
Yafan. Lu
University of Windsor

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[4+3] CYCLOADDITIONS AND TANDEM [4+3]
CYCLOADDITION/NUCLEOPHILIC TRAPPING
REACTIONS OF PROPARGYLIC DIETHER DICOBALT
COMPLEXES VIA SEQUENTIAL NICHOLAS
REACTIONS

BY
YAFAN LU

FACULTY OF GRADUATE STUDIES AND RESEARCH
UNIVERSITY OF WINDSOR
2001
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CYCLOADDITION/NUCLEOPHILIC TRAPPING REACTIONS OF
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SEQUENTIAL NICHOLAS REACTIONS

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Yafan Lu

A Thesis
Submitted to the Faculty of Graduate Studies and Research
through the School of Physical Sciences in Partial
Fulfillment of the Requirements for the Degree
of Master of Science at the University of Windsor

Windsor, Ontario, Canada
2001
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ABSTRACT

The origin of the fluorinative [4+3] cycloaddition in the course of [4+3] cycloaddition of butyne-1,4-diether-Co₂(CO)₆ complex 75a was investigated. The fluorinated cycloadduct 76a was found to come from the initial destannylation of silylstannane 59 to give allylsilane 113. This destannylation is facilitated by [EtOBF₃], which is formed in the course of normal [4+3] cycloaddition. The resultant allylsilane 113 then reacts with the substrate 75a in the presence of BF₃-OEt₂ to form 76a via a cyclic 2° alkyl cationic intermediate 117. Despite the extreme sensitivity of [4+3] cycloaddition to the moisture, the normal cycloadditions free of fluorination were performed successfully with substrates 75a and 111. In the [4+3] cycloaddition of 111 with 59, regioisomeric mixture of cycloadducts 69b and 69b' was obtained in a ratio of 69b:69b'=1:1.3. This is in comparison with a regioisomeric ratio of 69b:69b'>30:1, obtained with substrate 68d. It was found that the substitution at the propargyl site and the bulkiness of the alkoxy group in the substrates are the major factors in determining the sequence of the two steps in the normal [4+3] cycloaddition.

Substantial efforts were focused on the trapping reactions of the cationic intermediate 117 and its methyl- and phenyl- substituted analogues, obtained by the use of the allyltrimethylsilane. Various trapping nucleophiles were employed, such as "F−", "Cl−", "Br−", benzene, toluene and chlorobenzene. The resultant trapping products 125a, 125b, 125c, 127a, 127b, 127c, 129, 130a, 130b, 130c, 135a and 135b were produced; good yields were achieved in most cases.
DEDICATION

I dedicate this thesis to my parents.
ACKNOWLEDGEMENTS

First of all I would like to show my first and most sincere thanks to my supervisor, Dr. James Green. His consistent support, effective instruction and true friendship in the past two years are greatly appreciated and will be remembered for ever.

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ABBREVIATIONS

ABq  AB quartet
br   broad
Bu   butyl
δ    chemical shift in ppm
d    doublet
dd   doublet of doublet
dt   doublet of triplet
EI   electron impact
equiv. equivalents
Et   ethyl
HRMS high resolution mass spectrometry
'Pr  isopropyl
IR   infrared spectroscopy
LDA  lithium diisopropylamide
m    multiplet
MAO  methylaluminum oxide
Me   methyl
Mp   melting point
MS   mass spectrometry
M.S. molecular sieves
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<td>Naph</td>
<td>naphthyl</td>
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<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
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<tr>
<td>NOE</td>
<td>nuclear Overhauser effect</td>
</tr>
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<td>NOESY</td>
<td>nuclear overhauser and exchange spectroscopy</td>
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<tr>
<td>Nu</td>
<td>nucleophile</td>
</tr>
<tr>
<td>q</td>
<td>quartet</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>p-TsOH</td>
<td>para-toluenesulphonic acid</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>s</td>
<td>singlet</td>
</tr>
<tr>
<td>TBDMS</td>
<td>'butyldimethylsilyl</td>
</tr>
<tr>
<td>Tf</td>
<td>triflic (-SO$_2$CF$_3$)</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TIPS</td>
<td>triisopropylsilyl</td>
</tr>
<tr>
<td>TLC</td>
<td>thin layer chromatography</td>
</tr>
<tr>
<td>TMS</td>
<td>trimethylsilyl</td>
</tr>
<tr>
<td>TMSOTf</td>
<td>trimethylsilyl triflate</td>
</tr>
<tr>
<td>TS</td>
<td>transition state</td>
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<td>triplet of triplet</td>
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INTRODUCTION

Cycloheptane derivatives have been of great interest in the past few decades due to the frequent occurrence of the cycloheptane structure in natural compounds and the difficulty in synthesis of these compounds.\textsuperscript{[1, 2]}

There are four general synthetic routes for the synthesis of cycloheptane ring systems (Figure 1): acyclic ring closure, ring size alteration (including ring expansion and contraction), ring scission and cycloaddition. This classification is based on the different type of starting materials; that is, each different route has a different change in complexity. In the synthetic perspective, the best strategy is the route which has least steps and has largest increase in the complexity from starting materials to products.\textsuperscript{[1]} Therefore, cycloaddition is superficially the best strategy among these four routes as two bonds are formed in only one operation.

![Figure 1. Synthetic Routes for Cycloheptane System](image)

There are two major types of cycloadditions for the construction of the cycloheptane ring structure. One is the [4+3] cycloaddition;\textsuperscript{[3 -11]} the other is the [5+2] cycloaddition.\textsuperscript{[12]}

1
1. [4+3] Cycloaddition Reactions

1.1. Cycloadditions of Allyl Cations

Fort reported the first [4+3] cycloaddition. He prepared a bridged bicyclic ketone (2) by the base induced reaction of α-chloro ketone (1) and furan via an oxyallyl cation (Figure 2).[13]

![Figure 2. The First Reported [4+3] Cycloaddition](image)

The accurate mechanism of such [4+3] cycloadditions using stabilized allyl cations depends on the nucleophilicity of the dienes, the electrophilicity of the allyl cation species and the electronic property of the heteroatom X on the C2 of the allyl cation.[14] Hoffman proposed three types of possible mechanisms for [4+3] cycloaddition reactions. Type A features concerted bond formation, whereas Type B involves a stepwise bond formation. Type C leads to five-membered cyclization products or electrophilic substitution products (Figure 3).[9]

![Figure 3. Mechanisms for [4+3] Cycloadditions of Allyl Cations](image)
Two types of transition states for the concerted version of the [4+3] cycloaddition have been proposed. One is an extended (chair-like) transition state, another is a compact (boat-like) transition state (TS) (Figure 4). Furan prefers the compact transition state to a greater degree than cyclopentadiene.\[5\]

![Diagram of compact and extended modes of transition state]

**Figure 4.** Transition State models for Concerted [4+3] Cycloadditions

The stereochemistry of these [4+3] cycloaddition reactions is more complicated than that of its isoelectronic analogue, the Diels-Alder reaction. The main reason is that the configuration of the allyl cation intermediate has several alternatives. There are three possible structures for substituted acyclic allyl cations, the U form (3), the sickle form (4), and the W form (5).

![Structures of allyl cations]

Generally, the W form is preferred.\[5\] Despite the complexity in the stereochemical parameters, a wise choice of reactants and reaction conditions
can still effect the [4+3] cycloaddition reaction with good yield and good stereoselectivity.

So far, most of the research work in [4+3] cycloadditions has concentrated on the methods of the preparation of allyl cations. The most widely used allyl cations are the 2-oxyallyl cations (6) (Figure 5). The most widely used diene partners are furan, cyclopentadiene and pyrrole derivative, etc.

One of most useful methods of preparing (6) is to reduce $\alpha,\alpha'$-dihaloketones (7) with an agent (Figure 5) such as Zn-Cu couple,[15] Fe$_2$(CO)$_5$[16,17] or Cu/Nal[18]. Under these conditions, halogenated metal enolates (8) are formed first, and then 2-oxyallyl cations (6) are obtained by the departure of a halide anion (Figure 5).[7]

\[
\begin{align*}
\text{Zn/Cu} & \quad \text{or Fe}_2\text{(CO)}_5 \\
\text{or Cu/Nal} & \quad \text{or Cu/Nal}
\end{align*}
\]

Figure 5. Preparation of 2-Oxyallyl Cations

The course of [4+3] cycloaddition depends greatly on the choice of the reducing agent. The Cu/Nal reduction conditions are believed to produce the least electrophilic oxyallyl cation, as compared with Zn/Cu and Fe$_2$(CO)$_5$ reduction conditions. Fe$_2$(CO)$_5$ is believed to produce the most electrophilic oxyallyl cation.[9] It can be seen from the reaction of 2,4-dibromopentan-3-one with furan (Figure 6) that the least electrophilic oxyallyl cation leads to a cycloaddition of Type A with a compact transition state to give 9 predominantly. Product 10 came from an extended TS, while 11 was believed to come from the
stepwise cycloaddition (Type B). With the increase of the oxyallyl cation electrophilicity, Type B cycloadditions were promoted. When N-methylpyrrole was employed as diene partner, only the Cu/NaI protocol gave cyclization.

![Cycloadditions with Different Reducing Agents](image)

The [4+3] cycloaddition of acyclic dienes with oxyallyl cation was also investigated. The efficiency was not good, but when the corresponding η⁴-butadienetricarbonyliiron(0) complex was used as diene partner, a 90% yield was achieved (Figure 7). It is believed that tricarbonyliiron(0) moiety can lock the 1,3-butadiene in its S-cis configuration required for the cycloaddition.

![Cycloaddition of Acyclic Dienes](image)

When cycloadditions of C₂-substituted furans were investigated, cis stereoselectivity and excellent endo diastereoselectivity were observed (Figure
8). The electron donating group increased both the yield and diastereoselectivity.\textsuperscript{[22]}

\begin{center}
\begin{tabular}{|c|c|c|c|}
\hline
X & Yield \% & \textit{cis}:\textit{trans} & \textit{endo}:\textit{exo} \\
\hline
Ph & 60 & 100:0 & 97:3 \\
OSiMe\textsubscript{3} & 86 & 100:0 & 95:5 \\
OCO\textsubscript{}Bu & 93 & 100:0 & 95:5 \\
OCOEt & 100 & 100:0 & 100:0 \\
\hline
\end{tabular}
\end{center}

Figure 8. Cycloadditions of C\textsubscript{2}-substituted Furans

Lewis acid or silver salt promoted heterolysis of allyl halides are very direct methods to generate allyl cations.\textsuperscript{[23, 24]} For the 2-methoxyallyl and 2-silyloxyallyl cation systems, however, the efficiency for the [4+3] cycloaddition is modest.\textsuperscript{[24, 25]} The choice of solvent has a great influence on the course of the [4+3] cycloaddition of the 2-silyloxyallyl system, changing the cycloaddition mechanism from a concerted pathway in nitromethane to a stepwise pathway in THF/Et\textsubscript{2}O mixed solvent.\textsuperscript{[26]}

Excellent efficiency has been achieved in the Lewis acid (TiCl\textsubscript{4}) promoted [4+3] cycloaddition of (trimethylsilyl)methylallyl acetals with furan or cyclopentadiene (Figure 9). Only one diastereomer was obtained with all substrates employed. It is noteworthy that even a catalytic amount of TMSOTf can achieve a 65\% yield in the cycloaddition with furan.\textsuperscript{[27]}
Lewis acid TMSOTf has been used in the cycloaddition of α,α-dimethoxy silyl enol ethers with furan or 2,5-dimethylfuran. High diastereoselectivity and high yield can be achieved separately, but not simultaneously.\textsuperscript{[28]}

2-(Silyloxy)acroleins have been used in the Lewis acid mediated cycloaddition of furan and its derivatives.\textsuperscript{[29, 30]} Catalytic amounts of scandium triflate (10 mol%) effected these cycloadditions in good yields and 100% diastereoselection (Figure 10).\textsuperscript{[30]}

Chiral furan derivatives have been used in asymmetric intermolecular cycloadditions with 2,4-dibromopentan-3-one. De's at ≥90% were consistently achieved with medium to good yields (Figure 11). It is noteworthy that diaxial cycloadducts were consistently obtained in these cases. They were believed to stem from the chelation of ZnEt\textsubscript{2} with the oxygen atom on furan and the oxygen atom in oxyallyl cation. This chelation made the cycloaddition proceed with extended TS in a concerted pathway leading to the formation of diaxial cycloadducts.\textsuperscript{[31]}
The Lewis acid mediated asymmetric intermolecular cycloadditions of chiral allyl cations have been studied. Synthetically useful chiral allyl cations have been generated from $\alpha,\alpha'$-dialkoxy silyl enol ethers in reactions promoted by catalytic amounts of TMSOTf. The best diastereoselection was 100% de (Figure 12). In these systems, the aromatic group (Ph or Naph) was proposed to block one $\pi$-face of the allyl cation. The diene partner could only approach the allyl cation from the other $\pi$-face, so the stereoselectivity was achieved.

The use of basic conditions to generate oxyallyl cations from $\alpha$-haloketones is still a popular protocol for [4+3] cycloadditions, particularly for cyclic precursors, where the reductive conditions show low efficiencies. Base-mediated asymmetric cycloaddition of cyclic oxyallyl cations bearing adjacent
chiral centers has been tried with modest success, although >90% de was achieved once with an unknown yield.\footnote{41}

\[
\begin{align*}
\text{Br} & \quad \text{Ko} & \quad \text{Br} & \quad \text{Fe}_2(\text{CO})_9, \text{C}_6\text{H}_6 & \quad \text{R} = \text{H} & \quad 41\
\text{R} & \quad \text{O} & \quad \text{Me} & \quad 80^\circ\text{C}, 3\text{h} & \quad \text{Me} & \quad 38%
\end{align*}
\]

Figure 13. The First Reported Intramolecular [4+3] Cycloaddition

Noyori reported the first example of intramolecular [4+3] cycloaddition, although yields were low (Figure 13).\footnote{42} Better yields and good diastereoselectivity were first achieved by LiClO\(_4\) mediated intramolecular cycloadditions of dihaloketones. Curiously, the excellent simple diastereoselectivity (94:6 at the ring juncture) of \(\alpha,\alpha\)-dichloro substrate (Figure 14) decreased substantially upon substitution of a methyl group for one chloro function (a:b:c:d = 40:36:23:1), despite the excellent yield (84%).\footnote{43, 44}

\[
\begin{align*}
\text{Cl} & \quad \text{Ko} & \quad \text{Cl} & \quad \text{LiClO}_4, \text{ether} & \quad \text{H} & \quad \text{Cl} & \quad \text{a: } \alpha\text{-Cl} & \quad \text{b: } \beta\text{-Cl} & \quad \text{c: } \alpha\text{-Cl} & \quad \text{d: } \beta\text{-Cl}
\end{align*}
\]

Figure 14. LiClO\(_4\) Mediated Intramolecular Cycloaddition

Giguere found that the stereochemistry of allylic cations has large effect on the course of the cycloaddition. Treatment of 12 with triflic anhydride and 2,6-lutidine under high dilution conditions afforded 13 as a major isomer with excellent diastereoselectivity (92:5:3). Conversely 14, the isomer of 12, formed
[3+2] cycloadducts 15 as a major product in a ratio of 93:7, instead of the [4+3] cycloadducts (Figure 15).[^45]

![Chemical structures showing cycloaddition](image)

Figure 15. Cycloaddition Affected by Stereochemistry of Allylic Cation

Harmata introduced sulfur to the alkoxyallylic sulfone substrates to facilitate the formation of oxyallyl cations and therefore for the improvement of the yield.[^46] For example, when substrate 16 was treated with titanium tetrachloride, epimers 17 and 18 were formed with 86% yield (Figure 16).[^47]

![Chemical structures showing titanium tetrachloride mediated intramolecular cycloaddition](image)

Figure 16. Titanium Tetrachloride Mediated Intramolecular Cycloaddition of Sulphur-substituted Alkoxyallylic Sulfone Substrates

Harmata has reported the first non-photochemical intramolecular cycloaddition of a cyclic oxyallyl cation. In the event, 19 was subjected to LDA
followed by triflyl chloride to form chloroketone, which was then treated with lithium perchlorate and triethylamine to afford cycloadducts 20 in 54% yield; diastereoselection was 16:1 in favour of the product from the compact TS (Figure 17).[^48] [^49]

![Figure 17. First Non-photochemical Intramolecular Cycloaddition of Cyclic Oxyallyl Cation](image)

Larger ring cyclic oxyallylic cations have also been studied. Substrate 21 was subjected to the same conditions as that for 19, giving 1:2.5 mixture of cycloadduct stereoisomers 22a and 22b in 61% yield (Figure 18). It is noteworthy that the major stereoisomer was formed from the extended TS. Some other larger ring cyclic oxyallylic cations were also found to cycloadd via an extended TS.[^50] This is opposite to the corresponding intermolecular cycloaddition case, where the major product came from the compact TS.[^50]

![Figure 18. Larger Ring Cyclic Oxyallyl Cation [4+3] Cycloaddition](image)
In the intramolecular cyclic cation case, substituted butadiene substrates can
cycloadd in good yield. Treatment of substrate 23 with titanium tetrachloride
afforded 24a and 24b in a ratio of 2.4:1 in good yield (Figure 19).\[^{40}\] Recently,
some efforts have focused on the employment of intramolecular [4+3]
cycloaddition for the preparation of natural products such as aphanamol,\[^{51}\]
racemic lasidiol,\[^{52}\] (+)-dactylol\[^{53}\] and 5,7-fused ring systems.\[^{54}\]

![Cycloaddition of Substituted Butadiene Substrates](image)

Figure 19. Cycloaddition of Substituted Butadiene Substrates

The photochemical generation of cyclic allylic cations for the intramolecular
cycloaddition has been investigated more thoroughly and more successfully than
that for acyclic cations. Substrate 25 was irradiated in benzene to product 26 as
a single diastereomer in 80% yield (Figure 20). Under the same conditions,
substrate 27 cycloadded to form product 28 with quantitative yield (Figure 20).\[^{55, 56}\]
Figure 20. Photochemical Intramolecular [4+3] Cycloadditions

1.2. Cycloadditions of 1,4-Dicarboxyls

A distinctly different type of Lewis acid promoted [4+3] cycloaddition has been developed by Molander.\textsuperscript{[57-54]} These cycloadditions use 1,4-dicarbonyl electrophiles 29 and bis(trimethylsilyl) enol ethers 30 as 1,3-dinucleophiles (Figure 21).\textsuperscript{[58]} The regioselectivity of cycloadducts 31 comes from the initial attack of the terminal carbon of bis(trimethylsilyl) enol ethers at the more sterically hindered carbonyl center of 29. The Molander cycloadditions of 1,4-ketoacetals gave the same type of regiochemistry.\textsuperscript{[60]} For the 1,4-ketoaldehyde, extremely high regioselectivities (>200:1) were always achieved.\textsuperscript{[58, 59]} For the unsymmetrical 1,4-diketones, the regioselectivity was much lower (Figure 21).\textsuperscript{[58]}

A mechanism was proposed by Molander, which invokes a unique neighboring group participation which blocks the less sterically hindered carbonyl function using the carbonyl oxygen of the larger carbonyl, thereby activating the latter group to attack (Figure 22).\textsuperscript{[58, 59, 60]}
Figure 21. Molander [4+3] Cycloadditions

<table>
<thead>
<tr>
<th>R₂</th>
<th>R₃</th>
<th>Yield %</th>
<th>Diastereoselectivity (regioselectivity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>H</td>
<td>53</td>
<td>&gt;200:1</td>
</tr>
<tr>
<td>n-Pr</td>
<td>H</td>
<td>78-90</td>
<td>&gt;200:1</td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td>87</td>
<td>&gt;200:1</td>
</tr>
<tr>
<td>t-Bu</td>
<td>H</td>
<td>88</td>
<td>&gt;200:1</td>
</tr>
<tr>
<td>t-Bu</td>
<td>Me</td>
<td>74</td>
<td>28:1</td>
</tr>
<tr>
<td>n-Pr</td>
<td>Me</td>
<td>73</td>
<td>7:1</td>
</tr>
</tbody>
</table>

Figure 22. Mechanism for Molander [4+3] Cycloaddition

The regiochemistry for Molander cycloaddition was reversed by the use of another Lewis acid, TiCl₄ (Figure 23). This reaction likely proceeds in a different pathway which does not involve neighboring group participation.

Figure 23. Reversing of Regiochemistry of Molander Cycloaddition by TiCl₄
1,4-Acylsilane dicarbonyl substrates 32 have been subjected to the Molander cycloaddition conditions with bis(trimethylsilyl) enol ether 30. Cycloadducts 33 were formed with extremely high regioselectivity and good yield (Figure 24).[61]

![Chemical diagram showing the cycloaddition reaction](image)

**Figure 24.** Molander Cycloaddition of 1,4-Acylsilane Dicarbonyl Substrates

1.3. Cycloadditions via Tandem Cyclopropanation/Cope Rearrangement

A third class of [4+3] cycloadditions was first reported by Davies, who effected a rhodium(II) acetate mediated stereospecific [4+3] cycloaddition of vinyl diazo compounds 34a and furans with modest yields (Figure 25). This cycloaddition proceeds by a tandem cyclopropanation/Cope rearrangement mechanism via intermediate 34b.[65] When chiral vinyl diazo compound 34 was used with furans, cycloadducts 35 were obtained with excellent diastereoselectivity and good yield (Figure 25).[65] The chiral auxiliary X_c was believed to block one face of the rhodium-stabilized vinylcarbenoids, causing the furan to approach the carbene from the other face, and therefore giving high %de.[65] The intramolecular version of this cycloaddition was also investigated by Davies, and gives good yields.[67, 68]
Figure 25. Rhodium(II) Carboxylate Catalysed Davies Cycloaddition

The [4+3] cycloadditions of 2-aminobuta-1,3-dienes with vinylchromium Fischer type carbenes also have been investigated.\textsuperscript{69, 70, 71} For example, cycloaddition of 2-aminobuta-1,3-diene 36 with vinyl chromium Fischer carbenes proceeded in MeCN at room temperature to produce cycloheptadiene derivative 38 as the only diastereoisomer in 86-91% yield. Complete regiocontrol was achieved (Figure 26). The reaction was believed to follow a similar tandem cyclopropanation/Cope rearrangement mechanism via 39.\textsuperscript{80} Good diastereoselectivity (86% ee) was achieved when chiral aminodienes were used\textsuperscript{70}. Vinylmolybdenum Fischer carbenes also may be employed in the [4+3] cycloaddition of dienynes, with good yields being obtained.\textsuperscript{72, 73, 74}
Figure 26. Cycloaddition of Vinylchromium Fischer Carbene with Dienes

The [4+3] cycloaddition of $\alpha,\beta$-unsaturated acylsilanes with enolates of $\alpha,\beta$-unsaturated methyl ketones has been reported by Takeda. It proceeds stereospecifically and regiospecifically with good yield.$^{[75, 76]}$ For example, (E)-[\(\beta\)-(trimethylsilyl)acryloyl]-silane 40 cycloadded with the lithium enolate of $\alpha,\beta$-unsaturated methyl ketone 41 to form cycloheptenone derivative 42, as the only diastereoisomer, in 84% yield (Figure 27). The mechanism involves the formation of 41c by a Brook rearrangement$^{[77]}$/cyclopropanation process (41a $\rightarrow$ 41b $\rightarrow$ 41c) followed by a stereospecific Cope rearrangement (41c $\rightarrow$ 42) (Figure 27).$^{[75, 76]}$
2. Nicholas Reactions

Reppe\textsuperscript{[76]} first reported the transition metal organometallic chemistry of alkynes. Since then, many metals have been used to form complexes with alkynes, including Co,\textsuperscript{[79]} Pt,\textsuperscript{[80]} Mo,\textsuperscript{[81]} Ni,\textsuperscript{[82]} and several others. Generally speaking, there are three kinds of coordination possible to the triple bond: mononuclear coordination, dinuclear coordination and trinuclear coordination (Figure 28). In each case, the C-C-C bond angle is less than 180° due to metal coordination.

Figure 28. Three Kinds of Metal Coordination to Alkynes

Among these transition metal-alkyne complexes, alkyne-Co\textsubscript{2}(CO)\textsubscript{8} complexes are the most widely used complexes. The structure of the alkyne-
dicobalt hexacarbonyl complex features a pseudo-tetrahedral geometry (43 in Figure 28, M = Co(CO)₃) with C-C-C bond angle $\alpha \approx 140^\circ$. In this thesis, the abbreviation as in 44 will be used to represent this structure.

The Nicholas reaction was first reported in 1972 by Nicholas. Treatment of the carbinol 44 with a catalytic amount of trifluoroacetic acid in trifluoroethanol afforded trifluoroethyl ether 45 with quantitative yield (Figure 29). It was believed that this transformation proceeded via a Co₂(CO)₆ stabilized propargyl cation intermediate 46. Since this initial report, many nucleophiles have been successfully employed for Nicholas reactions. These nucleophiles include ketones and their enol derivatives, $\beta,\beta'$-dicarbonyls, electron rich aromatic rings, allylsilanes, hydrides, amines, sulfonamides, and others. Most importantly, the nucleophiles always attacked at the propargyl carbon and no allenic by-product was found. The formation of allenic by-products had been interfering with general propargylation reactions for a long time.

![Figure 29. The First Reported Nicholas Reaction](image)

The dicobalt hexacarbonyl propargyl cations are thermodynamically very stable cations, with $pK_a$ values of ca. −7 ($pK_a$ for $\text{Ph}_3\text{C}^+$ is ca. −6.6). The stability comes from the delocalization of the positive charge into the Co₂(CO)₆ moiety. These cations exist as unsymmetrical structures (Figure 30).
Figure 30. Unsymmetrical Structures for Co$_2$(CO)$_6$ Stabilized Propargyl Cations

Dicobalt hexacarbonyl complexes of 1,3-enynes 47 have been used as precursors for the Nicholas reaction. Other electrophiles such as acylium ions are then needed to generate Co$_2$(CO)$_6$ stabilized propargylic cations 48 for the subsequent Nicholas reaction (Figure 31).$^{[90, 91, 92]}$

Figure 31. Nicholas Reaction with 1,3-Enynes as Precursors

Schreiber first reported the Lewis acid promoted Nicholas reaction of cobalt-complexed propargylic ethers.$^{[93]}$ The reaction of substrate propargylic ethers 49 with silyl enol ether nucleophiles 50 afforded syn product syn-51 with high diastereoselectivity and >85% yield. The Z enol ether provided higher level of diastereoselection than the E-isomer (Figure 32). A transition state 52 was proposed to explain the high syn selectivity (Figure 32). There are two stereoisomers (syn and anti) for the cationic complex formed from 49; the syn isomer is formed preferentially. The silyl enol ether approaches the cationic complex with the former's H atoms synclinal to both the propargyl substituent and the cobalt cluster, giving transition state 52 and ultimate formation of syn-51.$^{[93]}$
The diastereoselective Nicholas reaction with cyclic enol silanes has also been investigated. Syn products were also preferred. The reaction of dicobalt hexacarbonyl complexes of acetylenic acetal 53 with cyclic enol silane 54 produced predominantly syn β-alkoxyacetylenic ketone complexes syn-55 in a ratio of syn:anti = 8:1 with 89% yield (Figure 33).^{[64]}

The diastereoselective Bu₂BOTf mediated Nicholas reactions with acyl oxazolidinone derived (Evans) enolates have been reported by Schreiber; good diastereoselectivities and good yields were achieved with syn product preferred (Figure 34).^{[68]}
Figure 34. Diastereoselective Nicholas Reactions of Evans Enolates

Six to eight-membered cycloalkyne-cobalt complexes have been produced via intramolecular Nicholas reactions with allylsilane containing substrates. For example, treatment of allylsilane substrate 56 with BF₃·OEt₂ afforded cycloheptyne-cobalt complex 57 with 55% yield (Figure 35). Oxidative removal of Co₂(CO)₆ moiety with Me₃NO did not lead to a cycloalkyne,[63] as simple cycloheptynes and cyclohexynes have not been isolated so far. By contrast, their dicobalt complexes may be obtained as pure and stable compounds,[63] because the change in the formally sp carbon bond angle alleviates the strain.[65]

Figure 35. Cycloalkyne-cobalt Complexes Produced via Intramolecular Nicholas Reaction

In 1998 Green reported the Bu₂BOTf mediated Nicholas reaction of γ-methoxyalkynoate and γ-methoxyalkynone dicobalt complexes 58 with stannylsilane 59 or 59' (Figure 36).[66] The reaction of propargyl ether 58a with
allylstannane 59' gave allylsilane product 60a as the major product, contaminated with vinylsilane product 61a (84%, 60a :61a = 78 :22). If a nucleophile with a bulkier silyl group (59) was employed, excellent regioselectivity was achieved in favour of the allylsilane product 60b (63%, 60b :61b =96:4) (Figure 36). \[86\]

![Chemical Reaction Diagram](attachment:image.png)

Figure 36. Stepwise Preparation of Cycloheptenyne Complexes

After reduction of the carbonyl function in 60 with \(^1\text{Bu}_2\text{AlH}\) and trapping of the resultant alkoxide intermediate with acetic anhydride, acetate products 62 were obtained in excellent yield. A BF₃-OEt₂ mediated intramolecular Nicholas reaction of the acetates 62 gave cycloheptenyne dicobalt complexes 63 in excellent yields (Figure 36). \[86\]

In the final cyclization step above, tiny amounts of silyl fluorocycloheptyne complexes 64 were obtained in the case of R=Ph, Me (Figure 36). \[86\] Desilylated fluorocycloheptyne complexes 65 were formed in the BF₃-OEt₂ mediated intramolecular Nicholas reaction of 66 in 44% or 8% depending on the addition procedure (Figure 37). \[86\]
In 1999, Green reported a successful synthesis of cycloheptenyne dicobalt complexes 69 + 69' in good yield via double Nicholas reactions of alkyne 1,4-diether complexes 68 with nucleophilic stannylsilanes 59. For unsubstituted substrate 68a, product 69a was obtained in 62% yield. For unsubstituted substrate 68b in which slightly large alkoxy groups were used, an even higher yield (72%) was achieved (Figure 38). Takano had also tried to produce cycloheptenyne complexes in 1992 via double Nicholas reaction of alkyne 1,4-diethers with the analogous disilyl nucleophiles in the presence of BF3·OEt2, but this attempt failed totally.

Figure 37. Desilylated Fluorocycloheptyne Formed in Intramolecular Cyclization

Figure 38. First Synthesis of Cycloheptenyne Complex via Double Nicholas Reactions by Green
Green's cycloheptenyne synthetic route was believed to be stepwise [4+3] cycloaddition via two Nicholas reactions (Figure 39).\(^{[67, 99]}\) The mechanism involves initial formation of carbocation 70, followed by nucleophilic trapping by the stannylsilane to form 71. The formation of another carbocationic intermediate (72) followed by ring closure affords cyclic intermediate 73. Finally cycloheptenyne complex is produced by the elimination of the formal Et₂Si⁺ moiety. Regioisomer product 69' comes from a similar route via carbocation intermediate 74 (Figure 39).\(^{[99]}\)

![Diagram of the reaction mechanism](image)

**Figure 39. Mechanism for Green [4+3] Cycloaddition**

For the methyl substituted propargylic diether 68c, a regioisomeric mixture of cycloheptenyne complexes 69b and 69b' (2.2:1) was obtained in 54% yield (Figure 38). When a larger ether function was placed at the more substituted propargylic site (for example ¹Pr ether 68d), cycloheptenyne complex 69b was
formed as the major product with only a trace amount of 69b'. The TBDMS ether 68a gave the same regiochemical results (Figure 38).\[97\]

When 5 equivalents of BF$_3$-OEt$_2$ was added to a highly dilute solution (10$^{-3}$ M) of 75 and 59 over a period of 12h at 0°C, fluorocycloheptyne complexes 76 were formed exclusively in good yield (Figure 40). The mechanism for the fluorination was unclear.\[97\]

![Chemical Reaction](image)

**Figure 40.** Fluorocycloheptyne Complex Produced from Green [4+3] Cycloaddition

Recently, Green reported regioselective Nicholas reactions of skipped bis(propargyl) diether complexes 77 with a series of nucleophiles, such as allylmetalts, silyl enol ethers, electron rich arenes, etc. Monocondensation products 78 were produced with good yield (Figure 41).\[100\]

![Chemical Reaction](image)

**Figure 41.** Regioselective Nicholas Reaction of 1,4-Diyne Tetracobalt Complex
When substrate 79 was subjected to similar conditions with a series of electron rich arenes as nucleophiles in highly dilute CH$_2$Cl$_2$ solutions, a variety of metacycophanediynes were isolated in only one synthetic step in good yields. For example, with 1,3,5-trimethoxybenzene as the nucleophile, metacycophanediyne 80 was produced in a 92% yield. The decomplexation of 80 has been achieved despite the substantial strain in the metal free cyclophanediynes (Figure 42).

![Figure 42. Green One-step Synthesis of Metacycophanediyne](image)

3. Nucleophilic Trapping of Carbocations from Reaction of Unactivated Alkenes

When cationic species react with unactivated alkenes, other cationic intermediates are formed. These cationic intermediates usually eliminate to form other alkenes. For example, when Co$_2$(CO)$_6$ stabilized propargylic cation 84 from 81 reacts with alkene 82, intermediate 85 was generated. A mixture of regioisomeric alkenes 83a-c were then produced by elimination and oxidative decomplexation (Figure 43).
The cationic carbocations from reaction with unactivated alkenes can also undergo rearrangement.\cite{103} For example, treatment of 86 with Lewis acid afforded intermediate 87, which then underwent rearrangement to form 88 (Figure 44).\cite{103}

The carbocations from reactions of unactivated alkenes can also be trapped intramolecularly. For example, the reaction of alkenyl esters and acids 89 with \text{Co}_2(\text{CO})_6 stabilized propargylic cations 84 afforded cationic intermediate 90,
which underwent intramolecular trapping by the carbonyl oxygen to form lactone 91. Decomplexation gave 92 in good overall yields (Figure 45). \[102\]

\[
\begin{align*}
\text{TMS-} & \quad \text{BF}_3\text{-OEt}_2 \\
\text{Co}_2(\text{CO})_8 \quad \text{CH}_2\text{Cl}_2, 0^\circ\text{C} \quad \rightarrow \quad \text{TMS-} \\
58 \quad & \quad \text{OAc} \\
& \quad \text{TMS-} \\
64 \quad & \quad \text{OR} \\
& \quad \text{OR} \\
90 \quad & \quad \text{OR} \\
& \quad \text{OR}
\end{align*}
\]

\[
\begin{align*}
\text{TMS-} & \quad \text{CAN} \\
\text{R} = \text{H} \quad \text{CH}_2\text{CH}_2\text{TMS} \quad 82\% \\
\text{CH}_2\text{CH}_2\text{TMS} \quad 65\%
\end{align*}
\]

Figure 45. Intermolecular Trapping of Cationic Intermediate

The intermolecular trapping reactions of such cationic intermediates by halogen ion have been reported recently. Lewis acids are always the sources of trapping agents, \(F^-\) and \(Cl^-\).\[104\] In cobalt chemistry, this was first reported by Tyrrell's group. They found that \(\text{Co}_2(\text{CO})_8\) stabilized propargylic cation 94, when generated from 93 in the presence of a Lewis acid, underwent a cyclization to form tertiary carbocation intermediate 95, which then was trapped by halide anion to produce 96 (Figure 46). Fluoride containing Lewis acids such as HBF$_4$, BF$_3$-OEt$_2$ and TiF$_4$ lead to fluoride trapping product 96a, whereas chloride containing Lewis acids such as AlCl$_3$, SnCl$_4$ and HCl lead to chloride trapping product 96b (Figure 46).\[104\]
Fluoride trapping reactions also have been reported in the Fe(CO)_3 stabilized pentadienyl cation system.\textsuperscript{105,106} The Lewis acid BF\textsubscript{3}-OEt\textsubscript{2} induced ionization of \textit{\textit{\Psi}} endo alcohol 97 with anchimeric assistance from the iron atom afforded Fe(CO)_3 stabilized pentadienyl cation 98. The pendant unactivated alkene then attacked the cation center from the face opposite to Fe(CO)_3 moiety to form cyclohexyl cation 99, which was trapped by \textit{\textit{\textit{\textit{F}}}^-} to form a mixture of fluorocyclohexanes 100a and 100b (Figure 47).\textsuperscript{105}
Figure 47. Fluoride Trapping in (Pentadienyl)-Fe\((\text{CO})_3\) Cation System

Chloride trapping has been reported in the synthesis of functionalized tetrahydropyrans via indium trichloride mediated cyclizations involving the reaction between cations with unactivated alkenes.\(^{107, 108}\) For example, homoallylic alcohol 101 reacted with aldehyde to form cation 102. Cyclization of 102 afforded cationic intermediates 103 and 104, which were then trapped by chloride anion to produce 105 and 106 respectively (Figure 48).\(^{108}\)

Figure 48. Chloride Trapping in Other Reaction System
RESULTS AND DISCUSSION

1. Regiochemistry of Green [4+3] Cycloadditions

Green has reported the [4+3] cycloaddition of substrate 68d with silylstannane 59 (Figure 38). The cycloadducts 69b and 69b' were obtained in a 68% yield in a ratio of 69b : 69b' > 30:1.\cite{97} Given the apparent effect of substrate sterics on the timing of the condensation steps in the [4+3] cycloaddition, we were interested in the possibility of reversing the regioselectivity of the cycloaddition. As a result we investigated the [4+3] cycloaddition reaction on substrate 111, which is the regioisomer of substrate 68d.

The synthesis of 111 is shown in Figure 49. Propargyl ether 107 was prepared from the commercially available 3-butyn-2-ol.\cite{106} Lithiation of 107 with MeLi, followed by a reaction with paraformaldehyde, gave hydroxypropargyl ether 108.\cite{96} Complexation of 108 with Co$_2$(CO)$_6$ in Et$_2$O at 0° C afforded complex 109\cite{109} which then was reacted with $^1$PrOH in the presence of 4Å molecular sieves and excess p-TsOH to produce propargyl diisopropyl diether complex 110. Treatment of 110 with p-TsOH in methanol afforded substrate 111. It is noteworthy that the attempt was made to monoisopropoxylate 109 selectively to produce 111 in one step using several equivalents of p-TsOH, but it failed. Isopropoxylation always happened preferentially on the more substituted side to form 109a (Figure 49)
Nucleophile silylstannane 59 was prepared according to a protocol previously developed in our laboratory (Figure 50).\textsuperscript{[56]}

\[
\text{MeBr} \xrightarrow{\text{Et}_3\text{SiCl}} \xrightarrow{\text{Et}_2\text{O}, \Delta} \text{SiMe}_3 \xrightarrow{\text{nBuLi/TMEDA}} \xrightarrow{\text{hexane, 20h}} \left[ \text{Me} \equiv \text{SiMe}_3 \right] \xrightarrow{\text{Bu}_3\text{SnCl}} \xrightarrow{-78^\circ\text{C}} \text{Bu}_3\text{Sn} \equiv \text{SiMe}_3 \equiv \text{59}
\]

Figure 50. Preparation of Silylstannane

The BF\textsubscript{3}-OEt\textsubscript{2} mediated [4+3] cycloaddition of substrate 111 with silylstannane 59 was carried out in CH\textsubscript{2}Cl\textsubscript{2} dried in the standard fashion (see Experimental Section), and gave substantial amounts of fluorinated cycloheptyne complexes. The source of fluorination will be addressed separately. Use of 'super-dry'\textsuperscript{[110]} (see Experimental Section) CH\textsubscript{2}Cl\textsubscript{2} gave a regioisomeric mixture of 69b and 69b' in a ratio of 69b : 69b' = 1 : 1.3 (Figure 51).
Figure 51. Green Cycloaddition of 111 with Silylstannane

Figure 52. The Origin of Regiochemistry for Green Cycloaddition

It can be seen that the exchange of the positions of \(^{1}\)PrO group with MeO group in the substrates 68d and 111 made a large difference in the regioisomeric ratio of the cycloadducts. According to the mechanism of the Green [4+3] cycloaddition (Figure 39), cycloadduct 69b comes from the initial attack of silylstannane 59 on the propargylic cation 70b (Figure 52), while cycloadduct 69b' comes from the initial attack of silylstannane 59 on the propargylic cation 74a (Figure 52).

There are two major factors which influence the formation of 70b and 74a. One set is the thermodynamic factors. Nicholas has found a greater stability of less substituted Co\(_2\)(CO)\(_6\) stabilized propargylic cations according to their pK\(_R^+\) values.\(^{[89]}\) Presuming this may be extended to the systems under study, 70b might be expected to form preferentially over 74a. The second factor is a kinetic one involving the bulkiness of the alkoxide group. The departure of the alkoxide group to form the Co\(_2\)(CO)\(_6\) stabilized propargylic cation is affected by the interaction between Lewis acid (BF\(_3\)-OEt\(_2\)) and the oxygen atom of an alkoxy
group. The bulkier the alkoxide group, the more difficult it is for BF$_3$-OEt$_2$ to approach it. As far as the MeO and $^1$PrO groups are concerned, BF$_3$-OEt$_2$ would be expected to be complexed by the MeO group preferentially over $^1$PrO group, as a result generating the corresponding propargyl cobalt cation. In the substrate 68d case (Figure 38), both thermodynamic and kinetic factors favour the formation of 70b over 74a; predominance of 70b over 74a in the reaction system leads to the predominance of cycloadduct 69b over 69b' (>30:1). In the substrate 111, thermodynamic factors favour the formation of 70b; however, kinetic factors favour the formation of 74a. The overall effect of these two factors leads to a mixture of two regioisomeric cycloadducts 69b and 69b', in a ratio of 1:1.3.


Green has reported a fluorinative [4+3] cycloaddition of propargyl diether complexes 75 with silylstannane 59 under high dilution, slow Lewis acid addition conditions. Although the fluorocycloheptyne complexes 76 were obtained exclusively in good yields (Figure 40), the mechanism of fluorination was not fully understood."}[97]

Unsubstituted substrate 75a was employed in the investigation of the mechanism for the fluorinative Green [4+3] cycloaddition. It was prepared according to a protocol previously developed in our laboratory (Figure 53)."}[99] For comparison sake, trityl ethyl ether 112 was also chosen for investigation. It was prepared by one-step reaction of triphenylcarbenium tetrafluoroborate with ethanol (Figure 54).
Figure 53. Synthesis of Unsubstituted Substrate 75a

\[
\begin{align*}
\text{HO} & \quad \text{Et}_2\text{SO}_4, \text{NaOH} \quad \text{EtO} \quad \Delta \quad 87\% \quad \text{EtO} \quad \text{Co}_2(\text{CO})_8, \text{Et}_2\text{O} \quad \text{EtO} \quad \text{Co}_2(\text{CO})_8 \\
\text{HO} & \quad \text{Et}_2\text{SO}_4, \text{NaOH} \quad \text{EtO} \quad \Delta \quad 87\% \quad \text{EtO} \quad \text{Co}_2(\text{CO})_8, \text{Et}_2\text{O} \quad \text{EtO} \quad \text{Co}_2(\text{CO})_8 \\
\end{align*}
\]

**Figure 54.** Synthesis of Trityl Ethyl Ether

In order to determine whether silylstannane 59 is stable in the presence of BF$_3$-OEt$_2$, some NMR experiments were carried out. In one of these, 1 equivalent of BF$_3$-OEt$_2$ was added to a solution of silylstannane 59 in commercial CDCl$_3$ at room temperature. After 7 min, the $^1$H NMR showed that the system contained allyltriethylsilane (113) and 59 in a ratio of 25:75, by integration of the δ 5.80 resonance of a vinyl H of 113 vs. the δ 6.19 resonance of a vinyl H of 59. In other words, 25% of 59 had been decomposed to allyltriethylsilane (113). When an analogous experiment was carried out in CD$_2$Cl$_2$ which had been purified by stirring with CaH$_2$ at room temperature for 0.5 h followed by distillation over CaH$_2$, only 4% of allylstanlennane 59 was decomposed to allyltriethylsilane (Figure 55), and 96% of 59 was still present, even after extended exposure times.

**Figure 55.** BF$_3$-OEt$_2$ Mediated Decomposition of Silylstannane in CDCl$_3$ and CD$_2$Cl$_2$
The difference in the BF\(_3\)-OEt\(_2\) mediated decompositions of silylstannane 59 in the two solvents can be attributed to different levels of dryness. Due to the well known futility in ‘drying’ CHCl\(_3\) (or CDCl\(_3\)),\(^{[11]}\) no special attempts were made here. It can be inferred that the moisture in the solvent is responsible for the BF\(_3\)-OEt\(_2\) mediated decomposition of silylstannane 59. The results in CD\(_2\)Cl\(_2\) support the conclusion that 59 is for all intents and purposes stable to BF\(_3\)-OEt\(_2\) in the absence of water.

In order to get further insight into the decomposition of silylstannane 59 in the Green cycloaddition environment, another NMR experiment was carried out in which trityl ethyl ether 112 was used to replace propargyl diether complex 75a in imitation of the Green cycloaddition conditions. The reason why 112 was chosen as a substitute for 75a was based on the consideration that the trityl cation has a similar pK\(_{a}\) to that of a Co\(_2\)(CO)\(_6\) stabilized propargyl cation.\(^{[86]}\) As a result, 112 was believed to undergo BF\(_3\)-OEt\(_2\) mediated ionization in the most similar way possible to its analogue 75a (Figure 56).

![Figure 56. BF\(_3\)-OEt\(_2\) Mediated Formation of [EtOBF\(_3\)]\(^+\)\n](attachment:image)

In this NMR experiment, silylstannane 59, trityl ethyl ether 112 and BF\(_3\)-OEt\(_2\) (5 equiv.) were mixed in a NMR tube. The \(^1\)H NMR spectrum showed that allyltriethylsilane 113, 114 and 115 were formed in a ratio of
113:114:115=0.41:0.50:1.00 in about 8 min (Figure 57), by integration of the δ 4.89 resonance of 113, the δ 3.46 resonance of 114 and the δ 3.52 resonance of 115. Product 114 is believed to result from the further reaction of allyltriethylsilane with trityl cation. It can be seen clearly that 113 keeps transforming to 114 during the period of 8-45 min with the ratio of (113+114):115 almost constant at 0.91:1.00 (Figure 57). Silylated product 115 is believed to be the consequence of Lewis acid mediated rearrangement of the silylstannane 59 to regioisomer 59a, followed by its reaction with the trityl cation (Figure 58). Although 59a itself has not been observed, it has been implicated previously in acyclic Nicholas reactions in this group. Therefore, about 48% the silylstannane 59 was decomposed to allyltriethylsilane in 8 min in this case.

\[
\text{Bu}_3\text{Sn} \quad \text{SiEt}_3 \quad \xrightarrow{\text{BF}_3\text{-OEt}_2(\text{eq})} \quad \begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array} \quad \begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array} \text{ dry CD}_2\text{Cl}_2. 8-45 \text{ min} \\
\text{113} + \text{114} + \text{115}
\]

\[
\begin{align*}
113 & : 114 : 115 \\
8 \text{ min} & : 0.41 : 0.50 : 1.00 \\
18 \text{ min} & : 0.29 : 0.63 : 1.00 \\
45 \text{ min} & : 0.16 : 0.75 : 1.00
\end{align*}
\]

Figure 57. Decomposition of Silylstannane in Presence of Trityl Ethyl Ether and BF\text{OE}t_2

\[
\begin{align*}
\text{Bu}_3\text{Sn} & \quad \text{SiEt}_3 \\
\text{59} & \xrightarrow{\text{BF}_3\text{-OEt}_2} \\
\text{SiEt}_3 & \quad \text{Ph} \\
\text{59a} & \quad \text{SnBu}_3 \xrightarrow{\text{Ph} \quad \text{Ph}} \text{115}
\end{align*}
\]

Figure 58. The Origin of 115

In comparison with the NMR experiment in dry CD\text{2}Cl\text{2} (Figure 55) in which there was almost no decomposition of silylstannane 59, this represents an
extensive amount of silylstannane decomposition. The levels of dryness are the same in these two cases.

In evaluation of the differences with the simple reaction of the silylstannane 59 with BF₃-OEt₂, and the similarities with the fluorinative [4+3] cycloaddition, attention must be drawn to the counterion of the propargyl cation or trityl cation, namely [EtO-BF₃]⁺. This species is noteworthy, given the possibility for the transfer of fluoride ion from the ate complex, and the ability of fluoride ion to form hypervalent complexes and ultimately demetallate both organotinns and organosilanes.¹¹³,¹¹⁴ As a result, it is likely that the allyldimetal reagent forms a tin ate complex. We believe that this ate complex is highly unstable with respect to loss of tin, giving an allylsilane (Figure 59). It is further possible that the same process may be occurring on the resultant allylsilane.

\[
\begin{align*}
H_2O & \quad + \quad BF_3 \quad \longrightarrow \quad H_2O-BF_3 & \quad \Leftrightarrow \quad HOBF_3 & \quad + \quad H^+ \\
\text{[EtO-BF₃]⁺} & \quad \text{Bu₃Sn} & \quad \text{SiEt₃} & \quad \text{Bu₃Sn}^- & \quad \text{SiEt₃} & \quad + \quad H^+ & \quad \longrightarrow \quad \text{SiEt₃} \\
\text{OEt} & \quad \text{Ph} & \quad \text{Ph} & \quad \text{ate complex} & \quad \text{Ph} & \quad \text{Ph} & \quad \text{113}
\end{align*}
\]

Figure 59. Mechanism for BF₃-OEt₂ Mediated Decomposition of Silylstannane

We recognize that the actual H⁺ source is not entirely accounted for; a 10⁻² M allyldimetal (1 mL CH₂Cl₂ solution) would require solvent that is ca 140 ppm (0.14%) in H₂O or other H⁺ source for complete consumption, and this is unlikely in CH₂Cl₂ distilled from CaH₂. The residual water in CH₂Cl₂ distilled from CaH₂ is unknown, but commercial ‘anhydrous’ CH₂Cl₂ is < 50 ppm in H₂O. Nevertheless,
there is a clear correlation between the rigour which the solvent is dried and the level of fluorination in the [4+3] cycloadditions. Some source of moisture is likely implicated.

Taking the above into account in the [4+3] cycloaddition, it can be speculated that 76a likely results from the trapping of cationic intermediate 117 by some source of fluoride anion (i.e. [EtO-BF$_3$]). The cationic intermediate 117 would then result from 116, which in turn results from the reaction of Co$_2$(CO)$_6$ stabilized propargyl cation 70a with the destannyalted allylsilane (Figure 60).

![Figure 60. Initial Speculation on the Mechanism](image)

According to the proposal above, allylsilanes themselves should prove to be participants in the fluorinative [4+3] cycloaddition. Therefore, the BF$_3$-OEt$_2$ mediated reaction of 75a with allylsilane was carried out. Fluorocycloheptyne complex 76a was obtained in good yields (Figure 61).

![Figure 61. Fluorinative [4+3] Cycloaddition with Allylsilane](image)

This concern with solvent purity dependent destannylation has led to re-establishment of conditions for [4+3] cycloadditions. Unfortunately, when the
CH₂Cl₂ distilled from a bulk still over CaH₂ was used as solvent, fluorinative cycloadduct 76a was always obtained and always the major product for this reaction, which gave cycloadduct 69a as a minor one (Figure 62).

![Chemical structure](image)

Figure 62. Green Cycloaddition in CH₂Cl₂ from Still

In order to determine whether or not the CH₂Cl₂ from the still was dry enough for the Green [4+3] cycloaddition, the BF₃-OEt₂ mediated decomposition experiment of silylstannane 59 was carried out in CH₂Cl₂ (from still)+dry CD₂Cl₂ (2:1) and monitored by NMR. In the event, about 18% of the silylstannane 59 was decomposed to allylsilane during a period of 7-21min (Figure 63). This experiment shows that the CH₂Cl₂ distilled from still was not dry enough for the Green [4+3] cycloaddition reaction.

![Chemical structure](image)

Figure 63. Decomposition of Silylstannane in CH₂Cl₂ from Still

4Å Molecular sieves were then added to the reaction system to absorb any moisture. For the substrate 75a, the situation gave improved results, as the reaction of substrate 75a with silylstannane 59 afforded predominantly cycloadduct 69a as a major product in a 43% yield with fluorinative cycloadduct 76a in only 3% yield (Figure 64). However, for substrate 111, fluorinative
cycloaduct 119 was produced (23%), although a mixture of cycloaducts 69b and 69b' predominated (32%) (Figure 64).

```
4A molecular sieves
EtO
BF₃·OEt₂ (5eq), CH₂Cl₂
Co₂(CO)₆
Bu₃Sn
SiEt₃
60°C, 0.5h
69a 43%
69b 32%
76a 3%
76b 6%

Figure 64. Green Cycloadditions with 4A M. S. in CH₂Cl₂ from Still

'Super-dry' CH₂Cl₂ was needed for this purpose. It was prepared by violent refluxing of small amounts of still-dried CH₂Cl₂ from still with excess of CaH₂ for >3 h followed by re-distillation over CaH₂. The cycloaddition of substrate 75a with silylstannane 59 was carried out in this 'super-dry' CH₂Cl₂. No fluorinative cycloadduct was formed. Cycloaduct 69a was obtained in a 72% yield (Figure 65). Also, no fluorination was observed for the substituted substrate 111 (Figure 51).

```

```
5min addition
BF₃·OEt₂ (5eq), RT, 13min
Bu₃Sn
SiEt₃
CH₂Cl₂
super-dry
69a 72%

Figure 65. Green [4+3] Cycloaddition in Super-dry CH₂Cl₂

When the Green cycloaddition was carried out at 0°C in super-dry CH₂Cl₂, fluorinative cycloadduct 76a emerged again as a minor side-product in 14% yield,
although cycloadduct 69a was formed predominantly (42% yield) (Figure 66). This is in contrast to the same reaction in CH₂Cl₂ distilled from still (Figure 62) in which fluorinative product 76a was obtained as the major one in a 37% yield. The improvement from the employment of super-dry CH₂Cl₂ was obvious.

![Diagram of cycloaddition reaction](image)

Figure 66. Green Cycloaddition in Super-dry CH₂Cl₂ at 0°C

In terms of the [4+3] cycloaddition, it is quite possible that the reaction of the Co₂(CO)₆ stabilized propargyl cation with silylstannane 59 proceeds in the same way as the decomposition reaction of silylstannane 59 with H⁺ (Figure 67 v.s. Figure 58), with [EtOBF₃⁺] also facilitating the Green [4+3] cycloaddition. In short, the formation of [EtOBF₃⁺] can facilitate both the cycloaddition and fluorination.

![Diagram of initial step of green cycloaddition](image)

Figure 67. Initial Step of Green Cycloaddition

As a result, the Green [4+3] cycloaddition free of fluorination (Figure 65 and 51) can only be achieved by fast formation of intermediate 71 (Figure 39) before the destannylation of silylstannane 59 occurs due to the presence of moisture.
and Lewis acid. Intermediate 71 will finally lead to the cycloaddition without fluorination. For all successful Green cycloadditions free of fluorination (Figure 61 and 51), the addition of BF$_3$-OEt$_2$ to the reaction system was accomplished in about 5 min at room temperature.

When the addition of BF$_3$-OEt$_2$ was carried out at 0°C over 0.5 h, the fluorination was obtained as a minor product even with super-dry CH$_2$Cl$_2$ (Figure 62). This could be explained if the lower temperature slows formation of intermediate 71a (Figure 67) to a greater degree than it slows the reaction of silylstannane 59 with moisture. If a spurious source of moisture is present (i.e., in the ‘inert’ gas), it may also make feasible the condensation of small amounts of moisture into the reaction system.

It can be further concluded that for the Green [4+3] cycloaddition, a fast reaction can lower the water sensitivity of the reaction system, and a slow reaction increases the water sensitivity of the reaction system. At this point, it is also easy to understand why the fluorinative cycloadducts were obtained exclusively at 0°C in the condition of very slow addition and very high dilution.$^{[87]}$

In short, the mechanism for the fluorinative [4+3] cycloaddition can be summarized as shown in Figure 68. Decomposition of silylstannane 59 generates allyltriethylsilane (Figure 59). The presence of [EtOBF$_3$]$^-$ species facilitates the decomposition. The reaction of allyltriethylsilane with 70a forms 120 which reacts with BF$_3$-OEt$_2$ to form 116. The cyclization of 116 affords 117, which then trapped by some source of fluoride anion, of which [EtO-BF$_3$]$^-$ is the most likely candidate.
3. Tandem [4+3] Cycloaddition/Nucleophilic Trapping Reactions

During the investigation on the mechanism for the formation of fluorinative cycloadducts in the Green [4+3] cycloaddition of propargyl diether cobalt complexes with silylstannanes, it was found that the fluorinative cycloadduct 76a likely stems from the trapping of cationic intermediate 117 by "F⁻" (Figure 68). This result has led us to study whether the use of the more readily available allylsilanes will allow trapping of intermediate 117 by other nucleophiles.

Figure 69. Syntheses of Substituted Substrates for Trapping
Unsubstituted substrate 124a (=75a in Figure 53) was employed most intensively for this purpose. Methyl and phenyl substituted substrates 124b and 124c were also studied. The syntheses of 124b and 124c are shown in Figure 69. Lithiation of propargyl alcohols 121 with 2-3 equivalents of "BuLi in THF at low temperature, followed by reaction with aldehydes RCHO afforded propargyl diols 122.\[^{115}\] Complexation of 122 with Co\(_2\)(CO)\(_6\) in Et\(_2\)O at 0°C formed propargyl diol complexes 123,\[^{98}\] which were then reacted with ethanol in the presence of excess p-TsOH to produce methyl and phenyl substituted substrates 124b and 124c in good yields.

Generally speaking, three modes of addition were employed for investigation of the trapping reactions: Mode A, addition of Lewis acid to a mixture of allylsilane and substrate; Mode B, addition of allylsilane/Lewis acid mixture to substrate; Mode C, addition of allylsilane to a mixture of Lewis acid and substrate. Mode A reduces the destruction of substrate by Lewis acid, and promotes the formation of the diallyl side product (i.e. 126 in Figure 70), but slow addition can lower the yield of diallyl side-product. Mode C reduces the formation of diallyl side-product, and increases the destruction of the substrate by Lewis acid; but fast addition can alleviate the destruction of the substrate. Mode B is between Mode A and C in these two respects.
The reactions of substrates 124 with allyltrimethylsilane were carried out in the presence of BF$_3$-OEt$_2$ in CH$_2$Cl$_2$ at room temperature. Fluoride trapping products 125 could be obtained in good yield by judicious choice of conditions. The major side products were diallyls 126 (Figure 70).

For the unsubstituted substrate 124a, fluorinative cycloadduct 125a was formed in 75%. The reaction was finished in 6 h with addition of allyltrimethylsilane to a mixture of 124a/ BF$_3$-OEt$_2$ (5 equiv.) over 2 h (Mode C). The fast reaction was also tried with addition of a mixture of allyltrimethylsilane/BF$_3$-OEt$_2$ to 124a CH$_2$Cl$_2$ solution over 10 min (Mode B). Product 125a was obtained also in a 75% yield, but diallyl 126a was increased substantially to 20%. For the methyl-substituted substrate 124b, fluoride trapping product 125b was also produced in a good yield (74%) (Mode A). For phenyl-substituted substrate 124c, fluorinative cycloadduct 125c was obtained in a lower yield (67%) (Mode A). It seemed that the final cyclization step proceeded very slowly according to observation by TLC.
For the substituted substrates 124b or 124c, a separable diastereoisomeric mixture of 125b or 125c was produced in a ratio of trans:cis=1.5-1.6:1 (Figure 70); the trans isomers were major products in both methyl and phenyl substituted cases. This result is consistent with the case reported by Green & Patel,[97] in which the reactions of methyl substituted substrate 75b and phenyl substituted substrate 75c with silylstannane 59 produced 125b (76b=125b), 125c (76c=125c) both in a ratio of trans:cis=2.5:1 at 0°C (Figure 40). The difference in the ratios likely result from the differences in the reaction conditions. The assignment of two diastereomers was based on 1H NMR spectra obtained previously in the Green group.[97]

![Chemical Reaction Diagram]

Figure 71. Chloride Trapping Reactions

The chloride trapping reactions of substrate 124 with allyltrimethylsilane in the presence of SnCl₄ were carried out in CH₂Cl₂ at room temperature. Chloride trapping products 127 were obtained in good yields; the major side products were diallyls 126 (Figure 71).

For the unsubstituted substrate 124a and methyl-substituted substrate 124b, the chloride trapping reactions proceeded very smoothly to completion within
about 30 min. Addition of allyltrimethylsilane to a mixture of SnCl₄ (5 equiv.) and 124a or 124b over 20 min (Mode C) afforded chloride trapping products 127a and 127b in 78% and 76% yields, respectively. For 127b, a separable mixture of diastereomers (trans:cis=1:1.9) was isolated. The chloride trapping reaction of unsubstituted substrate 124a was also tried with slower addition of allyltrimethylsilane to a CH₂Cl₂ solution of SnCl₄ (5 equiv.) and 124a (over 2 h). Chloride trapping product 127a was obtained in only a 43% yield. Substantial destruction of substrate 124a was believed to be responsible for this low yield.

\[
\text{SiMe}_3 \xrightarrow{\text{SnCl}_4 \text{, CDCl}, \text{RT}} \text{SnCl}_3
\]

Figure 72. Metathesis of Allyltrimethylsilane with SnCl₄

It has been reported that SnCl₄ reacts with allyltrimethylsilane to form allyltribromostannane 128 (Figure 72). The reaction is about 40% complete after 25 min, 75% complete after 80 min and nearly complete after 140 min. However, in our case, it can not be ruled out that allyltribromostannane 128 can also react with the Co₂(CO)₉ stabilized propargylic cation in the same way as allyltrimethylsilane does.

In view of destruction of substrates and transmetallation of allyltrimethylsilane by SnCl₄, it is a wise choice to do chloride trapping reactions with a fast addition. However, this is not the case for the chloride trapping reaction of phenyl-substituted substrate 124c with allyltrimethylsilane, as the final cyclization step of this reaction turned out to much slower than that of the reactions of unsubstituted or methyl-substituted substrates. The chloride trapping reaction of 124c with a fast addition of allyltrimethylsilane to a mixture of 124c
and SnCl₄ (over ca. 20 min) afforded diallyl 126c as a major product in a 30% yield, and chloride trapping product 127c only 27% yield. The total yield was also lower. In view of this situation, this trapping reaction was also attempted with a slow addition of SnCl₄ (3.5 equiv.) to a mixture of 124c and allyltrimethylsilane (over 2.25 h) (Mode A). Under these conditions, chloride trapping product 127c was obtained on a 60% yield, as a mixture of separable diastereomers (trans:cis=1:1.9), and with only tiny amounts of diallyl 126c (Figure 71). It is worth noting that in both the methyl-(124b) and phenyl-(124c) substituted cases, the cis isomer predominated. This is the opposite situation to the fluorinated cases.

The assignments of the diastereomers were based on their ¹H NMR spectra. It is believed that the trapping products exist in a cyclohexane-like chair conformation, by virtue of the observed coupling constants and by related work of other authors. It has been reported that their analogues, the cycloheptenes, exist in the chair conformation. In order to determine if the methyl groups in trans- and cis-127b are in the equatorial position, decoupling experiments were carried out. When the δ 1.33 (d, J=6.8, 3H) resonance from methyl group of trans-127b was irradiated, the geminal H resonance at δ3.40 (m, 1H) became simplified (dd, J=11.2, J=3.4, 1H), which is a typical axial H pattern, when the δ 1.35 (d, J=6.7, 3H) resonance from the methyl group of cis-127b was irradiated, the geminal H resonance at δ 2.94 (m, 1H) also became simplified (dd, J=11.5, 3.9), which is also a typical axial H pattern. Therefore, the methyl groups in trans- and cis-127b are in an equatorial orientation. For the phenyl-substituted case, the H's geminal to phenyl groups are also apparently in an axial orientation [δ
4.52 (dd, J=12.0, J=3.6, 1H) in trans-127c and δ 4.00 (dd, J=12.2, J=3.5, 1H) in cis-127c]. Therefore, the phenyl groups are in the equatorial orientation. The chemical shift of the axial H atom geminal to chlorine in cis-127b is relatively upfield compared with that in trans-127b (δ 3.99 in cis-127b vs. δ 4.67 in trans-127b ); furthermore, the vicinal coupling constant for that axial H in cis-127b is larger than that in trans-127b (J_{ax,ax} =11.1\text{Hz} in cis-127b vs. J_{eq,eq}=6.4\text{Hz} in trans-127b).

The corresponding bromination product 129 could be obtained in the reaction of 124a with allyltrimethylsilane in the presence of SnBr₄, but the best yield for 129 was only 26% (Figure 73) with the Mode C addition protocol. Other bromide containing Lewis acids, such as BBr₃, SiBr₃, and AlBr₃ were also tried, but no 129 was isolated and extensive decomposition occurred.

![Figure 73. Bromide Trapping Reaction](image)

While studying the conditions for the improvement of the fluoride trapping reaction, the reaction of 124a with allyltrimethylsilane in the presence of BF₃-OEt₂ was carried out in benzene as solvent. In addition to a small amount (21%) of fluoride trapping product 125a, benzene trapping product 130a was obtained as the major product in 48% yield (Figure 74). The benzene trapping product almost
certainly comes from the Friedel-Crafts reaction of cationic intermediate 117 (Figure 68) on benzene.

![Chemical Reaction Diagram]

Figure 74. Benzene and Fluoride Trapping Reaction

We then focused on finding a new Lewis acid to improve the yield of the benzene trapping reaction. Many Lewis acid were screened for their efficiency in promoting the benzene trapping reaction; these Lewis acids included Bu₂BOTf, TMSOTf, Et₃B, B(OAc)₃,[120, 121] Me₃Al, MAO, Al(OAc)₃, Ti(OiPr)₄. Bu₂BOTf. Me₃Al caused extensive destruction of the cobalt complexes. Et₃B, B(OAc)₃ MAO, Al(OAc)₃, and Ti(OiPr)₄ caused almost no reaction. TMSOTf did cause some desired benzene trapping product, but the efficiency was very low. 130a was produced in only 15% yield in the reaction of 124a and allyltriethylsilane in the presence of TMSOTf (5 equiv.) during a period of ca. 5 h. B(C₆F₅)₃ was found to be the best Lewis acid for the benzene trapping reaction.
The benzene trapping reactions of substrates 124 with allyltrimethylsilane in the presence of B(C₆F₅)₃ were carried out in benzene as solvent at room temperature. The benzene trapping products 130 were formed in fair to good yields. Very small amounts (<6%) of dialylts 126 were produced (Figure 75). For the unsubstituted substrate 124a, a 70% yield was achieved for benzene trapping product 130a. It was contaminated by a small amount (<6%) of unidentified substances which were likely propargyl trapping products (i.e. 131 and 136). This compound formed because the reaction was carried out by addition of allyltrimethylsilane to benzene solution of 124a and B(C₆F₅)₃ (Mode C); this addition mode was believed to promote the formation of 131 and 136 due
to the long term exposure of the propargyl cation to benzene. For methyl-
substituted 124b, Mode C, the addition of allylsilane to the mixture of
124b/B(C₆F₅)₃, was totally unsuited for this reaction. A substantial amount (28%)
of elimination product 132 was produced while the yield of trapping product 130b
was only 39%, even though a fast addition protocol (over 10 min) was employed.
Mode A (slow addition) was the only effective method for performing this trapping
reaction, giving good yields (61%) for 130b (Figure 75). The benzene trapping
reaction for the phenyl-substituted substrate 124c occurred with poor efficiency in
benzene, perhaps due to the slow final cyclization step, as in the fluoride and
chloride trapping cases. A yield of 52% was achieved by the addition of CH₂Cl₂ (CH₂Cl₂:benzene=1:4) after the addition of the Lewis acid (Mode A) was finished
(Figure 75).

It is noteworthy that only cis-130b and cis-130c were obtained for the
methyl- and phenyl-substituted substrates 124b or 124c. Given that the cyclic
cationic intermediates for the trapping reactions of substituted substrates (124b
and 124c) with allyltrimethylsilane also assume a cyclohexane-like chair
confirmation, its structure can be represented as 133, in which the phenyl or
methyl group is in the equatorial orientation due to its bulkiness. Another possible
conformer, 134, is believed to be too unstable to exist in substantial amounts
compared with 133. When benzene attacks 133 from the equatorial direction, cis-
130b and cis-130c are formed, whereas trans-130b and trans-130c are formed if
benzene attack 133 from the axial direction. The axial attack is prohibited
because the large phenyl group can not overcome the steric hindrance from 1, 3-diaxial H's. Therefore, only cis-130b and cis-130c were produced.

Figure 76. Stereoselectivity for Benzene Trapping Reaction of Substituted Substrates

According to Mayr's nucleophilicity chart,[122] this trapping process could only be extended to some other arenes within a limited nucleophilicity scope, such as toluene and chlorobenzene. This is because if the nucleophilicity is greater than that of an unactivated alkene, the nucleophile will trap the propargyl cation intermediate 116 (in Figure 68) before 117 is formed.
The toluene trapping reaction of 124a with allyltrimethylsilane in the presence of B(C₆F₅)₃ was carried out in toluene as solvent (Mode A). Toluene trapping products 135a were obtained as an inseparable regioisomeric mixture in a ratio of ortho:para:meta = 1.4:1:1 in a 58% yield (Figure 77). The assignment of the isomers was based on the NOESY (Nuclear Overhauser and Exchange Spectroscopy). In the 'H NMR spectrum of 135a, resonances at δ 2.80, δ 2.56 and δ 2.55 are believed to correspond to the H atoms geminal to arenne groups in ortho, para and meta isomers of 135a, respectively. NOESY shows that only the H atom resonating at δ 2.80 has an NOE effect enhancement with the nearby CH₃ group. Therefore, the 'H absorption at δ 2.80 is believed to come from ortho–135a (Figure 78). The corresponding H atoms in para-135a or meta-135a are too far away from the CH₃ group to produce an NOE effect. The ratio of para-135a and meta-135a was assigned by integration of the combined resonances at 2.56 and 2.55, as well as integration of the resonance at 7.07 ppm (d, J=8.0). The latter resonance is attributed to two arenne protons of para-135a.
The chlorobenzene trapping reaction of 124a with allyltrimethylsilane in the presence of B(C₆F₅)₃ also was carried out in chlorobenzene as solvent. Chlorobenzene trapping products 135b were obtained as a contaminated regioisomeric mixture in a ratio of ortho : para : meta = 1.8:1:0.3 in 51% yield (Figure 77). Isomerically pure ortho-135b could then be isolated after repeated chromatography. The inseparable mixture of para-135b and meta-135b was contaminated by side-product 136 (8%). The assignment of para-135b and meta-135b was based on the ¹H NMR spectrum. The δ 2.57 resonance (t, J=10.6 Hz, 1H) is believed to correspond to the H atom geminal to aryl group in para-135b. The δ 7.05 resonance (d, J=7.5 Hz, 1H) is believed to correspond to the aromatic H atom para to the Cl atom in meta-135b.

4. Conclusion
It has been found that the substitution in the propargyl position and the bulkiness of the alkoxy group in the substrates are the major factors in determining the sequence of the two steps in the Green [4+3] cycloaddition.

A mechanism has been proposed for the formation of fluorinative cycloadducts in the Green [4+3] cycloaddition reaction. Moisture in the reaction system causes BF$_3$-OEt$_2$ mediated decomposition of the silylstannane to an allylsilane, facilitated by [EtO-BF$_3$]$^-$. The resultant allylsilane then reacts with the propargyl diether cobalt complex in the presence of BF$_3$-OEt$_2$ to form a fluorinated cycloadduct via a cyclic 2° alkyl cationic intermediate. The Green [4+3] cycloadditions free of fluorination have been achieved with fast addition reactions in super-dry CH$_2$Cl$_2$ solvent.

We have successfully trapped the cyclic cationic intermediates with some nucleophiles other than F$^-$. These nucleophiles include Cl$^-$, Br$^-$, benzene, toluene, chlorobenzene. The influence of the substitution in the substrates on the trapping reactions has been investigated.

5. Future Work

For the decomposition of silylstannane 59, the actual H$^+$ source is not entirely accounted for. Further work is needed in finding out other H$^+$ sources.

In order to make synthetic use of the various trapping products, it is suggested that these trapping products be used as precursors for the Pauson-Khand reaction with alkenes such as norbornene or norbornadiene. The
Co$_2$(CO)$_6$ moiety will be removed in the process, and [7,5] fused ring systems will be produced (Figure 79).

![Chemical structure](image)

**Figure 79. Suggested Pauson-Khand Reaction with Trapping Products**

Intramolecular trapping is also an interesting possibility. This can provide a rapid access to a fused [7, 5] or [7,6] ring systems. It is possible that even BF$_3$-OEt$_2$ can be used in this reaction to achieve excellent yields, because intramolecular arene trapping may be fast enough to compete with the intermolecular fluoride trapping step (Figure 80).

![Chemical structure](image)

**Figure 80. Suggested Intramolecular Trapping Reaction**
EXPERIMENTAL

General Methods

NMR spectra were obtained on a Bruker Avance 500 Spectrometer at 500MHz for $^1$H and 125MHz for $^{13}$C, in CDCl$_3$ solution (unless otherwise indicated) at 25°C, or a Bruker Avance 300 Spectrometer at 300MHz for $^1$H and 75MHz for $^{13}$C, in CDCl$_3$ solution at 25°C. NOESY spectra were obtained on a Bruker Avance 500 spectrometer. The coupling constant (J) is in Hz unless otherwise indicated. Infrared spectra were obtained on a Bomem Michelson 100 spectrometer or a Bruker Vector 22 spectrometer. Mass spectra were obtained on a Kratos MS-80 instrument in electron impact mode.

All solvents were used after distillation from the appropriate drying agent in a still. Diethyl ether, benzene, toluene and THF were distilled from sodium benzophenone ketyl immediately before use. Dichloromethane and chlorobenzene were distilled from calcium hydride in a still immediately before use. ‘Super-dry’ dichloromethane was prepared by violently refluxing a small amount of dry dichloromethane freshly from the still with excess of calcium hydride for more than 3 h, followed by a distillation from calcium hydride immediately before use. Boron trifluoride diethyl etherate was distilled before use. 4Å molecular sieves were activated under vacuum at 60-80°C for 2-3 h and then cooled down under vacuum to room temperature immediately before use.
Preparative thin layer chromatography was performed with Analtech silica gel GF* 1000 micron plates. Analytical thin layer chromatography (TLC) was preformed with Merck precoated silica gel 60 F_{254} aluminum sheets. Flash chromatography was performed as described by Still\(^{123}\) with (230-240 mesh) silica gel 60.

All reactions were carried out under nitrogen or argon. The term "conventional workup" refers to extraction of the product from the aqueous phase with an organic solvent, such as dichloromethane or diethyl ether, drying of the organic extract with anhydrous magnesium sulfate and filtration of the resultant mixture, followed by evaporation of the solvent under reduced pressure to obtain the crude products.

The term "at \(-78^\circ\text{C}\)" refers to the temperature of an acetone-CO\(_2\) bath. The term "at \(-30^\circ\text{C}\)" refers to the temperature of a 50% ethanol-CO\(_2\) bath. The term "at 0\(^{\circ}\text{C}\)" refers to the temperature of an ice bath.

4-Methoxy-2-pentyn-1-ol (108)

\[
\begin{align*}
\text{Me} &\quad \text{OMe} \\
107 &\quad 1)\text{MeLi, Et}_2\text{O, -78}^\circ\text{C} \\
\text{Me} &\quad \text{HO} \\
2)\text{HCHO} &\quad 3)\text{H}_2\text{O} \\
61\% &\quad \text{OMe} \\
108 &\quad \text{Me}
\end{align*}
\]

To a stirred solution of 3-methoxy-1-butyn\(^{109}\) (107) (0.840 g, 10.0 mmol) in dry THF (20 mL) at \(-78^\circ\text{C}\) was added methylmagnesium (10.0 mL of 1.5 M solution, 15 mmol) dropwise over 20 min. After stirring for 10-15 min, paraformaldehyde
(0.353 g, 1.5 equiv.) in THF was added. The reaction mixture was allowed to come to RT and then quenched with water. After conventional workup with diethyl ether, bulb-to-bulb distillation of the crude product afforded 108 (0.693 g, 61%): IR (neat, NaCl) νmax 3419 (br), 2987, 2937, 2870, 2824, 1449, 1373, 1332, 1205, cm⁻¹; ¹H NMR δ 4.29 (d, J=1.6, 2H), 4.10 (qt, J=6.6, 1.5, 1H), 3.38 (s, 3H), 2.33 (s, 1H) (br), 1.41 (d, J=6.6, 3H); ¹³C NMR δ 84.6, 83.5, 66.8, 56.0, 50.4, 21.6.

 Hexacarbonyl[µ-η⁴-(4-methoxy-2-pentyn-1-ol)]dicobalt(Co-Co) (109)

![Chemical Reaction Diagram]

**Procedure A**

Compound 108 (1.000 g, 8.76 mmol) was dissolved in anhydrous ethyl ether (80 mL) and cooled to 0°C. An excess of dicobalt octacarbonyl was added and after 1 h the reaction mixture was allowed to warm up to room temperature. The resulting mixture was filtered through Celite® and the solvent was removed in vacuo. Flash chromatography (2:1 petroleum ether :diethyl ether) afforded 109 (3.290 g, 94%): IR (neat, NaCl) νmax 3424, 2984, 2933, 2828, 2094, 2051, 2021 cm⁻¹; ¹H NMR δ 4.74 (d, J=5.9, 2H), 4.48 (q, J=6.3, 1H), 3.65 (t, J=5.9, 1H), 3.41 (s, 3H), 1.43 (d, J=6.3, 3H); ¹³C NMR δ 199.5(br), 98.3, 96.2, 77.7, 63.4, 56.9.
21.7; MS m/e 400 (M⁺), 372 (M⁺-CO), 344 (M⁺-2CO), 316 (M⁺-3CO), 288 (M⁺-4CO), 260 (M⁺-5CO), 232 (M⁺-6CO); HRMS m/e for C₁₂H₁₀Co₂O₆ calcld (M⁺-CO) 371.9091, found 371.9083, calcld (M⁺-2CO) 343.9141, found 343.9146.

Hexacarbonyl[µ-η⁴-(1, 4-diisopropoxy-2-pentyne)]dicobalt(II-Co-Co) (110)

To a stirred solution of compound 109 (1.200 g, 3.00 mmol) in isopropanol (15 mL) and 4Å molecular sieves at RT was added para-toluenesulphonic acid (10 g). The reaction mixture was stirred for about 20 h. The reaction was monitored by TLC. When complete, saturated sodium bicarbonate solution was added slowly with stirring. The organic layer was separated and aqueous layer was washed twice with dichloromethane. The combined organic layers were dried over magnesium sulphate and concentrated under reduced pressure to yield a dark red oil. The residue was purified by flash chromatography (30:1, petroleum ether :diethyl ether) to afford 110 (1.080 g, 77%): IR (neat, NaCl) ν max 2975, 2934, 2874, 2093, 2051, 2024 cm⁻¹; ¹H NMR δ 4.67 (q, J=6.3, 1H), 4.61 (1/2ABq, J=12.9, 1H), 4.59 (1/2ABq, J=12.9, 1H), 3.87 (septet, J=6.1, 1H), 3.79 (septet, J=6.1, 1H), 1.45 (d, J=6.3, 3H), 1.20 (m,12H); ¹³C NMR δ 200.0 (br), 99.9, 93.8, 72.2, 71.8, 69.7, 68.1, 23.5, 22.4, 22.3, 21.9; MS m/e 414 (M⁺-2CO), 386
(M*-3CO), 358 (M*-4CO), 330 (M*-5CO), 302 (M*-6CO); HRMS m/e for C_{17}H_{20}Co_{2}O_{6} calcd (M*-3CO) 385.9975, found 385.9973.

Hexacarboxyl[μ-η^4-(1-isopropoxy-4-methoxy-2-pentyne)]dicobalt(Co-Co)

(111)

To a stirred solution of compound 110 (1.080 g, 2.13 mmol) in methanol (15 mL) at RT was added para-toluenesulphonic acid (1.4 g). The reaction mixture was stirred for about 5 h. The reaction was monitored by TLC. When complete, saturated sodium bicarbonate solution was added slowly with stirring. After a conventional workup with dichloromethane, flash chromatography (30:1 petroleum ether : diethyl ether) afforded 111 (0.714 g, 70%): IR (neat, NaCl) ν_{max} 2976, 2934, 2876, 2824, 2092, 2051, 2017 cm^{-1}; ¹H NMR δ 4.64 (1/2ABq, J=12.8, 1H), 4.61 (1/2ABq, J=12.8, 1H), 4.50 (q, J=6.3, 1H), 3.80 (septet, J=6.1, 1H), 3.48 (s, 3H), 1.49 (d, J=6.3, 3H), 1.21 (d, J=6.1, 6H); ¹³C NMR δ 199.8 (br), 98.1, 94.2, 71.8, 68.1, 57.1, 29.7, 22.3, 21.9; MS m/e 386 (M*-2CO), 358 (M*-3CO), 330 (M*-4CO), 302 (M*-5CO), 274 (M*-6CO); HRMS m/e for C_{15}H_{16}Co_{2}O_{6} calcd (M*-2CO) 385.9611, found 385.9615, calcd (M*-3CO) 357.9662, found 357.9659.
Hexacarbonyl[μ-η⁴-{2-pentyne-1,4-diol}]dicobalt(Co-Co) (123b)

\[
\begin{align*}
\text{HO} & \quad \text{OH} & \quad \text{Co}_2(\text{CO})_6 \\
122b & \quad \text{Et}_2\text{O}, 0^\circ\text{C} & \quad \text{HO} & \quad \text{OH} \\
& & \quad \text{Me} & \quad \text{Co}_2(\text{CO})_6 \\
123b
\end{align*}
\]

Compound 122b (0.659 g, 6.58 mmol) was complexed in diethyl ether (50 mL) via Procedure A. Flash chromatography (6:5 petroleum ether: diethyl ether) afforded the desired product 123b (2.33 g, 92%): IR (neat, NaCl) ν\text{max} 3342, 2978, 2928, 2852, 2094, 2052, 2021 cm⁻¹; ¹H NMR δ 5.05 (q, J=6.1, 1H), 4.89 (s, 2H), 3.00 (s, 2H) (br), 1.59 (d, J=26.5, 3H); ¹³C NMR δ199.3(br), 101.6, 94.9, 68.4, 63.9, 24.8; MS m/e 358 (M⁺-CO), 330 (M⁺-2CO), 302 (M⁺-3CO), 274 (M⁺-4CO), 246 (M⁺-5CO), 218 (M⁺-6CO); HRMS m/e for C₁₁H₆Co₂O₈ calc (M⁺-CO) 357.8934, found 357.8934.

Hexacarbonyl[μ-η⁴-{1,4-diethoxy-2-pentyne}]dicobalt(Co-Co) (124b)

\[
\begin{align*}
\text{HO} & \quad \text{OH} & \quad \text{Me} & \quad \text{Co}_2(\text{CO})_6 \\
123b & \quad \text{EtOH} & \quad \text{EtOH} \text{ (excess)} & \quad \text{EtO} & \quad \text{Me} & \quad \text{Co}_2(\text{CO})_6 \\
& & & \quad \text{124b}
\end{align*}
\]

Procedure B
To a stirred solution of compound 123b (1.360 g, 3.52 mmol) in ethanol (14 mL) at RT was added para-toluenesulphonic acid (34 g). The reaction mixture was stirred for 0.5 h. The reaction was monitored by TLC. When complete, saturated sodium bicarbonate solution was added slowly with stirring until the bubbling stopped. After a conventional workup with dichloromethane, flash chromatography (40:1 petroleum ether :diethyl ether afforded 124b (1.220 g, 78\%): IR (neat, NaCl) \( \nu_{\text{max}} \) 2980, 2932, 2869, 2093, 2051, 2022 cm\(^{-1}\); \(^1\)H NMR \( \delta \) 4.62 (s, 2H), 4.58 (q, J=6.4, 1H), 3.65 (m, 4H), 1.48 (d, J=6.3, 3H), 1.24 (t, J=7.0, 3H); 13C NMR \( \delta \) 199.8 (br), 99.0, 93.1, 75.2, 70.7, 66.5, 64.9, 22.8, 15.2, 15.0; MS \( m/e \) 442 (M\(^+\)), 414 (M\(^+\)-CO), 386 (M\(^+\)-2CO), 358 (M\(^+\)-3CO), 330 (M\(^+\)-4CO), 302 (M\(^+\)-5CO), 274 (M\(^+\)-6CO); HRMS \( m/e \) for C\(_{15}\)H\(_{16}\)Co\(_2\)O\(_8\) calcld (M\(^+\)-CO) 413.9560, found 413.9560.

**Hexacarbonyl[\(\mu-\eta^4\)-(1-phenyl-2-butyn-1,4-diol)]dicobalt(Co-Co) (123c)**

\[
\begin{align*}
\text{HO} & \quad \text{OH} \\
\text{122c} & \quad \text{Co}_2(CO)_6 & \quad \text{HO} & \quad \text{OH} \\
\text{Ph} & \quad \text{Et}_2\text{O}, \quad 0^\circ\text{C} & \quad \text{Ph} & \quad \text{Co}_2(CO)_6 \\
\text{123c} &
\end{align*}
\]

Compound 122c (1.000 g, 6.17 mmol) was complexed via Procedure A. Flash chromatography (7:1 petroleum ether :diethyl ether) afforded the desired product 123c (2.60 g, 94\%): IR (neat, NaCl) \( \nu_{\text{max}} \) 3346, 3090, 3067, 3032, 2924, 2854, 2095, 2054, 2023 cm\(^{-1}\); \(^1\)H NMR \( \delta \) 7.42 (d, J=7.2, 2H), 7.37 (t, J=7.2, 2H), 7.31 (t, J=7.2, 1H), 5.86 (d, J=2.9, 1H), 4.77 (d of 1/2ABq, J=5.5, 14.1, 1H), 4.74
(d of 1/2ABq, J= 4.9, 14.1, 1H), 4.30 (d, J=3.1, 1H), 3.88 (t, J=5.1, 1H); $^{13}$C NMR δ198.8(br), 143.7, 128.5, 128.1, 125.3, 101.3, 94.8, 74.6, 63.5; MS m/e 364 (M$^+$-3CO), 336 (M$^+$-4CO), 280 (M$^+$-6CO); HRMS m/e for C$_{16}$H$_{10}$Co$_2$O$_8$ calcd (M$^+$-3CO) 363.9192, found 363.9195.

**Hexacarbonyl[µ-η$^4$-{1, 4-diethoxy-1-phenyl-2-butyne}]dicobalt(0-CO) (124c)**

![Chemical structure](image)

Compound 123c (2.600 g, 5.80 mmol), ethanol (10 mL) and para-toluene sulphonic acid (30 g) were added together as described in Procedure B. Flash chromatography (80:1 petroleum ether :diethyl ether) afforded 124c (2.330 g, 80%): IR (neat, NaCl) νmax 3064, 3031, 2978, 2931, 2868, 2093, 2052, 2022 cm$^{-1}$; $^1$H NMR δ 7.44 (d, J=7.1, 2H), 7.40 (t, J=7.3, 2H), 7.32 (t, J=7.3, 1H), 5.47 (s, 1H), 4.57 (1/2ABq, J=13.2, 1H), 4.52 (1/2ABq, J=13.2, 1H), 3.58-3.73 (m, 4H), 1.31 (t, J=6.6, 3H), 1.30 (t, J=7.0, 3H); $^{13}$C NMR δ199.4(br), 142.5, 128.4, 127.9, 126.1, 99.4, 92.6, 81.5, 70.6, 66.4, 64.9, 15.0; MS m/e 504 (M$^+$), 476 (M$^+$-CO), 448 (M$^+$-2CO), 420 (M$^+$-3CO), 392 (M$^+$-4CO), 364 (M$^+$-5CO), 336 (M$^+$-6CO); HRMS m/e for C$_{20}$H$_{18}$Co$_2$O$_8$ calcd (M$^+$-CO) 475.9716, found 475.9719.

**Triphenylmethyl ethyl ether (112)**
Triphenylcarbenium tetrafluoroborate (1.084 g, 3.28 mmol) and ethanol (20-30 mL) were added together at RT. The resultant mixture was stirred for 1.5 h and then quenched with saturated aqueous sodium bicarbonate solution. Precipitate was formed upon quenching. A yellowish solid crude product was obtained by filtration. Flash chromatography (10: 1 petroleum ether : diethyl ether) afforded a white solid product **112** (0.770 g, 81%): mp 83.5-84.0°C/1 atm; Lit. mp 84.5°C.[124]

**((E)-Triethyl-[4,4,4-triphenyl-1-butene]silane (115)**

To a mixture of silylstannane **59** (0.215 g, 0.48 mmol) and trityl ethyl ether **112** (0.167 g, 0.58 mmol) at RT was added BF$_3$-OEt$_2$ (0.137 g, 2 equiv.) in dichloromethane (1.4 mL). The reaction mixture was stirred for 2 h and then quenched with saturated sodium bicarbonate solution. After a conventional workup with dichloromethane, flash chromatography (100% petroleum ether) afforded **115** (0.119 g, 62%): IR (neat, NaCl) $\nu_{max}$ 3057, 3030, 3019, 2951, 2909, 2873, 1612, 1597, 1493, 1446, cm$^{-1}$; $^1$H NMR $\delta$ 7.23-7.29 (m, 12H), 7.20 (tt,
J = 6.7, 1.8, 3H), 5.87 (dt, J = 18.7, J = 6.2, 1H), 5.61 (dt, J = 18.8, 1.2, 1H), 3.52 (dd, J = 6.2, J = 1.3, 2H), 0.81 (t, J = 7.9, 9H), 0.42 (q, J = 7.9, 6H); $^{13}$C NMR $\delta$ 147.4, 145.3, 129.7, 129.4, 127.7, 125.9, 56.5, 48.8, 7.2, 3.4; MS m/e 370 (M$^+$-C$_2$H$_5$), 245 (M$^+$-2 C$_6$H$_5$), 168 (M$^+$-3C$_6$H$_5$); HRMS m/e for C$_{28}$H$_{34}$Si calcld (M$^+$-C$_2$H$_5$) 369.2039, found 369.2044.

**Hexacarbonyl[μ-η$^4$-(cyclohept-1-en-4-ynyl)]dicobalt(Co-Co) (69a)**

```
EtO  5min addition  72%
75a  BF$_3$-OEt$_2$ (5eq), 75a
      CH$_2$Cl$_2$
Co$_2$(CO)$_6$ super-dry

Procedure C

Substrate 75a and silylstannane 59 were kept on vacuum for more than 2.5 h immediately before reaction. Substrate 75a (0.052 g, 0.12 mmol) and 59 (0.070 g, 1.3 equiv.) were dissolved in super-dry dichloromethane (1.9 mL) at RT. The mixture was stirred for 0.5 min. BF$_3$-OEt$_2$ (0.086 g, 5 equiv) in super-dry dichloromethane (0.8 mL) was added dropwise over 5 min. The reaction mixture was stirred for 8 min and then quenched with saturated sodium bicarbonate solution. After a conventional workup with dichloromethane, flash chromatography (100% petroleum ether) afforded 69a (0.033 g, 72%) without fluorination. The product was spectroscopically identical to that reported previously in our group.$^{[69]}$
Hexacarbonyl[μ-η⁴-(6-methylcyclohept-1-en-4-yne)]dicobalt(Co-Co) (69b)
and Hexacarbonyl[μ-η⁴-(3-methylcyclohept-1-en-4-yne)]dicobalt(Co-Co) (69b')

Substrate 111 (0.054 g, 0.12 mmol), silylstannane 59 (0.060 g, 1.1 equiv.) and BF₃·OEt₂ (0.087 g, 5 equiv) were added together as described in Procedure C (the reaction mixture was stirred for 40 min before quenching instead of 8 min). Flash chromatography (100% petroleum ether) afforded 69b and 69b' as an inseparable mixture (0.026 g, 57%, 1:1.3) without fluorination. The ratio 69b:69b'=1:1.3 was obtained by the integration ratio of the δ 3.69 (d, J=4.4, 2H) resonance of 69d to the δ 3.80 (m, 1H) resonance of 69d'. The products were spectroscopically identical to those reported previously in our group.⁶⁶

Hexacarbonyl[μ-η⁴-(5-fluorocycloheptyne)]dicobalt(Co-Co) (125a)
To a stirred solution of 124a (0.052 g, 0.12 mmol) in dichloromethane (2.4 mL) at RT was added dropwise a mixture of allytrimethylsilane (0.021 g, 1.5 equiv.) and BF$_3$-OEt$_2$ (0.172 g, 10 equiv.) in dichloromethane (1.0 mL) over 10 min. The reaction mixture was stirred for 10 min and then quenched with saturated sodium bicarbonate solution. After a conventional workup with dichloromethane, flash chromatography (100% petroleum ether) afforded sequentially diallyl 118 (0.010 g, 20%) and 125a (0.036 g, 75%). The product was spectroscopically identical to that reported previously in our group.[98]

Alternative Procedure:

To a stirred solution of 124a (0.065 g, 0.15 mmol) and BF$_3$-OEt$_2$ (0.108 g, 5 equiv.) in dichloromethane (6.3 mL) at RT was added dropwise allyltrimethylsilane (0.026 g, 1.5 equiv.) in dichloromethane (1.0 mL) over 2 h. The reaction mixture was stirred for 6 h and then quenched with saturated sodium bicarbonate solution. After a conventional workup with dichloromethane, flash chromatography (100% petroleum ether) afforded 125a (0.045 g, 75%).

Hexacarbonyl[$\mu$-$\eta^4$-(5-fluoro-3-methylcycloheptyne)]dicobalt(Co-Co) (125b)
To a stirred solution of 124b (0.049 g, 0.11 mmol) and allyltrimethylsilane (0.019 g, 1.5 equiv.) in dichloromethane (2.2 mL) at RT was added dropwise BF$_3$-OEt$_2$ (0.079 g, 5 equiv.) in dichloromethane (1.0 mL) over 1.5 h. The reaction mixture was stirred for 0.25 h and then quenched with saturated sodium bicarbonate solution. After a conventional workup with dichloromethane, flash chromatography (100% petroleum ether) afforded a mixture of trans-125b and cis-125b (0.034 g, 74%, 1.6:1). The ratio 1.6:1 (trans:cis) was obtained by the integration ratio of the 5.10 resonance (dt, J=44.3 Hz, 7.2, 1H) of trans-125b to the 4.55 resonance (dt, J=44.0 Hz, 10.9, 1H) of cis-125b. Further separation afforded pure trans-125b and cis-125b. The products were spectroscopically identical to those reported previously in our group.$^{[99]}$

Hexacarbonyl[μ-η$^4$-(5-fluoro-3-phenylcycloheptyne)]dicobalt(Co-Co) (125c)
To a stirred solution of 124c (0.045 g, 0.089 mmol) and allyltrimethylsilane (0.011 g, 1.1 equiv.) in dichloromethane (1.8 mL) at RT was added dropwise BF_3·OEt_2 (0.063 g, 5 equiv.) in dichloromethane (1.0 mL) over 2.2 h. The reaction mixture was stirred for 0.75 h and then quenched with saturated sodium bicarbonate solution. After a conventional workup with dichloromethane, flash chromatography (100% petroleum ether) afforded a mixture of trans-125c and cis-125c (0.028 g, 67%, 1.5 :1). The ratio 1.5:1 (trans:cis) was obtained by the integration ratio of the δ 5.30 resonance (dt, J=44.4_H, 6.9, 1H) of trans-125c to the δ 4.71 resonance (dt, J=44.1_H, 10.8, 1H) of cis-125c. Further separation afforded pure trans-125c and cis-125c. The products were spectroscopically identical to those reported previously in our group.\textsuperscript{[69]}

Hexacarbonyl[\mu-\eta^4-(5-chlorocycloheptyne)]dicobalt(Co-Co) (127a)
Procedure D

Substrate 124a (0.038 g, 0.089 mmol) and tin tetrachloride (0.116 g, 5 equiv.) were dissolved in dichloromethane (2.2 mL) at RT. The resultant mixture was stirred for 1 min. Allyltrimethylsilane (0.020 g, 2.0 equiv.) in dichloromethane (1.0 mL) was added dropwise over 20 min. The reaction mixture was stirred for 7 min and then quenched with saturated sodium bicarbonate solution. After a conventional workup with dichloromethane, flash chromatography (100% petroleum ether) afforded 127a (0.029 g, 78%): IR (neat, KBr) ν_{max} 2950, 2918, 2088, 2044, 2018, 1991 cm\(^{-1}\); \(^1\)H NMR δ 4.58 (t, J = 7.3, 1H), 3.26 (ddd, J = 16.6, 10.6, 4.1, 2H), 3.03 (apparent dt, J = 16.6, 4.4, 2H), 2.27 (m, 2H), 2.07 (m, 2H); \(^{13}\)C NMR δ 198.8 (br), 99.0, 62.1, 37.1, 30.0; MS m/e 414 (M\(^+\)), 386 (M\(^+\)-1CO), 358 (M\(^+\)-2CO), 330 (M\(^+\)-3CO), 302 (M\(^+\)-4CO), 274 (M\(^+\)-5CO), 246 (M\(^+\)-6CO); HRMS m/e for C\(_{13}\)H\(_8\)ClCo\(_2\)O\(_6\) calcd (M\(^+\)) 413.8752, found 413.8755.

Hexacarbonyl[μ-η\(^4\)-(5-chloro-3-methylcycloheptyne)]dicobalt(Co-Co) (127b)
Substrate 124b (0.039 g, 0.088 mmol), tin tetrachloride (0.115 g, 5 equiv.) and allyltrimethylsilane (0.020 g, 2.0 equiv.) were added as described in Procedure D (the reaction mixture was stirred for 15 min before quenching instead of 7 min). Flash chromatography (100% petroleum ether) afforded a mixture of trans-127b and cis-127b (0.029 g, 76%, 1:1.9). The ratio 1:1.9 (trans:cis) was obtained by the integration ratio of the δ 4.67 resonance (t, J = 6.4, 1H) of trans-127b to the δ 3.99 resonance (tt, J = 11.1, 1.7, 1H) of cis-127b. Further separation afforded pure trans-127b and cis-127b. (trans-127b): IR (neat, KBr) νmax 2961, 2929, 2852, 2090, 2045, 2017 cm⁻¹; ¹H NMR δ 4.67 (t, J = 6.4, 1H), 3.40 (m, 1H), 3.33 (ddd, J = 16.6, 12.4, 4.2, 1H), 3.08 (apparent dt, J = 16.6, 3.4, 1H), 2.25-2.35 (m, 2H), 1.93 (m, 1H), 1.68 (dd, J = 14.4, 1.3, 1H), 1.33 (d, J = 6.8, 3H); ¹³C NMR δ 200.2 (br), 106.4, 98.1, 61.3, 44.1, 35.8, 33.2, 29.4, 21.6; MS m/e 428 (M⁺), 400 (M⁺-1CO), 372 (M⁺-2CO), 344 (M⁺-3CO), 316 (M⁺-4CO), 288 (M⁺-5CO), 260 (M⁺-6CO); HRMS m/e for C₁₄H₁₁ClCo₂Os calcld (M⁺-2CO) 371.9010, found 371.9006.

(cis-127b): IR (neat, KBr) νmax 2964, 2929, 2852, 2090, 2046, 2015 cm⁻¹; ¹H NMR δ 3.99 (tt, J = 11.1, 1.7, 1H), 3.22 (dt, J = 16.6, 3.4, 1H), 2.94 (m, 1H), 2.87
(ddd, J = 16.6, 12.7, 4.0, 1H), 2.52 (m, 1H), 2.48 (m, 1H), 1.99 (m, 1H), 1.79 (m, 1H), 1.35 (d, J = 6.7, 3H); $^{13}$C NMR δ 200.1 (br), 105.5, 97.0, 61.8, 49.0, 40.4, 36.9, 32.8, 22.0; MS m/e 428 (M$^+$), 372 (M$^+$-2CO), 344 (M$^+$-3CO), 316 (M$^+$-4CO), 288 (M$^+$-5CO), 260 (M$^+$-6CO); HRMS m/e for C$_{14}$H$_{11}$ClCo$_2$O$_6$ calcd (M$^+$-2CO) 371.9010, found 371.9006.

**Hexacarbonyl[μ-η$^4$-(5-chloro-3-phenylcycloheptyne)]dicobalt(Co-Co) (127c)**

To a stirred solution of substrate 124c (0.046 g, 0.091 mmol) and allyltrimethylsilane (0.013 g, 1.2 equiv.) in dichloromethane (3.0 mL) at RT was added dropwise tin tetrachloride (0.083 g, 3.5 equiv.) in dichloromethane (1.0 mL) over 2.25 h. The reaction mixture was stirred for 5 min and then quenched with saturated sodium bicarbonate solution. After a conventional workup with dichloromethane, flash chromatography (100% petroleum ether) afforded a mixture of trans-127c and cis-127c (0.027 g, 60%, 1 :1.9). The ratio 1:1.9 (trans:cis) was obtained by the integration ratio of the δ 4.75 resonance (t, J=6.3, 1H) of trans-127c to the δ 4.14 resonance (tt, J=11.0, 1.8, 1H) of cis-127c. Further separation afforded pure trans-127c and cis-127c. (trans-127c): IR
(neat, NaCl) $\nu_{\text{max}}$ 3036, 2962, 2933, 2090, 2048, 2027 cm$^{-1}$; $^1$H NMR $\delta$ 7.37 (t, J = 7.5, 2H), 7.28-7.35 (m, 3H), 4.85 (t, J = 6.3, 1H), 4.52 (dd, J = 12.0, 3.6, 1H), 3.40 (ddd, J = 16.6, 12.5, 4.1, 1H), 3.15 (dt, J = 16.6, 3.3, 1H), 2.52 (m, 1H), 2.42 (m, 1H), 2.36 (apparent t, J = 13.5, 1H), 2.08 (m, 1H); $^{13}$C NMR $\delta$ 199.9 (br), 142.7, 128.5, 127.6, 127.2, 106.6, 99.1, 51.4, 43.9, 40.9, 36.0, 29.5; MS m/e 462 (M$^+$-CO), 434 (M$^+$-2CO), 406 (M$^+$-3CO), 378 (M$^+$-4CO), 350 (M$^+$-5CO), 322 (M$^+$-6CO); HRMS m/e for C$_{19}$H$_{18}$ClCo$_2$O$_6$ calcd (M$^+$-2CO) 433.9166, found 433.9162.

(cis-127c) IR (neat, NaCl) $\nu_{\text{max}}$ 3030, 2940, 2092, 2048, 2028, 2016 cm$^{-1}$; $^1$H NMR $\delta$ 7.37 (t, J = 7.4, 2H), 7.25-7.35 (m, 3H), 4.14 (tt, J = 11.0, 1.8, 1H), 4.00 (dd, J = 12.2, 3.5, 1H), 3.29 (tt, J = 16.8, 3.4, 1H), 2.95 (ddd, J = 16.8, 12.7, 4.1, 1H), 2.74 (m, 1H), 2.63 (m, 1H), 2.45 (m, 1H), 2.15 (m, 1H); $^{13}$C NMR $\delta$ 199.5 (br), 142.6, 128.6, 127.3, 127.2, 105.7, 98.0, 62.0, 47.5, 45.8, 40.7, 32.9; MS m/e 462 (M$^+$-1CO), 434 (M$^+$-2CO), 406 (M$^+$-3CO), 378 (M$^+$-4CO), 350 (M$^+$-5CO), 322 (M$^+$-6CO); HRMS m/e for C$_{19}$H$_{18}$ClCo$_2$O$_6$ calcd (M$^+$-2CO) 433.9166, found 433.9164.

Hexacarbonyl[μ-$\eta^4$-(5-Bromocycloheptyne)]dicobalt(Co-Co) (129)

$$
\begin{align*}
\text{EtO} & \quad \text{CO}_2(\text{CO})_6 \\
124a & \quad \text{SnBr}_4(\text{Bq}), \text{CH}_2\text{Cl}_2 \\
& \quad \text{SiMe}_3 \\
& \quad \text{RT} \\
& \quad 26\% \\
\end{align*}
$$
Substrate 124a (0.044 g, 0.10 mmol) and tin tetrabromide (0.360 g, 8 equiv.) were dissolved in dichloromethane (1.0 mL) at RT. The resultant mixture was stirred for 35-40 min. Allyltrimethylsilane (0.014 g, 1.2 equiv.) in dichloromethane (0.5 mL) was added dropwise over 1 h. The reaction mixture was stirred for 1 h, and the reaction was stopped by passing through a silica gel column with pure petroleum ether as eluent. The product fraction was collected and concentrated under reduced pressure to afford the crude product. Flash chromatography (100% petroleum ether) afforded 129 (0.012 g, 26%): IR (neat, KBr) νmax 2930, 2090, 2046, 2016 cm⁻¹; ¹H NMR δ 4.75 (t, J = 6.9, 1H), 3.27 (ddd, J = 16.7, 10.7, 3.7, 2H), 3.09 (dt, J = 16.7, 3.7, 2H), 2.33 (m, 2H), 2.07 (m, 2H); ¹³C NMR δ 200.0 (br), 98.8, 56.6, 37.5, 31.5; MS m/e 458 (M⁺), 402 (M⁺-2CO), 374 (M⁺-3CO), 348 (M⁺-4CO), 318 (M⁺-5CO), 290 (M⁺-6CO); HRMS m/e for C₁₃H₆Br⁷⁸Co₂O₆ calcd (M⁺) 457.8246, found 457.8242.

Hexacarbonyl[µ-η⁴-{5-phenylcycloheptyne}]dicobalt(Co-Co) (130a)

![Chemical structure](image)

Substrate 124a (0.050 g, 0.12 mmol) and B(C₆F₅)₃ (0.149 g, 2.5 equiv.) were dissolved in benzene (1.2 mL) at RT. The resultant mixture was stirred for 5
min. Allyltrimethylsilane (0.020 g, 1.5 equiv.) in benzene (0.5 mL) was added dropwise over 1 h. The reaction mixture was stirred for 0.5 h and then quenched with saturated sodium bicarbonate solution. After a conventional workup with dichloromethane, flash chromatography (100% petroleum ether) afforded contaminated 130a 0.040 g, with 6% impurities attributed to propargyl trapping products (131 and 136), gives an estimated yield of 70% for 130a: IR (neat, KBr) \( \nu_{\text{max}} \) 3028, 2087, 2043, 1303 cm\(^{-1}\); \(^1\)H NMR \( \delta \) 7.31 (t, \( J = 7.4, 2H \)), 7.21 (t, \( J = 7.5, 1H \)), 7.17 (d, \( J = 7.6, 2H \)), 3.29 (dt, \( J = 16.5, 3.2, 2H \)), 2.91 (dd, \( J = 16.5, 12.5, 4.1, 2H \)), 2.59 (t, \( J = 10.6, 1H \)), 2.14 (dt, \( J = 13.9, 3.4, 2H \)), 1.88 (m, \( 2H \)); \(^{13}\)C NMR \( \delta \) 200.0 (br), 149.5, 128.7, 126.3, 126.0, 100.4, 49.3, 38.1, 34.7; MS \( m/e \) 456 (M\(^+\)), 400 (M\(^+\)-2CO), 372 (M\(^+\)-3CO), 344 (M\(^+\)-4CO), 316 (M\(^+\)-5CO), 288 (M\(^+\)-6CO); HRMS \( m/e \) for \( \text{C}_{19}\text{H}_{14}\text{Co}_2\text{O}_6 \) calcd (M\(^+\)-2CO) 371.9607, found 371.9604.

Hexacarbonyl[\( \mu-\eta^4\)-(3-methyl-5-phenylcycloheptene)]dicobalt(Co-Co) (130b)

\[ \text{EtO} \quad \text{OEt} \quad \text{SiMe}_3 \quad \text{Me} \quad \text{Me} \quad \text{B(C}_6\text{F}_5)_3 \quad \text{RT} \quad \text{Co}_2(\text{CO})_6 \]

\( \text{124b} \quad \text{cis-130b} \)

To a stirred solution of substrate 124b (0.040 g, 0.091 mmol) and allyltrimethylsilane (0.016 g, 1.5 equiv.) in benzene (1.9 mL) at RT was added
dropwise $\text{B(C}_6\text{F}_5)_3$ (0.237 g, 5 equiv.) in benzene (1.0 mL) over 2.5 h. The reaction mixture was stirred for 0.25 h and then quenched with saturated sodium bicarbonate solution. After a conventional workup with dichloromethane, flash chromatography (100% petroleum ether) afforded cis-130b (0.026 g, 61%): IR (neat, KBr) $\nu_{\text{max}}$ 3030, 2088, 2044, 2021 cm$^{-1}$; $^1$H NMR $\delta$ 7.31 (m, 2H), 7.20 (m, 1H), 7.15 (d, $J = 7.1$, 2H), 3.29 (dt, $J = 16.4$, 3.1, 1H), 3.03 (m, 1H), 2.95 (ddd, $J = 16.6$, 12.6, 4.0, 1H), 2.66 (t, $J = 10.7$, 1H), 2.10 (dt, $J = 14.1$, 3.6, 1H), 2.03 (dd, $J = 14.0$, 3.9, 1H), 1.86 (m, 1H), 1.65 (m, 1H), 1.33 (d, $J = 6.8$, 3H); $^{13}$C NMR $\delta$ 200.4 (br), 149.6, 128.7, 126.2, 126.0, 107.4, 99.1, 48.4, 46.6, 39.1, 37.8, 35.0, 22.3; MS m/e 434 ($M^+$), 414 ($M^+-\text{CO}$), 386 ($M^+-\text{CO}_2$), 358 ($M^+-\text{CO}_3$), 330 ($M^+-\text{CO}_4$), 302 ($M^+-\text{CO}_5$); HRMS m/e for $C_{20}H_{16}Co_2O_6$ calcd ($M^+-\text{CO}_3$) 385.9763, found 385.9766.

**Hexacarbonyl[μ-η$^4$-(3, 5-diphenylcycloheptene)]dicobalt(Co-Co) (130c)**

![Chemical Structure](image)

To a stirred solution of substrate 124c (0.047 g, 0.093 mmol) and allyltrimethylsilane (0.011 g, 1 equiv.) in benzene (1.9 mL) at RT was added dropwise $\text{B(C}_6\text{F}_5)_3$ (0.167 g, 3.5 equiv.) in benzene (1.0 mL) over 2.5 h. A dark-
red precipitate was found on the inner wall of the flask. After the reaction mixture was stirred for 1 h, dichloromethane (ca. 0.7 mL) was added to the reaction mixture, and most of the dark-red precipitate dissolved. The reaction was stirred for 15 min and then quenched with saturated sodium bicarbonate solution. After a conventional workup with dichloromethane, flash chromatography (100% petroleum ether) afforded cis-130c (0.026 g, 52%): IR (neat, KBr) \( \nu_{\text{max}} \) 3029, 2089, 2045, 2026, 2008 cm\(^{-1}\); \(^1\)H NMR \( \delta \) 7.18-7.37 (m, 10H), 4.11 (m, 1H, simplifies to dd, \( J = 9.7, 5.6 \) upon irradiation at \( \delta 2.83 \)), 3.37 (dt, \( J = 16.4, 3.2, 1H \)), 3.03 (ddd, \( J = 16.4, 12.6, 4.1, 1H \)), 2.83 (br t, \( J = 10.7, 1H \)), 2.28-2.37 (m, 2H), 2.22 (dt, \( J = 14.1, 3.1, 1H \)), 2.04 (m, 1H); \(^{13}\)C NMR \( \delta \) 199.9 (br), 149.3, 143.7, 128.7, 128.4, 127.3, 127.0, 126.3, 126.1, 107.4, 100.3, 50.0, 48.9, 43.5, 37.9, 35.1; MS \( m/e \) 504 (M\(^+\)-1CO), 448 M\(^+\)-3CO), 420 (M\(^+\)-4CO), 392 (M\(^+\)-5CO), 364 (M\(^+\)-6CO); HRMS \( m/e \) for C\(_{25}\)H\(_{18}\)Co\(_2\)O\(_6\) calcd (M\(^+\)-3CO) 447.9920, found 447.9917.

**Hexacarbonyl\([\mu-\eta^4-(5\text{-}(2\text{-methylphenyl})\text{cycloheptyne})]\)dicobalt(Co-Co) (ortho-135a), Hexacarbonyl\([\mu-\eta^4-(5\text{-}(4\text{-methylphenyl})\text{cycloheptyne})]\)dicobalt(Co-Co) (para-135a), Hexacarbonyl\([\mu-\eta^4-(5\text{-}(3\text{-methylphenyl})\text{cycloheptyne})]\)dicobalt(Co-Co) (meta-135a)**
To a stirred solution of substrate 124a (0.039 g, 0.091 mmol) and allyltrimethylsilane (0.012 g, 1.2 equiv.) in toluene (1.8 mL) at RT was added dropwise B(C_{6}F_{5})_{3} (0.117 g, 2.5 equiv.) in toluene (1.0 mL) over 1.25 h. The reaction was stirred for 0.75 h and then quenched with saturated sodium bicarbonate solution. After a conventional workup with dichloromethane, flash chromatography (100% petroleum ether) afforded ortho-135a, para-135a and meta-135a as an inseparable mixture (0.025 g, 58%, ortho:para:meta = 1.4:1:1). The ratio of regioisomers was assigned by integration of the $^1$H NMR resonance at $\delta$ 2.80 and the combined resonances at $\delta$ 2.56 and $\delta$ 2.55, as well as integration of the resonance at 7.07 ppm (d, J=8.0), which is attributed to two arene protons of para-135a. (ortho+para+meta-135a): IR (neat, KBr) $\nu_{\text{max}}$ 3022, 2088, 2043, 2017 cm$^{-1}$; $^1$H NMR $\delta$ 6.92-7.22 (m, 4H), 3.29 (m, 2H), 2.90 (m, 2H), 2.80 (t, J = 10.2), 2.56 (t, J = 10.6) and 2.55 (t, J = 10.6) (1H), 2.35 (s), 2.34 (s), and 2.33 (s) (3H), 2.11 (m, 2H), 1.86 (m, 2H); $^{13}$C NMR $\delta$ 200.7 (br), 200.0 (br), 149.5, 147.6, 146.6, 138.3, 135.5, 133.7, 130.4, 129.3, 128.6, 127.1, 126.8, 126.4, 126.2, 125.7, 123.3, 100.4, 100.2, 49.3, 48.8, 38.3, 38.2, 37.7, 35.1, 34.8,
34.7; MS m/e 470 (M$^+$), 414 (M$^+$-2CO), 386 (M$^+$-3CO), 358 (M$^+$-4CO), 330 (M$^+$-5CO), 302 (M$^+$-6CO); HRMS m/e for C$_{20}$H$_{16}$Co$_2$O$_6$ calcd (M$^+$ -3CO) 385.9763, found 385.9767.

**Hexacarbonyl[μ-η$^4$-(5-{2-chlorophenyl)cycloheptyne})dicobalt(Co-Co)** (ortho-135b), **Hexacarbonyl[μ-η$^4$-(5-{4-chlorophenyl)cycloheptyne})dicobalt(Co-Co)** (para-135b), **Hexacarbonyl[μ-η$^4$-(5-{3-chlorophenyl)cycloheptyne})dicobalt(Co-Co)** (meta-135b)

![Chemical structure](image)

To a stirred solution of substrate 124a (0.041 g, 0.096 mmol) in chlorobenzene (1.0 mL) at RT was added dropwise a solution of B(C$_5$F$_5$)$_3$ (0.123 g, 2.5 equiv.) and allyltrimethylsilane (0.016 g, 1.5 equiv.) in chlorobenzene (1.0 mL) over 1.25 h. The reaction was stirred for 1 h and then quenched with saturated sodium bicarbonate solution. After a conventional workup with dichloromethane, the resultant chlorobenzene solution was kept under vacuum for 2-5 min to evaporate the remaining chlorobenzene. Flash chromatography
(100% petroleum ether) afforded a contaminated regioisomeric mixture 135b 0.028 g, with 8% impurity attributed to 136, gives a 51% yield for 135b (ortho:para:meta=1.8:1:0.3). The ratio was determined by the integration of the δ 3.14 (br s, 1H) resonance of ortho-135b, the δ 2.57 (t, J=10.6, 1H) resonance of para-135b and the δ 7.05 (d, J=7.5, 1H) resonance of meta-135b. Pure ortho-135b was obtained by repeated preparative TLC separations. (ortho-135b): IR (neat, KBr) v_max 2925, 2848, 2096, 2048, 2030, 2015, 1994 cm^{-1}; 1H NMR δ 7.38 (dd, J = 8.0, 1H), 7.19-7.27 (m, 2H), 7.14 (m, 1H), 3.30 (dt, J = 16.4, 3.1, 2H), 3.14 (br, 1H), 2.97 (dd, J = 16.4, 12.6, 4.2, 2H), 2.13 (dt, J = 13.9, 3.3, 2H), 1.85 (br m, 2H); 13C NMR δ 200.2 (br), 151.0, 146.2, 132.4, 129.6, 127.1, 127.0, 100.3, 44.0, 37.3, 34.8; MS m/e 434 (M^{+}-2CO), 406 (M^{+}-3CO), 378 (M^{+}-4CO), 350 (M^{+}-5CO), 322 (M^{+}-6CO); HRMS m/e for C_{19}H_{13}ClCO_2O_6 calcd (M^{+}-2CO) 433.9166, found 433.9168.

(para- +meta-135b): IR (neat, KBr) v_max 2925, 2848, 2103, 2097, 2089, 2045, 2013, 1086 cm^{-1}; Peaks attributable to the para isomer could be observed in the 1H NMR at δ 7.28 (d, J = 8.3, 2H), 7.09 (d, J = 8.3, 2H), 3.28 (m, obscured, 2H), 2.90 (ddd, J = 16.5, 12.6, 4.1, 2H), 2.57 (t, J = 10.6, 1H), 2.09 (dt, J = 14.0, 3.4, 2H), 18.3 (m, 2H); 13C NMR δ 200.6 (br), 147.8, 131.7, 128.8, 127.6, 100.1, 48.6, 38.1, 34.6. Peaks from the meta isomer could be observed in 1H NMR at δ 7.24 (apparent t, J = 7.7, 1H), 7.18 (br d, J = 8.5, 1H), 7.16 (br s, 1H), 7.04 (d, J = 7.6, 1H), 2.12 (m, obscured, 2H); 13C NMR δ 151.3, 134.3, 130.0, 126.6, 126.1, 124.5, 105.5 48.9, 38.0; MS m/e 490 (M^{+}), 434 (M^{+}-2CO), 406 (M^{+}-3CO), 378
(M*-4CO), 350 (M*-5CO), 322 (M*-6CO); HRMS m/e for C_{19}H_{13}ClCo_{2}O_{5} calcd (M*-2CO) 433.9166, found 433.9162.
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VITA AUCTORIS

NAME: Yafan Lu

PLACE OF BIRTH: Hengnan, P. R. China

YEAR OF BIRTH: 1964

EDUCATION:
Zhongshan University, Guangzhou, China
1985, B. Sc., Chemistry

Zhongshan University, Guangzhou, China
1988, M. Sc., Chemistry

University of Windsor, Windsor, Ontario
2001, M. Sc., Chemistry