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

BY

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UNIVERSITY OF WINDSOR

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A Thesis

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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-$Co_2(CO)_6$ 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 [EtO-BF_3]$^-$, 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 BF_3-OEt_2 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**.[97] 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.

I would like to thank Dr. John McIntosh and Dr. Philip Dutton for their advice and help whenever needed. I would also like to thank Mike Fuerth for his help in the NMR experiments.

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The other people in the Department are also thanked for their help whenever needed.

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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
^{i}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

Naph	naphthyl
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
NOESY	nuclear overhauser and exchange spectroscopy
Nu	nucleophile
q	quartet
Ph	phenyl
ppm	parts per million
p-TsOH	para-toluenesulphonic acid
RT	room temperature
s	singlet
TBDMS	^{t}butyldimethylsilyl
Tf	triflic (-SO_2CF_3)
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TLC	thin layer chromatography
TMS	trimethylsilyl
TMSOTf	trimethylsilyl triflate
TS	transition state
tt	triplet of triplet

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.[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.[1] Therefore, cycloaddition is superficially the best strategy among these four routes as two bonds are formed in only one operation.

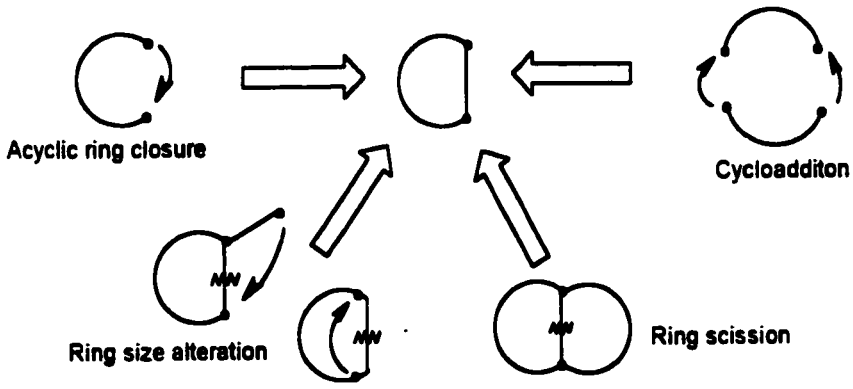


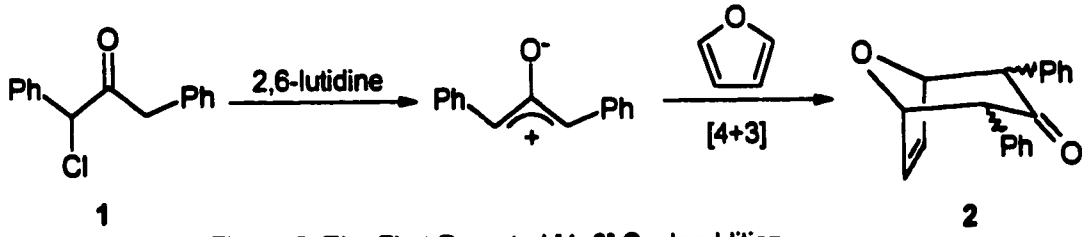
Figure 1. Synthetic Routes for Cycloheptane System

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

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]



1 **2**

Figure 2. The First Reported [4+3] Cycloaddition

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 C_2 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]

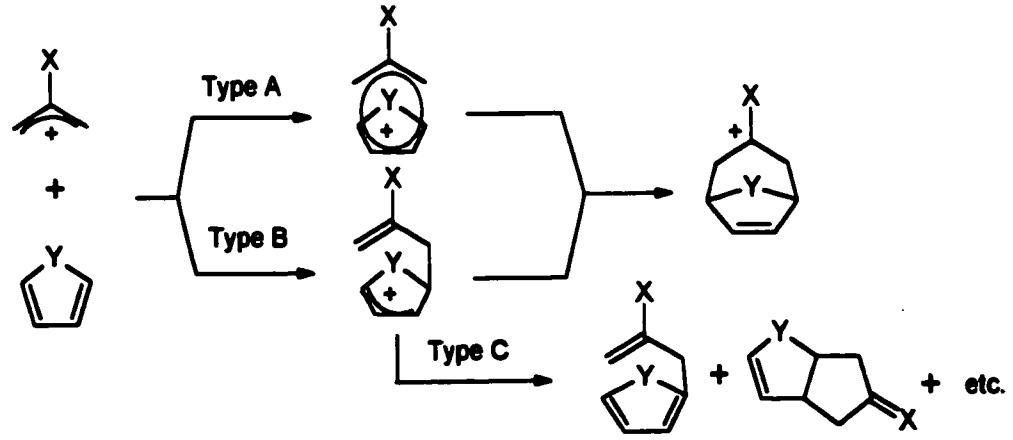


Figure 3. Mechanisms for [4+3] Cycloadditions of Allyl Cations

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.[9]

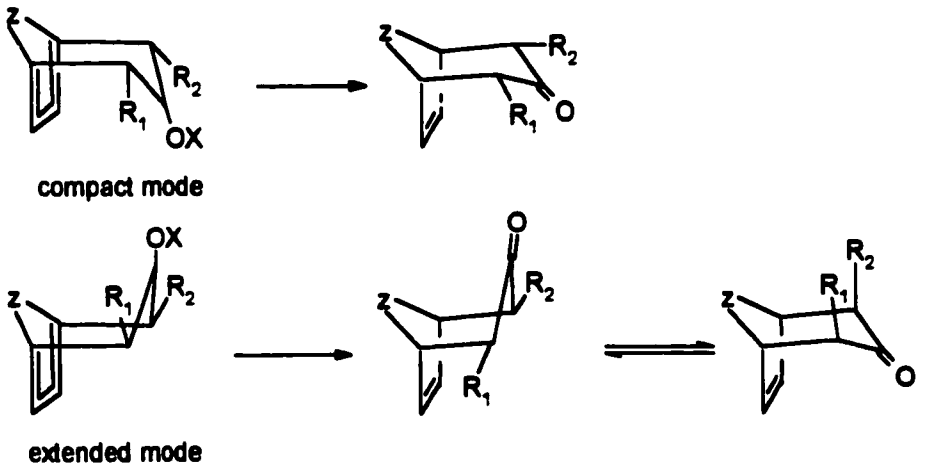
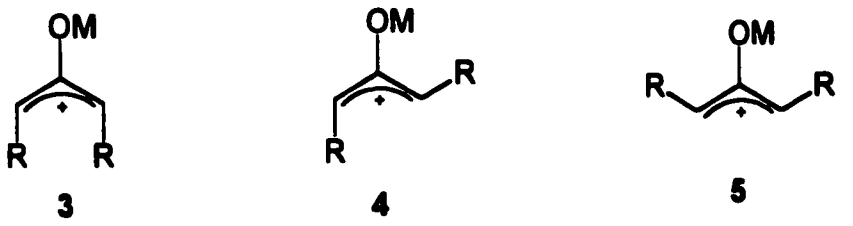


Figure 4. Transition State models for Concerted [4+3] Cycloadditions

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**).



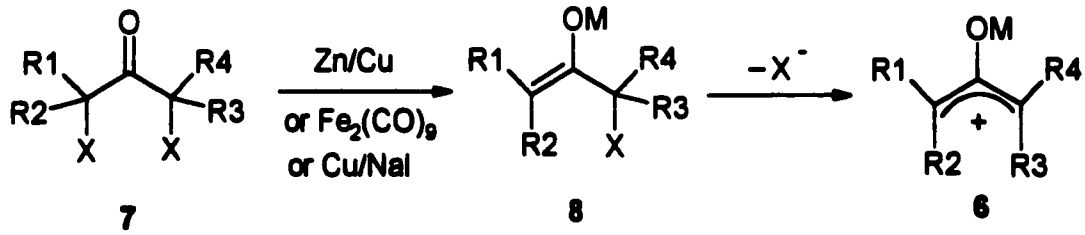
3 **4** **5**

Generally, the W form is preferred.[9] 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 α,α'-dihaloketones (**7**) with an agent (Figure 5) such as Zn-Cu couple,[15] $Fe_2(CO)_9$[16, 17] or Cu/NaI[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]

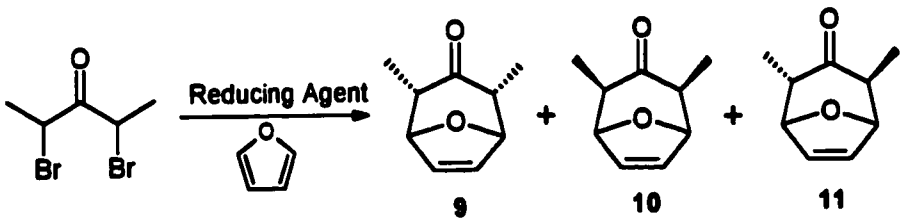


7 **8** **6**

Figure 5. Preparation of 2-Oxyallyl Cations

The course of [4+3] cycloaddition depends greatly on the choice of the reducing agent. The Cu/NaI reduction conditions are believed to produce the least electrophilic oxyallyl cation, as compared with Zn/Cu and $Fe_2(CO)_9$ reduction conditions. $Fe_2(CO)_9$ 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.[15,16,19] When N-methylpyrrole was employed as diene partner, only the Cu/NaI protocol gave cyclization.[16,20,21]



Reducing Agent	9	10	11
Cu/NaI	48%	5%	-
Zn/Cu	69%	8%	7%
$Fe_2(CO)_9$	40%	-	50%

Figure 6. Cycloadditions with Different Reducing Agents

The [4+3] cycloaddition of acyclic dienes with oxyallyl cation was also investigated. The efficiency was not good, but when the corresponding η^4-butadienetricarbonyliron(0) complex was used as diene partner, a 90% yield was achieved (Figure 7). It is believed that tricarbonyliron(0) moiety can lock the 1,3-butadiene in its S-*cis* configuration required for the cycloaddition.[16]

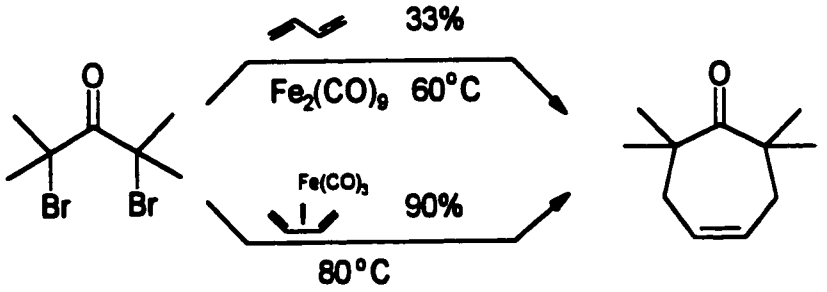
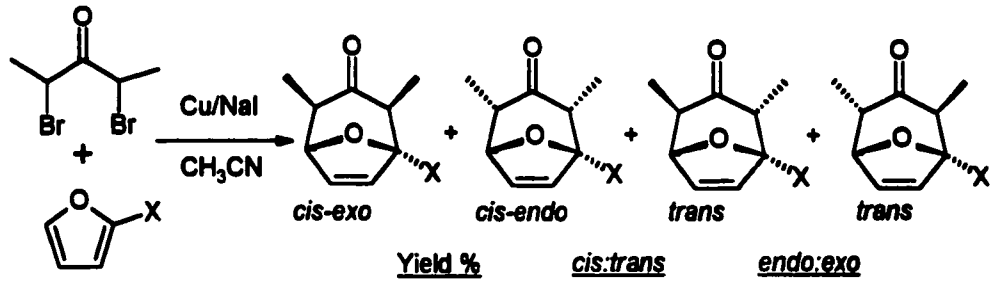


Figure 7. Cycloaddition of Acyclic Dienes

When cycloadditions of C_2-substituted furans were investigated, *cis* stereoselectivity and excellent *endo* diastereoselectivity were observed (Figure

8). The electron donating group increased both the yield and diastereoselectivity.[22]



	Yield %	cis:trans	endo:exo
X = Ph	60	100 : 0	97 : 3
$OSiMe_3$	86	100 : 0	95 : 5
OCO^tBu	93	100 : 0	95 : 5
OCOOEt	100	100 : 0	100 : 0

Figure 8. Cycloadditions of C_2-substituted Furans

Lewis acid or silver salt promoted heterolysis of allyl halides are very direct methods to generate allyl cations.[23, 24] For the 2-methoxyallyl and 2-silyloxyallyl cation systems, however, the efficiency for the [4+3] cycloaddition is modest.[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_2O mixed solvent.[26]

Excellent efficiency has been achieved in the Lewis acid ($TiCl_4$) promoted [4+3] cycloaddition of (trimethysilyl)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.[27]

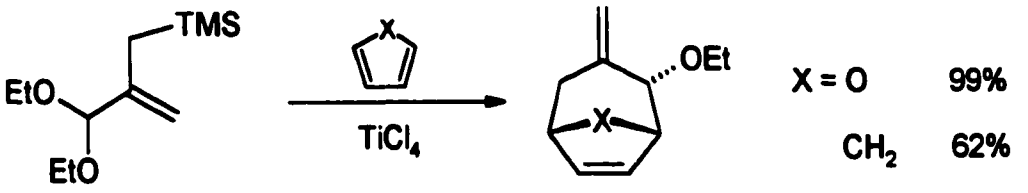


Figure 9. Lewis Acid Promoted Cycloaddition of (Trimethylsilyl)methylallyl Acetals

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.[28]

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

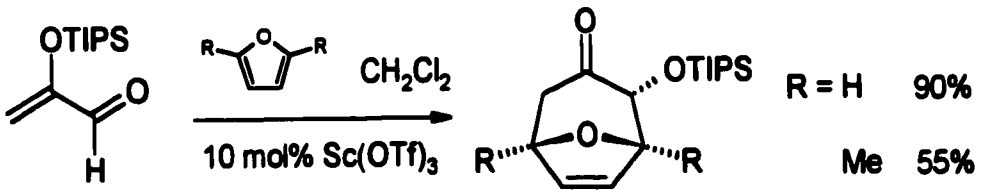
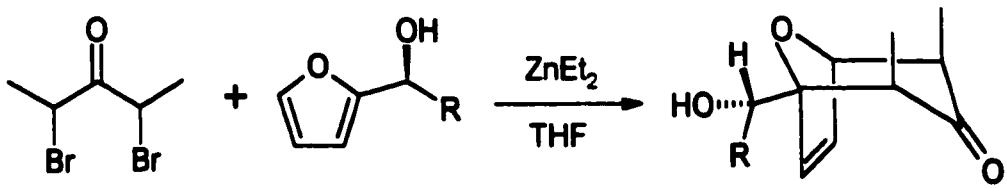


Figure 10. Cycloaddition of 2-(Silyloxy)acroleins

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 $ZnEt_2$ 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.[31]



	Yield %	diastereoselection
R = ^{t}Bu	80	96 : 4
c-Hexyl	80	95 : 5

Figure 11. Asymmetric Cycloaddition of Chiral Furan Derivatives

The Lewis acid mediated asymmetric intermolecular cycloadditions of chiral allyl cations have been studied.[32-36] Synthetically useful chiral allyl cations have been generated from α,α-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 π-face of the allyl cation. The diene partner could only approach the allyl cation from the other π-face, so the stereoselectivity was achieved.[35, 36]

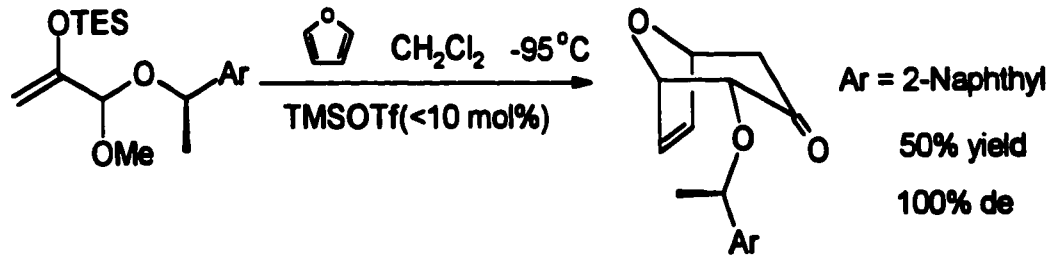


Figure 12. TMSOTf-mediated Asymmetric Intermolecular Cycloaddition

The use of basic conditions to generate oxyallyl cations from α-haloketones is still a popular protocol for [4+3] cycloadditions,[37,38] particularly for cyclic precursors,[39] where the reductive conditions show low efficiencies.[40] 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.[41]

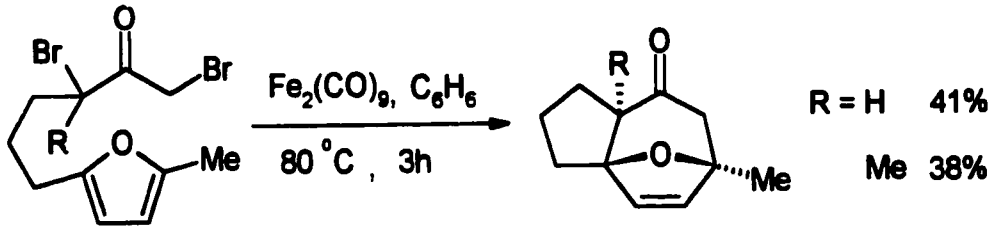


Figure 13. The First Reported Intramolecular [4+3] Cycloaddition

Noyori reported the first example of intramolecular [4+3] cycloaddition, although yields were low (Figure 13).[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 α,α-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%).[43, 44]

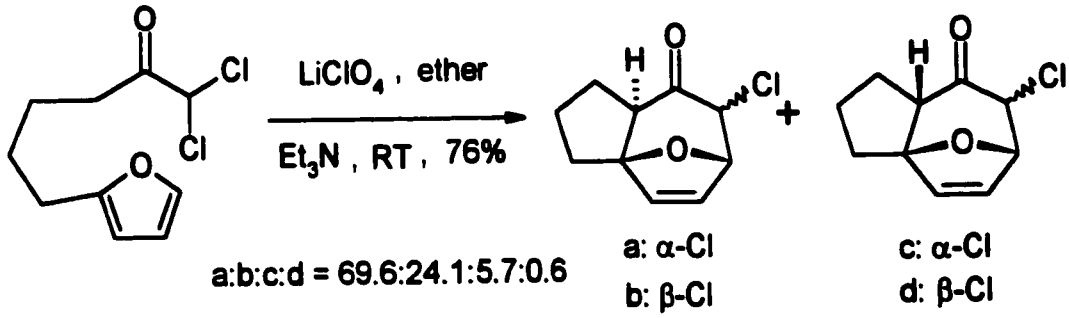


Figure 14. $LiClO_4$ Mediated Intramolecular Cycloaddition

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]

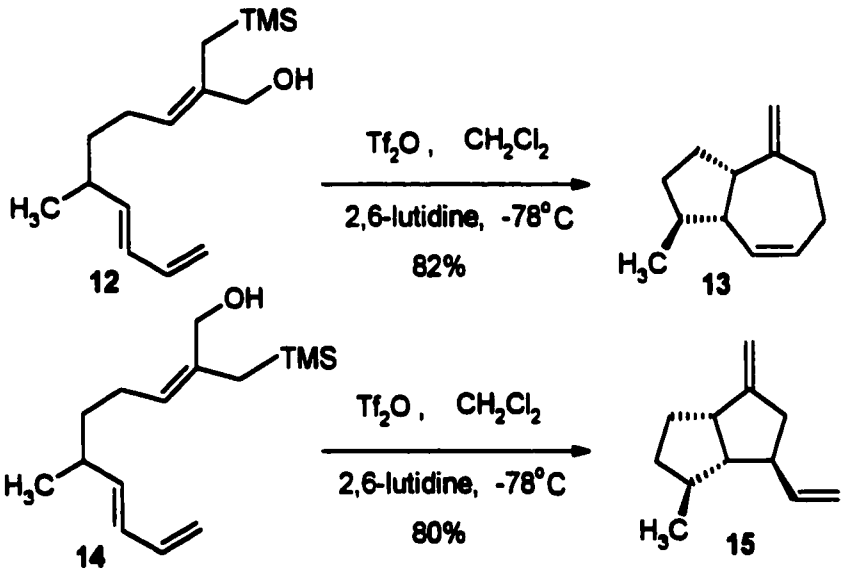


Figure 15. Cycloaddition Affected by Stereochemistry of Allylic Cation

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

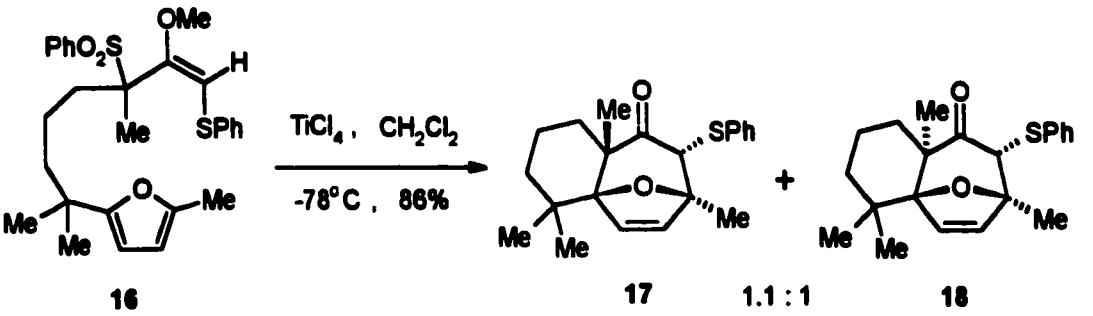


Figure 16. Titanium Tetrachloride Mediated Intramolecular Cycloaddition of Sulphur-substituted Alkoxyallylic Sulfone Substrates

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]

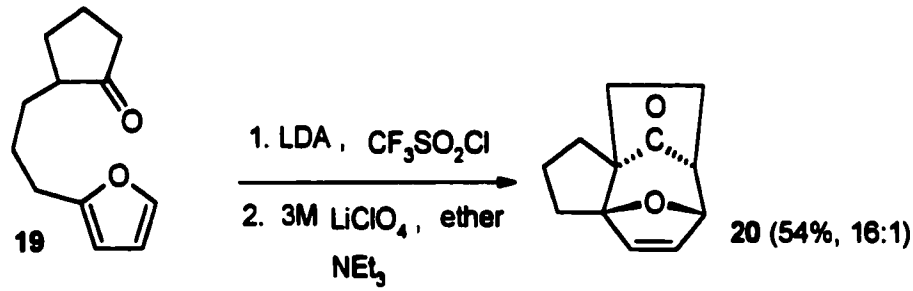


Figure 17. First Non-photochemical Intramolecular Cycloaddition of Cyclic Oxyallyl Cation

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.[39]

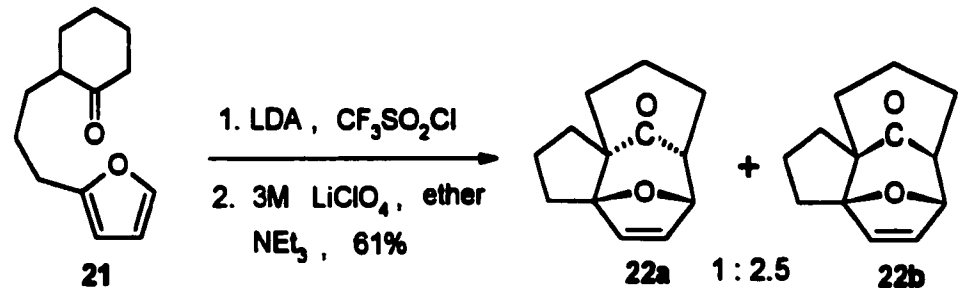


Figure 18. Larger Ring Cyclic Oxyallyl Cation [4+3] Cycloaddition

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).[49] 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]

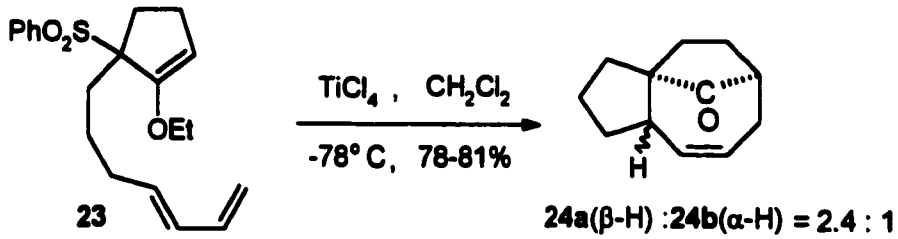


Figure 19. Cycloaddition of Substituted Butadiene Substrates

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]

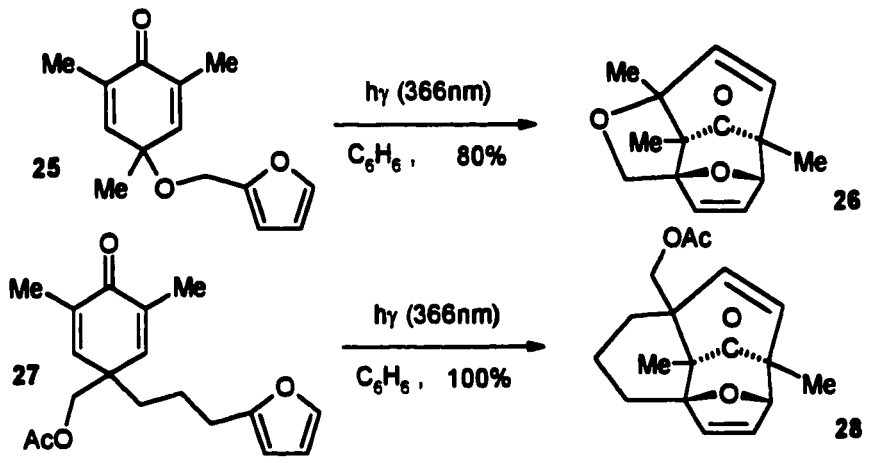
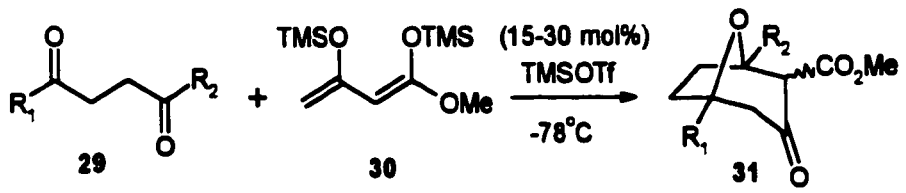


Figure 20. Photochemical Intramolecular [4+3] Cycloadditions

1.2. Cycloadditions of 1,4-Dicarbonyls

A distinctly different type of Lewis acid promoted [4+3] cycloaddition has been developed by Molander.[57 -64] These cycloadditions use 1,4-dicarbonyl electrophiles **29** and bis(trimethylsilyl) enol ethers **30** as 1,3-dinucleophiles (Figure 21).[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.[60] For the 1,4-ketoaldehyde, extremely high regioselectivities (>200:1) were always achieved.[58, 59] For the unsymmetrical 1,4-diketones, the regioselectivity was much lower (Figure 21).[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).[58, 59, 60]



R_1	R_2	Yield %	Diastereoselectivity (regioselectivity)
Me	H	53	>200:1
n-Pr	H	78-90	>200:1
Ph	H	87	>200:
t-Bu	H	88	>200:1
t-Bu	Me	74	28:1
n-Pr	Me	73	7:1

Figure 21. Molander [4+3] Cycloadditions

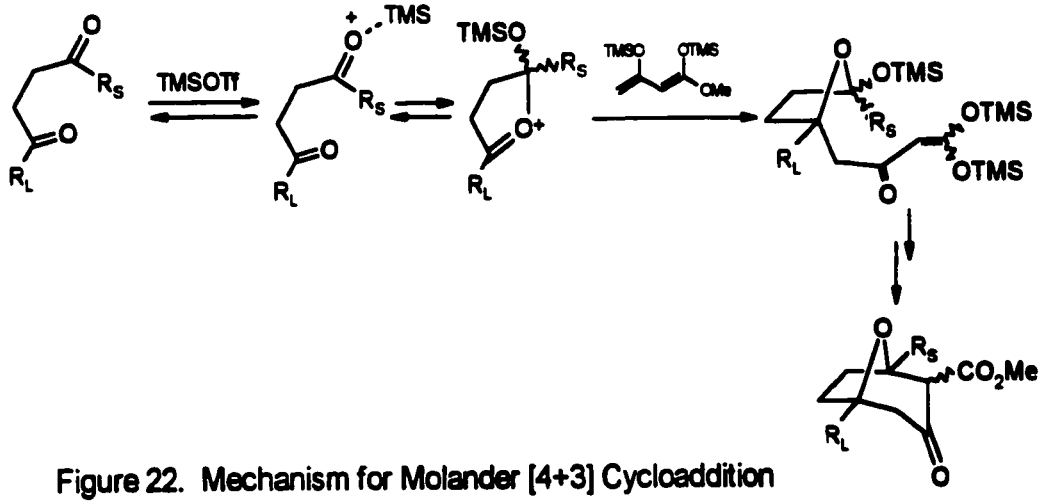


Figure 22. Mechanism for Molander [4+3] Cycloaddition

The regiochemistry for Molander cycloaddition was reversed by the use of another Lewis acid, $TiCl_4$ (Figure 23).[57] This reaction likely proceeds in a different pathway which does not involve neighboring group participation.[64]

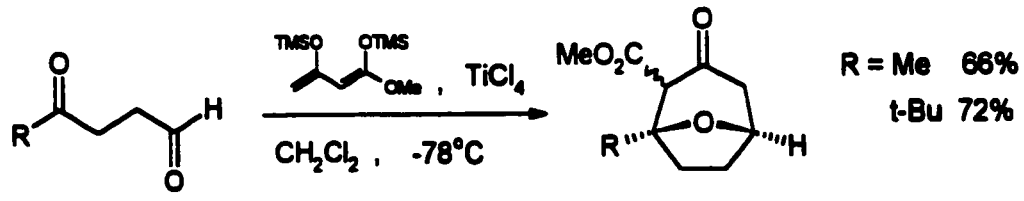
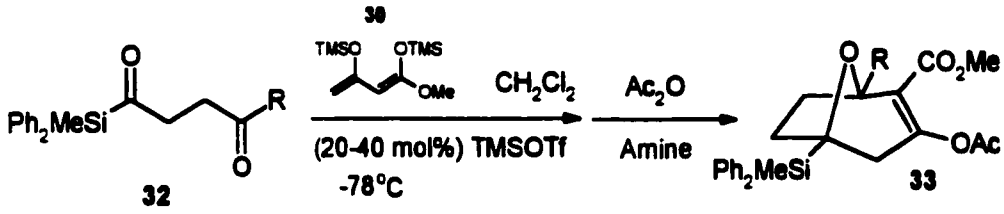


Figure 23. Reversing of Regiochemistry of Molander Cycloaddition by $TiCl_4$

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]

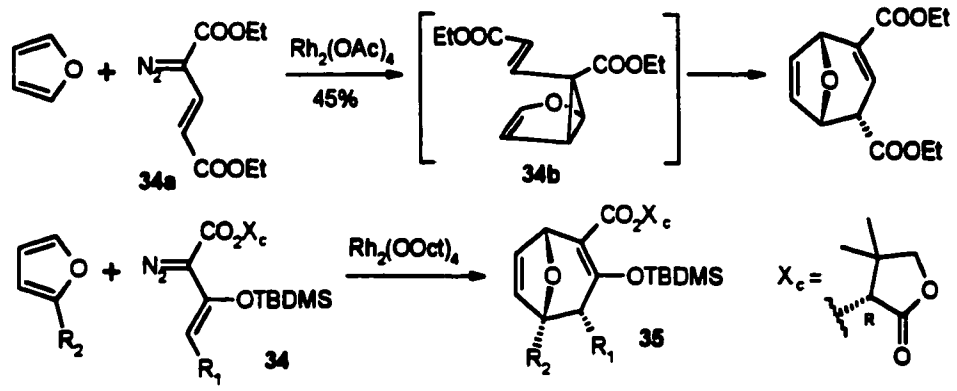


	Yield %	diastereoselectivity
R = H	82	>200:1
Me	70	>200:1

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).[66] 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.[66] The intramolecular version of this cycloaddition was also investigated by Davies, and gives good yields.[67, 68]



R_1	R_2	Yield %	de % (abs stereochem)
H	H	82	94 (1R)
Me	H	75	95 (1R)
Me	Me	69	94 (1R)

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.[69, 70, 71] For example, cycloaddition of 2-aminobuta-1,3-diene **36** with vinyl chromium Fischer carbenes **37** 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**.[69] Good diastereoselectivity (86% ee) was achieved when chiral aminodienes were used[70]. Vinylmolybdenum Fischer carbenes also may be employed in the [4+3] cycloaddition of dienynes, with good yields being obtained.[72, 73, 74]

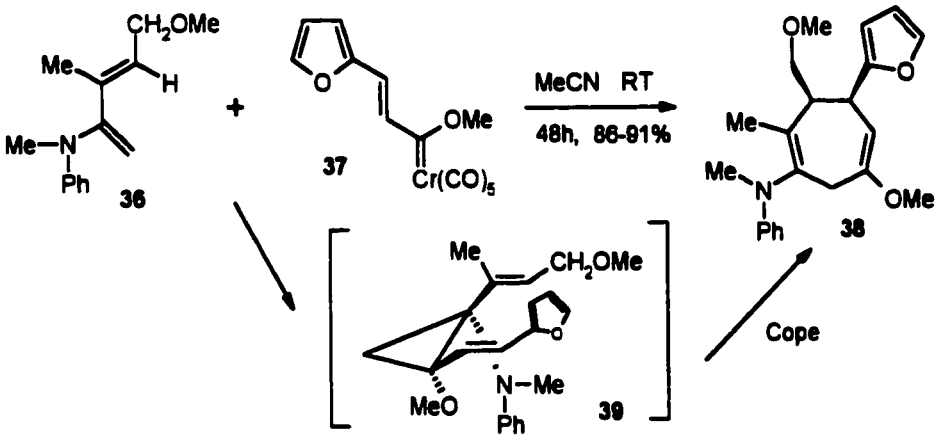


Figure 26. Cycloaddition of Vinylchromium Fischer Carbene with Dienes

The [4+3] cycloaddition of α,β-unsaturated acylsilanes with enolates of α,β-unsaturated methyl ketones has been reported by Takeda. It proceeds stereospecifically and regiospecifically with good yield.[75, 76] For example, (E)-[β-(trimethylsilyl)acryloyl]-silane **40** cycloadded with the lithium enolate of α,β-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** → **41b** → **41c**) followed by a stereospecific Cope rearrangement (**41c** → **42**) (Figure 27).[75, 76]

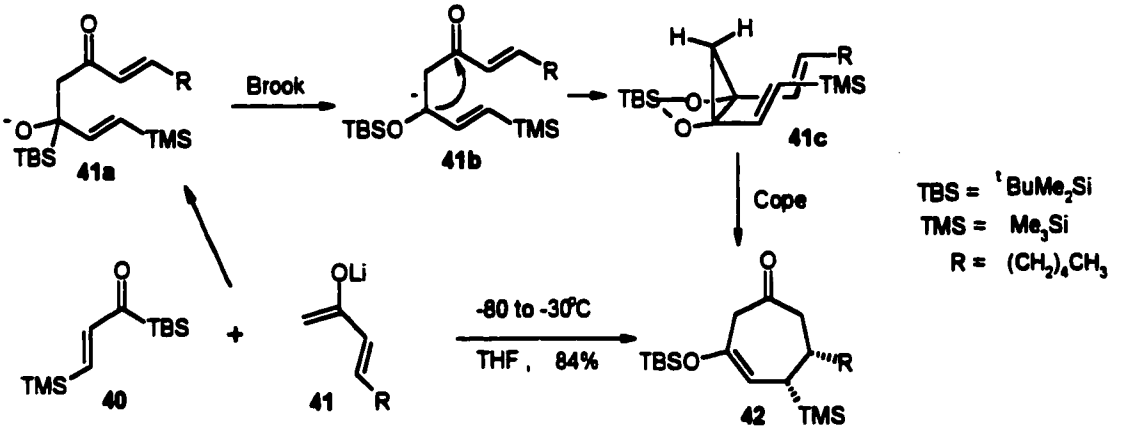
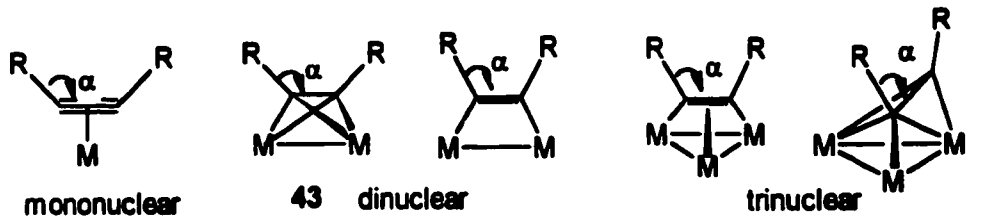


Figure 27. Takeda [4+3] Cycloaddition

2. Nicholas Reactions

Reppe[78] first reported the transition metal organometallic chemistry of alkynes. Since then, many metals have been used to form complexes with alkynes, including Co,[79] Pt,[80] Mo,[81] Ni,[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.



mononuclear 43 dinuclear trinuclear

Figure 28. Three Kinds of Metal Coordination to Alkynes

Among these transition metal-alkyne complexes, alkyne-$Co_2(CO)_6$ 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 $\alpha \approx 140°$. 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 $Co_2(CO)_6$ stabilized propargyl cation intermediate **46**.[83] Since this initial report, many nucleophiles have been successfully employed for Nicholas reactions. These nucleophiles include ketones and their enol derivatives, β,β'-dicarbonyls, electron rich aromatic rings, allylsilanes, hydrides, amines, sulfonamides, and others. Most importantly, the nucleophiles always attacked at the propargyl carbon,[84] and no allenic by-product was found. The formation of allenic by-products had been interfering with general propargylation reactions for a long time.[85]

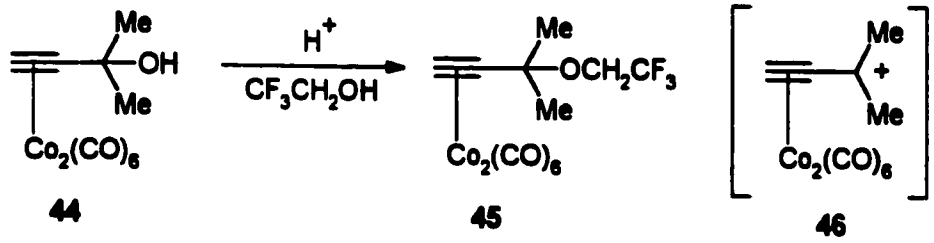


Figure 29. The First Reported Nicholas Reaction

The dicobalt hexacarbonyl propargylic cations are thermodynamically very stable cations, with pK_{R+} values of ca. –7 (pK_{R+} for Ph_3C^+ is ca. –6.6).[86] The stability comes from the delocalization of the positive charge into the $Co_2(CO)_6$ moiety. These cations exist as unsymmetrical structures (Figure 30).[87, 88, 89]

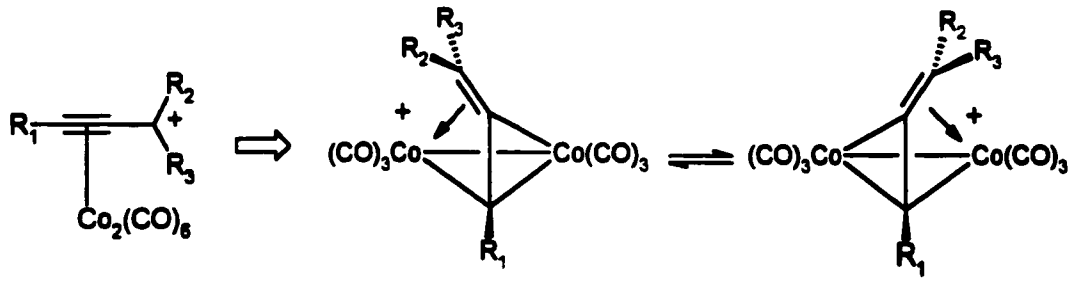


Figure 30. Unsymmetrical Structures for $Co_2(CO)_6$ Stabilized Propargyl Cations

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]

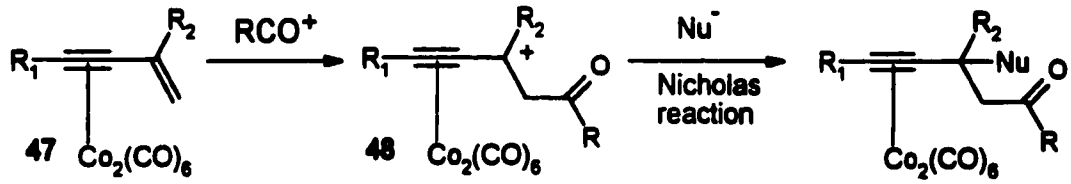


Figure 31. Nicholas Reaction with 1,3-Enynes as Precursers

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]

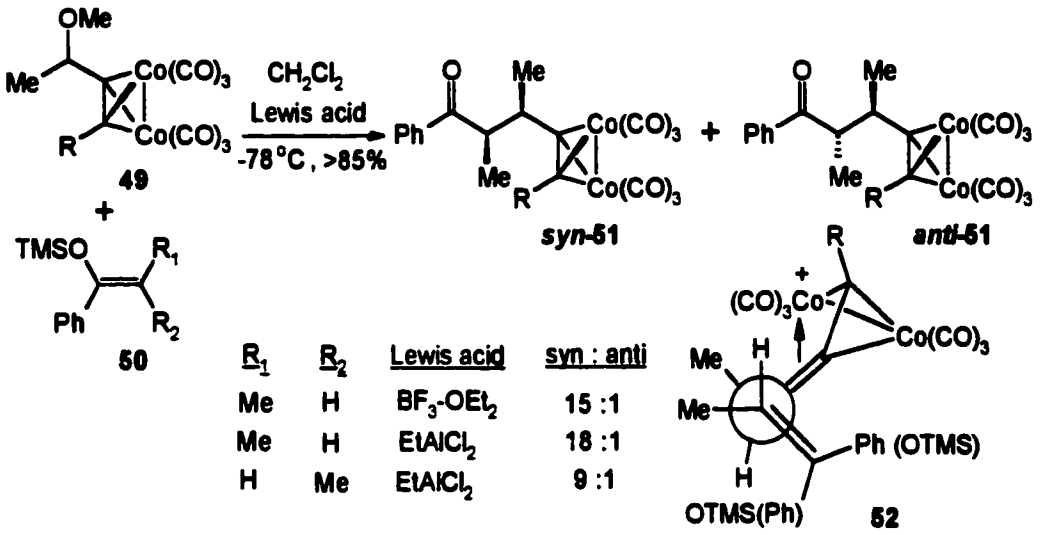


Figure 32. Nicholas Reaction with High *Syn* Diastereoselectivity

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).[94]

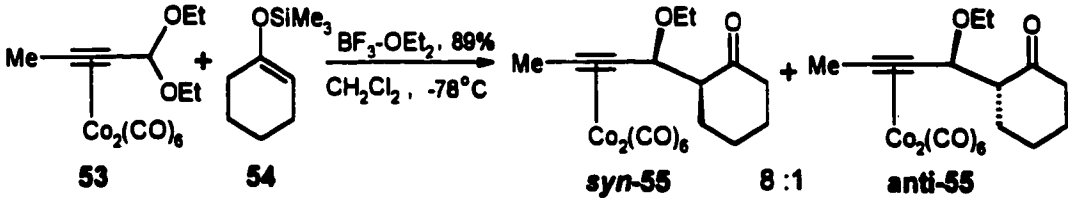


Figure 33. Diastereoselective Nicholas Reaction of Cyclic Enolsilane

The diastereoselective Bu_2BOTf 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).[86]

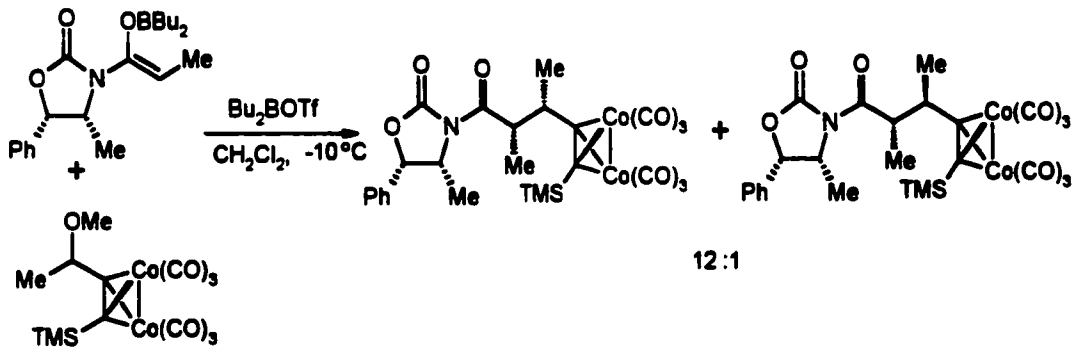


Figure 34. Diastereoselective Nicholas Reactions of Evans Enolates

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 BF_3-OEt_2 afforded cycloheptyne-cobalt complex **57** with 55% yield (Figure 35). Oxidative removal of $Co_2(CO)_6$ moiety with Me_3NO did not lead to a cycloalkyne,[93] as simple cycloheptynes and cyclohexynes have not been isolated so far. By contrast, their dicobalt complexes may be obtained as pure and stable compounds,[93] because the change in the formally sp carbon bond angle alleviates the strain.[95]

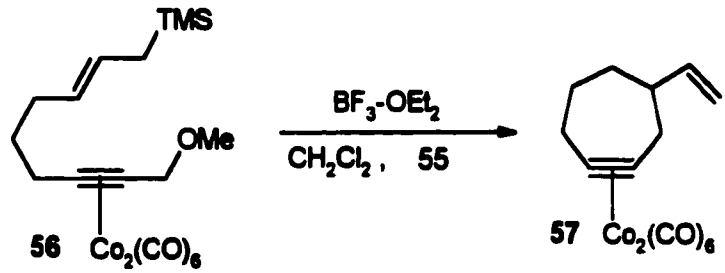


Figure 35. Cycloalkyne-cobalt Complexes Produced via Intramolecular Nicholas Reaction

In 1998 Green reported the Bu_2BOTf mediated Nicholas reaction of γ-methoxyalkynoate and γ-methoxyalkynone dicobalt complexes **58** with stannylsilane **59** or **59'** (Figure 36).[96] 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).[96]

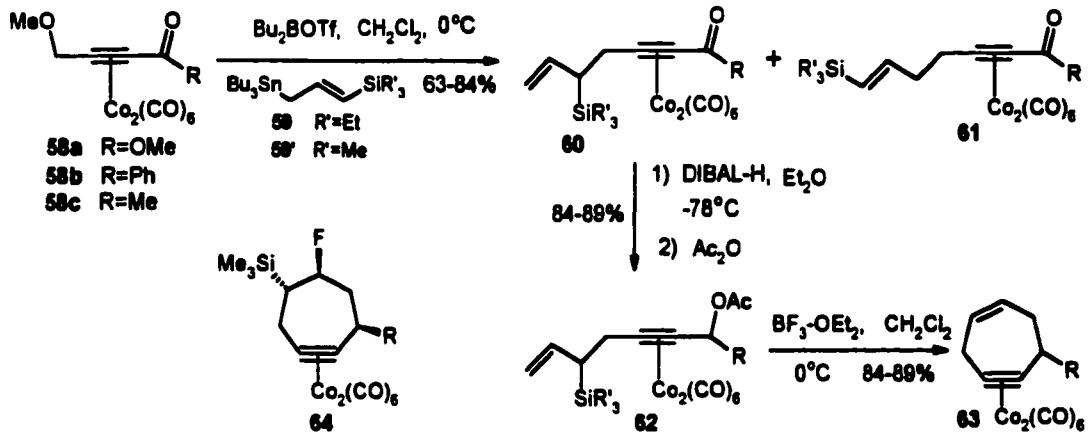
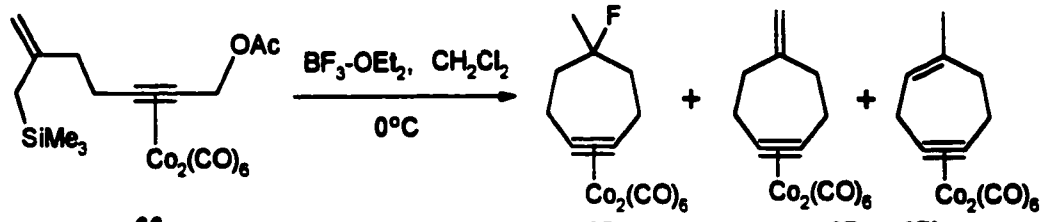


Figure 36. Stepwise Preparation of Cycloheptenyne Complexes

After reduction of the carbonyl function in **60** with $^{i}Bu_2AlH$ and trapping of the resultant alkoxide intermediate with acetic anhydride, acetate products **62** were obtained in excellent yield. A BF_3-OEt_2 mediated intramolecular Nicholas reaction of the acetates **62** gave cycloheptenyne dicobalt complexes **63** in excellent yields (Figure 36).[96]

In the final cyclization step above, tiny amounts of silyl fluorocycloheptyne complexes **64** were obtained in the case of R=Ph, Me (Figure 36).[96] Desilylated fluorocycloheptyne complexes **65** were formed in the BF_3-OEt_2 mediated intramolecular Nicholas reaction of **66** in 44% or 8% depending on the addition procedure (Figure 37).[96]

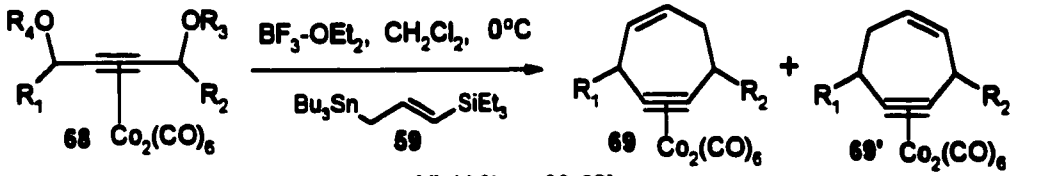


66 65 67a + 67b

Slow additionof66 to BF_3-OEt_2(excess)	44%	46%
Slow addition of BF_3-OEt_2(5equiv) to 66	8%	55%

Figure 37. Desilylated Fluorocycloheptyne Formed in Intramolecular Cyclization

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).[97] 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 BF_3-OEt_2 , but this attempt failed totally.[96]



	R_1	R_2	R_3	R_4	Yield %	69:69'	
68a	H	H	Me	Me	62	–	69a
68b	H	H	Et	Et	72	–	69a
68c	H	Me	Me	Me	54	2.2 :1	69b : 69b'
68d	H	Me	iPr	Me	68	>30 :1	69b : 69b'
68e	H	Me	TBMS	Me	62	>30 :1	69b : 69b'

	R_1	R_2
69a	H	H
69b or 69b'	H	Me

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).[97, 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 Et_3Si^+ moiety. Regioisomer product **69'** comes from a similar route via carbocation intermediate **74** (Figure 39).[99]

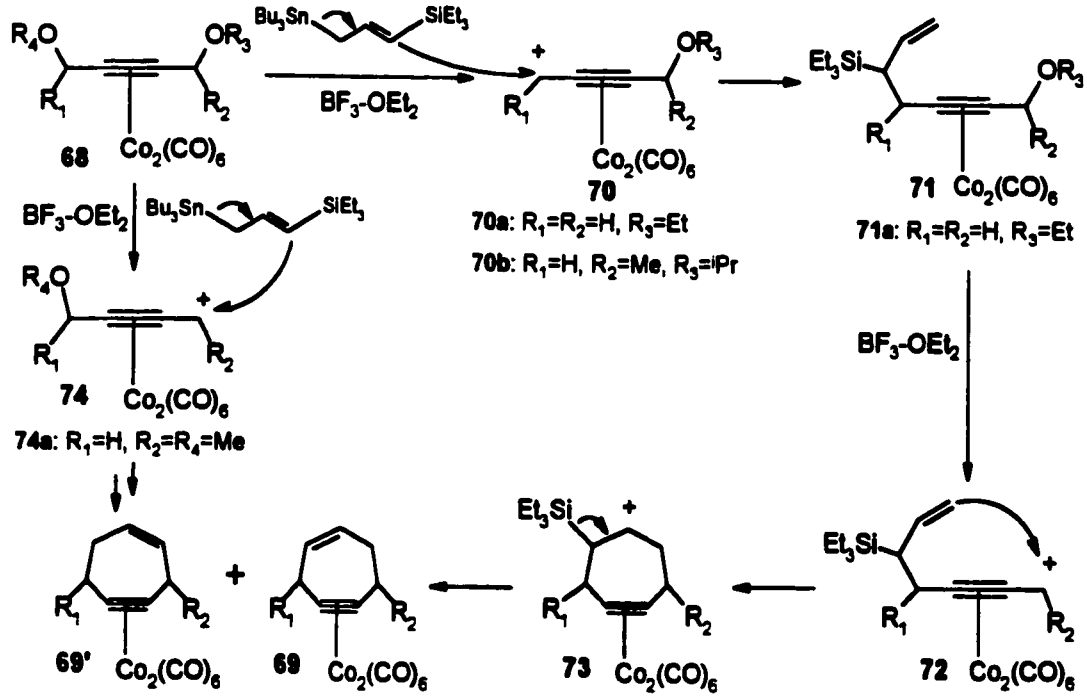
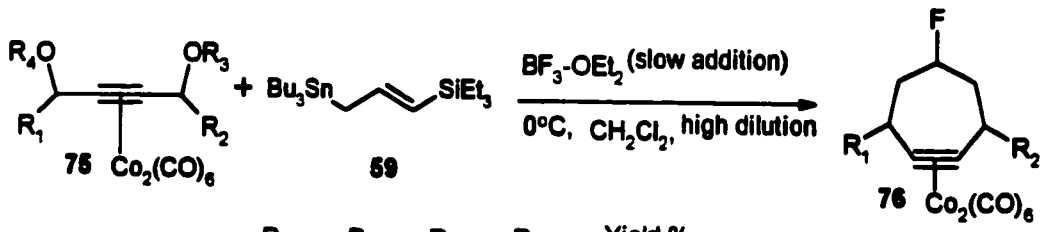


Figure 39. Mechanism for Green [4+3] Cycloaddition

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 ^{i}Pr ether **68d**), cycloheptenyne complex **69b** was

formed as the major product with only a trace amount of **69b'**. The TBDMS ether **68e** 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]



	R_1	R_2	R_3	R_4	Yield %	
75a	H	H	Et	Et	70	
75b	H	Me	Me	Me	57	trans:cis=2.6:1
75c	H	Ph	Me	Me	55	trans:cis=2.4:1
75d	Me	Me	Et	Et	80	trans,trans:cis,cis:trans,cis =1.9:1:0.14

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 allylmetals, silyl enol ethers, electron rich arenes, etc. Monocondensation products **78** were produced with good yield (Figure 41).[100]

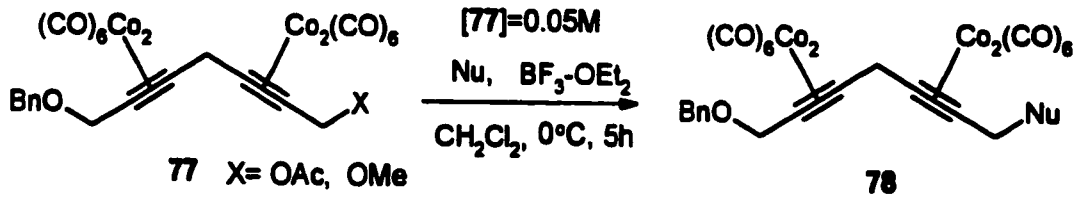


Figure 41. Regioselective Nicholas Reaction of 1,4-Diyne Tetracobalt Complex

When substrate **79** was subjected to similar conditions with a series of electron rich arenes as nucleophiles in highly dilute CH_2Cl_2 solutions, a variety of metacyclophanediynes were isolated in only one synthetic step in good yields. For example, with 1,3,5-trimethoxybenzene as the nucleophile, metacyclophanediyne **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).[101]

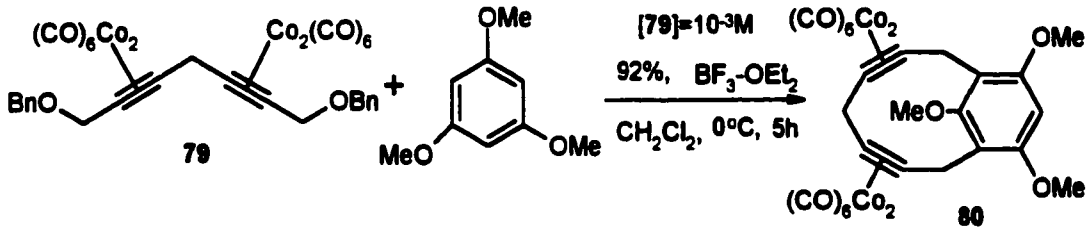


Figure 42. Green One-step Synthesis of Metacyclophanediyne

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).[102]

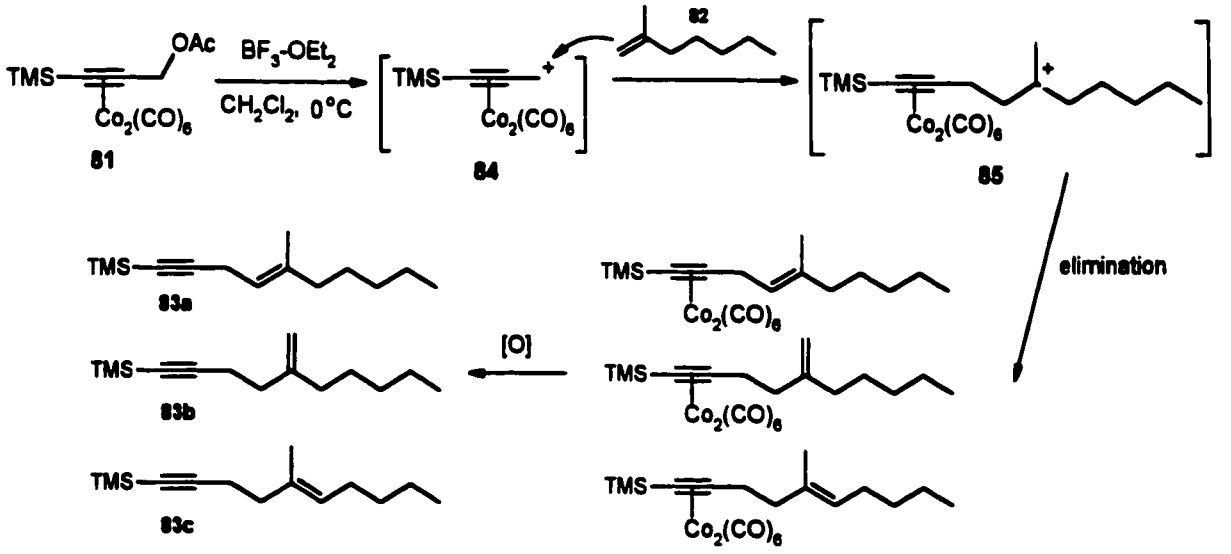


Figure 43. Reaction of Propargyl Cations with Unactivated Alkenes

The cationic carbocations from reaction with unactivated alkenes can also undergo rearrangement.[103] For example, treatment of **86** with Lewis acid afforded intermediate **87**, which then underwent rearrangement to form **88** (Figure 44).[103]

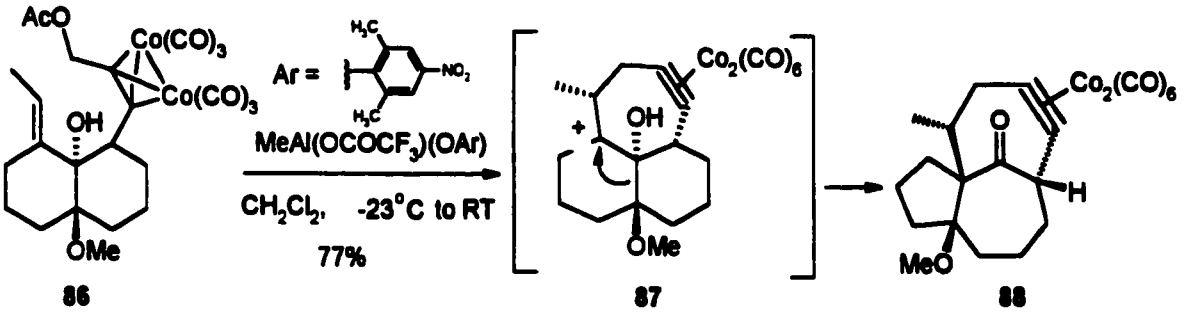


Figure 44. Rearrangement of Cationic Intermediate

The carbocations from reactions of unactivated alkenes can also be trapped intramolecularly. For example, the reaction of alkenyl esters and acids **89** with $Co_2(CO)_6$ 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]

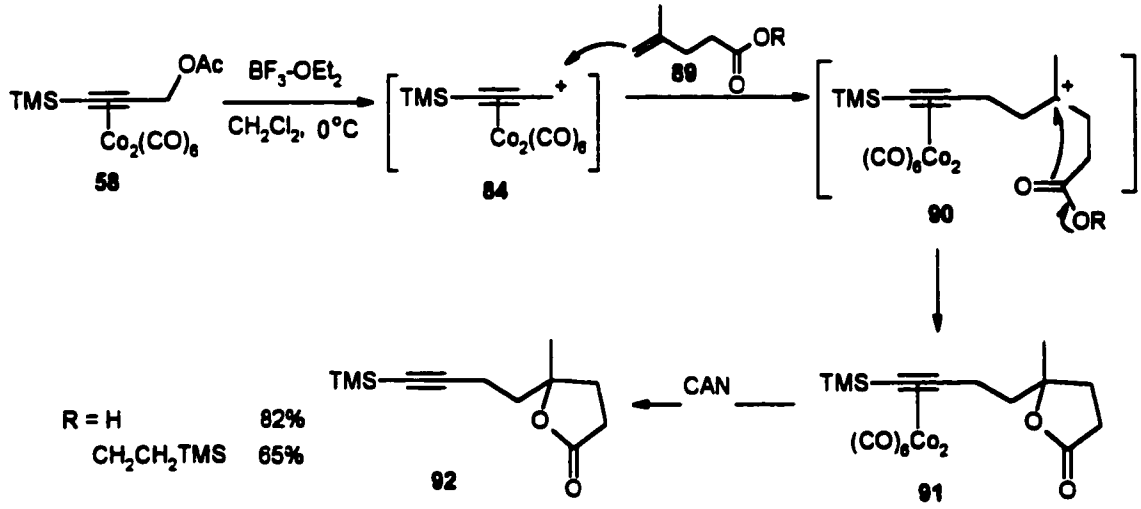


Figure 45. Intermolecular Trapping of Cationic Intermediate

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^- ".[104-108] In cobalt chemistry, this was first reported by Tyrrell's group. They found that $Co_2(CO)_6$ 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]

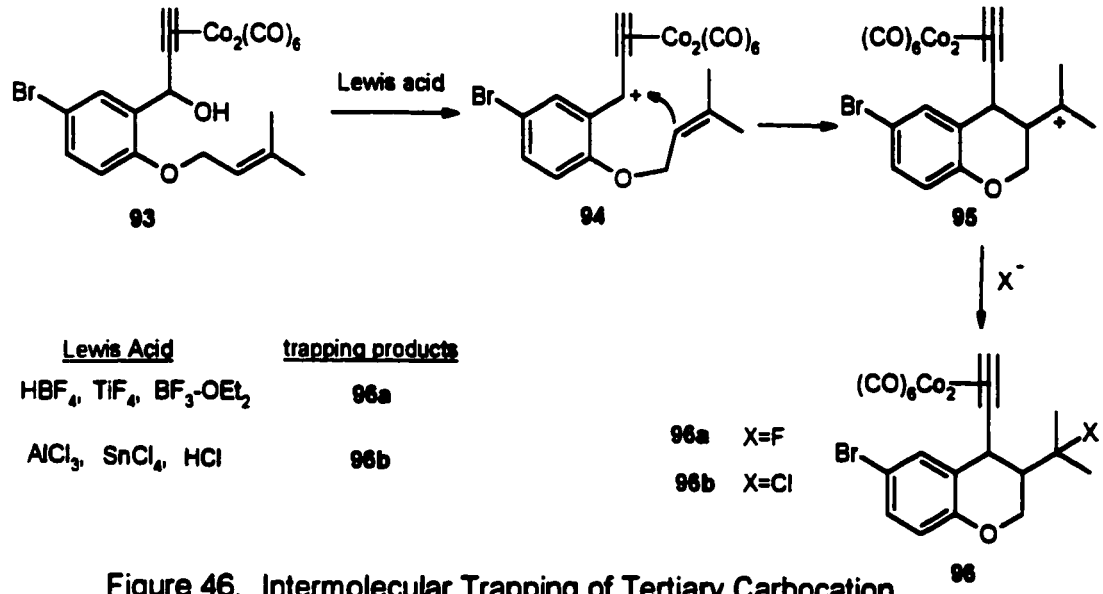


Figure 46. Intermolecular Trapping of Tertiary Carbocation by Halogen Anions

Fluoride trapping reactions also have been reported in the $Fe(CO)_3$ stabilized pentadienyl cation system.[105, 106] The Lewis acid BF_3-OEt_2 induced ionization of Ψ *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 " F^- to form a mixture of fluorocyclohexanes **100a** and **100b** (Figure 47).[105].

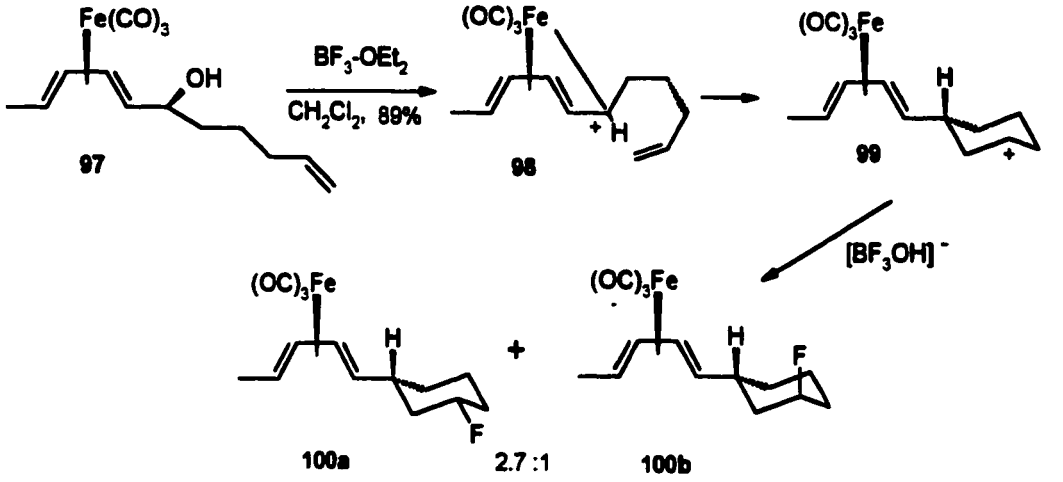


Figure 47. Fluoride Trapping in (Pentadienyl)-$Fe(CO)_3$ Cation System

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]

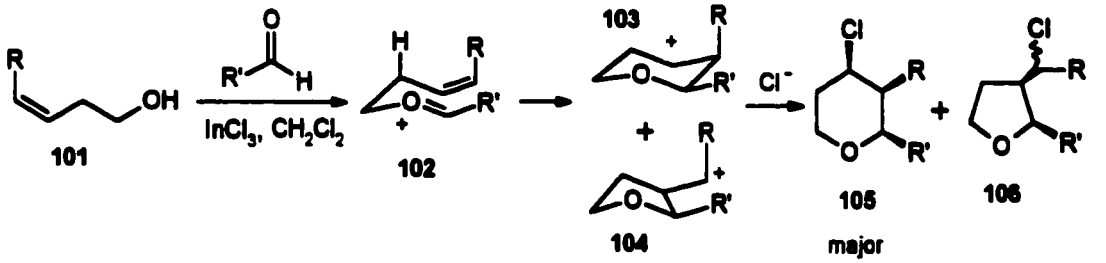


Figure 48. Chloride Trapping in Other Reaction System

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.[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.[109] Lithiation of **107** with MeLi, followed by a reaction with paraformaldehyde, gave hydroxypropargyl ether **108**.[96] Complexation of **108** with $Co_2(CO)_8$ in Et_2O at 0° C afforded complex **109**[96] which then was reacted with ^iPrOH 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)

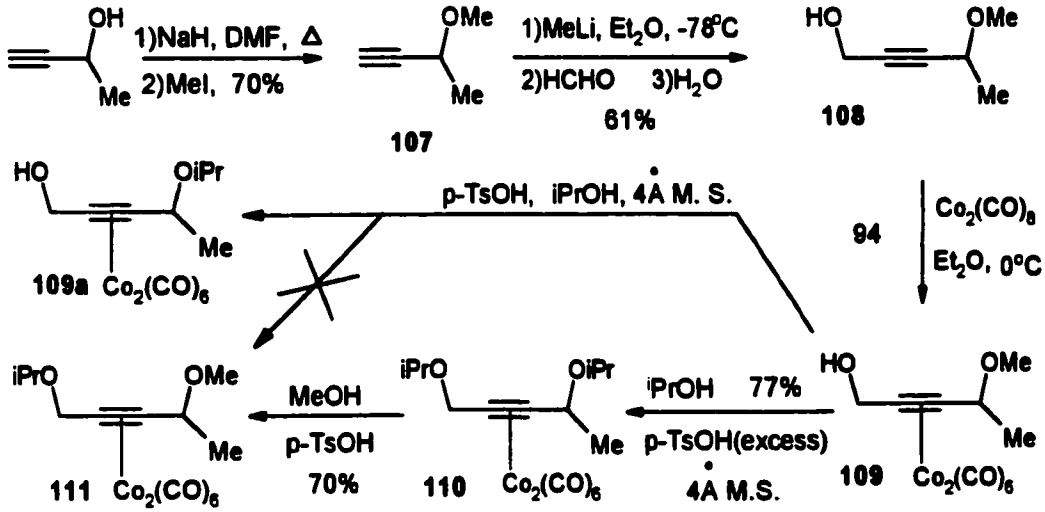


Figure 49. Synthesis of Substrate for [4+3] Cycloaddition

Nucleophile silylstannane **59** was prepared according to a protocol previously developed in our laboratory (Figure 50).[99]

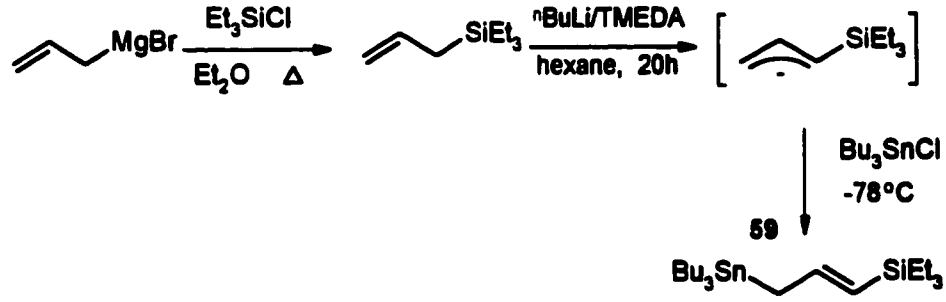


Figure 50. Preparation of Silylstannane

The BF_3-OEt_2 mediated [4+3] cycloaddition of substrate **111** with silylstannane **59** was carried out in CH_2Cl_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'[110] (see Experimental Section) CH_2Cl_2 gave a regioisomeric mixture of **69b** and **69b'** in a ratio of **69b** :**69b'**= 1 :1.3 (Figure 51).

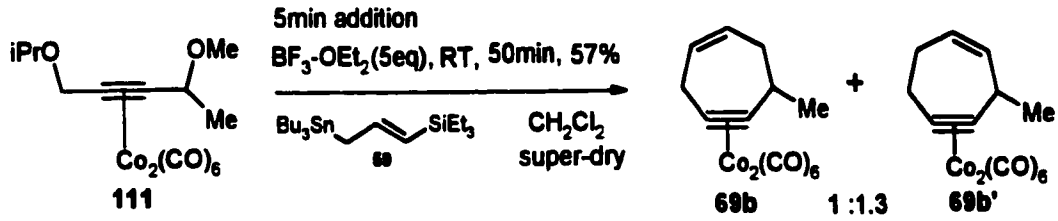


Figure 51. Green Cycloaddition of **111** with Silylstannane

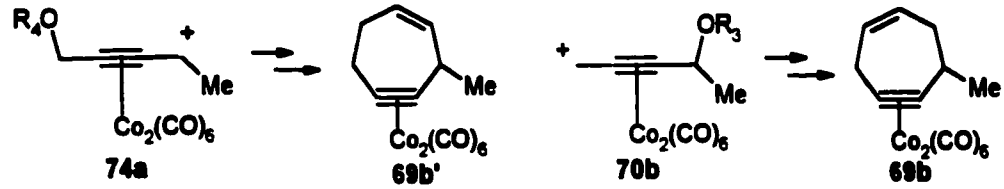


Figure 52. The Origin of Regiochemistry for Green Cycloaddition

It can be seen that the exchange of the positions of ^{i}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.[86] 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 ^{i}PrO groups are concerned, BF_3-OEt_2 would be expected to be complexed by the MeO group preferentially over ^{i}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 regiomeric cycloadducts **69b** and **69b'**, in a ratio of 1 :1.3.

2. Mechanism of Fluorinative Green [4+3] Cycloaddition

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).[98] 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).

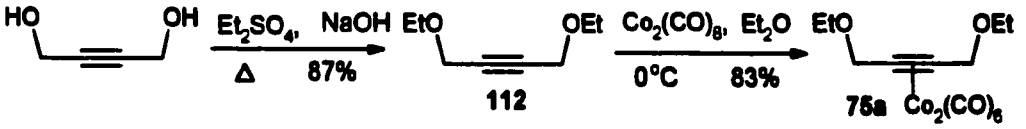


Figure 53. Synthesis of Unsubstituted Substrate **75a**

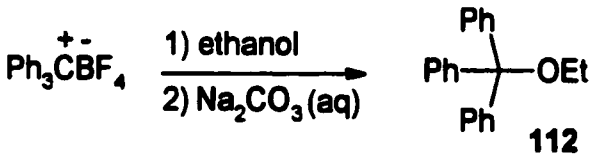


Figure 54. Synthesis of Trityl Ethyl Ether

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 ^1H 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_2Cl_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 allylstannane **59** was decomposed to allyltriethylsilane (Figure 55), and 96% of **59** was still present, even after extended exposure times.

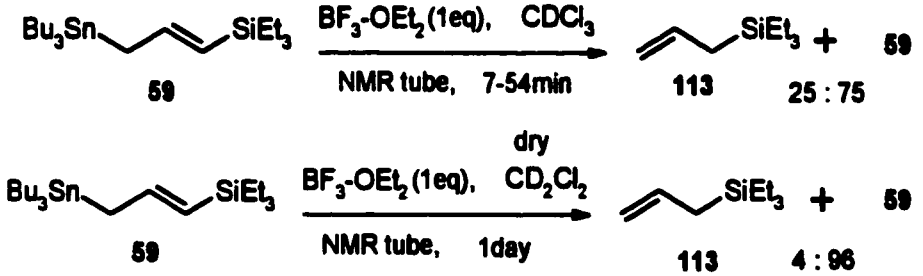


Figure 55. BF_3-OEt_2 Mediated Decomposition of Silylstannane in $CDCl_3$ and CD_2Cl_2

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 $CDCl_3$),[111] 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_2Cl_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_{R^+} 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).

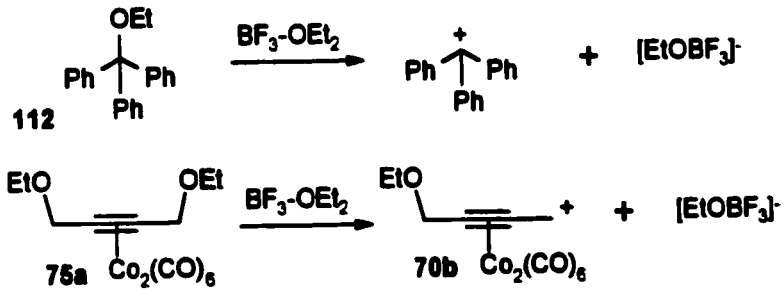
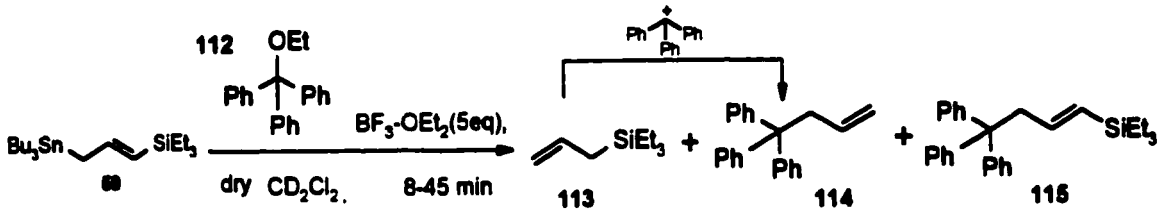


Figure 56. BF_3-OEt_2 Mediated Formation of $[EtOBF_3]^-$

In this NMR experiment, silylstannane **59**, trityl ethyl ether **112** and BF_3-OEt_2 (5 equiv.) were mixed in a NMR tube. The ^1H 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**[112] 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.[96] Therefore, about 48% the silylstannane **59** was decomposed to allyltriethylsilane in 8 min in this case.



	113 : 114 : 115
8 min	0.41 : 0.50 : 1.00
18 min	0.29 : 0.63 : 1.00
45 min	0.16 : 0.75 : 1.00

Figure 57. Decomposition of Silylstannane in Presence of Trityl Ethyl Ether and BF_3OEt_2

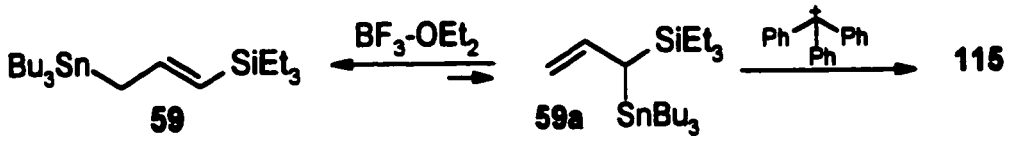


Figure 58. The Origin of **115**

In comparison with the NMR experiment in dry CD_2Cl_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 BF_3-OEt_2 , and the similarities with the fluorinative [4+3] cycloaddition, attention must be drawn to the counterion of the propargyl cation or trityl cation, namely $[EtO\text{-}BF_3]^-$. 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 organotins 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.

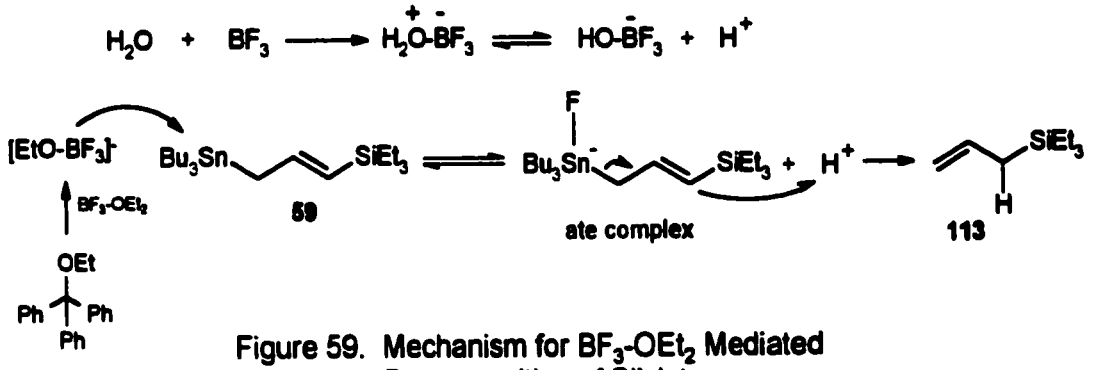


Figure 59. Mechanism for BF_3-OEt_2 Mediated Decomposition of Silylstannane

We recognize that the actual H^+ source is not entirely accounted for; a 10^{-2} M allyldimetal (1 mL CH_2Cl_2 solution) would require solvent that is ca 140 ppm (0.14%) in H_2O or other H^+ source for complete consumption, and this is unlikely in CH_2Cl_2 distilled from CaH_2. The residual water in CH_2Cl_2 distilled from CaH_2 is unknown, but commercial 'anhydrous' CH_2Cl_2 is < 50 ppm in H_2O. 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. $[EtO\text{-}BF_3]^-$). 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 destannylated allylsilane (Figure 60).

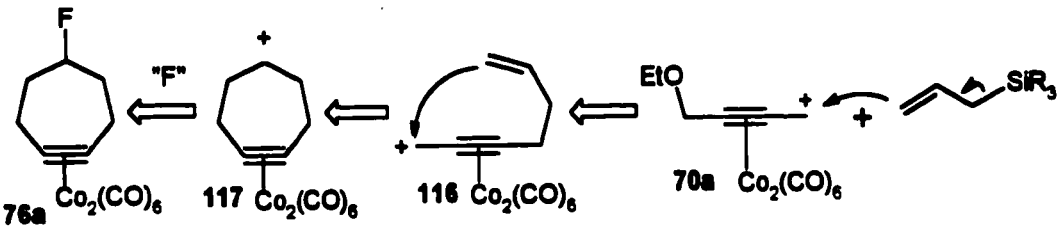


Figure 60. Initial Speculation on the Mechanism

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).

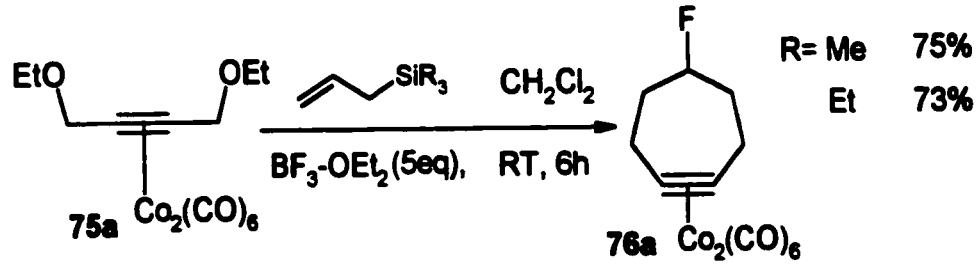


Figure 61. Fluorinative [4+3] Cycloaddition with Allylsilane

This concern with solvent purity dependent destannylation has led to re-establishment of conditions for [4+3] cycloadditions. Unfortunately, when the

CH_2Cl_2 distilled from a bulk still over CaH_2 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).

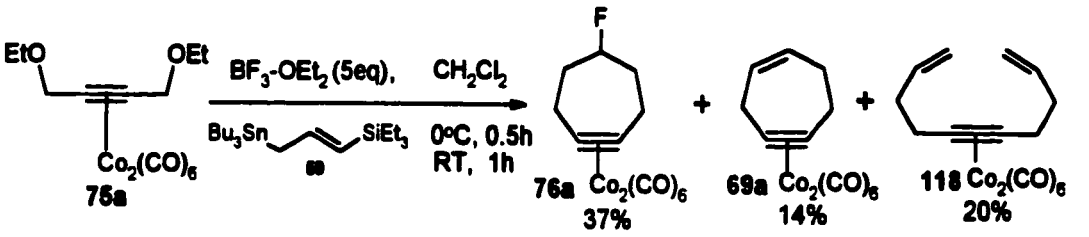


Figure 62. Green Cycloaddition in CH_2Cl_2 from Still

In order to determine whether or not the CH_2Cl_2 from the still was dry enough for the Green [4+3] cycloaddition, the BF_3-OEt_2 mediated decomposition experiment of silylstannane **59** was carried out in CH_2Cl_2 (from still)+dry CD_2Cl_2 (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 CH_2Cl_2 distilled from still was not dry enough for the Green [4+3] cycloaddition reaction.

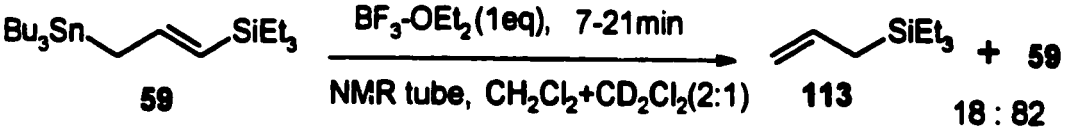


Figure 63. Decomposition of Silylstannane in CH_2Cl_2 from Still

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

cycloadduct **119** was produced (23%), although a mixture of cycloadducts **69b** and **69b'** predominated (32%) (Figure 64).

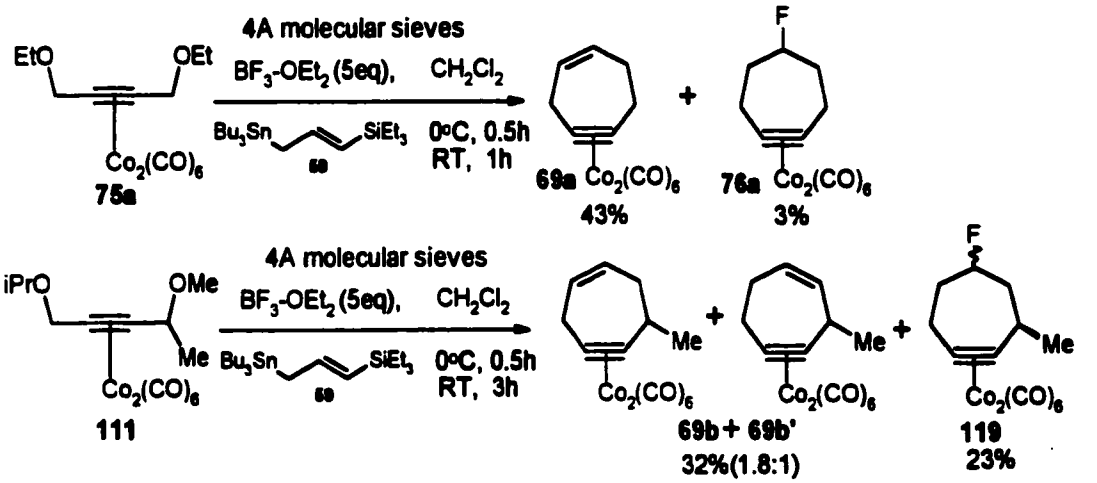


Figure 64. Green Cycloadditions with 4A M. S. in CH_2Cl_2 from Still

'Super-dry' CH_2Cl_2 was needed for this purpose. It was prepared by violent refluxing of small amounts of still-dried CH_2Cl_2 from still with excess of CaH_2 for >3 h followed by re-distillation over CaH_2. The cycloaddition of substrate **75a** with silylstannane **59** was carried out in this 'super-dry' CH_2Cl_2. No fluorinative cycloadduct was formed. Cycloadduct **69a** was obtained in a 72% yield (Figure 65). Also, no fluorination was observed for the substituted substrate **111** (Figure 51).

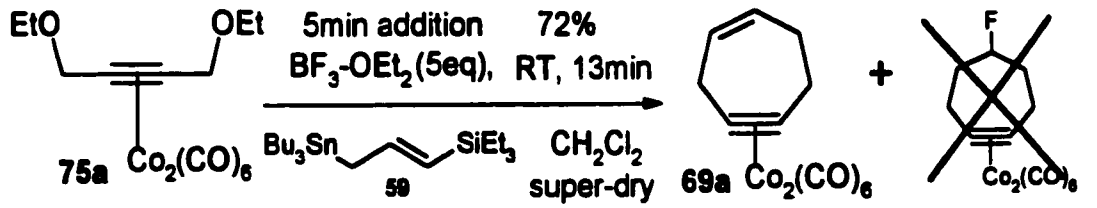


Figure 65. Green [4+3] Cycloaddition in Super-dry CH_2Cl_2

When the Green cycloaddition was carried out at 0°C in super-dry CH_2Cl_2, 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 CH_2Cl_2 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 CH_2Cl_2 was obvious.

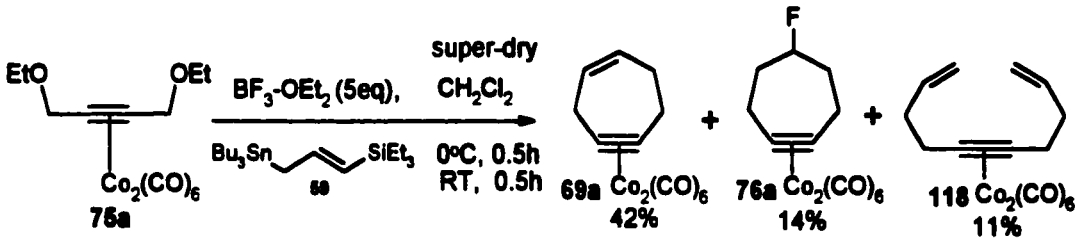


Figure 66. Green Cycloaddition in Super-dry CH_2Cl_2 at 0°C

In terms of the [4+3] cycloaddition, it is quite possible that the reaction of the $Co_2(CO)_6$ 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 $[EtOBF_3]^-$ also facilitating the Green [4+3] cycloaddition. In short, the formation of $[EtOBF_3]^-$ can facilitate both the cycloaddition and fluorination.

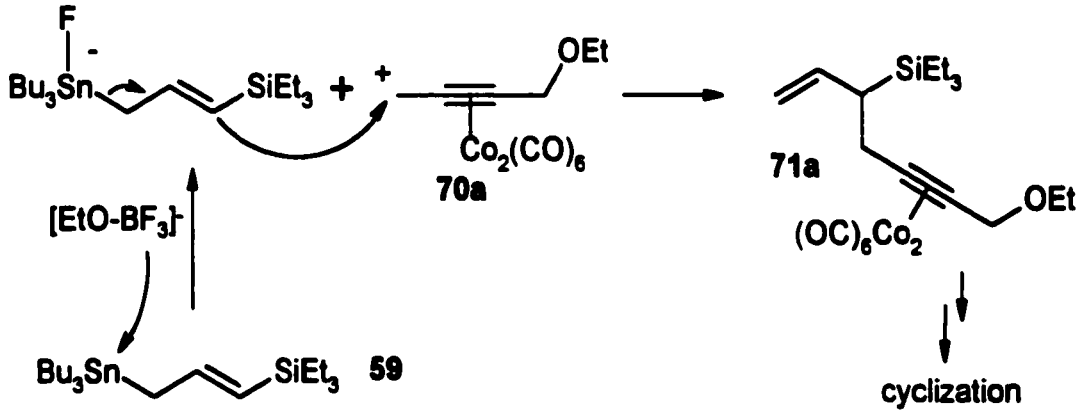


Figure 67. Initial Step of Green Cycloaddition

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_2Cl_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.[97]

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 $[EtO\text{-}BF_3]^-$ is the most likely candidate.

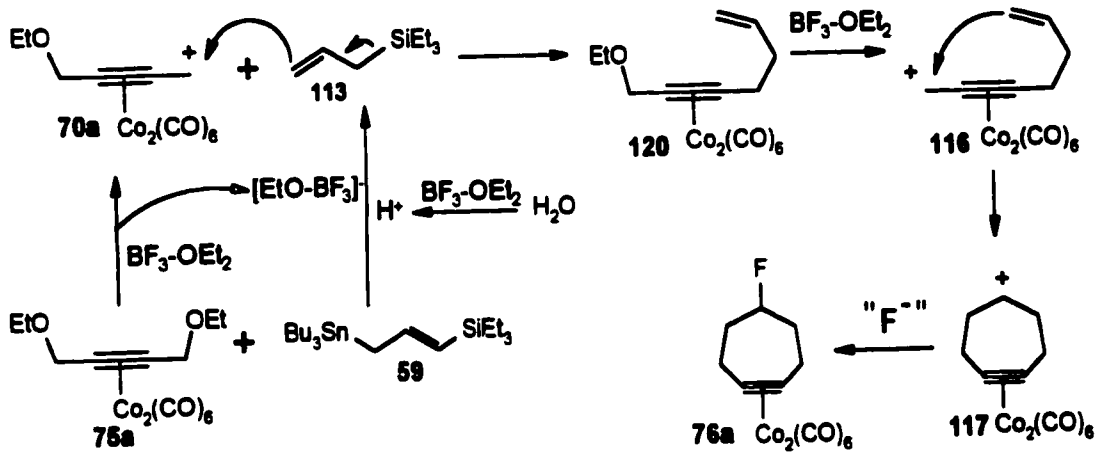


Figure 68. Mechanism for Fluorinative [4+3] Cycloaddition

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.

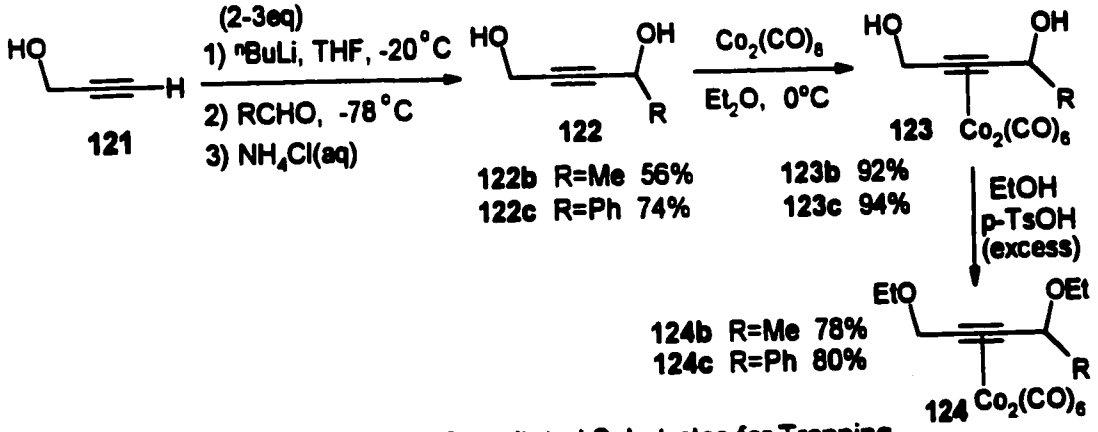
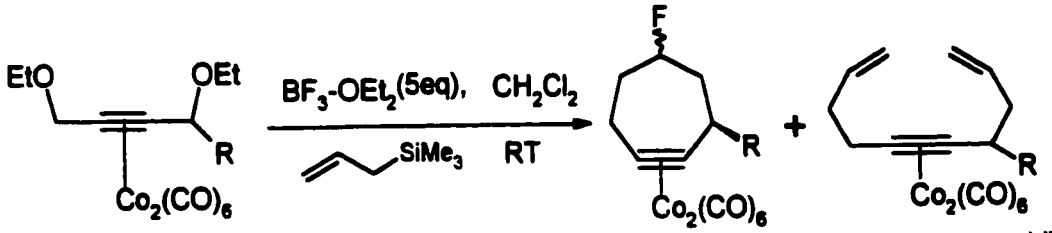


Figure 69. Syntheses of Substituted Substrates for Trapping

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 ^{n}BuLi in THF at low temperature, followed by reaction with aldehydes RCHO afforded propargyl diols **122**.[115] Complexation of **122** with $Co_2(CO)_8$ in Et_2O at 0°C formed propargyl diol complexes **123**,[99] 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.



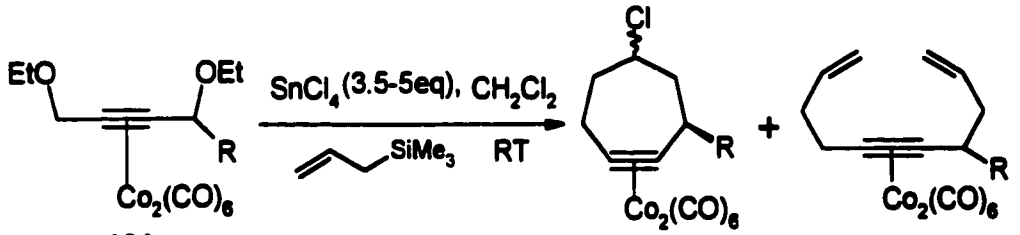
	R	125	trans:cis	126	addition Mode
124a	H	75%	–	8%	B, C
124b	Me	74%	1.6 :1	17%	A
124c	Ph	67%	1.5 :1	5%	A

Figure 70. Fluoride Trapping Reactions

The reactions of substrates **124** with allyltrimethylsilane were carried out in the presence of BF_3-OEt_2 in CH_2Cl_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_2Cl_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 ^{1}H NMR spectra obtained previously in the Green group.[97]



	R	127	trans:cis	126	addition Mode
124a	H	78%	-	11%	C
124b	Me	76%	1 :1.9	5%	C
124c	Ph	60%	1 :1.9	2%	A

Figure 71. Chloride Trapping Reactions

The chloride trapping reactions of substrate **124** with allyltrimethylsilane in the presence of $SnCl_4$ were carried out in CH_2Cl_2 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 $SnCl_4$ (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 CH_2Cl_2 solution of $SnCl_4$ (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 .

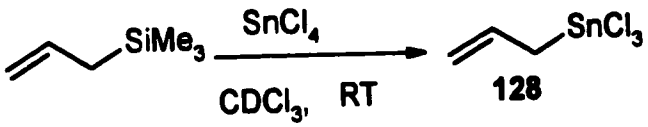


Figure 72. Metathesis of Allyltrimethylsilane with $SnCl_4$

It has been reported that $SnCl_4$ reacts with allyltrimethylsilane to form allyltrichorostannane **128** (Figure 72).[116] The reaction is about 40% complete after 25 min, 75% complete after 80 min and nearly complete after 140 min.[116] However, in our case, it can not be ruled out that allyltrichlorostannane **128** can also react with the $Co_2(CO)_6$ stabilized propargylic cation in the same way as allyltrimethylsilane does.

In view of destruction of substrates and transmetallation of allyltrimethylsilane by $SnCl_4$, 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 $SnCl_4$ (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 $SnCl_4$ (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.[117] It has been reported that their analogues, the cycloheptenes, exist in the chair conformation.[118, 119] 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** ($J_{ax\text{-}ax}$ =11.1Hz in *cis*-**127b** vs. $J_{eq\text{-}eq}$=6.4Hz in *trans*-**127b**).

The corresponding bromination product **129** could be obtained in the reaction of **124a** with allyltrimethylsilane in the presence of $SnBr_4$, but the best yield for **129** was only 26% (Figure 73) with the Mode C addition protocol. Other bromide containing Lewis acids, such as BBr_3, $SiBr_3$, and $AlBr_3$ were also tried, but no **129** was isolated and extensive decomposition occurred.

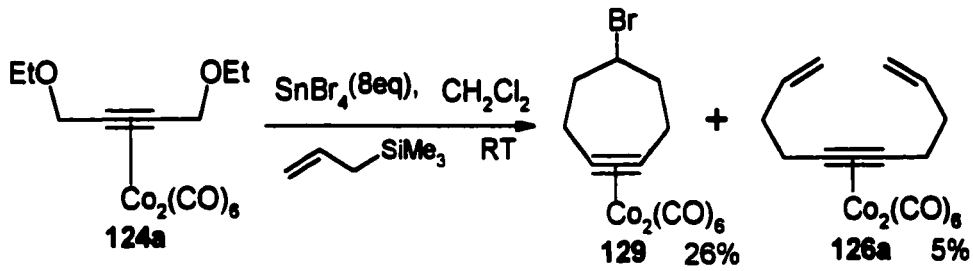


Figure 73. Bromide Trapping Reaction

While studying the conditions for the improvement of the fluoride trapping reaction, the reaction of **124a** with allyltrimethylsilane in the presence of BF_3-OEt_2 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.

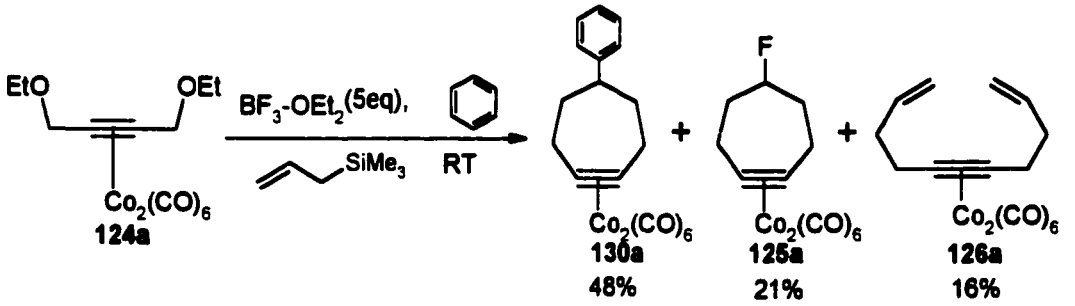
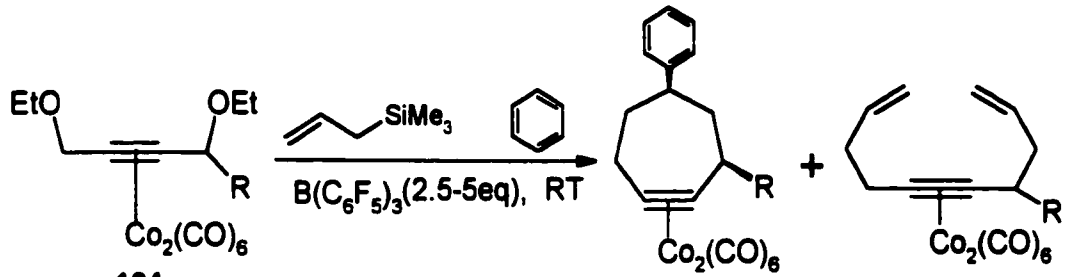


Figure 74. Benzene and Fluoride Trapping Reaction

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 Bu_2BOTf, TMSOTf, Et_3B, $B(OAc)_3$,[120, 121] Me_3Al, MAO, $Al(OAc)_3$, $Ti(OiPr)_4$. Bu_2BOTf. Me_3Al caused extensive destruction of the cobalt complexes. Et_3B, $B(OAc)_3$ 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. $B(C_6F_5)_3$ was found to be the best Lewis acid for the benzene trapping reaction.



	R	130	trans:cis	126	addition mode
124a	H	70%	-	6%	C
124b	Me	61%	0 :100	3%	A
124c	Ph	52%	0 :100	4%	A

Figure 75. Benzene Trapping Reactions

The benzene trapping reactions of substrates **124** with allyltrimethylsilane in the presence of $B(C_6F_5)_3$ 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 diallyls **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 $B(C_6F_5)_3$ (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**/$B(C_6F_5)_3$, 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 CH_2Cl_2 (CH_2Cl_2: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.

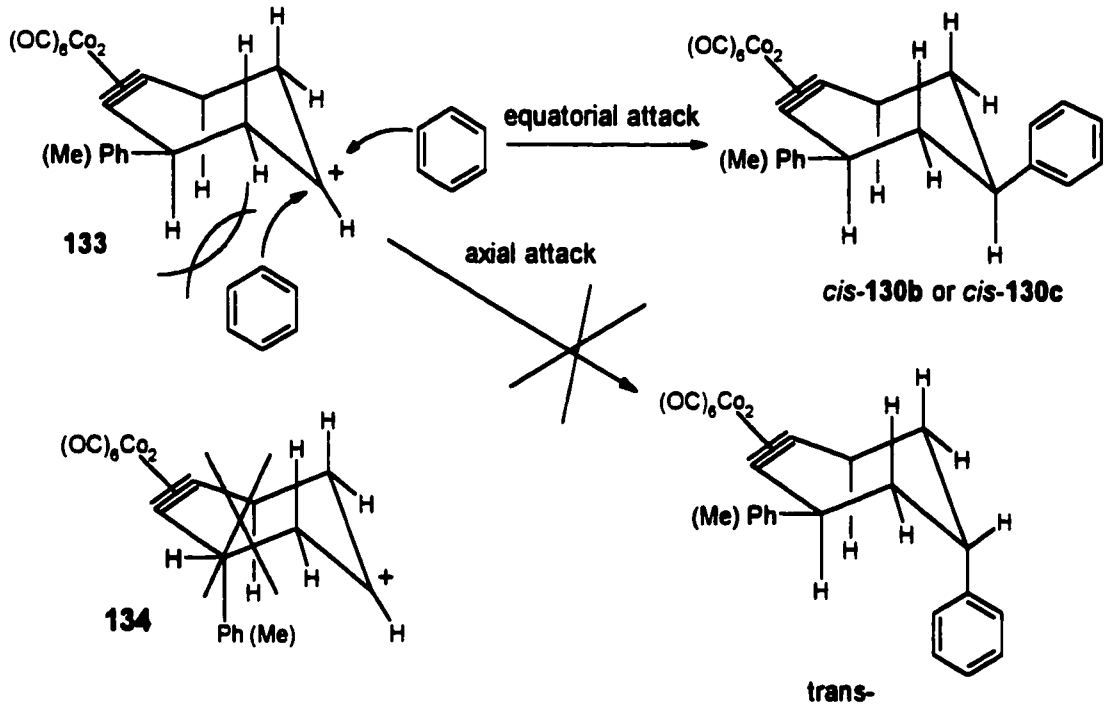
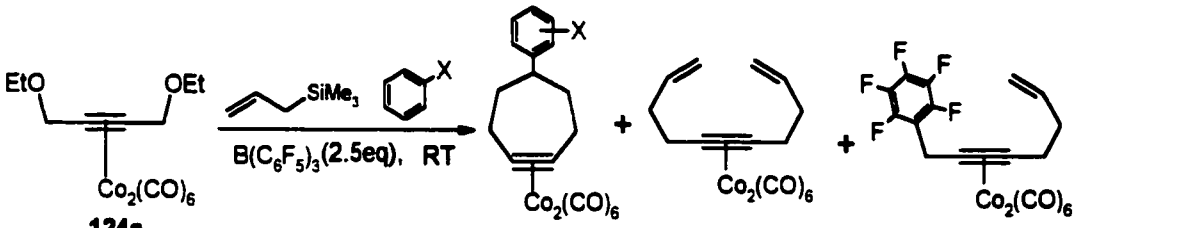


Figure 76. Stereoselectivity for Benzene Trapping Reaction of Substituted Substrates

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.



	135	**126a**	**136**	**addition mode**
X = Me	**58% (135a)** o:p:m=1.4:1:1	13%	0	A
Cl	**51% (135b)** o:p:m=1.8:1:0.3	5%	8%	B

Figure 77. Arene Trapping Reactions

The toluene trapping reaction of **124a** with allyltrimethylsilane in the presence of $B(C_6F_5)_3$ 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 ^1H 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 arene 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 CH_3 group. Therefore, the ^1H 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 CH_3 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 arene protons of *para*-**135a**.

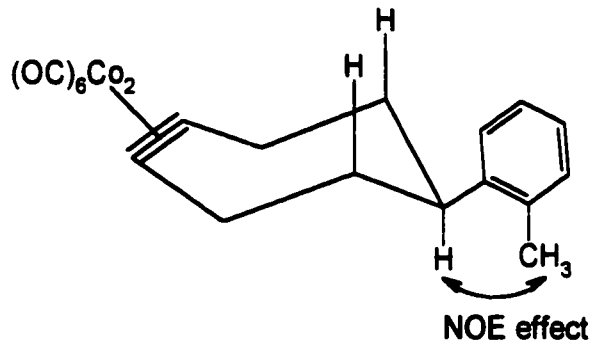


Figure 78. NOESY Assignment of *ortho*-**135a**

The chlorobenzene trapping reaction of **124a** with allyltrimethylsilane in the presence of $B(C_6F_5)_3$ 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 $[EtO\text{-}BF_3]^-$. 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_2Cl_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).

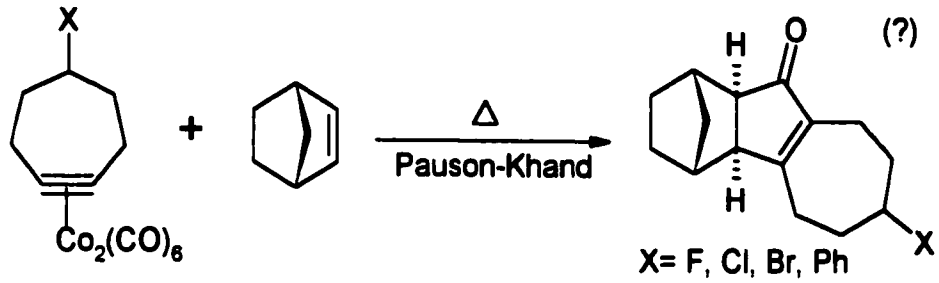


Figure 79. Suggested Pauson-Khand Reaction with Trapping Products

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).

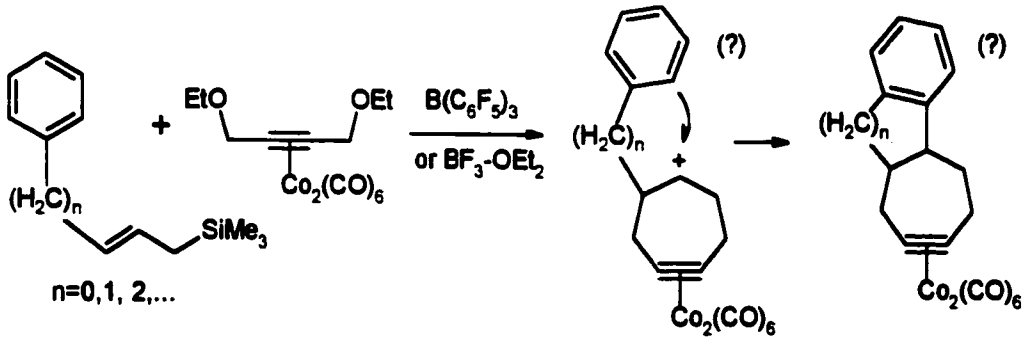


Figure 80. Suggested Intramolecular Trapping Reaction

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.

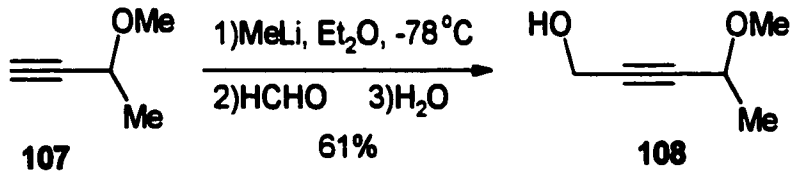
All solvents were used after distillation from the appropriate drying agent in a still. Diethyl ether, benzene, toluene and THF were distilled from sodium benzophenone ketyl immediately before use. Dichloromethane and chlorobenzene were distilled from calcium hydride in a still immediately before use. '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°C " refers to the temperature of an acetone-$CO_{2(s)}$ bath. The term "at –30°C " refers to the temperature of a 50% ethanol-$CO_{2(s)}$ bath. The term " at 0°C" refers to the temperature of an ice bath.

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

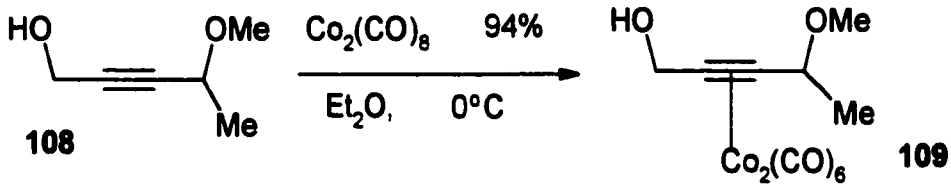


107 **108**

To a stirred solution of 3-methoxy-1-butyne[109] (**107**) (0.840 g, 10.0 mmol) in dry THF (20 mL) at –78°C was added methyllithium (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) ν_{max} 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); ^{13}C 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)

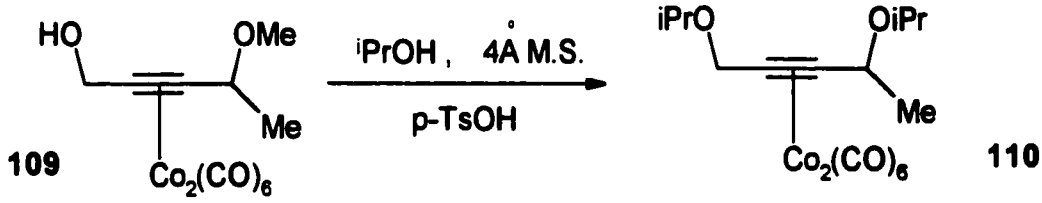


Procedure A

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) ν_{max} 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); ^{13}C NMR δ199.5(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 $C_{12}H_{10}Co_2O_8$ calcd (M^+-CO) 371.9091, found 371.9083, calcd (M^+-2CO) 343.9141, found 343.9146.

Hexacarbonyl[μ-η^4-(1, 4-diisopropyloxy-2-pentyne)]dicobalt(Co-Co) (110)

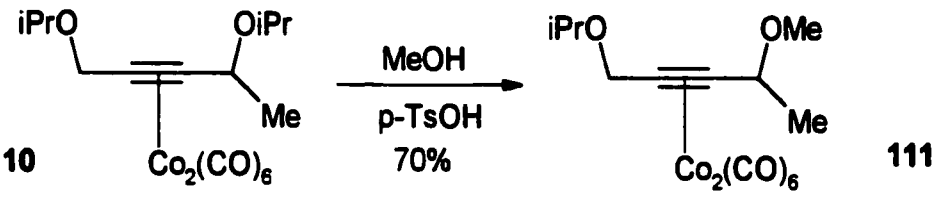


109 **110**

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}; ^{1}H 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); ^{13}C 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 $C_{17}H_{20}Co_2O_8$ calcd (M^+-3CO) 385.9975, found 385.9973.

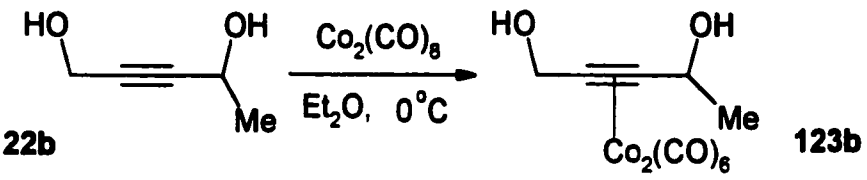
Hexacarbonyl[μ-η⁴-(1-isopropyloxy-4-methoxy-2-pentyne)]dicobalt(Co-Co) (111)



110 **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); ^{13}C 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 $C_{15}H_{16}Co_2O_8$ calcd (M^+-2CO) 385.9611, found 385.9615, calcd (M^+-3CO) 357.9662, found 357.9659.

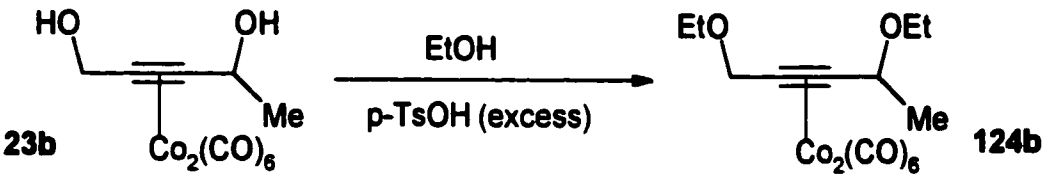
Hexacarbonyl[μ-η⁴-(2-pentyn-1,4-diol)]dicobalt(Co-Co) (123b)



122b **123b**

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_{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); ^{13}C 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 $C_{11}H_8Co_2O_8$ calcd (M^+-CO) 357.8934, found 357.8934.

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

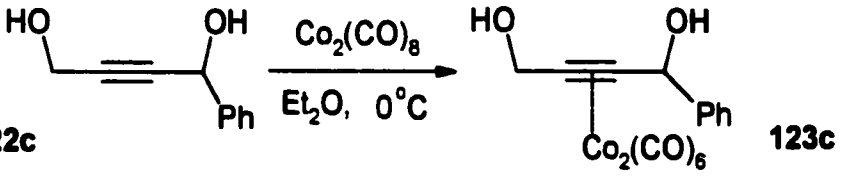


123b **124b**

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) ν_{max} 2980, 2932, 2869, 2093, 2051, 2022 cm^{-1}; ^1H NMR δ 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); 1.22 (t, J=7.0, 3H); ^{13}C NMR δ199.8 (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 $C_{15}H_{16}Co_2O_8$ calcd (M^+-CO) 413.9560, found 413.9560.

Hexacarbonyl[μ-η^4-(1-phenyl-2-butyn-1,4-diol)]dicobalt(Co-Co) (123c)

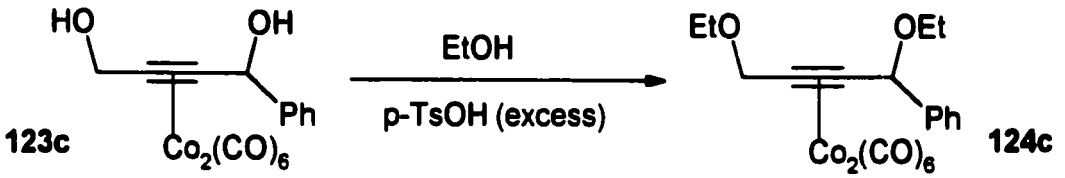


122c **123c**

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) ν_{max} 3346, 3090, 3067, 3032, 2924, 2854, 2095, 2054, 2023 cm^{-1}; ^1H NMR δ 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 $C_{16}H_{10}Co_2O_8$ calcd (M^+-3CO) 363.9192, found 363.9195.

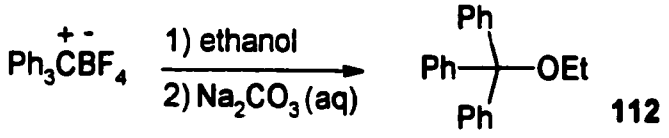
Hexacarbonyl[μ-η⁴-(1, 4-diethoxy-1-phenyl-2-butyne)]dicobalt(Co-Co) (124c)



123c **124c**

Compound **123c** (2.600 g, 5.80 mmol), ethanol (10 mL) and *para*-toluenesulphonic 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) ν_{max} 3064, 3031, 2978, 2931, 2868, 2093, 2052, 2022 cm^{-1}; ^1H 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 $C_{20}H_{18}Co_2O_8$ calcd (M^+-CO) 475.9716, found 475.9719.

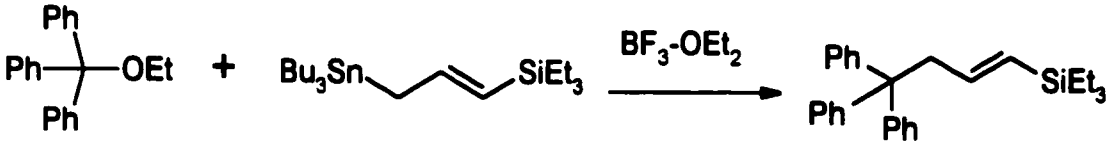
Triphenylmethyl ethyl ether (112)



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-butenyl]silane (115)

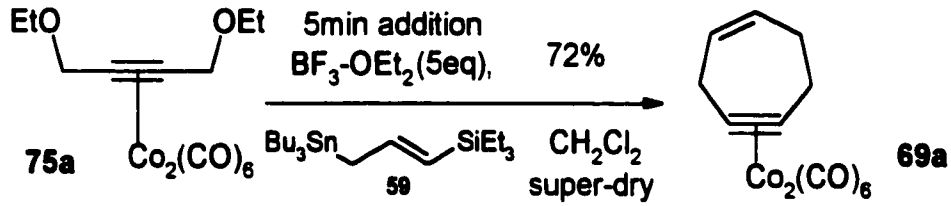


112 **59** **115**

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) ν_{max} 3057, 3030, 3019, 2951, 2909, 2873, 1612, 1597, 1493, 1446, cm^{-1}; ^1H NMR δ 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 δ 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_2H_5), 245 (M^+-2 C_6H_5), 168 (M^+-3C_6H_5); HRMS *m/e* for $C_{28}H_{34}Si$ calcd (M^+-C_2H_5) 369.2039, found 369.2044.

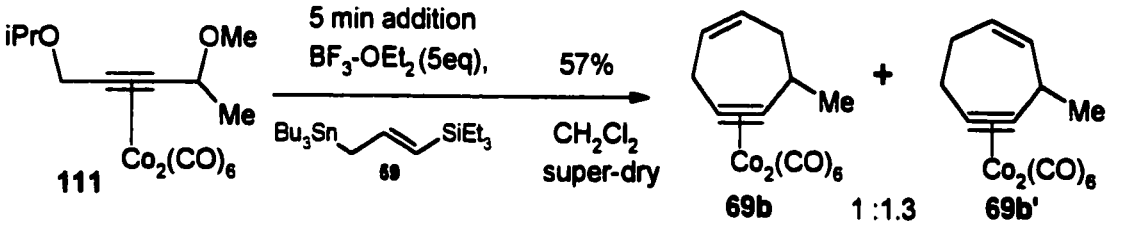
Hexacarbonyl[μ-η⁴-(cyclohept-1-en-4-yne)]dicobalt(Co-Co) (69a)



Procedure C

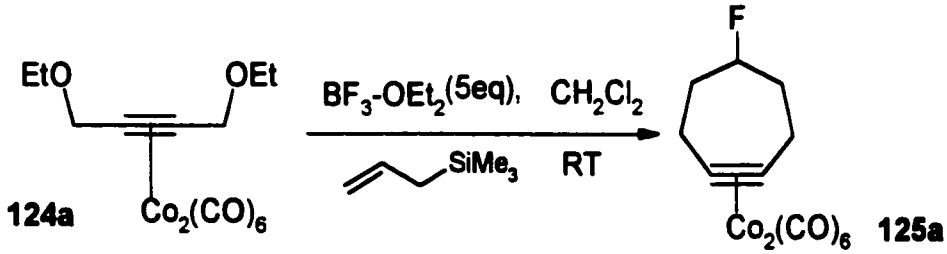
Substrate **75a** and silylstannane **59** were kept on vacuum for more than 2.5 h immediately before reaction. Substrate **75a** (0.052 g, 0.12 mmol) and **59** (0.070 g, 1.3 equiv.) were dissolved in super-dry dichloromethane (1.9 mL) at RT. The mixture was stirred for 0.5 min. BF_3-OEt_2 (0.086 g, 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.[99]

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 BF_3-OEt_2 (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.[99]

Hexacarbonyl[μ-η⁴-(5-fluorocycloheptyne)]dicobalt(Co-Co) (125a)

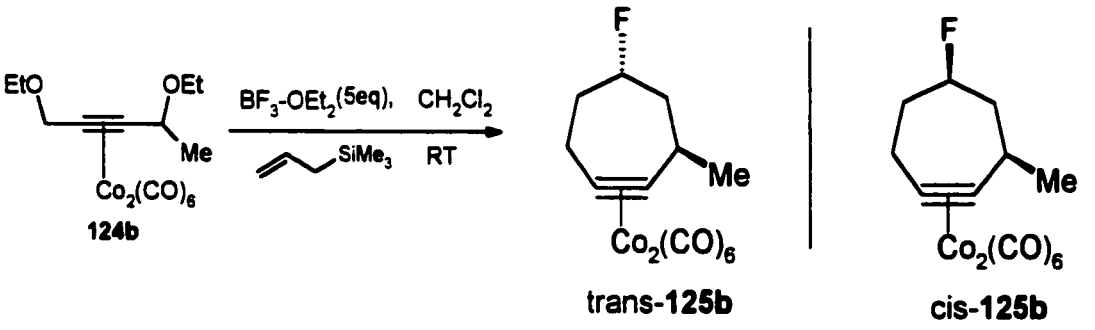


To a stirred solution of **124a** (0.052 g, 0.12 mmol) in dichloromethane (2.4 mL) at RT was added dropwise a mixture of allyltrimethylsilane (0.021 g, 1.5 equiv.) and BF_3-OEt_2 (0.172 g, 10 equiv.) in dichloromethane (1.0 mL) over 10 min. The reaction mixture was stirred for 10 min and then quenched 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.[99]

Alternative Procedure:

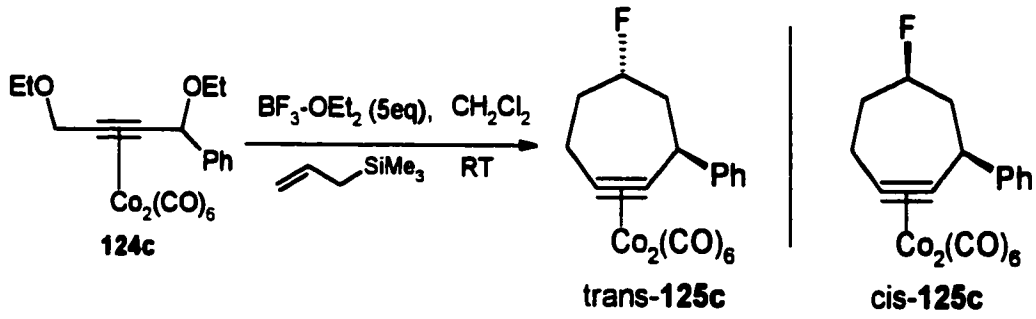
To a stirred solution of **124a** (0.065 g, 0.15 mmol) and BF_3-OEt_2 (0.108 g, 5 equiv.) in dichloromethane (6.3 mL) at RT was added dropwise allyltrimethylsilane (0.026 g, 1.5 equiv.) in dichloromethane (1.0 mL) over 2 h. The reaction mixture was stirred for 6 h and then quenched with saturated sodium bicarbonate solution. After a conventional workup with dichloromethane, flash chromatography (100% petroleum ether) afforded **125a** (0.045 g, 75%).

Hexacarbonyl[μ-η^4-(5-fluoro-3-methylcycloheptyne)]dicobalt(Co-Co) (125b)



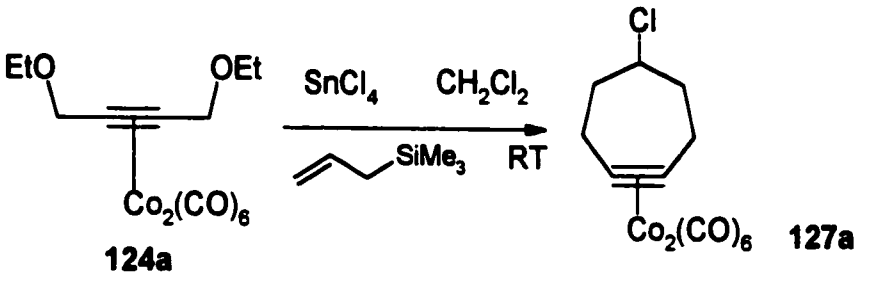
To a stirred solution of **124b** (0.049 g, 0.11 mmol) and allyltrimethylsilane (0.019 g, 1.5 equiv..) in dichloromethane (2.2 mL) at RT was added dropwise BF_3-OEt_2 (0.079 g, 5 equiv.) in dichloromethane (1.0 mL) over 1.5 h. The reaction mixture was stirred for 0.25 h and then quenched with saturated 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 δ 5.10 resonance (dt, $J=44.3_{HF}$, 7.2, 1H) of *trans*-**125b** to the δ 4.55 resonance (dt, $J=44.0_{HF}$, 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, $J=44.4_{HF}$, 6.9, 1H) of *trans*-**125c** to the δ 4.71 resonance (dt, $J=44.1_{HF}$, 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.[99]

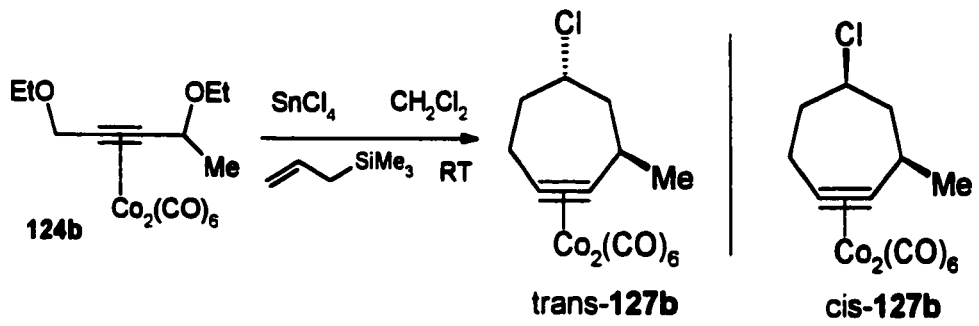
Hexacarbonyl[μ-η^4-(5-chlorocycloheptyne)]dicobalt(Co-Co) (127a)



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}; ^1H 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 $C_{13}H_9ClCo_2O_6$ calcd (M^+) 413.8752, found 413.8755.

Hexacarbonyl[μ-η^4-(5-chloro-3-methylcycloheptyne)]dicobalt(Co-Co) (127b)

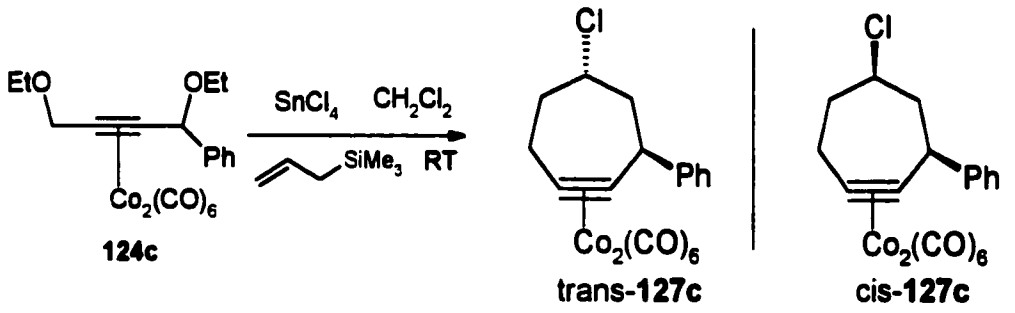


Substrate **124b** (0.039 g, 0.088 mmol), tin tetrachloride (0.115 g, 5 equiv.) and allyltrimethylsilane (0.020 g, 2.0 equiv.) were added as described in Procedure D (the reaction mixture was stirred for 15 min before quenching instead of 7 min). Flash chromatography (100% petroleum ether) afforded a 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) ν_{max} 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); ^{13}C 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 $C_{14}H_{11}ClCo_2O_6$ calcd (M^+-2CO) 371.9010, found 371.9006.

(*cis*-127b): IR (neat, KBr) ν_{max} 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 $C_{14}H_{11}ClCo_2O_6$ calcd (M^+-2CO) 371.9010, found 371.9006.

Hexacarbonyl[μ-η⁴-(5-chloro-3-phenylcycloheptyne)]dicobalt(Co-Co) (127c)

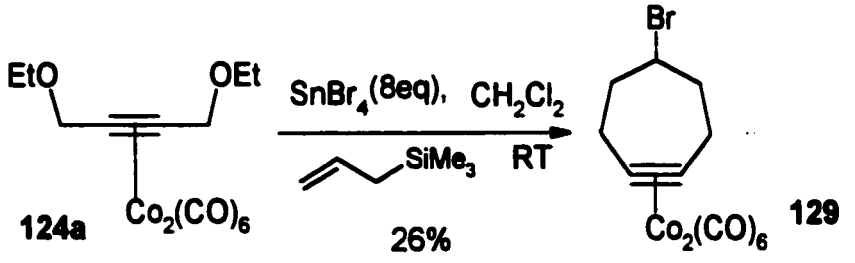


To a stirred solution of substrate **124c** (0.046 g, 0.091 mmol) and allyltrimethylsilane (0.013 g, 1.2 equiv.) in dichloromethane (3.0 mL) at RT was added dropwise tin tetrachloride (0.083 g, 3.5 equiv.) in dichloromethane (1.0 mL) over 2.25 h. The reaction mixture was stirred for 5 min and then quenched 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) ν_{max} 3036, 2962, 2933, 2090, 2048, 2027 cm^{-1}; ^1H NMR δ 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 δ 199.9 (br), 142.7, 128.5, 127.6, 127.2, 106.6, 99.1, 61.4, 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 $C_{19}H_{13}ClCo_2O_6$ calcd (M^+-2CO) 433.9166, found 433.9162.

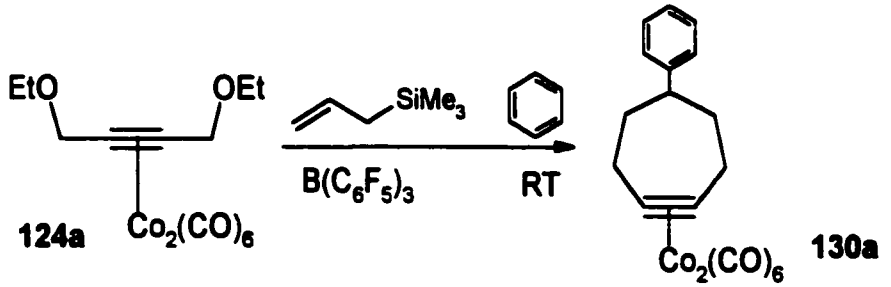
(*cis*-127c:) IR (neat, NaCl) ν_{max} 3030, 2940, 2092, 2048, 2028, 2016 cm^{-1}; ^1H NMR δ 7.37 (t, J = 7.4, 2H), 7.25-7.35 (m, 3H), 4.14 (tt, J = 11.0, 1.8, 1H), 4.00 (dd, J = 12.2, 3.5, 1H), 3.29 (tt, J = 16.8, 3.4, 1H), 2.95 (ddd, J = 16.8, 12.7, 4.1, 1H), 2.74 (m, 1H), 2.63 (m, 1H), 2.45 (m, 1H), 2.15 (m, 1H); ^{13}C NMR δ 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 $C_{19}H_{13}ClCo_2O_6$ calcd (M^+-2CO) 433.9166, found 433.9164.

Hexacarbonyl[μ-η⁴-(5-Bromocycloheptyne)]dicobalt(Co-Co) (129)



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 fluent. The product fraction was collected and concentrated under reduced pressure to afford the crude products. Flash chromatography (100% petroleum ether) afforded **129** (0.012 g, 26%): IR (neat, KBr) ν_{max} 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); ^{13}C 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 $C_{13}H_9Br^{79}Co_2O_6$ calcd (M^+) 457.8246, found 457.8242.

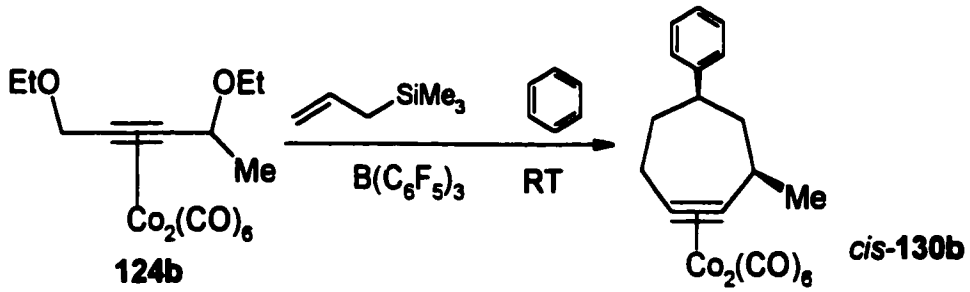
Hexacarbonyl[μ-η⁴-(5-phenylcycloheptyne)]dicobalt(Co-Co) (130a)



Substrate **124a** (0.050 g, 0.12 mmol) and $B(C_6F_5)_3$ (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) ν_{max} 3028, 2087, 2043, 2013 cm^{-1}; ^1H NMR δ 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 (ddd, 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 δ 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 $C_{19}H_{14}Co_2O_6$ calcd (M^+-2CO) 371.9607, found 371.9604.

Hexacarbonyl[μ-η⁴-(3-methyl-5-phenylcycloheptyne)]dicobalt(Co-Co) (130b)

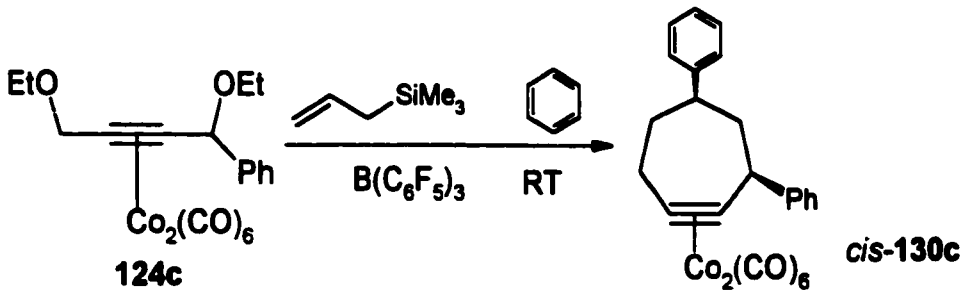


124b *cis*-**130b**

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 $B(C_6F_5)_3$ (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) ν_{max} 3030, 2088, 2044, 2021 cm^{-1}; ^1H NMR δ 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 δ 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^+-2CO), 386 (M^+-3CO), 358 (M^+-4CO), 330 (M^+-5CO), 302 (M^+-6CO); HRMS *m/e* for $C_{20}H_{16}Co_2O_6$ calcd (M^+-3CO) 385.9763, found 385.9766.

Hexacarbonyl[μ-η⁴-(3, 5-diphenylcycloheptyne)]dicobalt(Co-Co) (130c)

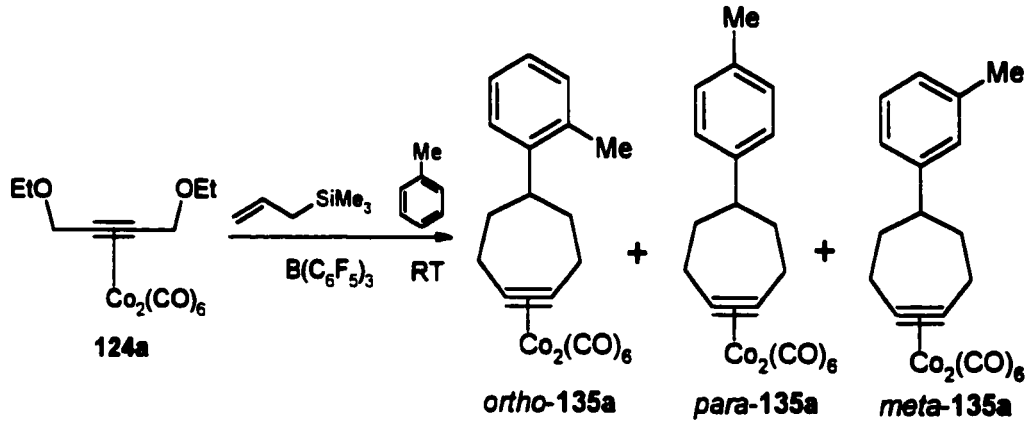


124c *cis*-**130c**

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 $B(C_6F_5)_3$ (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) ν_{max} 3029, 2089, 2045, 2026, 2008 cm^{-1}; ^1H NMR δ 7.18-7.37 (m, 10H), 4.11 (m, 1H, simplifies to dd, J = 9.7, 5.6 upon irradiation at δ 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 δ 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 $C_{25}H_{18}Co_2O_6$ calcd (M^+-3CO) 447.9920, found 447.9917.

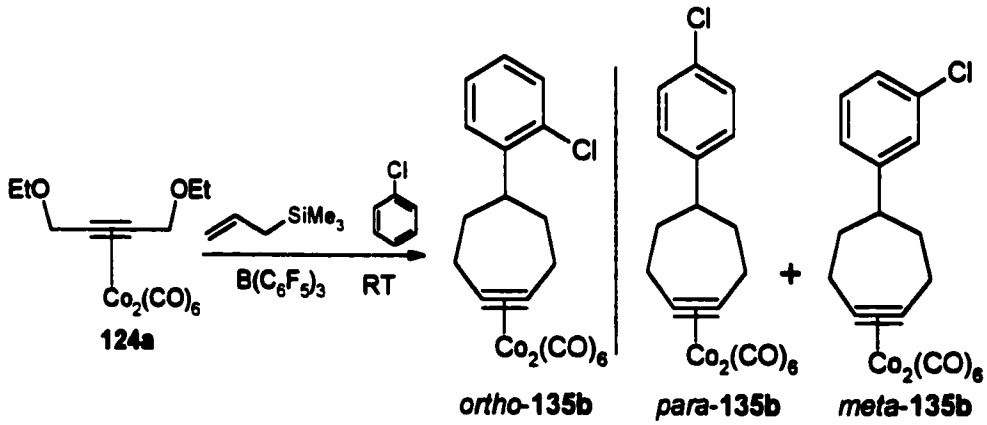
Hexacarbonyl[μ-η⁴-(5-(2-methylphenyl)cycloheptyne)]dicobalt(Co-Co) (*ortho*-135a), Hexacarbonyl[μ-η⁴-(5-(4-methylphenyl)cycloheptyne)] dicobalt(Co-Co) (*para*-135a), Hexacarbonyl[μ-η⁴-(5-(3-methylphenyl) cycloheptyne)] dicobalt(Co-Co) (*meta*-135a)



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 $B(C_6F_5)_3$ (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 ^1H NMR resonance at δ 2.80 and the combined resonances at δ 2.56 and δ 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) ν_{max} 3022, 2088, 2043, 2017 cm^{-1}; ^1H NMR δ 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 δ 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 $C_{20}H_{16}Co_2O_6$ calcd (M^+ -3CO) 385.9763, found 385.9767.

Hexacarbonyl[μ-η⁴-(5-(2-chlorophenyl)cycloheptyne)]dicobalt(Co-Co) (*ortho*-135b), Hexacarbonyl[μ-η⁴-(5-(4-chlorophenyl)cycloheptyne)] dicobalt(Co-Co) (*para*-135b), Hexacarbonyl[μ-η⁴-(5-(3-chlorophenyl) cycloheptyne)] dicobalt(Co-Co) (*meta*-135b)



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 $B(C_6F_5)_3$ (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) ν_{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 (ddd, J = 16.4, 12.6, 4.2, 2H), 2.13 (dt, J = 13.9, 3.3, 2H), 1.85 (br m, 2H); ^{13}C 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) ν_{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) ; ^{13}C 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); ^{13}C 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 $C_{19}H_{13}ClCo_2O_6$ calcd (M^+-2CO) 433.9166, found 433.9162.

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