1}$-TEMPOH)($^{\kappa^1}$-CCPh), 5.3c in toluene-$d_8$. The $^{15}$N chemical shift is with reference to liquid NH$_3$.

Figure D.3. $^1$H NMR spectrum of Ni($^{\eta^2}$-TEMPO)($^{\kappa^1}$-TEMPOH)($^{\kappa^1}$-CCPh), 5.3c (black) and Ni($^{\eta^2}$-TEMPO)($^{\kappa^1}$-TEMPOD)($^{\kappa^1}$-CCPh), 5.3c-$d_1$ (red). * denotes acetylene hydrogen now on TEMPO nitrogen N2.
Figure D.4. $^1$H NMR spectrum of 5.1$t$ plus a 6:6 mixture of PhCCH and PhCCD in toluene-$d_8$ solvent at room temperature.

Figure D.5. $^2$H NMR spectrum of 5.1$t$ plus a 6:6 mixture of PhCCH and PhCCD in toluene solvent at room temperature.
<table>
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<th>5.3c</th>
</tr>
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<td>NiO$<em>2$N$<em>2$C$</em>{18}$H$</em>{36}$</td>
<td>NiO$<em>2$N$<em>3$C$</em>{23}$H$</em>{45}$</td>
<td>NiO$<em>2$N$<em>2$C$</em>{26}$H$</em>{42}$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>371.20</td>
<td>454.33</td>
<td>473.33</td>
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<td>Crystal system</td>
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<td>Monoclinic</td>
<td>Triclinic</td>
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<tr>
<td>Lattice parameters</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>$a$ (Å)</td>
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<td>8.3519(3)</td>
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<td>$b$ (Å)</td>
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<td>$c$ (Å)</td>
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<td>$\alpha$ (deg)</td>
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<td>90.00</td>
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<tr>
<td>$\beta$ (deg)</td>
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<td>92.041(7)</td>
<td>95.8880(5)</td>
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<tr>
<td>$\gamma$ (deg)</td>
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<td>90.00</td>
<td>107.7300(4)</td>
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<tr>
<td>V (Å$^3$)</td>
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<td>2568.54(17)</td>
<td>1285.55</td>
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<tr>
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<td>$P2_1/n$ (# 14)</td>
<td>$P \overline{1}$ (# 2)</td>
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<tr>
<td>Z value</td>
<td>2</td>
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<td>2</td>
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<td>$\rho_{\text{calc}}$ (g / cm$^3$)</td>
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<td>$\mu$ (Mo K(\alpha)) (mm$^{-1}$)</td>
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<td>0.778</td>
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<td>Multi-scan</td>
<td>Multi-scan</td>
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<tr>
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*R = \(\sum_{hkl}(|F_{\text{obs}}| - |F_{\text{calc}}|) / \sum_{hkl}F_{\text{obs}}\); R\(_w\) = \(\sum_{hkl}w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / \sum_{hkl}wF_{\text{obs}}^2\)^{1/2};
\(w = 1/\sigma^2(F_{\text{obs}})\); GOF = \(\sum_{hkl}w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / (n_{\text{data}} - n_{\text{vari}})\)^{1/2}.
Table D.2. Crystallographic Data for compounds 5.4c, 5.5c and 5.7c.

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<th>5.7c</th>
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<td>NiO$<em>2$N$<em>2$C$</em>{20}$H$</em>{38}$</td>
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<td>Lattice parameters</td>
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<td>$a$ (Å)</td>
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<td>0.001</td>
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<td>0.0307; 0.0813</td>
<td>0.0275; 0.0757</td>
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<td>Absorption Correction, Max/min</td>
<td>Multi-scan</td>
<td>Multi-scan</td>
<td>Multi-scan</td>
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<tr>
<td>Largest peak in Final Diff. Map $e^3$ / Å$^3$</td>
<td>0.931</td>
<td>0.260</td>
<td>0.371</td>
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*R = \[ \Sigma_{hkl}(|F_{obs}| - |F_{calc}|)/\Sigma_{hkl}|F_{obs}|; R_w = [\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\Sigma_{hkl}wF_{obs}^2]^{1/2}, \\
w = 1/\sigma^2(F_{obs}); \text{GOF} = [\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|)^2/(n_{data} - n_{vari})]^{1/2}.


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<td>Lattice parameters</td>
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<td>b (Å)</td>
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<td>14.8196(6)</td>
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<td>c (Å)</td>
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<td>γ (deg)</td>
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<td>90.00</td>
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<td>V (Å³)</td>
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<td>4819.7(3)</td>
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<td>Pbca (# 61)</td>
</tr>
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<td>ρ&lt;sub&gt;calc&lt;/sub&gt; (g / cm³)</td>
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<td>1.241</td>
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<td>µ (Mo Kα) (mm⁻¹)</td>
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<td>2Θ&lt;sub&gt;max&lt;/sub&gt; (°)</td>
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<td>57.00</td>
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<td>Goodness of fit</td>
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<td>0.001</td>
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<tr>
<td>Residuals*: R1; wR2</td>
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<tr>
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<td>Multi-scan</td>
</tr>
<tr>
<td>Max/min</td>
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<td>0.9677/0.8137</td>
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<td>Largest peak in Final Diff. Map (e⁻ / Å³)</td>
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<td>0.340</td>
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*R = Σ<sub>hkl</sub>[(|F<sub>obs</sub>| - |F<sub>calc</sub>|)²/Σ<sub>hkl</sub>|F<sub>obs</sub>|²]; R<sub>w</sub> = [Σ<sub>hkl</sub>W(|F<sub>obs</sub>|² - |F<sub>calc</sub>|²)²/Σ<sub>hkl</sub>W²F<sub>obs</sub>²]¹/², w = 1/σ²(F<sub>obs</sub>); GOF = [Σ<sub>hkl</sub>W((|F<sub>obs</sub>| - |F<sub>calc</sub>|)²/(σ<sub>data</sub>² - σ<sub>var</sub>²))]¹/².
Table D.4. Solution-phase reaction free energies ($\Delta G_{\text{soln}}$ in kcal mol$^{-1}$) of bimetallic complexes and relative free energies ($\Delta\Delta G_{\text{soln}}$ in kcal mol$^{-1}$) of isomers of complex 5.8 (isomer 5.8cc is arbitrarily set to 0.0 kcal mol$^{-1}$).

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<th></th>
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<th>B3LYP</th>
</tr>
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<td>2 equiv 5.1t + HCCH → 5.6cc</td>
<td>5.4</td>
<td>14.4</td>
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<tr>
<td>5c + 5.1t → 5.6cc</td>
<td>9.2</td>
<td>15.8</td>
</tr>
<tr>
<td>5.8cc 5.8ct 5.8tt</td>
<td>0.0 4.1 9.2</td>
<td>0.0 3.3 5.6</td>
</tr>
<tr>
<td>2 equiv 5.1t + HCCPhCCH → 5.8cc</td>
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<td>-0.3</td>
</tr>
<tr>
<td>5.7c + 5.1t → 5.8cc</td>
<td>-0.8</td>
<td>1.1</td>
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Figure D.6. $^1$H NMR spectra for the addition of excess amounts of pyridine to 5.1t at room temperature.
Figure D.7. $^1$H NMR spectra at 400 MHz of compound Ni($\eta^2$-TEMPO)($\eta^1$-TEMPO)($\kappa^1$-N$_5$H$_5$), 5.9$t$ at various temperatures in toluene-$d_8$ solvent.
Table D.5. Relative free energies and energies of activation (in kcal mol⁻¹). Experimentally observed isomer is in bold.

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Scheme D.1. Addition of HCCH to 5.1t.

Scheme D.2. Addition of HCCH to 5.1c.
Scheme D.3. Addition of HCCSiMe$_3$ to form 5.4\textit{t}.

Scheme D.4. Addition of HCCSiMe$_3$ to form 5.4\textit{c}.
Scheme D.5. Addition of HCC(Ph)CCH to form 5.7t

Scheme D.6. Addition of HCC(Ph)CCH to form 5.7c.
Table D.6. Computed total dipole moments (in Debye).

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<th>5.8cc</th>
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<td>B3LYP</td>
<td>1.821</td>
<td>B3LYP</td>
<td>5.338</td>
<td>B3LYP</td>
<td>0.000</td>
</tr>
<tr>
<td>PBE</td>
<td>0.823</td>
<td>PBE</td>
<td>5.637</td>
<td>PBE</td>
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<td>6.753</td>
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<tr>
<td>PBE</td>
<td>1.280</td>
<td>PBE</td>
<td>4.877</td>
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Description of computed NMR spectra for complex 5.1

Computed NMR data shows the lowest energy conformers of both *cis* and *trans* isomers of 5.1 have fortuitously similar chemical shifts. The isomerization of *cis* and *trans* isomers of 5.1 is possible at room temperature but would not be observed in the VT NMR because the coalescence of peaks would not produce new chemical shifts different
than those already present in the spectrum. Our hypothesis derived from the computational results is that the only expected alteration in the spectrum would be a visually imperceptible change in the peak integrations. The NMR chemical shift computations rely upon a variety of approximations and the absolute chemical shift values are difficult to accurately compute. Organometallic complexes present even further challenges in accurately computing chemical shifts. Therefore, we will rely more heavily upon the differences in chemical shifts.

One would reasonably expect obvious and quantitative differences in the spectra of 5.1,t and 5.1,c. However, the results of the NMR computations are surprising. From the experimental NMR spectra, the two sets of four methyls have averaged chemical shifts of 2.39 and 1.36 ppm, respectively. The computed values for 5.1,t (chair/chair) are 2.10 and 1.18 ppm. Again, even though we expect to not as accurately compute the chemical shift, the placement of the peaks in the spectrum for 5.1,t still compare fairly well. The differences in these shifts (1.03 versus 0.92) are in excellent agreement (for computed NMR chemical shifts). For 5.1,t, the experimental propylene CH2 proton range is 1.40 – 1.25 ppm. The computed chemical shifts are computed to be more downfield, ranging from 1.69 – 1.52 ppm.

The “chair-axial/chair” form is the lowest energy conformation of the cis isomer of 5.1 (5.1,c) and is computationally determined to be ~ 4 kcal mol-1 less stable than the lowest energy conformation of the trans isomer of 5.1 (5.1,t - “chair/chair” form). Assume the isomerization to the lowest-energy cis form is possible at slightly elevated temperatures (as our computations indicate). At room temperature, approximately 0.1% of the complex in solution will be in the 5.1,c form. The detection limit for NMR is
typically considered to be in the parts per thousand. Even considering this detection limit, the range of the propylene proton chemical shifts for both the “chair” and “chair-axial” side (1.74 – 1.57 ppm) of 5.1c fall within or are very close to the computed range for 5.1t. More importantly, the “chair” side methyl protons of 5.1c have essentially the same chemical shift as the 5.1t isomer, and the “chair-axial” side proton chemical shifts (1.73 and 1.49 ppm) now overlap with the propylene-type proton chemical shifts (further leading to the experimentally observed broadened peaks). Therefore, 5.1c will not significantly contribute to the observed NMR spectrum.

**Table D.7.** Computed chemical shifts (in ppm) of complex 5.1t, "chair/chair"

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<tr>
<th>H type</th>
<th>chemical shift</th>
<th>average of unique H shifts</th>
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<tr>
<td>CH3–</td>
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<tr>
<td></td>
<td>2.5</td>
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<tr>
<td>–CH2–</td>
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<td>1.18</td>
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<tr>
<td>–CH2–</td>
<td>1.39</td>
<td>1.69</td>
</tr>
<tr>
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<td>1.79</td>
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</tr>
<tr>
<td>CH3–</td>
<td>1.59</td>
<td>1.52</td>
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<td></td>
<td>1.27</td>
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Table D.8. Computed chemical shifts (in ppm) of complex 5.1c, "chair-axial/chair"

<table>
<thead>
<tr>
<th>chair-axial H type</th>
<th>chemical shift</th>
<th>chair H type</th>
<th>chemical shift</th>
<th>chair-axial side average of unique H shifts</th>
<th>chair side average of unique H shifts</th>
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</thead>
<tbody>
<tr>
<td>CH3–</td>
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<td>CH3–</td>
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<td></td>
<td>0.41</td>
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<td>2.89</td>
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</tr>
<tr>
<td></td>
<td>3.1</td>
<td></td>
<td>0.97</td>
<td></td>
<td></td>
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<tr>
<td>–CH2–</td>
<td>1.71</td>
<td>–CH2–</td>
<td>1.84</td>
<td>1.49</td>
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</tr>
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<td></td>
<td>0.91</td>
<td></td>
<td>0.44</td>
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<td>–CH2–</td>
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<td>–CH2–</td>
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<tr>
<td>CH3–</td>
<td>1.58</td>
<td>CH3–</td>
<td>1.71</td>
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<td>1.84</td>
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Figure D.8. Complex 5.1t “chair/chair” – C2h symmetric chemical shifts are omitted
**Figure D.9.** Complex 5.1c “chair-axial/chair” – $C_5$ symmetric chemical shifts are omitted