ZIRCONIUM-GROUP 13 HETEROBIMETALLIC COMPOUNDS AND THE SYNTHESIS OF OXYSULFIDES IN SODIUM POLYSULFIDE

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

Doctor of Philosophy in Inorganic Chemistry
at the
Massachusetts Institute of Technology

June 1996

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Abstract

The reaction of main group (B, Al and Ga) alkoxides with zirconocene complexes of benzynes is used to prepare novel zirconium-group 13 heterobimetallic compounds. These complexes are characterized in solution by NMR spectroscopy and in the solid state *via* single crystal X-ray crystallography. The formation of the new compounds is discussed in light of the known insertion chemistry of small unsaturated molecules into the zirconium-carbon bonds of zirconocene stabilized benzynes.

The heterobimetallic compounds of zirconium and boron are used as intermediates in the "one pot" synthesis of substituted aromatic compounds. Methods for the synthesis of halophenols, α-bromoiodoarenes and brominated-biaryls are developed.

The compounds (LnO)CuS with Ln = La, Nd, Sm and Eu are made in a sodium polysulfide flux at 300 to 400 °C. The powdered products are characterized using Powder X-Ray Diffraction and indexed in the space group P4/nmm. The compounds form a layered structure in the *c* direction with atoms in the order $[\text{O-Ln-S-Cu-S-Ln}]_{\infty}$.

Thesis Supervisor:	Stephen L. Buchwald
Title:	Professor of Chemistry

Dedicated to those who make it all worthwhile;
Anna and Nicoletta

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PREFACE

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de Rege, F. M. G.; Buchwald, S. L. "The Regioselective Synthesis of Halophenols" *Tetrahedron* **1995**, 51, 4291-4296.

de Rege, F. M. G.; Davis, W. M.; Buchwald, S. L. "Synthesis and Structure of Zirconium-Group 13 Heterobimetallic Compounds" *Organometallics*, **1995**, 14, 4799-4807.

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INTRODUCTION

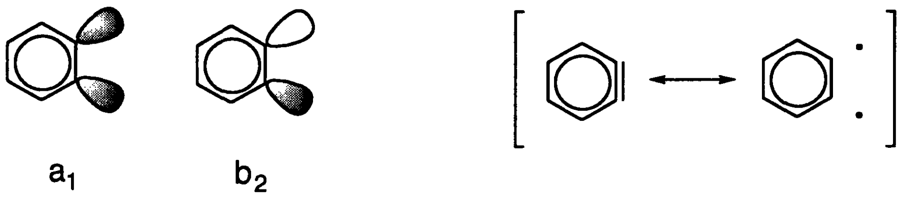
Chapter one of this thesis deals with the synthesis and characterization of some new heterobimetallic complexes of zirconium and main group metals. Chapter two is involved with an organic problem, the regioselective synthesis of substituted aromatic compounds. There is a direct relationship between first two chapters, since the methodology developed in chapter two relies on the organometallic chemistry developed in chapter one. Thus a common background is presented for chapters one and two. The third chapter stands somewhat alone as it deals with the synthesis of solid state materials. This thesis is perhaps unique for the Buchwald group in that topics in the different fields of organic, organometallic and inorganic chemistry are discussed. The common thread is that in all cases the work is devoted to synthesis.

BACKGROUND FOR
CHAPTERS ONE AND TWO

Many reactive organic fragments can be stabilized when complexed to a transition metal. Thus through bonding to the metal, the chemistry of an organic fragment can be profoundly changed. A case in point is benzyne, which cannot be isolated in the free state yet can form stable complexes with transition metals.[1-8] Furthermore, the complexed benzyne exhibits very different chemistry then the free benzyne. The Buchwald group has had a history of interest in zirconocene stabilized benzynes.[9] Chapters One and Two of this thesis expand the scope and usefulness of zirconocene benzyne complexes with the synthesis of heterobimetallic and substituted aromatic compounds. Some background will be presented here to place the new work in perspective.

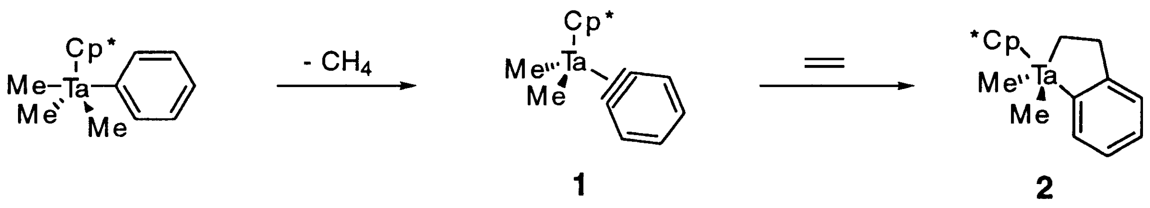
Free *o*-benzyne contains a weak triple bond, but the hexagonal geometry of the aromatic system essentially remains in tact. The strain energy of *o*-benzyne has been calculated to be approximately 80 Kcal/mol.[10] Due to poor overlap between the orbitals which form the triple bond, the singlet to triplet energy gap is small (~33 Kcal/mol).[11] Thus the benzyne is best described as having significant mixing of the a_1 and b_2 molecular orbitals (Figure 1). Alternatively, a resonance description, where the two important canonical structures are shown in Figure 1, can be used. These properties make free *o*-benzyne an unstable species which must be generated and reacted *in situ*. Benzynes will react with nucleophiles, undergo concerted [2+4] cycloaddition reactions or unconcerted [2+2] addition reactions. The last two reactions have been particularly useful in organic synthesis.[12-16]

Figure 1 Molecular Orbitals of *o*-benzyne and Resonance Description.

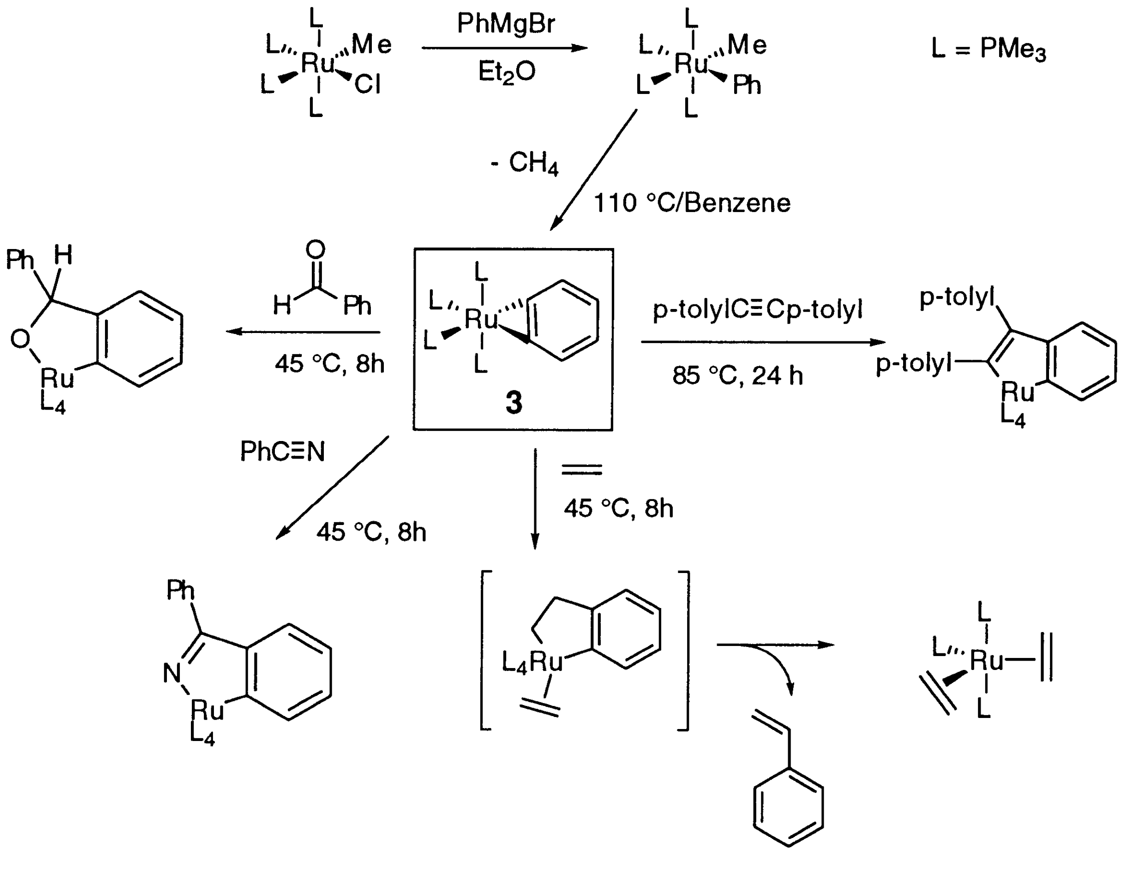


As previously noted, one way to stabilize benzynes is through forming a complex with a transition metal. Many late and early transition metal complexes of benzynes have been isolated and structurally characterized. The first structurally characterized complex, **1**, (Scheme 1) was reported by Schrock in 1973 and was generated by the loss of methane from $Cp^*Ta(Me)_3Ph$.[8] Compound **1** reacts with ethylene to give the metallocyclopentene **2**. Scheme 2 shows the generation and reactivity of another interesting benzyne complex.[6] This complex will insert many small organic molecules such as ketones, nitriles, alkenes and alkynes. A nickel benzyne complex isolated by Bennett,[17] is generated by a different method from the previous two examples as seen in Scheme 3. Oxidative addition of *o*-dibromobenzene followed by halogen metathesis and reduction leads to the compound **4**. The benzyne shows a similar insertion chemistry to the previous two examples. Recent work has shown that derivatives of **4** will insert small molecules twice leading to naphthalene compounds after reductive elimination from the Ni(II) cycloheptatrienes.[18] There are other known transition metal stabilized benzynes,[1,2,4,5,7] but these three are sufficient to show the similarities in the chemistry exhibited by the metal complexes, and that this chemistry is very different from the chemistry of free benzyne.

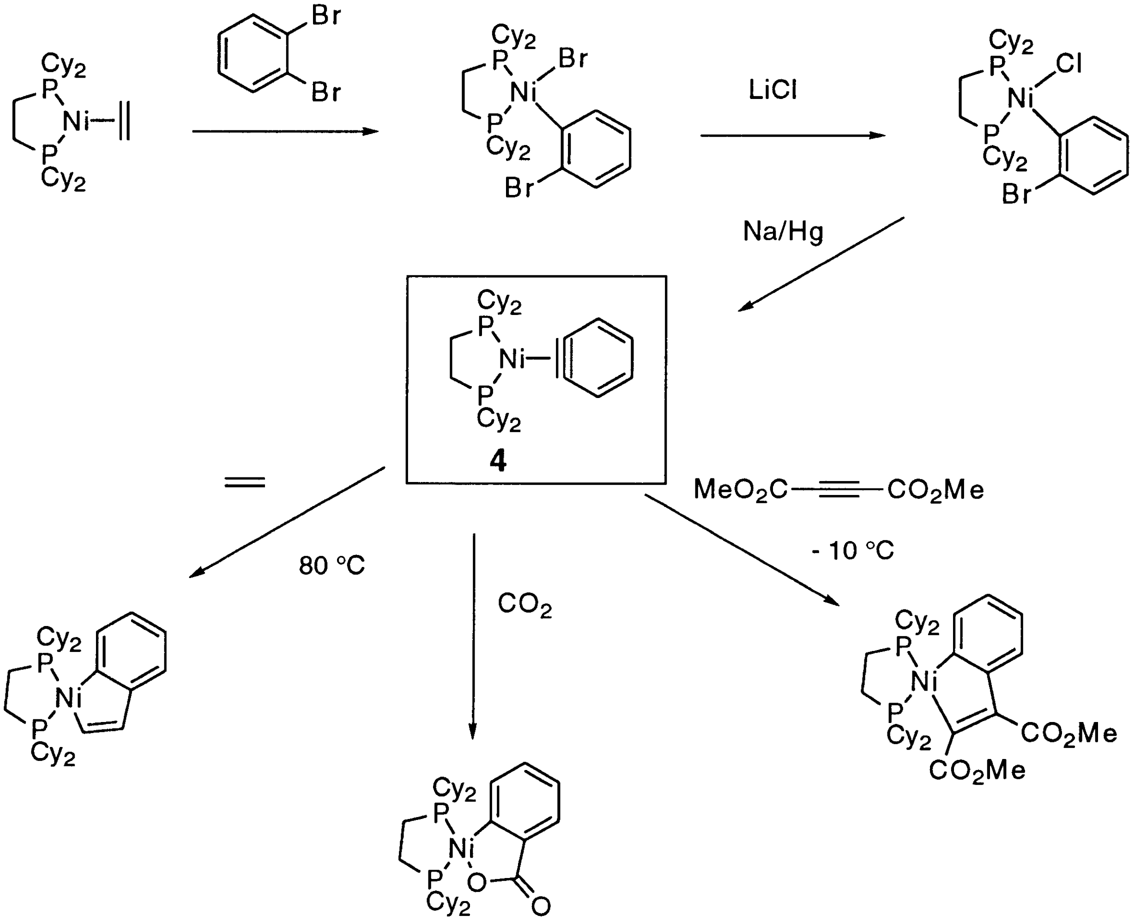
Scheme 1: Generation of **1** and reaction with ethylene.



Scheme 2: Generation of **3** and Insertion Reactions.

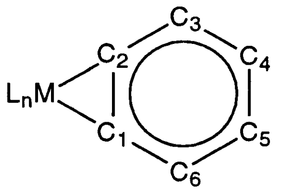


Scheme 3: Generation of **4** and Insertion Reactions.



Comparison of the structurally characterized metal benzyne complexes reveals some important similarities. The M - C_1 and M - C_2 bond lengths (Figure 2) are approximately equal in each complex, indicating a symmetrically bound benzyne. The C_1 - C_2 distances of approximately 1.36 Å are close to the C - C distance in a benzene ring indicating that there is no triple bond. The remaining C - C bonds are between 1.36 and 1.40 Å, and are consistent with an aromatic ring system where the strongest bonds to the metal do not involve the delocalized orbitals.

Figure 2: Important Structural Features of Metal Stabilized Benzynes.



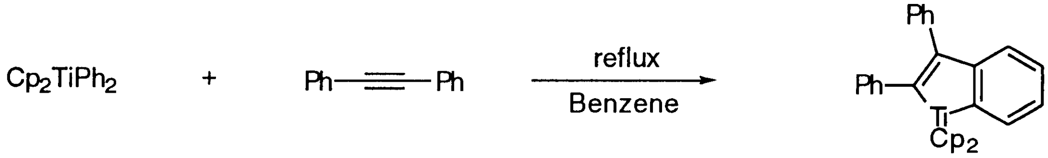
$M\text{-}C_1 = M\text{-}C_2$

$C_1 - C_2 \sim 1.36$ Å

$C_2 - C_3 \sim C_3\text{-}C_4 \sim C_4\text{-}C_5 \sim C_5\text{-}C_6 \sim C_6\text{-}C_7 = 1.36 - 1.4$

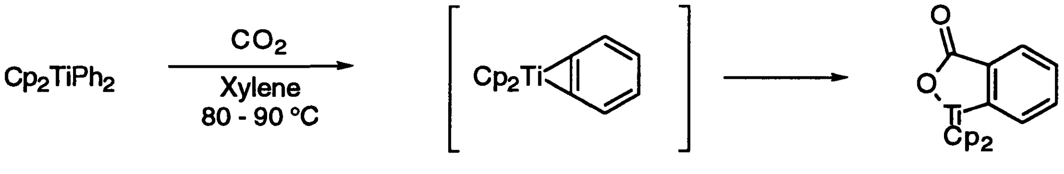
Group 4 metallocenes also form metal benzyne complexes which, however, are more difficult to isolate. In 1968 Hagihara noted that the reaction of diphenyl titanocene and diphenylacetylene led to the formation of the titanium metallacycle **5** (Scheme 4).[19] Some years later, Vol'pin studied the reaction of CO_2 with Cp_2TiPh_2 and found a similar insertion reaction occurred leading to **6** (Scheme 5).[20] He concluded that both **5** and **6** were the products of an insertion reaction with diphenylacetylene or carbon dioxide with the titanocene stabilized benzyne **7**.

Scheme 4: Hagihara's Synthesis of Metallacycle **5.**



5

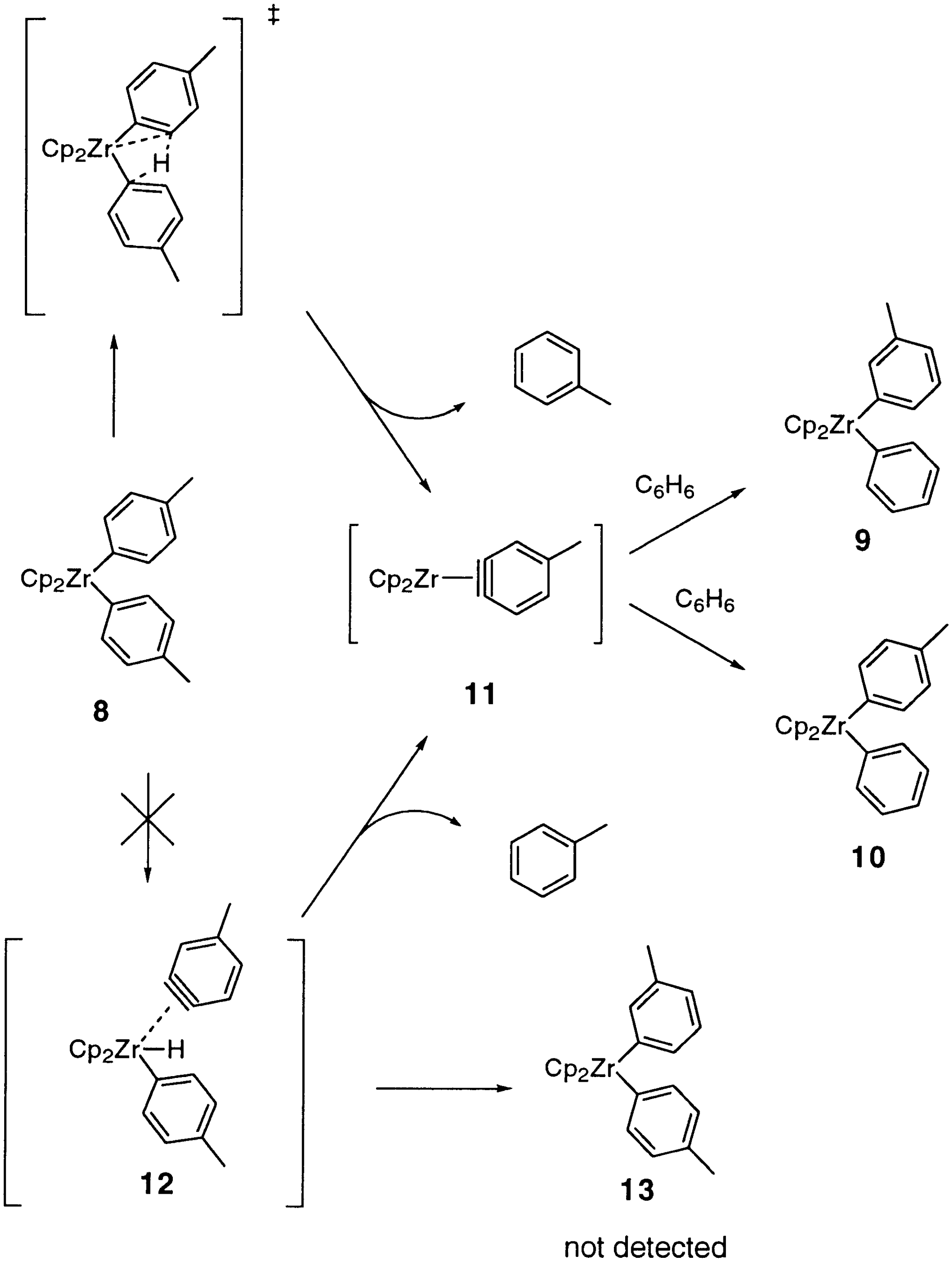
Scheme 5: Vol'pin's Proposed Benzyne Intermediate.



7 **6**

Erker showed that thermolysis of zirconocene aryne complexes leads to the generation of zirconocene stabilized benzynes through a concerted hydride abstraction from one of the phenyl groups.[21] In this study, he first showed that photolysis of biarylzirconocene intermediates quantitatively led to coupling of the aryl groups at the carbon originally bonded to the zirconocene fragment. This allowed a systematic analysis of the reaction products. Since the biphenyl originated from specific biarylzirconocene complexes, only the complexes will be discussed here with the understanding that the biaryl compounds were the actual observed products. Erker showed that heating zirconocene diaryl complex **8** in benzene lead to the generation of **9** and **10** (Scheme 6). This must occur through a benzyne intermediate such as **11** since the 3 and 4 positions of the tolyl groups become equivalent at some point in the reaction mechanism. At the time, two plausible mechanisms to generate **11** from a biaryl-metal complex were a β-hydride elimination or an *o*-hydrogen abstraction from one of the aryl ligands by the other aryl ligand. The intermediate **12**, would lead to the formation of some of **13** since the β-hydride elimination mechanism is reversible. The lack of any product **13** therefore excludes the β-hydride elimination pathway. Erker's conclusion was that **11** is formed through the concerted *o*-hydrogen abstraction mechanism.

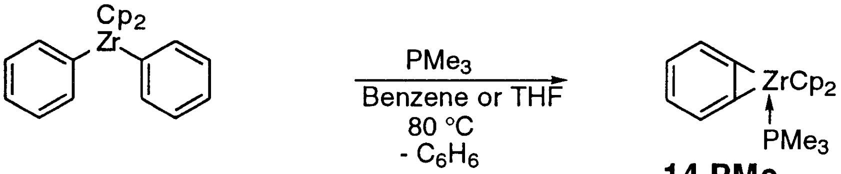
Scheme 6: Some of the Thermolysis Products of **8** in Benzene.



Zirconocene stabilized benzynes were only postulated as transient species until one was trapped *in situ*. This was done by generating the benzyne in the presence of excess PMe_3 which forms a the stable complex $Cp_2Zr(\eta^2\text{-}C_6H_4)PMe_3$,

14·PMe$_3$ (Scheme 7). Complex **14·PMe$_3$** has been isolated and characterized by single crystal X-ray crystallography[4] and was the first of the elusive group 4 metallocene benzynes to be structurally characterized.

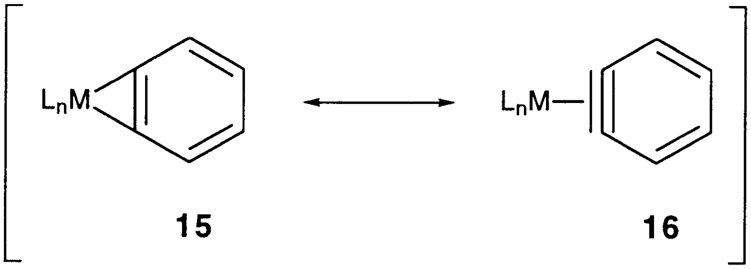
Scheme 7: The formation of $Cp_2Zr(\eta^2\text{-}C_6H_4)PMe_3$.



14·PMe$_3$

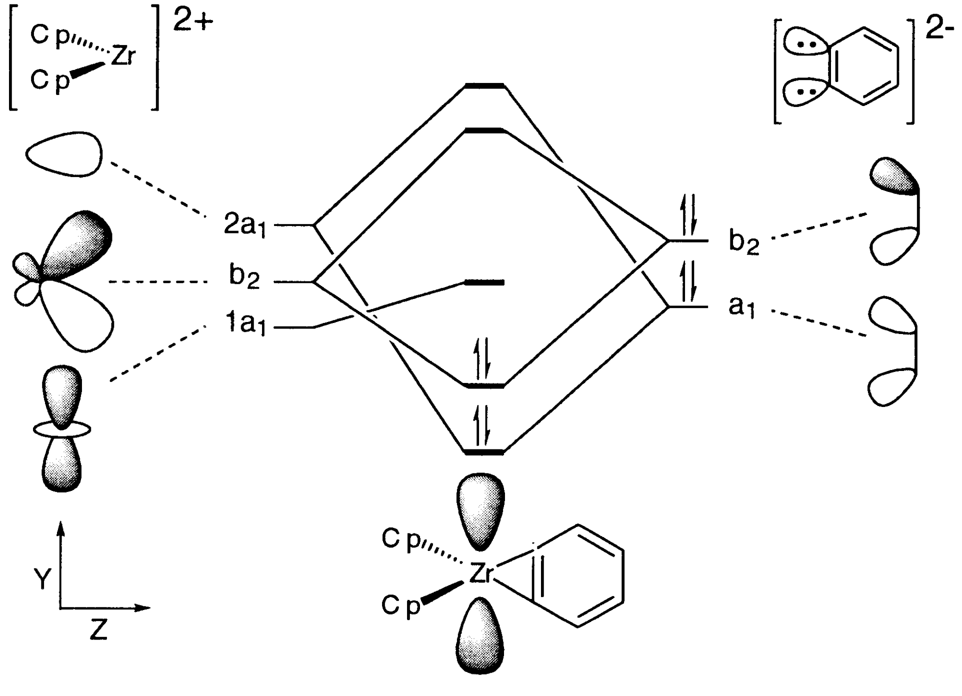
The bonding between the metal and the benzynes can be described by two canonical structures (Figure 3). Structure **15** can be described as a benzopropene while **16** is a benzyne.[9] In light of the observed properties of these complexes, we believe that the canonical structure **15** is the more important resonance contributor. This is especially true with zirconocene stabilized benzynes since the metal-carbon bonds are highly polarized. The metal stabilized benzyne is therefore thought of as a zirconium(IV) species with a benzyne-dianion ligand.

Figure 3: Canonical structure for the M-C bonding In Metal Stabilized Benzynes.



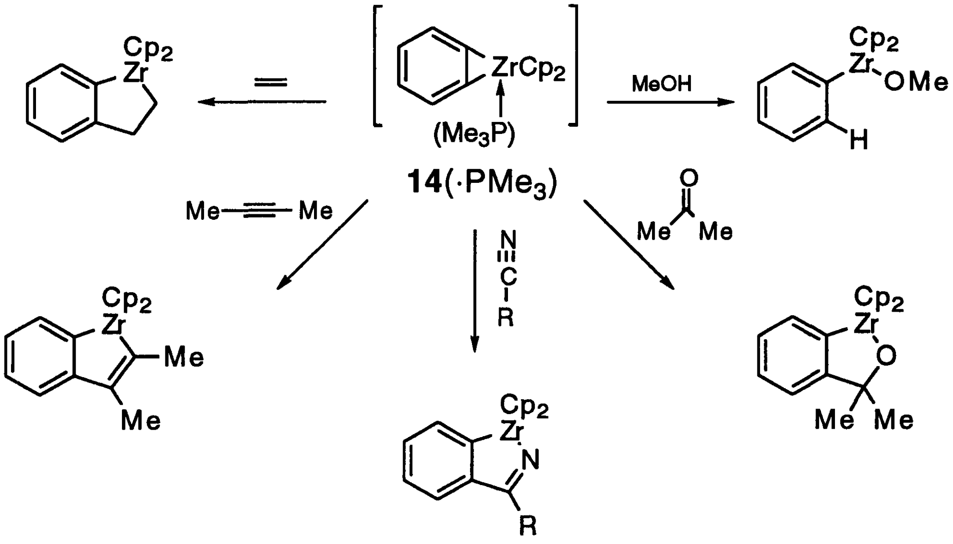
A molecular orbital description is helpful in understanding the structure and reactivity of the zirconocene stabilized benzyne complexes (Figure 4). Hoffman showed that bent early transition metal metallocenes have three frontier molecular orbitals.[22] Two orbitals have a_1 symmetry and the other has b_2 symmetry. A benzyne fragment would have two frontier molecular orbitals; one with a_1 symmetry and the other with b_2 symmetry.[22] All the frontier MO's lie in the YZ plane which bisects the angle made by the metal and the two cyclopentadiene ligands. Combination of frontier MO's of the same symmetry leads to two bonding orbitals, one of a_1 symmetry and the other of b_2 symmetry, and an empty metal based non-bonding orbital of a_1 symmetry. The non-bonding orbital is situated in the same plane as the benzene ring with density in the y and -y directions above and below the metal. From this MO description, it is expected that Lewis bases would interact above and below the zirconium where the approach has to be in the same plane as the aromatic ring.

Figure 4: Molecular Orbital Diagram for **14**.

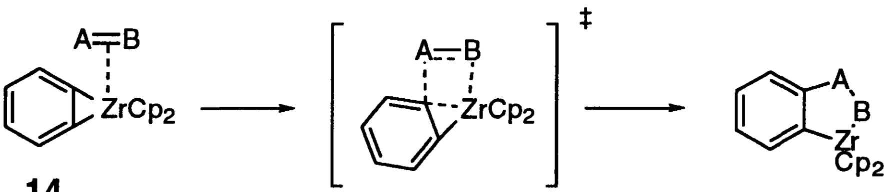


Zirconocene benzynes exhibit rich bond insertion chemistry with small organic fragments such as alkenes, alkynes, nitriles, ketones and alcohols (Scheme 8). We believe that this insertion occurs through first a σ like interaction with the empty zirconium orbital of **14** and then through a four centered transition state which leads to a metallocycle **17** (Scheme 9).[23]

Scheme 8: Insertion Chemistry of **14**.

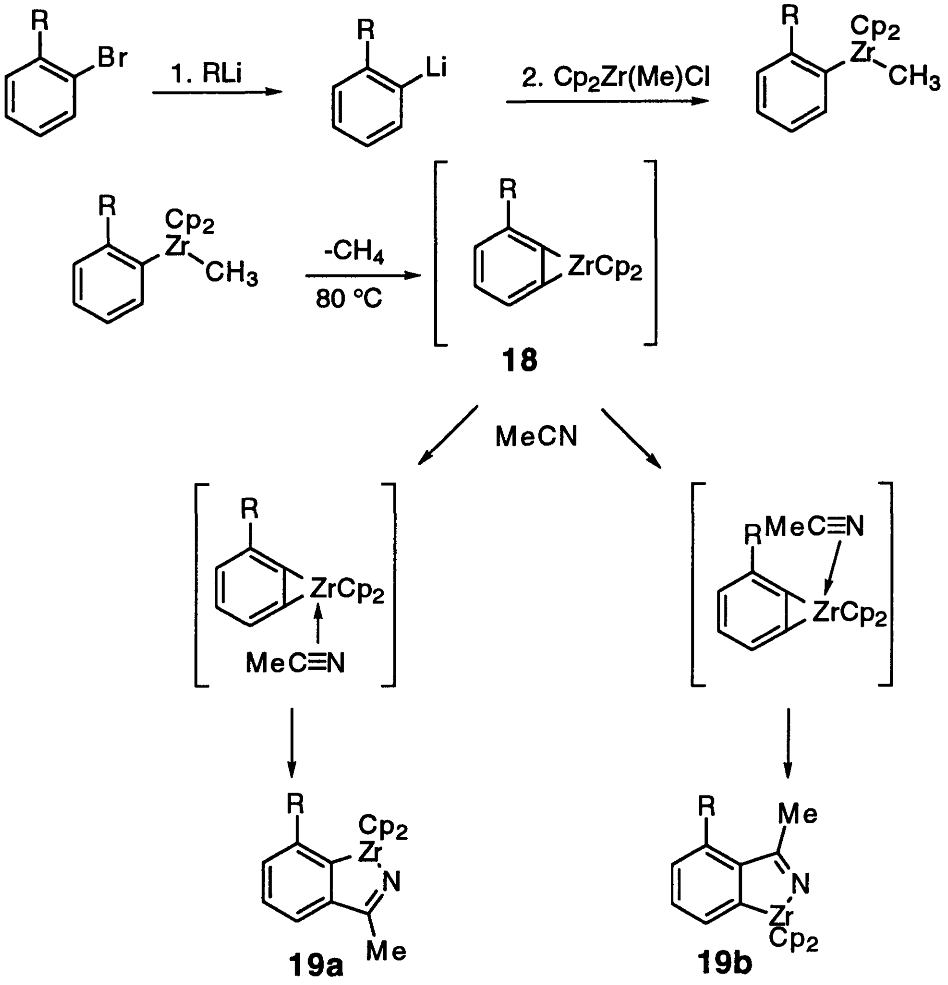


Scheme 9: Proposed Mechanism for Insertion Reaction.



An important contribution to zirconocene benzyne chemistry for use in organic synthesis was the development in our group of a method to make substituted benzynes.[23] Erker had found that it was not possible to make zirconocene compounds containing two *ortho*-substituted aromatic ligands.[21] This is probably due to steric constraints which would make such complexes unstable. It was reasoned that a substituted aromatic next to a methyl group on the zirconocene fragment would be stable. These compounds can be isolated from the reaction of an aryl lithium with zirconocene methyl chloride (Scheme 10).[9] The substituted benzyne **18** was generated from the aryl methyl zirconocene intermediate *via* the concerted loss of methane. The complex **18** is unstable but can be allowed to react *in situ* with small molecules leading to insertion products. Scheme 10 shows the reaction of **18** with MeCN, leading to the two possible isomers, **19a** and **19b**. The regioselectivity for the production of **19a** over **19b** was excellent.[23] This regioselectivity is a consequence of the constrained way in which the inserting fragment must approach the zirconium center. Insertion occurs almost exclusively from the less hindered side. Several methodologies for the synthesis of substituted aromatic compounds such as, the synthesis of aromatic ketones,[23] iodoacyclnaphthoquinones,[24] benzothiophenes[25] and tetrahydropyrroloquinolines[26] have been developed based on this chemistry. These methods use one equivalent of the cheap and readily available zirconocene methyl chloride, one equivalent of aryl bromide and lead to substituted aromatic compounds with excellent regioselectivity.

Scheme 10: Regioselective Insertion into Substituted Benzynes.



R = Me	100	0
R = MeO	98	2

In conclusion, several transition metals have been shown to stabilize benzynes and modify the chemistry of this reactive species. Where the reactivity has been studied, the key process seems to be the insertion of small organic fragments into the metal - aryl bonds. In particular, there has been a wealth of chemistry done in the area of zirconocene benzyne complexes. The discovery of a general method for the generation of substituted benzynes was particularly significant in organic synthesis. Several methods for the regioselective functionalization of aromatic compounds have been developed based on the zirconocene stabilized benzyne chemistry.

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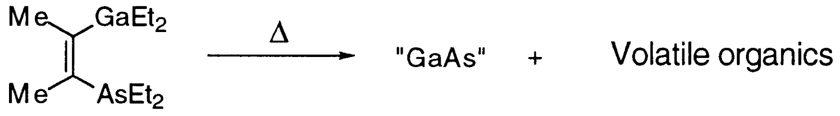
CHAPTER 1:

SYNTHESIS AND STRUCTURE OF ZIRCONIUM-GROUP 13 HETEROBIMETALLIC COMPOUNDS.

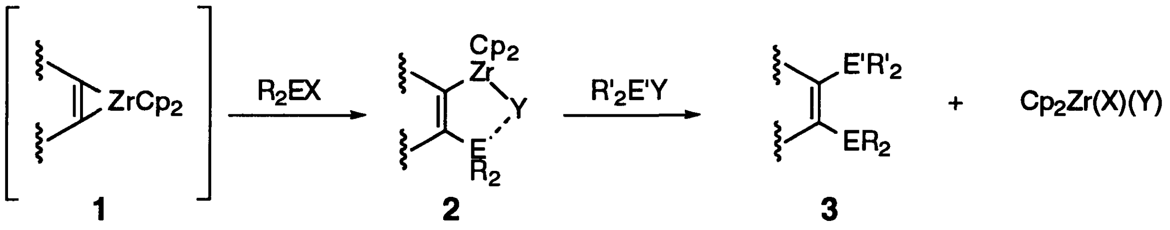
Introduction

Much of the current interest in main-group heterobimetallic complexes is due to their potential use as single source precursors for electronic, optical or refractory materials.[1-9] Likewise, vicinally disubstituted olefins or arenes with two main group fragments are potential precursors to ceramic materials (Scheme 1), but few of these compounds are known.[10-16] Since we had been interested in the synthesis of novel main group compounds *via* zirconocene-mediated routes for several years,[17-21] the synthesis of such main group complexes was an attractive goal. Scheme 2 shows our strategy for the synthesis of such compounds in two transmetallation steps from a zirconocene complex of an alkyne or aryne, possibly as a one pot procedure. In the first step a main group compound would react with a zirconocene aryne or alkyne complex **1** giving a heterobimetallic complex **2**. In the second step, the transmetallation from zirconium to a main group species then leads to the desired compounds **3**.

Scheme 1.1: An Example of a Single Source Precursor to Gallium Arsenide.



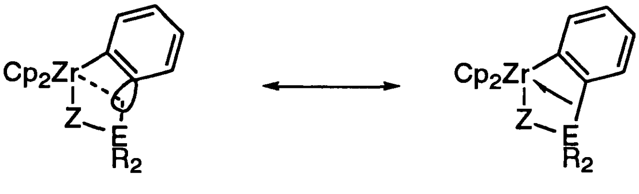
Scheme 1.2: Zirconocene Mediated Route to Mixed Main Group Compounds.



E, E' = group 13 or 15 element
X, Y = electronegative element

Insertion of a main-group fragment into a zirconium-carbon bond was previously observed by Erker in the synthesis of zirconium group 13 heterobimetallic compounds.[22-26] The structures of these and similar heterobimetallic products were determined by X-Ray crystallography and shown to possess a planar tetracoordinate carbon. In these compounds, a σ electron pair of the aryne anion bridges the two metals *via* a three centered two electron bond[27] (Figure 1). The structural alternative **2**, where the zirconium is bonded to only one carbon of the aryl group, is calculated to be 30 to 50 kcal/mol less stable.[27] Nevertheless, Erker's work indicated that a compound such as **2** might be obtained through careful selection of the main group reagent R_2EX.

Figure 1.1: Erker's Zirconium-Main group Heterobimetallic Compounds.



$Z = CH_3, CH_2CH_3$
E = Al, Ga

The second transmetallation step in Scheme 1.2 also has ample precedent for similar systems.[7, 28-30] The work of Fagan and Nugent is particularly relevant and comprehensive.[28]

Although we were not able to generate the mixed main group compounds **3** we initially desired, we were able to effect the first transmetallation depicted in Scheme 1.2. This chapter describes the isolation and characterization of several complexes with structures analogous to **2**, some of which were characterized by X-ray crystallography.

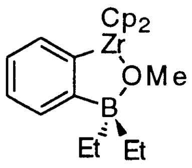
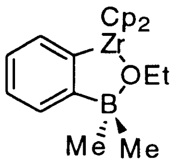
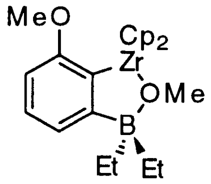
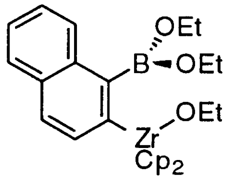
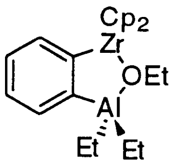
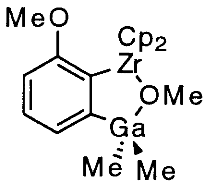
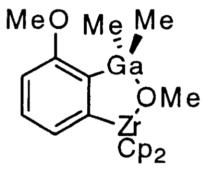
Results and Discussion

Synthesis and Characterization of Heterobimetallic Complexes.

The zirconium-group 13 heterobimetallic compounds that were prepared are listed in Table 1.1. These are all made by treating a group 13 alkoxide with an appropriate zirconocene complex of an aryne.[31] The products are obtained in 80 - 90 % yield (^{1}H NMR) and are isolated by recrystallization in 44 - 78 % yield (based on Cp_2ZrPh_2 for **4**, **5** and **8**, and based on $Cp_2Zr(Me)Cl$ for **6**, **7** and **9**).

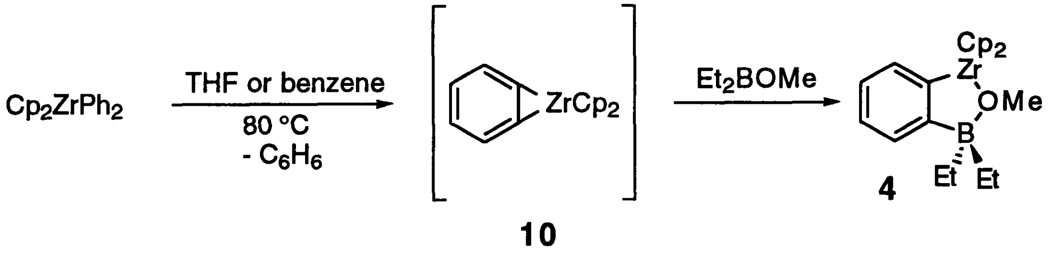
Treatment of **10**, generated *in situ* from diphenylzirconocene, with either Et_2BOMe or Me_2BOEt in THF or benzene leads to the isolation of **4** (78 %) or **5** (54 %) (Equations 1.1 and 1.2). Similarly, **6** (52 %) and **7** (55 %) are prepared from zirconocene-aryne complexes and Et_2BOMe or $(EtO)_3B$ (Equations 1.3 and 1.4). We were not able to isolate the benzene analog of **7** in pure form (it was ~80 % pure as estimated by ^{1}H NMR).

Table 1.1. Results for the Synthesis of Zirconium-Main Group Aromatic Compounds

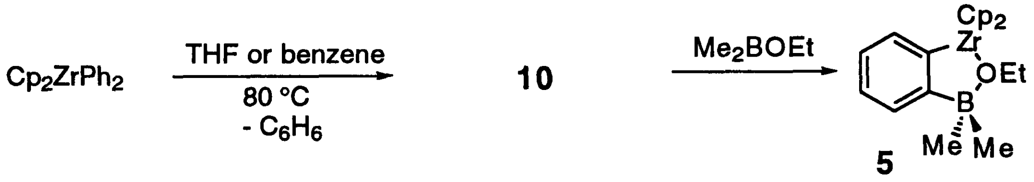
Compound	Structure	Isolated Yield
4		78 %
5		54 %
6		52 %
7		55 %
8		44 %
9	 **a**  **b**	52 %^{a}

^{a} Isolated as an inseparable 65:35 mixture of **9a** and **9b**.

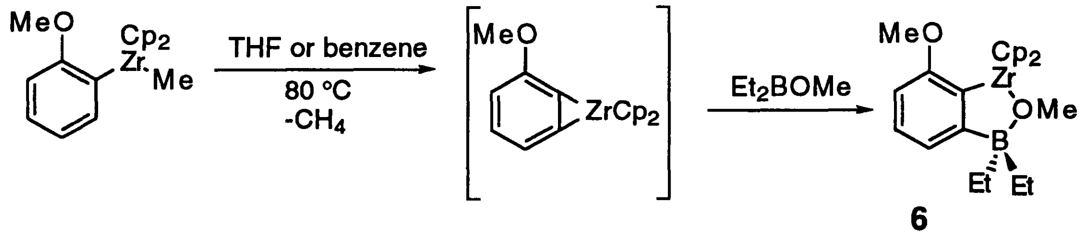
1.1)



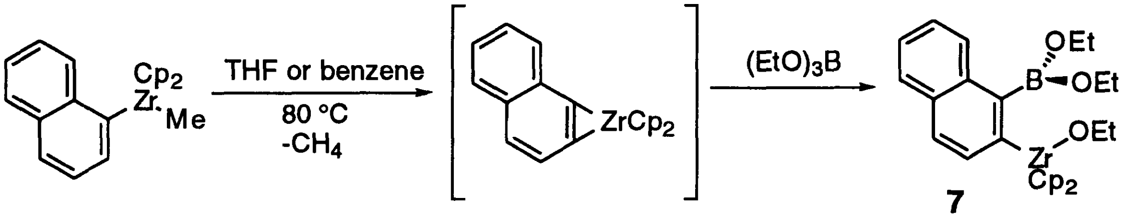
1.2)



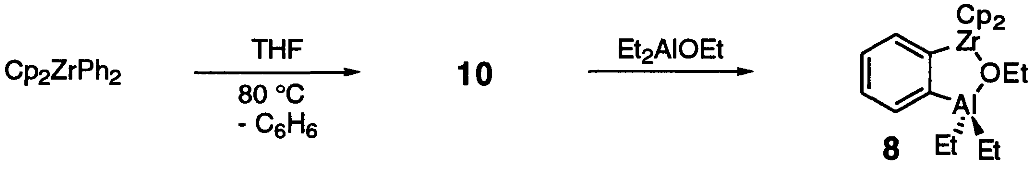
1.3)



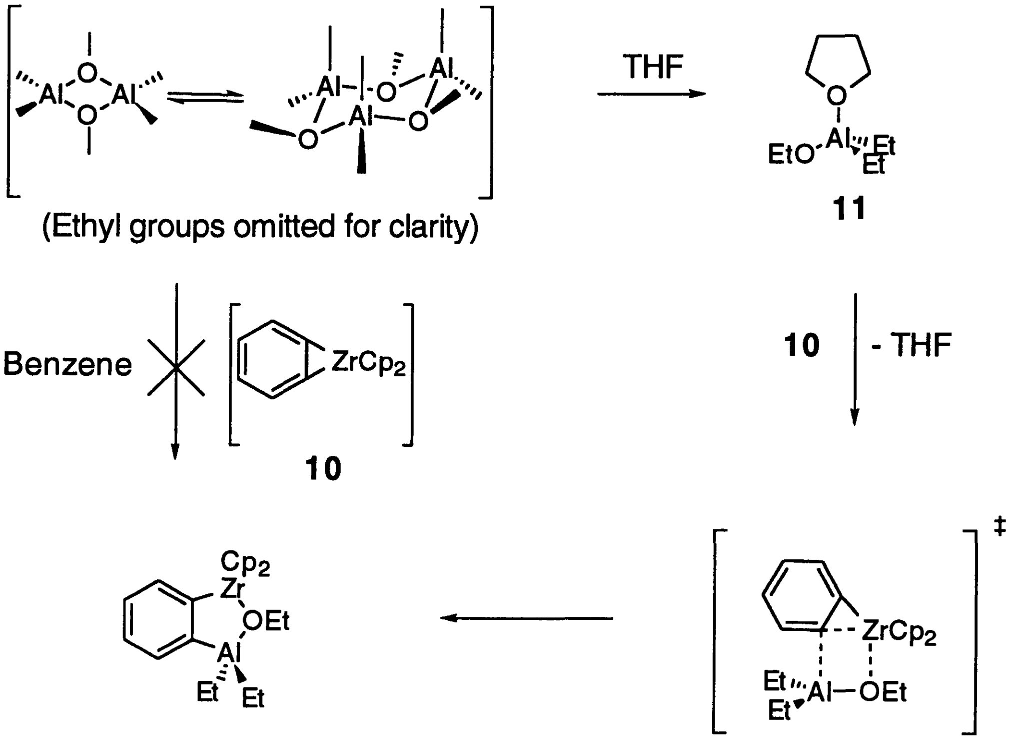
1.4)



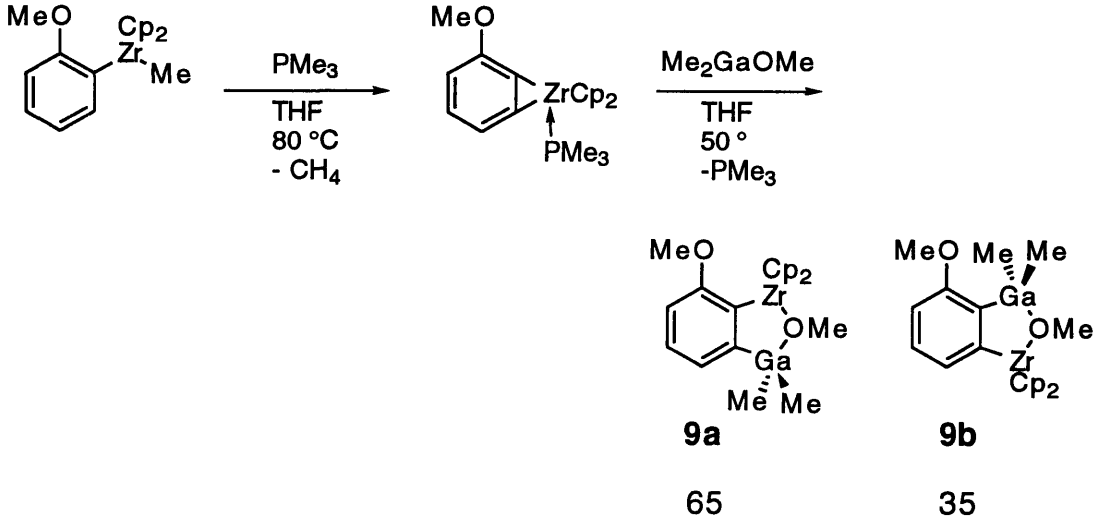
While the reactions of borates and borinates with **10** proceed in benzene, the reaction of Et_2AlOEt and **10** requires a more coordinating solvent and is therefore performed in THF (Equation 1.5). We attribute this solvent effect to the strong tendency of aluminum complexes to form heteroatom bridges.[32,33] These highly bridged structures presumably decrease the reactivity of the aluminum-oxygen bond towards the zirconium-carbon bond of **10** based on steric and electronic effects (Scheme 1.3). In a coordinating solvent such as THF, the oligomers are broken up by the interaction of THF forming a monomer such as **11** which then reacts with **10**.

1.5)


Scheme 1.3: Structure of Et_2AlOMe and Reaction with **10**.



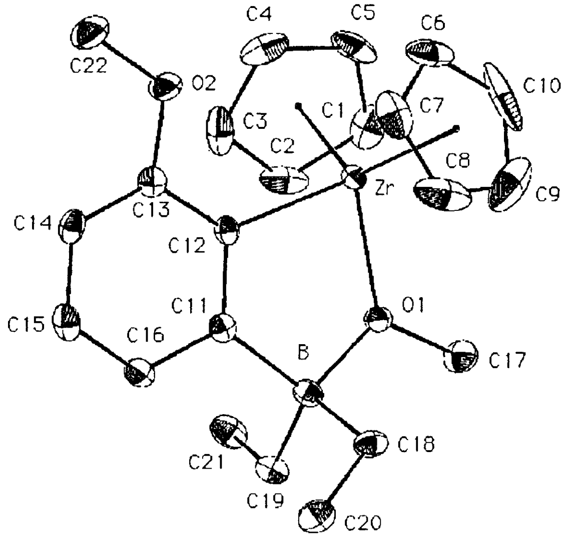
Facile ligand exchange between the phenyl ligands on Cp_2ZrPh_2 and the methoxy ligands on Me_2GaOMe precludes formation of the desired zirconium gallium heterobimetallic complex by the *in situ* generation of **10**. However, reaction of the PMe_3 adduct of **10** (**10·PMe_3**), with Me_2GaOMe forms the desired insertion product, although it was not possible to isolate the product cleanly (~ 80 % by ^{1}H NMR). The anisole derivative **9**, was isolated in a 52 % yield as a 65:35 mixture of isomers **a** and **b** (Equation 1.6).[33] The lack of regioselectivity is in contrast to the boron reagents.

1.6) 

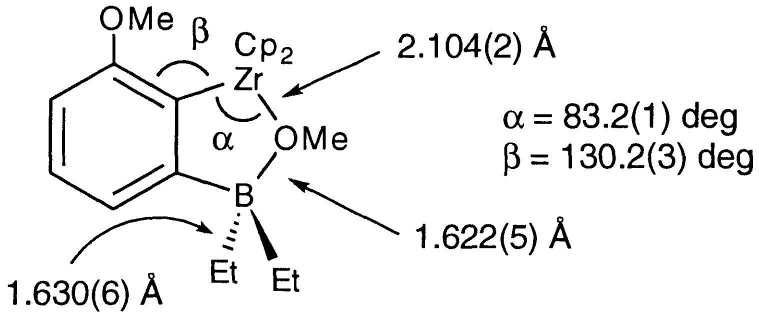
Structures of the Heterobimetallic Complexes.

Single crystals of **6** suitable for X-ray structure determination were obtained by the slow diffusion of pentane into a saturated toluene solution of **6**. An ORTEP diagram of **6** is shown in Figure 1.2 along with a pictorial representation showing some important bond lengths and angles.

Figure 1.2: ORTEP drawing and Picture of **6**.



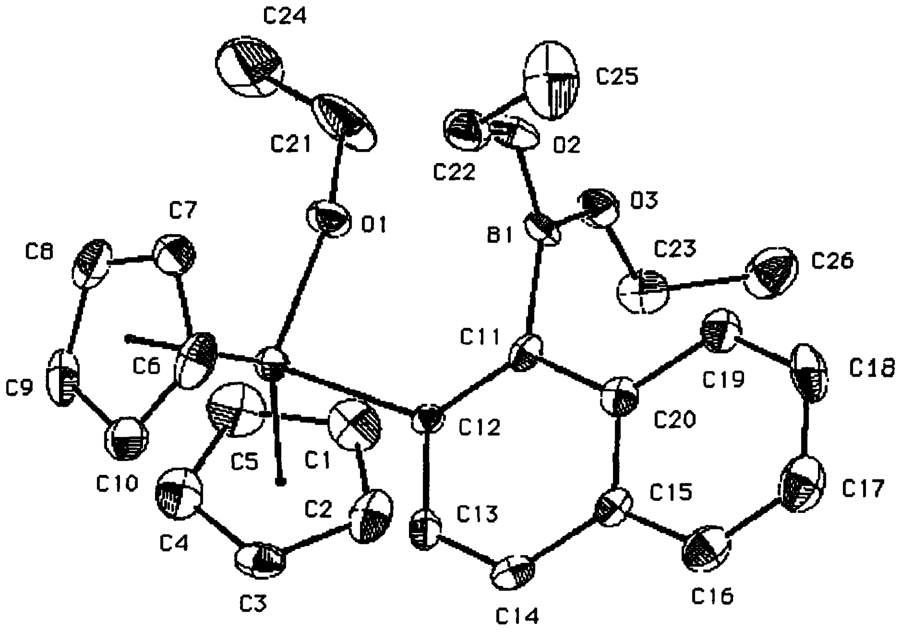
thermal ellipsoids at 35 % probability



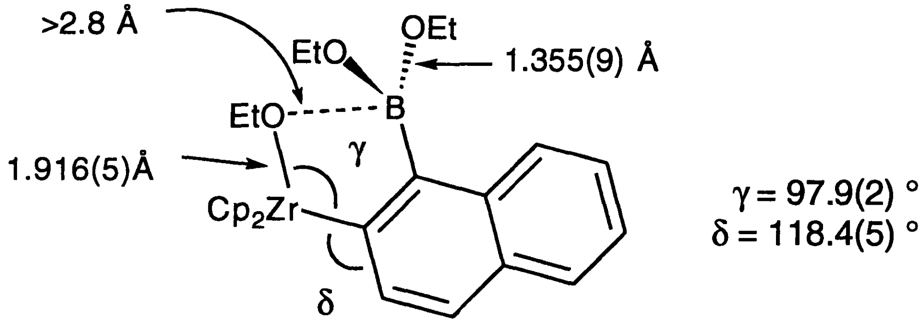
6

Likewise the structure of **7** was also determined by X-Ray crystallography. Single crystals of **7** were obtained by the diffusion of pentane into a saturated toluene solution of **7** at -40 °C over a two week period. There are two fragments in the unit cell of **7** where fragment 2 has some disorder in an ethyl group but otherwise is the same as fragment 1. Figure 1.3 shows an ORTEP diagram of **7** fragment 1 and a picture showing important bond lengths and angles.

Figure 1.3: ORTEP drawing of **7** (fragment 1) and Picture.



thermal ellipsoids at 35% probability



7

Comparison of **6** and **7** reveal some important differences. For example, the B-O(1) bond length in **6** of 1.622(5) Å is slightly longer than the sum of covalent radii of boron and oxygen (1.54 Å),[35-37] which is consistent with a dative interaction between these two atoms. In contrast, the B-O(1) distance in **7** is greater than 2.8 Å, implying that there is no significant bonding interaction. In **6**, the coordination environment of boron is almost tetrahedral with an average boron to carbon bond distance of 1.630(6) Å. This distance is characteristic for tetracoordinate boron compounds (typically 1.62 - 1.65 Å).[33] The average boron-oxygen (ethoxy ligands) bond distance in **7** is 1.355(9), which is a typical value for a tricoordinate alkoxy boron compound (1.38 Å for $(EtO)_3B$). In **6** the aryl ring, boron, zirconium and oxygen are nearly coplanar.[38] Due to this planar geometry, zirconium-oxygen multiple bonding cannot occur. Consequently, the Zr-O(1) bond length of 2.104(2) Å is close to that expected for a zirconium-oxygen single bond (~2.0 Å).[39] In comparison, **7** has a Zr-O(1) bond length of 1.916(5) Å implying that there may be some multiple bond character in the zirconium-oxygen bond due to π-donation from an oxygen lone pair to an empty orbital on zirconium. The C(12)-Zr-O(1) bond angle (γ, Scheme 1.3) in **7** of 97.9(2) ° is in the range expected for a d^0 Cp_2ZrR_2 complex,[40] while the corresponding angle in **6** (β, scheme 1.3) of 83.2(1) is smaller than theoretically expected but close to that seen for other oxa-zirconacycles.[41-44]

The solution structures of compounds **4**, **5**, **6** and **7** were probed by ^{11}B NMR. The chemical shifts indicated that the boron atoms in **4**, **5** and **6** are tetracoordinate while in **7** the boron center is tricoordinate. For comparison, the chemical shifts of these zirconium-boron complexes and some related boron compounds are listed (Table 1.2). The chemical shifts of compounds **4** to **6** resemble those of a rich boron center, such as a borate. This similarity is consistent with a bridging alkoxide between the boron and zirconium in **4**, **5** and **6**. Likewise, the ^1H NMR spectra of **4** and **6** displayed diasteriotopic methylene protons consistent with a bridging structure. In contrast, the ^{11}B NMR chemical shift for **7** suggests a boron center that is less electron rich, such as a borinate. For example, the chemical shift of **7** is very similar to that of $PhB(OMe)_2$.[35] These results suggest that there is no bridging alkoxy group between the boron and the zirconium of **7** in solution or in the solid state.

Table 1.2: Representative ^{11}B NMR Chemical Shifts.

Borane	δ (ppm,$BF_3{\cdot}Et_2O$ = 0)
$Li[B(Ph)_4]^a$	-16.6
$Li[B(OMe)_4]^a$	2.7
4	7.13
5	1.1
6	8.3
$PhB(OMe)_2^b$	28.7
7	29.7

[a]see ref 35. [b]see Ref 45

The difference in the structures of **4** - **6** relative to **7** can be rationalized by the electronic nature of the boron center. In **7**, π-donation from an oxygen lone pair partially fills the empty p-orbital on the boron and decreases its tendency to bridge. Since no π-donation is available for **4** to **6**, the electrophilic boron center takes on an additional ligand in the form of a bridging methoxy group.

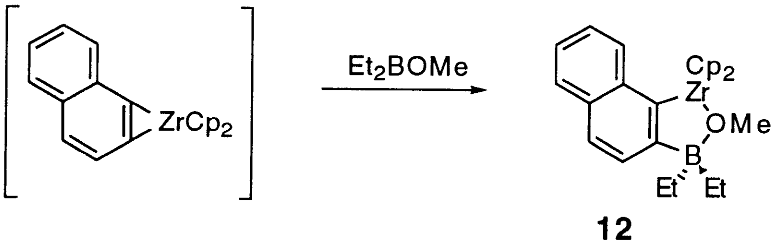
The structure of the Et_2AlOEt inserted product **8** was elucidated by ^1H NMR. The spectrum displays diasteriotopic methylene protons of the two ethyl groups attached to the Aluminum, consistent with a bridging alkoxy ligand between the zirconium and the aluminum. The bridging alkoxide is not surprising as aluminum is both larger and more oxophilic than boron.[46]

In the case of the gallium analog **9**, there is no firm evidence of an alkoxy bridge between the two metals. Although gallium is slightly smaller and less oxophilic than aluminum,[46] it still is more oxophilic and larger than boron. It is therefore reasonable to assign a connectivity where the methoxy group bridges between the two metals.

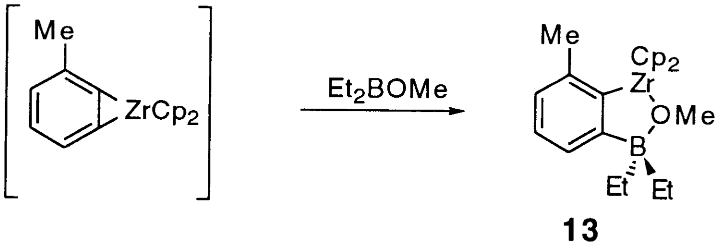
Reagent Controlled Regioselectivity and Regiochemistry.

The reaction of Et_2BOMe with zirconocene stabilized benzynes gives the expected kinetic products **6**, **12** and **13** (Equations 1.7 to 1.9). These insertion reactions are highly regioselective as seen by ^1H NMR. In contrast, the reaction of $(EtO)_3B$ with zirconocene stabilized benzynes leads to **7**, and **14** (Equations 1.10 and 1.11) where the boron reagent ultimately approaches from the more congested side of the benzyne. In the reaction of $(EtO)_3B$ with the zirconium complex of 3-methoxy benzyne, two isomers are obtained (**15a** and **15b**, Equation 1.12). The ratio of these isomers is temperature dependent (Table 1.3). At room temperature the reaction gives mostly **15b** (**a** to **b**, 5:95), while at 110 °C the ratio is reversed (**a** to **b**, 79:21). At 80 °C, equilibration is slow and the ratio after one week is 50:50. The product mixture obtained in the room temperature reaction is presumably under kinetic control while the mixture obtained at 110 °C represents a thermodynamic distribution.

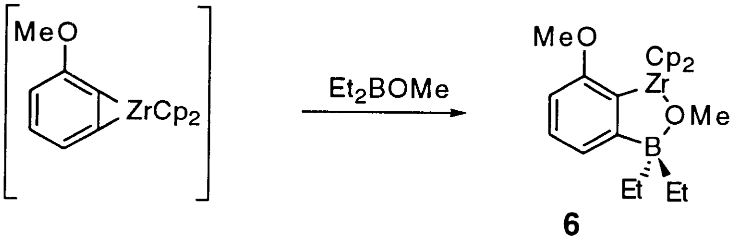
1.7)



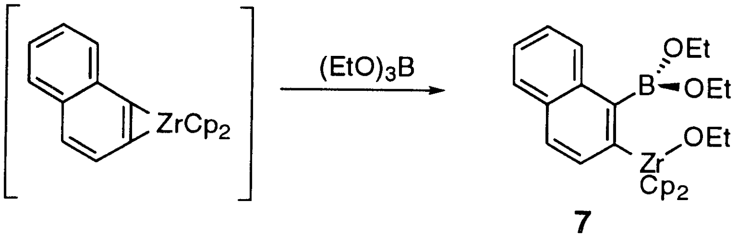
1.8)



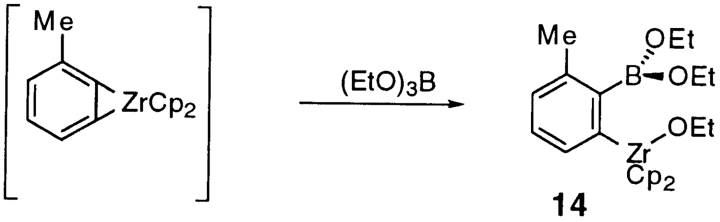
1.9)



1.10)



1.11)



1.12)

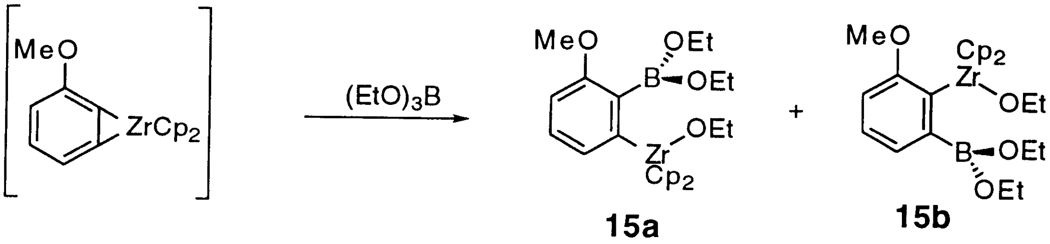
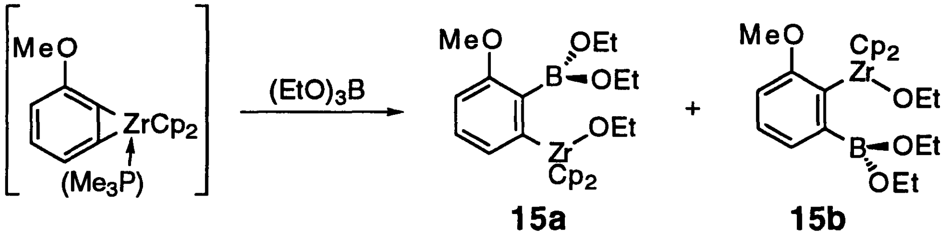
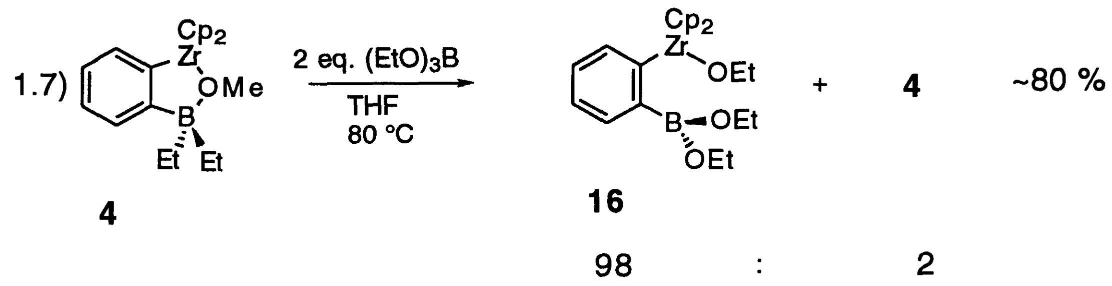


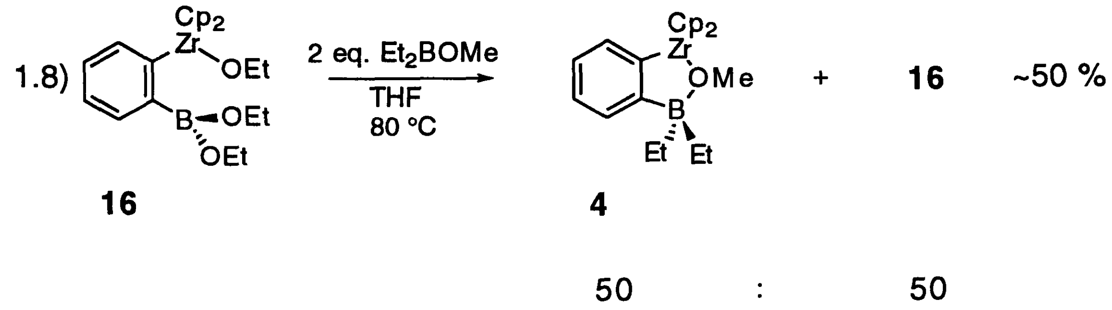
Table 1.3: Temperature Dependence on Ratio of **15a** to **15b**.



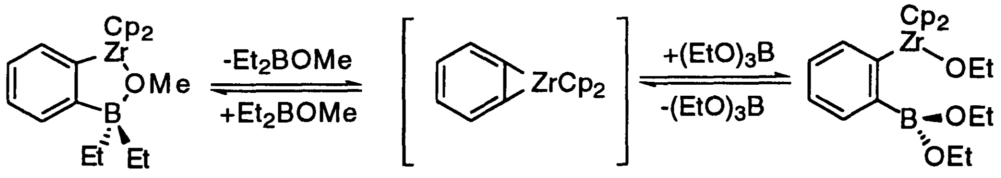
Temperature	Ratio	
25 °C	5	95
80 °C	50	50
110 °C	79	21

The insertion of the boron reagents into the zirconium-carbon bonds of benzynes is reversible. The reaction of **4** with excess Et$_2$BOMe gives **16** (Equation 1.7). This implies that **4** loses Et$_2$BOMe generating **10** which then reacts with (EtO)$_3$B (Scheme 1.4). Likewise, the reaction of **16** with excess (EtO)$_3$B leads to the generation of some **4** (Equation 1.8). Similarly, this indicates the formation of **10** as a transient species *via* the loss of (EtO)$_3$B from **16** (Scheme 1.4). The reversibility of these insertion reactions is not surprising in light of Erker's work on other insertion chemistry with zirconocene benzynes.[47]





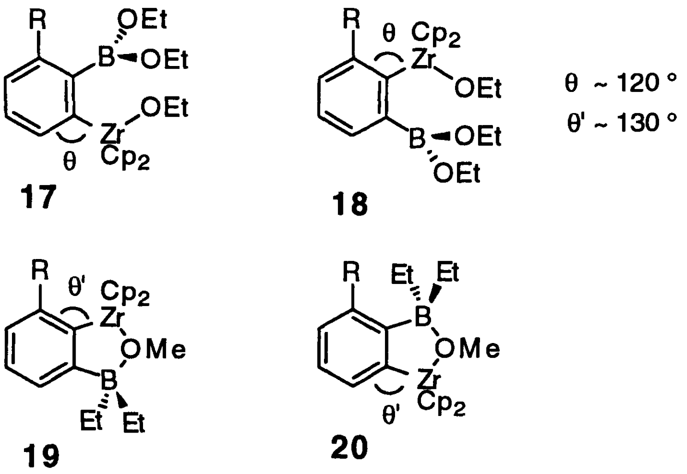
Scheme 1.4: Reversible Benzyne formation from **4** and **16**.



4 **10** **16**

The greater stability of **17** (Figure 1.4) and related compounds relative to the corresponding regioisomers (eg. **18**) is probably steric in nature. In **18** the substituent on the aromatic ring (R) is positioned close to the large zirconocene fragment while in **17** the aromatic substituent is positioned next to the relatively small $B(OEt)_2$ fragment (Figure 1.4). Similar arguments could be applied to compare the relative stabilities of **19** and **20** (Figure 1.4). As previously noted, however, only **19**[47] is observed when a substituted benzyne is generated in the presence of Et_2BOMe. This may be due to the methoxy group which bridges between the zirconium and boron in **19**, pulling the zirconium away from the substituent R, leading to a lessening of the steric interaction between R and the zirconocene fragment in **19**. The boron centered group in **20** is also effectively larger than that in **17**, since it is sp^3 hybridized, exacerbating the interaction of R with the BEt_2 fragment in **20** relative to that of R with the $B(OEt)_2$ fragment in **17**.

Figure 1.4: Regiochemistry.



In the case of the reaction between Me_2GaOMe with the methoxy substituted benzyne, it is not clear why two isomers (**9a** and **9b**) are observed. We suspected that **9a** might be favored kinetically while **9b** predominates under thermodynamic conditions. Heating the mixture **9a** and **9b** to higher temperatures leads to a change in the ratios of **9a** to **9b** (65:35 for **a** to **b** at 50 °C, 32:38 for **a** to **b** at 110 °C) but significant decomposition to unknown products also occurs, diminishing the relevance of this observation. The structure of **9** may be important in understanding the observed isomeric distribution, although attempts to grow single crystals of **9** or an analog suitable for X-ray crystallographic analysis have been unsuccessful.

Conclusion.

We have prepared a series of zirconium-group 13 heterobimetallic compounds by the reaction of zirconocene-aryne complexes and main group complexes containing alkoxy ligands. The crystal structures of zirconium-boron heterobimetallic complexes **6** and **7** as well as ^{11}B NMR show these to have very different structures both in the solid state and in solution. The most important difference in the structures of **6** and **7** is that **6** contains a methoxy ligand bonded to boron and zirconium while **7** has no bridging alkoxide. We believe that this structural difference causes different intermolecular steric interactions in **6** and **7**, accounting, at least in part, for the different regioselectivity observed in the reactions to form these complexes.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of purified argon or nitrogen using standard Schlenk techniques. Transfer and storage of air sensitive, moisture sensitive or hygroscopic materials were performed in a Vacuum Atmospheres Co. dry box under an atmosphere of nitrogen. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity-300 or a Varian XL-300 Fourier transform spectrometer. Melting points were determined with a Haake Buchler melting point apparatus and are uncorrected. Gas chromatography (GC) analyses were performed on a Hewlett-Packard model 5890 gas chromatograph with a flame ionization detector and a model 3392A integrator using a 25 meter capillary column with polymethylsiloxane (Hewlett-

Packard) as a stationary phase. Combustion analysis was performed by E&R Microanalytical Laboratory, Corona, NY.

Tetrahydrofuran (THF), toluene and pentane were dried and deoxygenated by refluxing and distilling from sodium / benzophenone ketyl under an argon atmosphere. Diphenylzirconocene was prepared by the reaction of zirconocene dichloride with phenylmagnesium bromide.[49, 50] Zirconocene methyl chloride[51] and Me_2GaOMe[52] were prepared by the published procedures. All other reagents were commercially available and used without further purification.

Preparation of $Et_2B(\mu\text{-}OMe)(\mu\text{-}1,2\text{-}benzene)ZrCp_2$ (4). A dry sealable Schlenk tube with a stirring bar was charged with diphenylzirconocene (0.376 g, 1 mmol) in a glove box. The flask was removed from the glove box and attached to a Schlenk line, and THF (10 mL) was added. Et_2BOMe (0.26 mL, 2 mmol) was added *via* syringe. The flask was sealed and heated in an oil bath at 80 °C for 18 h. After allowing the reaction mixture to cool to room temperature, the volatiles were removed *in vacuo* . The crude boron-zirconium complex was redissolved in toluene (5 mL) and pure product was precipitated from the solution upon slow addition of pentane (20 mL) and cooling in an ice bath. The solvents were decanted from the solids *via* cannula filtration and the product was washed twice with cold pentane (10 mL). Residual solvents were removed *in vacuo* to give **4**, 0.310g (78 %) as a bright yellow powder: ^1H NMR (300 MHz, CD_2Cl_2): δ 0.53 (m, 4H), 0.71 (t, J=7.2 Hz, 6H), 3.16 (s, 3H), 6.30 (s, 10H), 6.91 (m, 3H), 7.15 (d, J =6.3 Hz, 1H); ^{13}C NMR (300 MHz, THF-d_8): δ 11.66, 15.33 (broad), 52.71, 114.85, 124.09, 125.14, 133.75, 135.69, 193.80; ^{11}B NMR (300 MHz, C_6D_6, $BF_3{\cdot}OEt_2$ ext. ref.) δ 7.13; mp 118-124 °C; Anal. Calcd for $C_{21}H_{27}OZrB$: C, 63.46; H, 6.85. Found: C, 63.30; H, 6.63.

Preparation of $Me_2B(\mu\text{-}OEt)(\mu\text{-}1,2\text{-benzene})ZrCp_2$ (5). Compound **5** was made in a similar fashion as **4** except that Me_2BOEt (0.28 g, 2 mmol) was used instead of Et_2BOMe. The yield for **5** was 0.207g (54 %) of a bright yellow powder: ^1H NMR (300 MHz, CD_2Cl_2): δ -0.11(s, 6H), 1.24 (t, *J* =7.0 Hz, 3H), 3.83 (q, *J* =7.2 Hz, 2H), 6.16 (s, 10H), 6.88 (dd, *J* =7.2 Hz, 1H), 6.93 (dd, *J* =7.2 Hz, 1H), 7.16 (d, *J* =6.9 Hz, 1H), 7.20 (d, *J* =6.6 Hz, 1H); ^{13}C NMR (300 MHz, THF-d_8): δ 11.05 (broad), 18.40, 64.86, 113.43, 124.65, 125.84, 134.75, 136.02, 192.73; ^{11}B NMR (300 MHz, C_6D_6, $BF_3{\cdot}OEt_2$ ext. ref.) δ 1.14; mp 146-147 °C; Anal. Calcd for $C_{20}H_{25}OZrB$: C, 62.62; H, 6.57. Found: C, 62.30; H, 6.35.

Preparation of $Et_2B(\mu\text{-}OMe)(\mu\text{-}1,2\text{-anisole})ZrCp_2$ (6). A dry sealable Schlenk tube was charged with zirconocene (methyl) chloride (1.088 g, 4 mmol) in a glove box. The flask was removed from the glove box, attached to a Schlenk line, and THF (20 mL) was added. The flask was then charged with 2-bromoanisole (0.50 mL, 4 mmol) and cooled to -78 °C. Using a gas-tight syringe, *tert*-butyllithium (3.6 mL, 1.7 M in pentane, 6 mmol) was added. After 15 min, the flask was removed from the -78 °C bath and allowed to warm to room temperature. Et_2BOMe (1.05 mL, 8 mmol) was added *via* syringe, the flask was sealed and was then heated in an oil bath for 18 h at 80 °C. After allowing the reaction mixture to cool to room temperature, the volatiles were removed *in vacuo* . Residual THF was removed from the crude product by adding toluene (10 mL) and removing this under vacuum. The product was dissolved in toluene (10 mL) and the resulting solution cannula filtered from the solid impurities to a round bottom Schlenk flask. The toluene was removed *in vacuo* to give a solid which was dissolved in a minimal quantity of toluene (~5 mL). Product precipitated out of the solution upon slow addition of pentane (20 mL) and cooling in an ice bath. The solvents were decanted using a cannula filter and the remaining solid was washed twice with cold pentane (5 mL).

Residual solvents were removed *in vacuo* to give 0.889 g (52 %) of yellow product: ^{1}H NMR (300 MHz, C_6D_6): δ 0.94 (m, 4H), 1.20 (t, *J* =7.6 Hz, 6H), 2.65 (s, 3H), 3.40 (s, 3H), 5.98 (s, 10H), 6.43 (d, *J* =7.1 Hz, 1H), 7.28 (m, 2H); ^{13}C NMR (300 MHz, THF-d_8): δ 11.72, 15.26, 52.21, 54.56, 104.75, 114.65, 126.03, 127.37, 162.74, 178.04; ^{11}B NMR (300 MHz, C_6D_6, $BF_3{\cdot}OEt_2$ ext. ref.) δ 8.29; mp 149 - 154 °C; Anal. Calcd for $C_{22}H_{30}BO_2Zr$: C, 61.67; H, 7.06. Found: C, 61.62; H, 6.96.

Preparation of $(EtO)_2B(\mu$-1,2-naphthalene$)ZrCp_2(OEt)$ (7). A dry sealable Schlenk tube was charged with zirconocene (methyl) chloride (0.544 g, 2 mmol) in a glove box. The flask was removed from the glove box, attached to a Schlenk line, and THF (20 mL) was added. The flask was then charged with 1-bromonaphthalene (0.28 mL, 2 mmol) and cooled to -78 °C. Using a gas-tight syringe, *tert*-butyllithium (1.8 mL, 1.7 M in pentane, 3 mmol) was added. After 15 min, the flask was removed from the -78 °C bath and allowed to warm to 0 °C over 20 min. $(EtO)_3B$ (0.68 mL, 4 mmol) was added *via* syringe. The flask was sealed and was then heated in an oil bath for 5 h at 50 °C. After allowing the reaction mixture to cool to room temperature, the volatiles were removed *in vacuo*. Residual THF was removed from the crude product by the addition of toluene (10 mL) and removing this *in vacuo*. The product was dissolved in toluene (10 mL) and the resulting solution cannula filtered from the insoluble materials to a round bottom Schlenk flask where the filtrate was concentrated *in vacuo* . Crystals and powdered product were obtained from the crude product by diffusion of pentane into a concentrated solution of the product in toluene at -40 °C over two weeks. The solids were isolated and residual solvents were removed *in vacuo*, to yield 0.543 g (55 %) of a mixture of yellow powder and crystals. ^{1}H NMR (300 MHz, C_6D_6): δ 1.03 (t, *J* =7.1 Hz, 3H), 1.17 (t, *J* =7.1 Hz, 6H), 3.96 (m, 4H), 4.00 (q, *J* =7.0 Hz, 2H), 5.92 (s, 10H), 7.40 (m, 3H), 7.63 (d, *J* =8.1 Hz, 1H), 7.81 (d, *J* =8.1 Hz, 1H), 7.98 (d, *J*

=8.1 Hz, 1H); ^{13}C NMR (300 MHz, THF-d_8): δ 17.88, 20.79, 60.37, 69.81, 112.23, 123.48, 124.56, 125.23, 127.87, 129.15, 132.13, 136.73, 136.88, 180.68; ^{11}B NMR (300 MHz, C_6D_6, $BF_3{\cdot}OEt_2$ ext. ref.) δ 29.65; mp 115-120 °C; Anal. Calcd for Calcd for $C_{26}H_{31}O_3ZrB$: C, 63.27; H, 6.33. Found: C, 63.26; H, 6.58.

Preparation of $Et_2Al(\mu\text{-}OEt)(\mu\text{-}1,2\text{-benzene})ZrCp_2$ (8). A dry sealable Schlenk tube with a stirring bar was charged with diphenylzirconocene (0.376 g, 1 mmol) in a glove box. The flask was removed from the glove box, attached to a Schlenk line, and THF (10 mL) was added. Et_2AlOEt (0.63 mL, 1.6 M in toluene, 1 mmol) was added *via* syringe. The flask was sealed and the solution was heated in an oil bath for 18 h at 80 °C. After allowing the reaction mixture to cool to room temperature, the volatiles were removed *in vacuo*. Residual THF was removed from the crude product by addition of toluene (10 mL) and removing the solvent mixture under vacuum. Pentane (10 mL) was added to the crude aluminum-zirconium complex and the flask was sonicated for 30 min leading to a brown suspension in an orange solution. The solution was cannula filtered into a round bottom Schlenk flask and the solvents were removed under vacuum until approximately 2 mL of solution remained as well as an orange precipitate. The flask was cooled in an ice bath while the solvents were decanted from the solids. Residual solvents were removed *in vacuo* leaving 0.188 g (44 %) of a light orange-brown powder: ^1H NMR (300 MHz, C_6D_6): δ 0.27 (m, 4H), 1.15 (t, J=6.9 Hz, 3H), 1.35 (t, J=8.0 Hz, 6H), 3.34 (q, J=6.9 Hz, 2H), 5.54 (s, 10H), 7.21 (m, 2H), 7.56 (m, 1H), 7.98 (m, 1H); ^{13}C NMR (300 MHz, THF-d_8): δ 1.46 (broad), 10.36, 18.47, 67.27, 109.98, 126.55, 127.66, 133.70, 139.25, 201.81; mp 96 - 98 °C; Anal. Calcd for $C_{22}H_{29}OZrAl$: C, 61.79; H, 6.83. Found: C, 61.73; H, 6.90.

Preparation of $Me_2Ga(\mu\text{-}OMe)(\mu\text{-}1,2\text{-benzene})ZrCp_2$ (9a, b). A dry sealable Schlenk tube was charged with zirconocene(methyl)chloride (0.544 g, 2 mmol) in a glove box. The flask was removed from the glove box, attached to a Schlenk line, and THF (20 mL) was added. The flask was then charged with 2-bromoanisole (0.25 mL, 2 mmol) and cooled to -78 °C. Using a gas-tight syringe, *tert*-butyllithium (1.8 mL, 1.7 M in pentane, 3 mmol) was added. After 15 min, the flask was removed from the -78 °C bath and allowed to warm to room temperature. PMe_3 (1 mL, 10 mmol) was added to the solution *via* syringe. The flask was sealed and was then heated in an oil bath for 18 h at 80 °C. After allowing the reaction mixture to cool to room temperature, the volatiles were removed *in vacuo* . THF (20 mL) was added to dissolve the solids and Me_2GaOMe (0.288g, 2.2 mmol) was added to the solution. The flask was again sealed and was heated in an oil bath at 50 °C for 6 h. The flask was removed from the oil bath and after cooling to room temperature, the solvents were removed *in vacuo.* Residual THF was removed from the crude product by addition of toluene (10 mL) and removing this under vacuum. Pentane (50 mL) was added to the product and the flask was sonicated for 1 h. The solution was cannula filtered from the solids and concentrated to approximately 3 mL. The solution was cooled in an ice bath and decanted from the precipitates that had formed. Residual solvent was removed *in vacuo* leaving 0.477 g (52 %) of an off-white powder which was a mixture of the two isomers **9a** and **9b** in the ratio of 65:35[34] respectively. When the reaction was run at approximately 110 °C,[53], a yield of 0.266 g (29 %) was obtained where the ratio of **9a** to **9b** was 32:68: **9a**; ^1H NMR (300 MHz, C_6D_6): δ 0.01 (s, 6H), 3.09 (s, 3H), 3.49 (s, 3H), 5.78 (s, 10H), 6.38 (dd, *J* =6.0, 3.0 Hz, 2H), 7.23 (d, *J* =3.0 Hz, 1H), 7.24 (d, *J* =6.0 Hz, 1H);^{13}C NMR (300 MHz, THF-d_8): δ 7.32, 54.99, 58.29, 107.64, 128.60, 130.15, 163.10, 199.38; **9b;** ^1H NMR (300 MHz, C_6D_6): δ 0.08 (s, 6H), 3.15 (s, 3H), 3.43 (s, 3H), 5.66 (s, 10H), 6.42 (d, *J* =7.8 Hz, 1H), 7.10 (d, *J* =6.9 Hz, 1H), 7.28 (dd, *J* =7.5 Hz, 2H);^{13}C NMR (300 MHz, THF-d_8): δ 6.78, 55.22, 57,83, 106.77,112.21, 128.43, 129.59, 166.26, 199.38; Anal. Calcd for $C_{20}H_{25}O_2ZrGa$: C, 52.41 H, 5.50. Found: C, 52.23; H, 5.57.

Thermal Decomposition of 9. A 25 mg sample of **9** made at 50 °C as outlined above was loaded into a sealable NMR tube. The sample was dissolved in THF-d_8 and excess Me_2GaOMe was added to the sample. The NMR tube was sealed. Heating at 80 °C for 12 h led to a 10 % decomposition of **9** and appearance of impurities as seen by ^1H NMR.

Preparation of $(EtO)_2B(\mu$-1,2-anisole)$ZrCp_2(OEt)$ (13a, 15a). The procedure used is the same as that for **6** except that: (1) $(EtO)_3B$ (0.34 mL, 2 mmol) was used instead of Et_2BOMe, (2) three different reaction temperatures were used leading to different ratios of **15a** to **15b** and, (3) the product could not be isolated cleanly and so its structure was deduced by conversion to methoxy phenol. Integration of ^1H NMR cyclopentadiene resonances of **15a** (δ 5.81) and **15b** (δ 6.00) were used for determination of the isomeric ratios listed in Table 5.

Temperature dependence of the product ratio: These experiments were done in toluene-d_8[54] with mesitylene as an internal standard. The room temperature reaction was done using the PMe_3 stabilized methoxy substituted benzyne as in the synthesis of **9**, and the ratio of **15a** to **15b** observed was 95:5. The reaction run at 80 °C gave a ratio of **15a** to **15b** of 50:50 after heating for one week. At 110 °C,[53] the product ratio of **15a** and **15b** was 21:79 after 18 hours.

Derivatization: The reaction to synthesize **15a** and **15b** was done at 110 °C in THF. The solvents were removed from the crude **15a** and **15b** product and this was redisolved in THF. An aqueous solution of HCl (2 mL, 10 %) was added *via* syringe. The reaction flask was cooled in an ice bath and NaOH (5 mL, 3 M) was added dropwise followed by the dropwise addition of H_2O_2 (3 mL, 30 %). This was allowed to stir for 15 min at 0 °C and then allowed to warm up to room temperature.

Excess sodium thiosulfate was used to quench the reaction and the crude product was extracted in ether (3 X 50 mL). The product was dried over magnesium sulfate and concentrated *in vacuo*. The GC and ^{1}H NMR showed two main products of > 95 % purity in a ratio of 7:3. Comparison with purchased materials showed 2-methoxyphenol (70 %) and 3-methoxyphenol (30 %).

Study on The Reversible Insertions of Et_2BOMe and $(EtO)_3B$.

Reaction of ***4*** *with* $(EtO)_3B$*:* Compound **4** (0.100 g, 0.23 mmol), $(EtO)_3B$ (85 µL, 0.50 mmol) and THF (2.0 mL) were loaded into a sealable Schlenk equipped with a stir bar. The Schlenk flask was sealed and set to heat at 80 °C for 12 h. Analysis of the products by ^{1}H NMR showed **16** in about 80 % yield and **4** in less than 5% yield. The rest of the products were not identified.

Reaction of ***16*** *with* Et_2BOMe*:* Compound **16** was made by the reaction of Cp_2ZrPh_2 with $(EtO)_3B$. Removal of volatiles gave crude **16** (~ 85 % clean by ^{1}H NMR). The crude **16** (0.100g, 0.25 mmol), Et_2BOMe (66 µL, 0.5 mmol) and THF (2 mL) were loaded into a sealable Schlenk tube. The mixture was heated at 80 °C for 12 h. Analysis by ^{1}H NMR showed about 50 % decomposition products that were not identified, 25 % **4** and 25 % **16**.

X-ray Data Collection, Structure Determination and Refinement.

General Comments

A summary of the data collection parameters is given in Table 1.4. The crystals were mounted on a glass fiber. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo $K\alpha$ radiation. Cell constants, listed in Table 1.4, and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range of $14.00 < 2\theta < 22.00$ °.

The data was collected at -86 °C using the ω-2θ scan technique. Moving crystal moving counter background measurements were made by scanning an additional 25 % above and below the scan range. The counter aperture consisted of a variable horizontal slit with a width ranging from 2.0 to 2.5 mm and a vertical slit set to 2.0 mm. The diameter of the incident beam collimator was 0.7 mm and the crystal to detector distance was 21 cm. For intense reflections an attenuator was automatically inserted in front of the detector.

An empirical absorption correction, using the program DIFABS,[55] was applied which resulted in the transmission factors listed in (Table 1.4). The intensities were corrected for Lorentz and polarization effects. A correction for secondary extinction was also applied. No decay corrections were required since the crystals displayed crystal and electronic stability.

The structure was solved using direct methods.[56,57] The non-hydrogen atoms were refined anisotropically.

Neutral atom scattering factors were taken from Cromer and Waber.[58] Anomalous dispersion effects were included in Fcalc; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[59] All calculations were performed using the TEXSAN[60] crystallographic software package of Molecular Structure Corporation.

Table 1.4: Crystal Data for **6** and **7**.

Compound	**6**	**7**
mol formula	$C_{22}H_{29}BO_2Zr$	$C_{26}H_{31}BO_3Zr$
Mol Wt	428.51	493.56
Crystal color	orange	orange
Crystal habit	prismatic	prismatic
Cryst dimens, mm	0.380 X 0.320 X 0.430	0.280 X 0.410 X 0.320
a (Å)	9.4805(8)	8.242(1)
b (Å)	14.300(1)	16.628(1)
c (Å)	15.204(1)	17.700(1)
α (°)		89.92(3)
β (°)	101.84(2)	90.63(2)
γ (°)		90.36(3)
Cell vol ($Å^3$)	2017.4(6)	2425.5(6)
Space group	$P2_1/c$	P-1
Z	4	4
Dcalc (g/cm^3)	1.411	1.352
Diffractometer	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4
Radiation	Mo Kα (0.71069 Å)	Mo Kα (0.71069 Å)
Temperature (K)	86	86
Attenuator	Zr foil (factor = 17.9)	Zr foil (factor = 17.9)
Take off angle (°)	2.8	2.8
Scan rate, (°/min)	1.9 - 16.5 (in ω)	1.9 - 16.5 (in ω)
Scan width	$0.80 + 0.35 \tan\theta$	$0.80 + 0.35 \tan\theta$
2θ max (°)°	49.9	45.1
Reflctns measd	3934	7041
Unique reflections	3700	607
Corrections:		
Lorenz-Polarization	0.87 - 1.19	0.94 - 1.05
abs	(trans. factors)	(trans. factors)
Secondary Extinctn	0.95402 X 10-7 (coeff)	0.26846 X 10-6 (coeff)
Obsd. reflctns	2791 (I > 3.00s(I))	(I > 3.00s(I))
No. Variables	236	569
R	0.039	0.049
Rw	0.041	0.052
Max/min in final diff. map (e-/$Å^3$)	0.41, -0.58	0.48, -0.67
GOF	3.64	1.43

*X-ray Data Collection, Structure Determination and Refinement for **6**.*

Based on the systematic absences of:

h0l: $l \neq 2n$

0k0: $k \neq 2n$

and the successful solution and refinement of the structure, the space group was determined to be $P2_1/c$.

The final cycle of full-matrix least-squares refinement was based on 2791 observed reflections ($I > 3.00s(I)$) and 236 variable parameters and converged (largest parameter shift was 0.00 times its esd) with $R = 0.039$ and $R_w = 0.041$.

The standard deviation of an observation of unit weight was 3.64. The weighting scheme was based on counting statistics and included a factor ($p = 0.02$) to downweight the intense reflections. Plots of $\Sigma\, w\, (|F_o| - |F_c|)^2$ *vs* $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.41 and -0.58 $e^-/Å^3$, respectively.

The final values for refined coordinates of **6** are given in Table 1.5. Some important bond lengths and angles are given in Table 1.6.

Table 1.5: Atomic Coordinates and B ($Å^2$) values for **6**.

Atoms	x	y	z	B(eq)
Zr	0.23690(4)	0.24212(2)	-0.00152(2)	1.54(1)
O(1)	0.4603(3)	0.2206(2)	0.0146(2)	1.8(1)
O(2)	0.0284(3)	0.3792(2)	-0.1646(2)	2.7(1)
C(1)	0.2416(6)	0.2876(3)	0.1588(3)	3.4(2)
C(2)	0.3100(5)	0.3604(4)	0.1224(3)	3.3(2)
C(3)	0.2053(7)	0.4036(3)	0.0566(3)	3.7(2)
C(4)	0.0759(5)	0.3574(4)	0.0535(3)	3.7(2)
C(5)	0.0981(5)	0.2876(4)	0.1157(3)	3.6(2)
C(6)	0.0154(5)	0.1469(4)	-0.0520(4)	3.9(2)
C(7)	0.0741(6)	0.1552(4)	-0.1271(3)	3.7(2)
C(8)	0.1988(7)	0.1086(5)	-0.1135(5)	5.3(3)
C(9)	0.2216(7)	0.0696(4)	-0.0311(7)	7.0(4)
C(10)	0.109(1)	0.0932(5)	0.0090(4)	6.3(3)
C(11)	0.4154(4)	0.3320(3)	-0.1209(2)	1.7(1)
C(12)	0.2679(4)	0.3306(3)	-0.1169(2)	1.7(1)
C(13)	0.1695(4)	0.3877(3)	-0.1749(3)	2.0(1)
C(14)	0.2119(5)	0.4467(3)	-0.2366(3)	2.2(2)
C(15)	0.3572(5)	0.4498(3)	-0.2394(3)	2.4(2)
C(16)	0.4564(4)	0.3947(3)	-0.1836(3)	2.2(2)
C(17)	0.5439(5)	0.1587(3)	0.0790(3)	2.7(2)
C(18)	0.5791(4)	0.1765(3)	-0.1213(3)	2.3(2)
C(19)	0.6820(4)	0.3186(3)	-0.0122(3)	2.3(2)
C(20)	0.6560(5)	0.2037(3)	-0.1959(3)	2.9(2)
C(21)	0.6635(5)	0.3905(3)	0.0586(3)	2.7(2)
C(22)	-0.0762(5)	0.4381(4)	-0.2181(4)	3.6(2)
B	0.5372(4)	0.2639(3)	-0.0623(3)	1.9(2)

Table 1.6: Bond Lengths and Angles in **6**.

Atoms	Length (A°)	Atoms	Angle (deg)
Zr-O(1)	2.104(2)	O(1)-Zr-C(12)	83.2(1)
Zr-C(12)	2.231(4)	Zr-C(12)-C(13)	130.2(3)
B-O(1)	1.622(5)	O(1)-B-C(11)	104.5(3)
B-C(18)	1.635(6)	O(1)-B-C(18)	107.4(3)
B-C(19)	1.627(6)	O(1)-B-C(19)	107.9(3)
B-C(11)	1.629(6)	C(11)-B-C(18)	112.4(3)
O(1)-C(17)	1.432(5)	C(11)-B-C(19)	113.8(3)
O(2)-C(22)	1.423(5)	C(18)-B-C(19)	110.3(3)
C(11)-C(12)	1.412(5)	C(11)-C(12)-C(13)	120.0(3)
C(12)-C(13)	1.406(5)	C(12)-C(13)-C(14)	122.2(4)
C(13)-C(14)	1.381(6)	C(13)-C(14)-C(15)	118.0(4)
C(14)-C(15)	1.388(6)	C(14)-C(15)-C(16)	121.3(4)
C(15)-C(16)	1.377(6)	C(11)-C(16)-C(15)	121.9(4)
C(16)-C(11)	1.420(6)	Zr-O(1)-B	116.8(2)
		Zr-O(1)-C(17)	124.9(2)
		B-O(1)-C(17)	117.5(3)

X-ray Data Collection, Structure Determination and Refinement for 7.

Based on the systematic absences of:

h0l: $l \neq 2n$

0k0: $k \neq 2n$

and the successful solution and refinement of the structure, the space group was determined to be $P2_1/c$.

The final cycle of full-matrix least-squares refinement was based on 4543 observed reflections (I > 3.00s(I)) and 569 variable parameters and converged (largest parameter shift was 0.00 times its esd) with R = 0.049 and R_w = 0.052.

The standard deviation of an observation of unit weight was 1.43. The weighting scheme was based on counting statistics and included a factor (p = 0.02) to downweight the intense reflections. Plots of Σ w $(|F_o| - |F_c|)^2$ *vs* $|F_o|$, reflection order in data collection, sin θ/λ, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.48 and -0.67 $e^-/\text{Å}^3$, respectively.

The final values for refined coordinates of **7** are given in Table 1.7. Some important bond lengths and angles are given in Table 1.8.

Table 1.7: Atomic Coordinates and B ($Å^2$) values for **7**.

Atoms	x	y	z	B(eq)
Zr(1)	0.22144(8)	0.02010(4)	0.79061(4)	1.95(3)
O(1)	-0.0045(5)	0.0392(3)	0.8068(3)	3.2(3)
O(2)	-0.2068(5)	-0.0096(3)	0.6626(3)	2.7(2)
O(3)	-0.2144(5)	-0.1064(3)	0.7513(3)	2.8(2)
C(1)	0.190(1)	-0.0750(5)	0.9021(5)	3.9(4)
C(2)	0.301(1)	-0.1104(4)	0.8553(4)	3.5(4)
C(3)	0.442(1)	-0.0616(5)	0.8544(4)	3.3(4)
C(4)	0.410(1)	0.0028(5)	0.9031(5)	3.8(4)
C(5)	0.256(1)	-0.0047(5)	0.9310(4)	4.0(5)
C(6)	0.319(1)	0.0902(4)	0.6715(4)	3.5(4)
C(7)	0.200(1)	0.1389(4)	0.6996(5)	3.2(4)
C(8)	0.253(1)	0.1698(4)	0.7680(5)	3.6(4)
C(9)	0.407(1)	0.1403(5)	0.7832(5)	3.9(4)
C(10)	0.449(1)	0.0912(4)	0.7235(5)	3.6(4)
C(11)	0.0457(8)	-0.1035(4)	0.6693(4)	2.0(3)
C(12)	0.1938(8)	-0.0758(4)	0.6975(4)	1.7(3)
C(13)	0.3367(8)	-0.1109(4)	0.6681(4)	2.4(3)
C(14)	0.3358(9)	-0.1693(4)	0.6137(4)	2.5(3)
C(15)	0.1869(9)	-0.1982(4)	0.5844(4)	2.3(3)
C(16)	0.181(1)	-0.2587(5)	0.5286(4)	3.5(4)
C(17)	0.037(1)	-0.2848(5)	0.5000(5)	4.1(5)
C(18)	-0.109(1)	-0.2513(5)	0.5240(4)	3.8(4)
C(19)	-0.1064(9)	-0.1937(4)	0.5791(4)	2.9(4)
C(20)	0.0419(9)	-0.1649(4)	0.6112(4)	2.3(3)
C(21)	-0.144(1)	0.0607(8)	0.8419(7)	9.9(8)
C(22)	-0.150(1)	0.0325(5)	0.5982(5)	3.6(4)
C(23)	-0.164(1)	-0.1747(5)	0.7930(4)	3.4(4)
C(24)	-0.149(1)	0.1292(7)	0.8855(7)	8.0(7)
C(25)	-0.254(1)	0.0149(6)	0.5312(5)	6.2(6)
C(26)	-0.286(1)	-0.2412(5)	0.7822(5)	4.6(5)
B(1)	-0.126(1)	-0.0707(5)	0.6966(4)	2.1(4)

Table 1.7: Continued.

Atoms	x	y	z	B(eq)
Zr(2)	0.22912(8)	0.51940(4)	0.71978(4)	1.82(3)
O(4)	0.4527(5)	0.5354(3)	0.6976(3)	2.5(2)
O(5)	0.6703(5)	0.4813(3)	0.8378(2)	2.2(2)
O(6)	0.6509(5)	0.3822(3)	0.7513(3)	2.7(2)
C(27)	0.134(1)	0.5889(4)	0.8392(4)	3.0(4)
C(28)	0.266(1)	0.6342(4)	0.8140(4)	3.1(4)
C(29)	0.224(1)	0.6693(4)	0.7444(5)	3.3(4)
C(30)	0.066(1)	0.6456(4)	0.7271(4)	3.0(4)
C(31)	0.0095(9)	0.5961(4)	0.7854(4)	2.9(4)
C(32)	0.172(1)	0.4948(5)	0.5809(4)	3.4(4)
C(33)	0.243(1)	0.4241(5)	0.6081(4)	3.3(4)
C(34)	0.137(1)	0.3884(4)	0.6595(4)	3.3(4)
C(35)	-0.0018(9)	0.4376(5)	0.6639(4)	3.0(4)
C(36)	0.021(1)	0.5014(4)	0.6141(4)	3.1(4)
C(37)	0.4052(8)	0.3938(4)	0.8410(4)	1.8(3)
C(38)	0.2577(8)	0.4238(4)	0.8143(4)	1.8(3)
C(39)	0.1124(8)	0.3922(4)	0.8467(4)	2.1(3)
C(40)	0.1144(8)	0.3364(4)	0.9024(4)	2.5(3)
C(41)	0.2615(8)	0.3051(4)	0.9306(4)	2.1(3)
C(42)	0.265(1)	0.2470(5)	0.9888(4)	3.4(4)
C(43)	0.409(1)	0.2187(5)	1.0164(5)	4.2(5)
C(44)	0.555(1)	0.2466(5)	0.9869(4)	3.8(4)
C(45)	0.5549(9)	0.3028(4)	0.9300(4)	2.9(4)
C(46)	0.4068(8)	0.3343(4)	0.9000(4)	2.0(3)
C(47)	0.597(1)	0.5564(6)	0.6627(5)	5.8(5)
C(48)	0.6320(9)	0.5255(4)	0.9035(4)	3.3(4)
C(49)	0.576(1)	0.3135(5)	0.7156(5)	4.3(5)
C(50)	0.588(1)	0.5980(7)	0.5942(6)	7.6(7)
C(51)	0.747(1)	0.5044(5)	0.9658(4)	4.0(4)
C(52)	0.644(3)	0.292(2)	0.648(1)	7(2)
C(52*)	0.715(3)	0.261(1)	0.694(2)	6(1)
B(2)	0.575(1)	0.4214(5)	0.8080(4)	1.9(4)

Table 1.8: Bond Lengths and Angles in **7**, fragment 1.

Atoms	Length (A°)	Atoms	Angle (deg)
Zr-O(1)	1.916(5)	O(1)-Zr-C(12)	97.9(2)
Zr-C(12)	2.302(6)	Zr-C(12)-C(13)	118.4(9)
B-O(1)	2.84(1)	Zr-O(1)-C(21)	160.2(6)
B-O(2)	1.357(9)	O(2)-B-C(11)	124.0(7)
B-O(3)	1.353(9)	O(3)-B-C(11)	123.5(7)
B-C(11)	1.60(1)	O(2)-B-O(3)	112.2(6)
O(1)-C(21)	1.36(1)	C(20)-C(11)-B	116.6(6)
O(2)-C(22)	1.417(9)	C(11)-C(12)-C(13)	117.3(6)
C(3)-C(23)	1.416(9)	C(12)-C(13)-C(14)	123.8(6)
C(11)-C(12)	1.391(9)	C(13)-C(14)-C(15)	119.7(6)
C(12)-C(13)	1.423(9)	C(14)-C(15)-C(16)	121.4(7)
C(13)-C(14)	1.368(9)	C(15)-C(16)-C(17)	120.7(7)
C(14)-C(15)	1.409(9)	C(16)-C(17)-C(18)	120.7(7)
C(15)-C(20)	1.407(9)	C(17)-C(18)-C(19)	119.8(7)
C(15)-C(16)	1.411(9)	C(18)-C(19)-C(20)	121.5(7)
C(16)-C(17)	1.35(1)	C(11)-C(20)-C(15)	120.6(6)
C(17)-C(18)	1.40(1)	C(11)-C(20)-C(19)	121.9(6)
C(18)-C(19)	1.37(1)	C(15)-C(20)-C(19)	117.5(6)
C(19)-C(20)	1.423(9)		
C(20)-C(11)	1.450(9)		

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CHAPTER 2:

THE REGIOSELECTIVE SYNTHESIS OF SUBSTITUTED AROMATIC COMPOUNDS.

Introduction

Aromatic rings are ubiquitous in organic chemistry, being found in molecules as diverse as alkaloids, nucleic acids and polymers. They are also found in many therapeutic agents as shown from the fact that of the top 20 pharmaceuticals prescribed in 1994 (US dollar value), 16 are compounds which contain aromatic rings.[1] Usually substituted aromatic compounds are used as synthons in organic chemistry rather than building the aromatic unit into the structure. Often, an aromatic compound is used as the starting reagent for the construction of more complex molecules. Although substituted aromatic compounds are found in many synthetic schemes, the synthesis of substituted aromatic compounds is not always a trivial endeavor. For example the synthesis of (aryloxy)cyclohexenone **1** (Scheme 2.1), the key intermediate for the tandem radical cyclization to the morphine like molecule **2**,[2] requires six steps starting from Isovanillin (3-hydroxy-4-methoxybenzaldehyde) **3** (32 % overall yield). Thus the synthesis of **1** hinges on the availability of a highly functionalized aromatic compound. Certainly many methods exist for the functionalization of aromatic systems, but regioselective synthesis are often difficult. One of the more elegant methods involves directed metallation.[3] The proportionally large need for substituted aromatic compounds as compared to their availability promises that there will be work in this area for some time to come. The insertion reactions of zirconocene benzene complexes are important in organic synthesis as a way to regioselectively synthesize substituted aromatic compounds. This has been the focus of some of the chemistry in the Buchwald group to date.[4,5] This chapter will deal with the use of the heterobimetallic compounds **4** and **5** (Figure 2.1), described in chapter 1, for the synthesis of 1,2,3-trisubstituted aromatic compounds.

Scheme 2.1: Radical Tandem Cyclization Approach to **2**

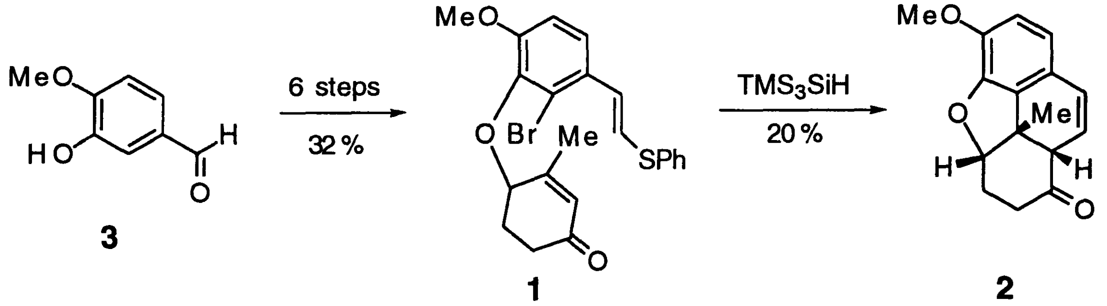
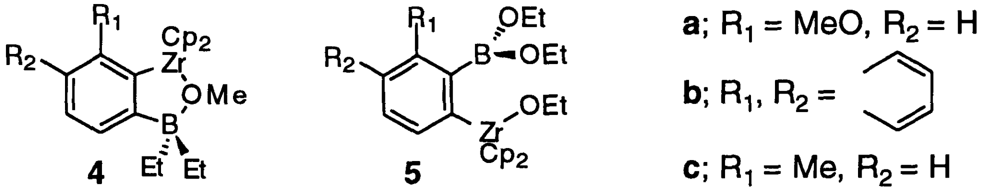


Figure 2.1: Heterobimetallic Compounds **4** and **5**.



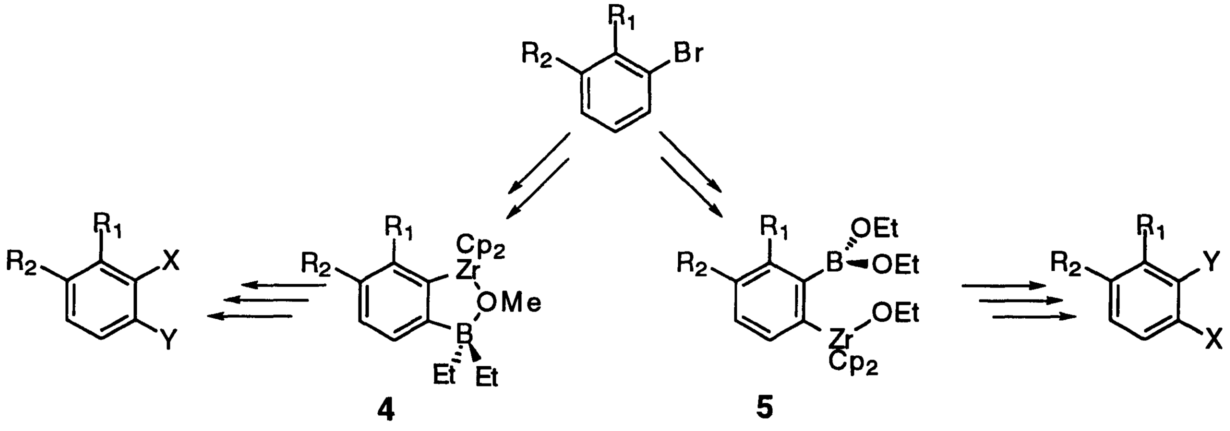
a; R_1 = MeO, R_2 = H

b; R_1, R_2 =

c; R_1 = Me, R_2 = H

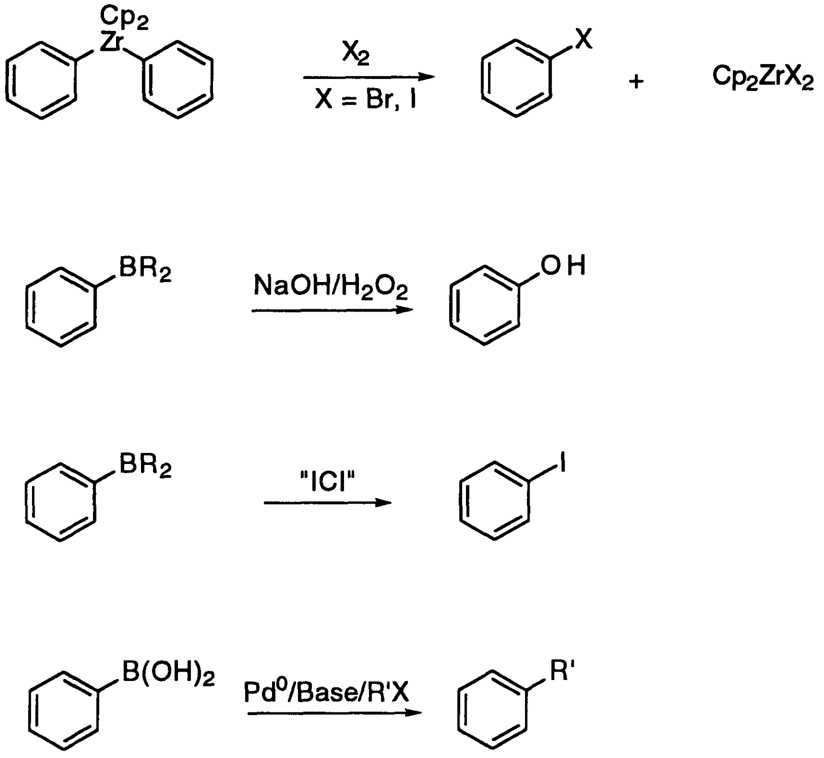
As noted in chapter 1, a significant difference from previous work in this area is that the regiochemistry of the insertion step is controlled to a great degree by the use of a borate or borinate respectively. This is particularly important for the development of an organic methodology for organic synthesis since different regioisomers can, in principle, be obtained using very similar reaction conditions and the same starting material (Scheme 2.2).

Scheme 2.2: Different Regioisomers Derived from the same Starting Material.



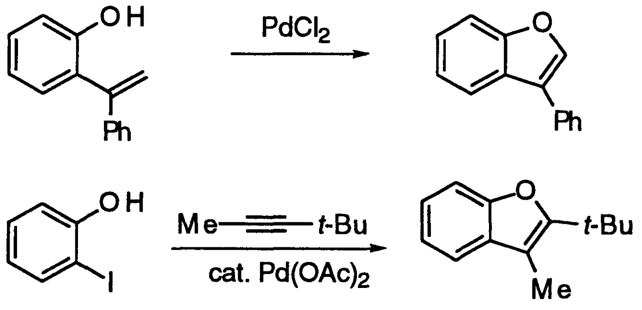
Compounds **4** and **5** allow for the independent transformations at both the zirconocene and boron fragment. Under appropriate conditions, a halognation cleaves the zirconium-aryl bond[6] but leaves the boron-aryl bond intact (Scheme 2.3). The boron-aryl bond can then be transformed via: oxidation to yield the phenol,[7] iodination to give the aryl iodide[8] and Suzuki coupling reactions to give biaryls[9]. The combination of halogenation and one of the previously mentioned transformations using **4** and **5**, therefore provides a method for the synthesis of halophenols, α-dihaloarenes and halogenated-biaryls.

Scheme 2.3: Some Possible Transformations at B-Aryl and Zr-Aryl bonds.

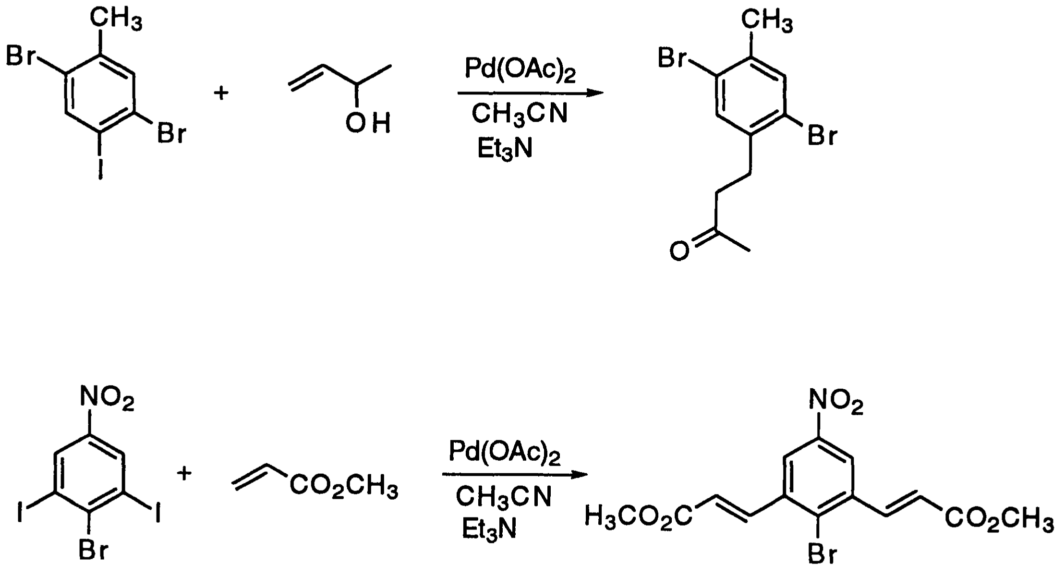


The first methodology discussed will be for the synthesis of halophenols which serve as important precursors in organic synthesis. For example, Larock has shown that benzofurans can be made from halophenols using various palladium mediated coupling reactions (Scheme 2.4).[10,11] The second method to be explored is for the synthesis of α-bromoiodoarenes. These compounds would be particularly useful as substrates in palladium-catalyzed cross-coupling reactions since Heck has shown that for polyhaloarenes, the reaction is faster at the iodide than at the bromide position (Scheme 2.5).[12] A third method allows for the synthesis of bromobiaryls. This method involves the coupling of an aryl halide with an aryl boronate ester (Suzuki cross-coupling reaction). The coupling of substituted biaryls is important for the synthesis of many natural products,[13] chiral auxiliaries[14] and polymeric materials.[15]

Scheme 2.4: Palladium Catalyzed Synthesis of Benzofurans From Phenols.



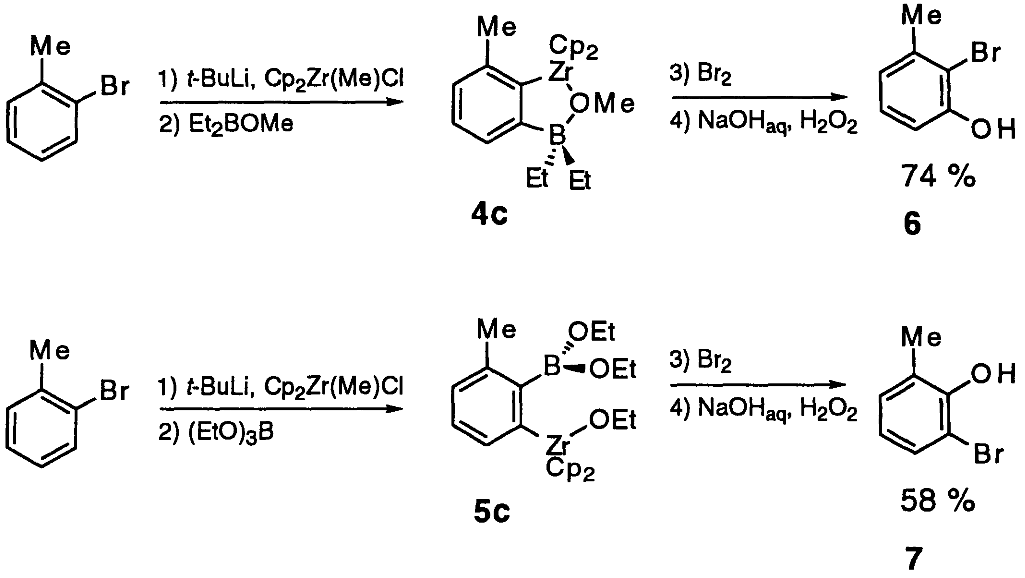
Scheme 2.5: Selective Alkylation of Polyhaloarenes.



Results and Discussion

Two examples of the construction of halophenols are the syntheses of 2-bromo-3-methylphenol and 2-bromo-5-methylphenol (Scheme 2.6). The first two steps leading to compounds **4c** and **5c** are discussed in chapter 1 (Scheme 1.4). Without isolation, compounds **4c** and **5c** are converted to **6** and **7** by bromination (iodination) followed by oxidation of the aryl borane. A list of the halophenols prepared by this method is given in Table 2.1. The yields are for the conversion of the aryl bromide substrate to the isolated product.

Scheme 2.6: The Synthesis of Halophenols **6** and **7**.



4c

74 %

6

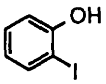
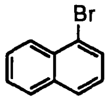
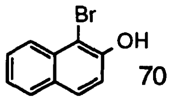
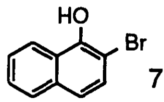
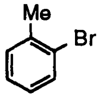
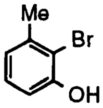
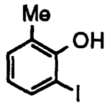
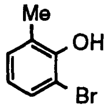
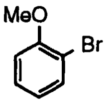
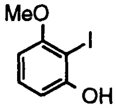
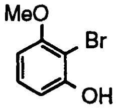
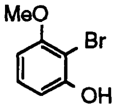
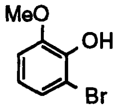
5c

58 %

7

The variety of methods reported for the synthesis of the products listed in Table 2.1 highlights the difficulty in making substituted halophenols in a regioselective fashion.[16-22] These methods often employ phenolic starting materials in which the hydroxyl substituent acts as a directing group for the halogenation. In this new method the starting material is an aryl bromide; therefore, the method is complementary to the previous strategy especially for systems where an aryl bromide is more readily available than the appropriate phenol. It is also a trivial conceptual leap to envision methods where directed metalation with a lithium reagent would provide halophenols from non-halogenated starting materials.[23] The key step in this new method is use of either Et_2BOMe or $(EtO)_3B$ which controls the regiochemistry of the following reactions. The strong features of this new method are its generality, ease of use, readily available starting materials, and excellent control of the regiochemistry.

Table 2.1: Yields for the Synthesis of Halophenols.

Substrate	Reagents	Isomer: A	B
Cp_2ZrPh_2	$(EtO)_3B$ I_2		 72 %
	Et_2BOMe Br_2	 70 %	
	$(EtO)_3B$ Br_2		 71 %
	Et_2BOMe Br_2	 58 %	
	$(EtO)_3B$ I_2		 61 %
	$(EtO)_3B$ Br_2		 74 %
	Et_2BOMe I_2	 51 %	
	Et_2BOMe Br_2	 61 %	
	$(EtO)_3B$ Br_2		 53 % 34/66

The first steps for the synthesis of α-bromoiodoarenes are similar to that for the synthesis of halophenols (Scheme 2.7). In the last step the aryldiethylborane **8** or aryldiethylboronate **9** is treated with ICl which is generated *in situ* by N-chloro-N-sodium-4-toluenesulfonamide (chloramine-T) and NaI.[8,24,25] This step cleaves the boron aryl bond, selectively iodinating the aromatic ring. As for the halophenols, no isolation of intermediate complexes is required. A list and yields of the compounds prepared by this method is shown in Table 2.2.

Scheme 2.7: The Synthesis of α-Bromoiodoarenes Compounds.

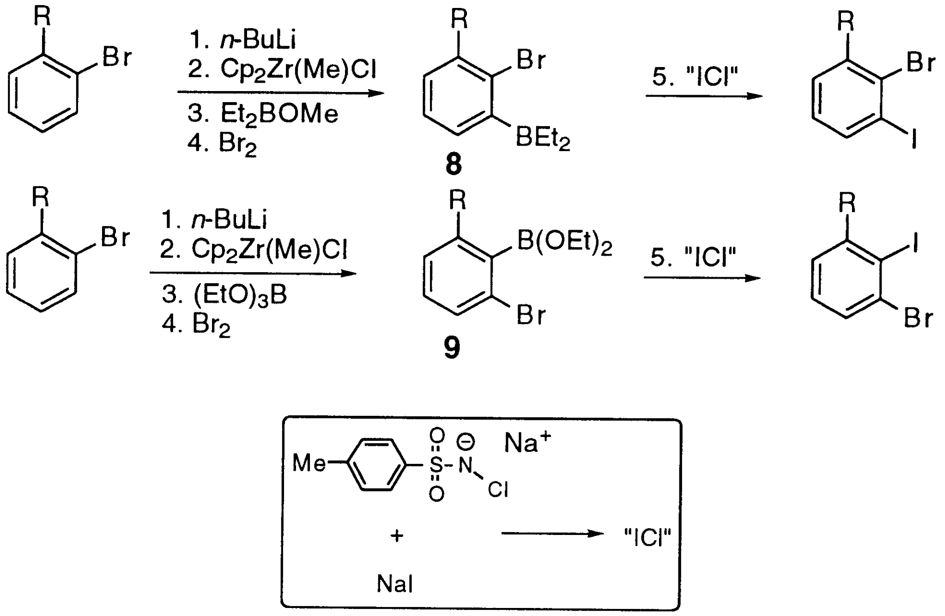
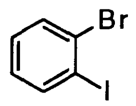
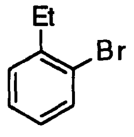
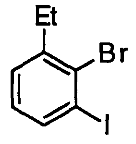
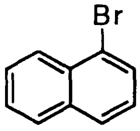
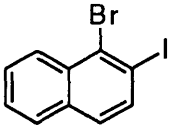
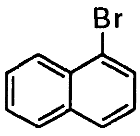
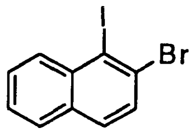
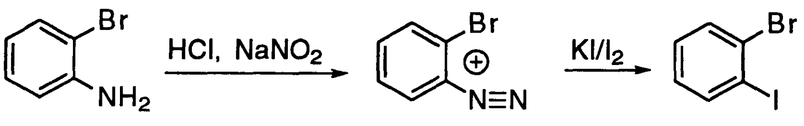


Table 2.2: Yields for the Synthesis of α-Bromoiodoarenes.

Substrate	Boron Reagent	Products	Yield
Cp_2ZrPh_2	$(EtO)_3B$ or Et_2BOMe		70 (GC) %
	Et_2BOMe		51 %
	Et_2BOMe		47 %
	$(EtO)_3B$		23 %

The only other general method for the synthesis of α-bromoiodoarenes is the Sandmeyer reaction (Scheme 2.8). This method relies on the availability of a primary aryl amine.[26] The method described here uses more readily available aryl halides as starting materials, as such may prove to be more general. The yields seen are moderate due to the difficulty in isolating the product in pure form away from impurities. Analysis by GC shows the crude products to be approximately 50 to 70 % pure.

Scheme 2.8: Synthesis of *o*-Bromoiodobenzene.



As pointed out previously, one major reason the synthesis of α-bromoiodoarenes is important is that they may be used in cross-coupling schemes where a new carbon-carbon bond could be formed at the aryl-iodide bond leaving the bromide intact. An alternative is to use the aryl boronic esters **9** and **10** in a Suzuki reaction leading to bromobiaryls. The boronic ester **10** can be prepared by oxidation of **8** with dioxygen. The boronic esters are generated and reacted *in situ* yielding the brominobiaryls **11** and **12** (Scheme 2.9 and Table 2.3).

Scheme 2.9: The Synthesis of Bromobiaryls.

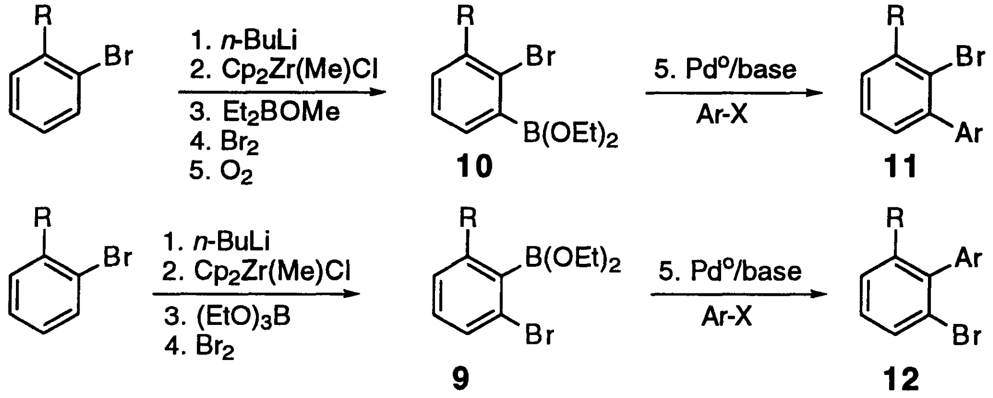
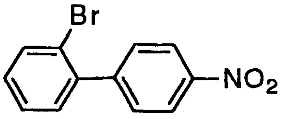
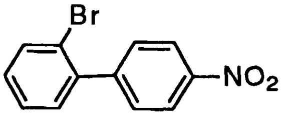
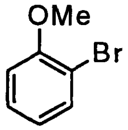
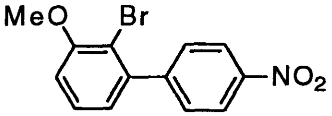
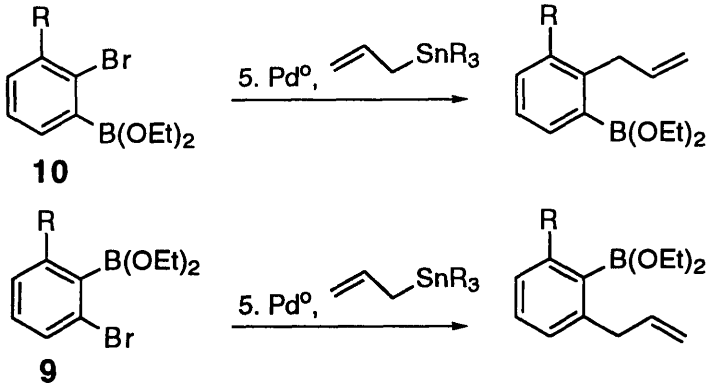


Table 2.3: Yields for Bromobiaryls.

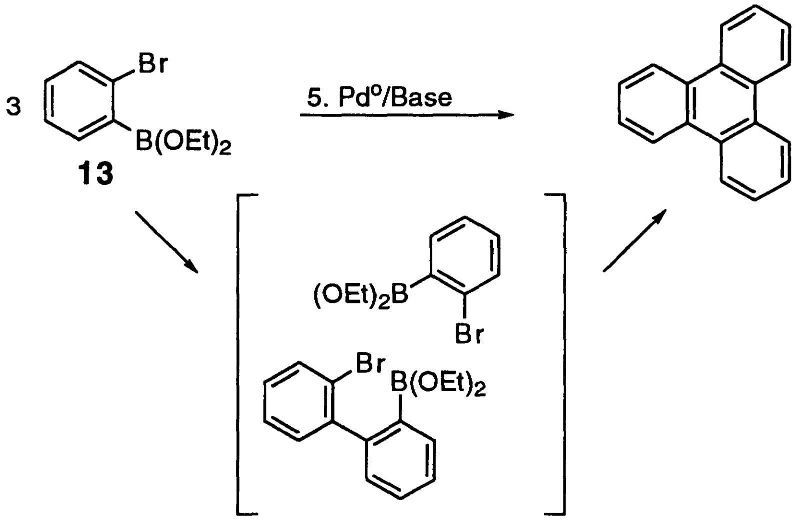
Substrate	Boron Reagent	Products	Yield
Cp_2ZrPh_2	Et_2BOMe		44 %
Cp_2ZrPh_2	$(EtO)_3B$		44 %
	Et_2BOMe		45 %

The boronic esters **9** and **10** should be good substrates in cross-coupling schemes other than the Suzuki reaction. For example, in the absence of a base, a Stille reaction[27] could be used to react at the bromine-aryl bond of **9** and **10** (Scheme 2.10). This would use the intermediates **9** and **10** as electrophiles in the coupling scheme rather than nucleophiles. This reversal of roles for the boron intermediate was shown in the synthesis of triphenylene (Scheme 2.11) from **13**. In this reaction, **13** acts as both nucleophile and electrophile.

Scheme 2.10: Intermediates **9** and **10** as Reagents in a Stille Coupling.



Scheme 2.11: Synthesis of Triphenylene from **13**.



New methods for making aryl boronic acids would be useful since even simple boronic acids available from chemical suppliers are very expensive. It should be possible to hydrolyze the boronic esters **9** and **10** to boronic acids. Hydrolysis of **9** and **10** and isolation of the aryl boronic acids[28,29] would give general reagents that could be used for making a variety of substituted aromatic compounds.

In summary the heterobimetallic compounds **4** and **5** are versatile intermediates for the synthesis of 1,2,3-trisubstituted aromatic compounds. This work demonstrates the one pot synthesis of halophenols, α-bromoiodoarenes and brominatedbiaryls. These syntheses are an extension of work previously done in our group on the syntheses of substituted aromatic compounds. The reactions available for an aryl boron bond and the control of regiochemistry, which is dependent upon whether Et_2BOMe or $(EtO)_3B$ is used in the insertion step, greatly add to the scope and novelty of this chemistry.

Experimental Section

General Considerations. Where the reagents or products were air or moisture sensitive, the reactions were carried out under an atmosphere of purified argon or nitrogen using standard Schlenk and glove box techniques. ^1H Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity-300 or a Varian XL-300 Fourier transform spectrometer. Gas chromatography (GC) analyses were performed on a Hewlett-Packard model 5890 gas chromatograph with a flame ionization detector and a model 3392A integrator using a 25 meter capillary column with polymethylsiloxane (Hewlett-Packard) as a stationary phase. Melting points were determined with a Haake Buchler melting point apparatus and are uncorrected.

Tetrahydrofuran (THF) was dried and deoxygenated by refluxing and distilling from sodium / benzophenone ketyl under an argon atmosphere. Preparative flash chromatography was performed on silica gel (E. M. Science Kieselgel 60, 230-400 mesh). All reagents were prepared according to published procedures or were commercially available and used without further purification.

General procedure for the preparation of iodo and bromophenols. A dry sealable Schlenk flask was charged with zirconocene(methyl)chloride (0.272 g, 1 mmol) in a glove box. The flask was removed from the glove box and attached to a Schlenk line, and THF (10 mL) was added. The flask was then charged with the aryl bromide (1 mmol) and cooled to -78 °C. Using a gas-tight syringe, *tert*-butyllithium (0.9 mL, 1.7 M in pentane) was added. After 15 min, the flask was removed from the -78 °C bath and allowed to warm to room temperature over 1 h (warm to 0 °C over 20 min in the case of the naphthalene derivative). The triethylborate (0.34 mL, 2 mmol) or diethyl methylborinate (0.26 mL, 2 mmol) was added *via* syringe. The flask was sealed and was then heated in an oil bath for 18 h at 80 °C (heated for 3 h at 50 °C in the case of the naphthalene derivative). After allowing the reaction mixture to cool to room temperature, the volatiles were removed *in vacuo* and the yellowish boron-zirconium complex was dissolved in THF (10 mL). A dry round bottom Schlenk flask equipped with a stirbar was attached to the Schlenk line. The round bottom flask was charged with iodine (0.254 g, 1 mmol) or bromine (0.2 mL, excess) and THF (10 mL). The boron-zirconium complex was added quickly to the halogen solution *via* cannula at room temperature with vigorous stirring. After this addition was complete, the cannula was removed and the flask was heated to 50 °C for 1 h. The flask was then cooled in an ice bath. Using a syringe, aqueous sodium hydroxide (2.6 mL, 3 M) was added dropwise immediately followed by dropwise addition of 30% hydrogen peroxide (3 mL). The flask was removed from the ice bath and was allowed to warm up for 15 min after which time the reaction mixture was quenched by the addition of excess saturated aqueous sodium thiosulfate solution. Some ammonium chloride was added at this time to ensure the pH of the solution was close to 7. The product was extracted in ether (3 x 70 mL), dried over magnesium sulfate and the solvents removed by rotary evaporation. The products were purified using preparative flash chromatography to afford the pure halophenols.

In the case of the synthesis of 2-Iodophenol, diphenyl zirconocene was used instead of the zirconocene(methyl)chloride and an aryl bromide substrate.

The spectral data for 2-bromo-6-methylphenol[16] and 2-bromo-6-methoxyphenol[17] have been reported in the literature. Spectral data of both 2-iodophenol and 1-bromo-2-napthol were compared with spectral data of material purchased from Aldrich Chemical Co., Inc. and Lancaster Synthesis, Inc. Spectral data of the 2-bromo-1-naphthol was compared with spectral data of material prepared by literature methods.[18] While all of the compounds in Table 2.1 are known,[16-22] the ^{1}H NMR and IR spectral data which were not available in the literature are listed below. Yields in Table 2.1 refer to isolated yields of products of greater than 95 % purity as determined by capillary GC and ^{1}H NMR spectrometry.

Spectral data for 2-Iodo-6-methylphenol[19] ^{1}H NMR (300 MHz, $CDCl_3$): d 2.30 (s, 3H), 5.28 (s, 1H), 6.57 (t, *J* =7.8 Hz, 1H), 7.07 (d, *J* =7.8 Hz, 1H), 7.47 (d, *J* =7.8 Hz, 1H). IR (KBr, cm^{-1}): 3484.

Spectral data for 2-Iodo-3-methoxyphenol[20] ^{1}H NMR (300 MHz, $CDCl_3$): d 3.87 (s, 3H), 5.48 (s, 1H), 6.39 (d, *J* =8.2 Hz, 1H), 6.67 (d, *J* =8.2 Hz, 1H), 7.18 (t, *J* =8.2 Hz, 1H). IR (KBr, cm^{-1}): 3463.

Spectral data for 2-Bromo-3-methylphenol[21] ^{1}H NMR (300 MHz, $CDCl_3$): d 2.39 (s, 3H), 5.60 (s, 1H), 6.80 (d, *J* =7.7 Hz, 1H), 6.87 (d, *J* =7.7 Hz, 1H), 7.10 (t, *J* =7.7 Hz, 1H). IR (KBr, cm^{-1}): 3396.

Spectral data for 2-Bromo-3-methoxyphenol[22] ^{1}H NMR (300 MHz, CDCl$_3$): d 3.879 (s, 3H), 5.68 (s, 1H), 6.47 (d, *J* =8.2 Hz, 1H), 6.67 (d, *J*=8.2 Hz, 1H), 7.16 (t, *J* =8.2 Hz, 1H). IR (KBr): 3489 cm^{-1}.

General procedure for the preparation of α-bromoiodoarenes. A dry sealable Schlenk flask was charged with zirconocene(methyl)chloride (0.272 g, 1 mmol) in a glove box. The flask was removed from the glove box and attached to a Schlenk line. The zirconocene(methyl)chloride was dissolved in THF (10 mL) and the mixture was cooled to -78 °C. A round bottom Schlenk flask was charged with the aryl bromide (1 mmol) and cooled to -78 °C. Using a gas-tight syringe, *n*-butyllithium (0.63 mL, 1 mmol, 1.6 M in hexane) was added. After 30 min, the contents of the round bottom flask were added to the sealable Schlenk flask containing the zirconocene(methyl)chloride using a cannula (all at -78 °C). The reaction was allowed to proceed for 15 min at -78 °C after which time the flask was removed from the -78 °C bath and allowed to warm to room temperature over 1 h (warm to 0 °C over 20 min in the case of the naphthalene derivative). The triethylborate (0.34 mL, 2 mmol) or diethyl methylborinate (0.26 mL, 2 mmol) was added *via* syringe, the flask was sealed and was then heated in an oil bath for 18 h at 80 °C (heated for 3 h at 50 °C in the case of the naphthalene derivative). After allowing the reaction mixture to cool to room temperature, the volatiles were removed *in vacuo* and the yellowish boron-zirconium complex was dissolved in THF (10 mL). A dry round bottom Schlenk flask equipped with a stirbar was attached to the Schlenk line. The round bottom flask was charged with bromine (72 µL, 1.4 mmol) and THF (5 mL). The boron-zirconium complex was added quickly to the halogen solution *via* cannula at room temperature with vigorous stirring. After this addition was complete, the cannula was removed and the flask was heated to 50 °C for 1 h. The flask was then cooled in an ice bath and distilled water (50 mL) was added to the solution. The intermediate was extracted in ether (3 x 50 mL), dried over magnesium sulfate and the solvents removed *in vacuo*. The intermediate was transferred to a round bottomed flask equipped with a magnetic stirrer and 50 mL of a mixture of methanol/water (50:50) was added. The solution was stirred in the absence of light while a solution of sodium iodide (1.25 mL, 1.25 mmol, 1 M) was added. Chloramine-T (0.455 g, 2 mmol), dissolved in 30 mL of methanol/water (50:50), was added in a dropwise fashion to the flask containing the intermediate and sodium iodide. The reaction was allowed to proceed for three hours after which 20 mL of brine was added to the flask. The crude product was extracted in ether (3 X 75 mL), dried over magnesium sulfate and the solvents were removed *in vacuo*. Both 2-bromo-3-iodoethylbenzene and 1-iodo-2-bromonaphthylene were purified by using spinning plate chromatography with pentane as eluent giving a 51 % and 23 % yield respectively based on the aryl bromide starting material. Recrystallization from hot hexane gave clean 1-bromo-2-iodonaphthylene in 47 % yield based on 1-bromonaphthylene starting material.

In the case of the synthesis of *o*-bromoiodobenzene, diphenyl zirconocene was used instead of the zirconocene(methyl)chloride and an aryl bromide substrate. The product was not isolated and a yield of 70 % was determined by GC. The retention time was the same as that of *o*-bromoiodobenzene purchased from Aldrich Chemical Co. 1-Bromo-2-iodoethylbenzene has been previously made although spectral data was not listed.[30] Spectral data of 2-bromo-3-iodoethylbenzene, 1-bromo-2-iodonaphthlene and 1-iodo-2-bromonaphthylene are listed below.

Spectral data for 2-bromo-3-iodoethylbenzene. The product was a yellow oil. ^1H NMR (300 MHz, C_6D_6): δ 0..91 (t, *J* =7.2, 3H), 2.52 (q, *J* =7.2, Hz, 2H), 6.40 (t, *J* =7.8, 1H), 6.641 (d, *J* =7.8, 1H), 7.44 (d, *J* =7.8, 1H); ^{13}C NMR (300 MHz, CD_2Cl_2):

δ 14.57, 32.79, 103.40, 129.33, 129.47, 131.36, 138.56, 146.19; Anal. Calcd for C_8H_8BrI: C, 30.90; H, 2.59. Found: C, 31.15; H, 2.68.

Spectral data for 1-bromo-2-iodonaphthylene.[30] The product was a while crystalline powder ^1H NMR (300 MHz, CD_2Cl_2): δ 7.57 (m, 3H), 7.81 (d, *J* =7.8 Hz, 1H), 7.89 (d, *J* =9.3 Hz, 1H), 8.30 (d, *J* =7.8 Hz, 1H); ^{13}C NMR (300 MHz, CD_2Cl_2): δ 101.36, 127.61, 128.84, 128.97, 129.32, 129.44, 130.33, 133.75, 133.92, 136.64; mp 93 °C; Anal. Calcd for $C_{10}H_6BrI$: C, 36.07; H, 1.82. Found: C, 36.08; H, 1.69.

Spectral data for 1-iodo-2-bromonaphthylene. The product was a while crystalline powder. ^1H NMR (300 MHz, CD_2Cl_2: δ 7.57 (m, 2H), 7.73 (m, 3H), 8.24 (d, *J* =7.2 Hz, 1H); ^{13}C NMR (300 MHz, CD_2Cl_2:): δ 106.95, 127.36, 128.99, 129.355, 130.08, 130.42, 130.57, 132.44, 134.26, 137.15; mp 61 °C; Anal. Calcd for $C_{10}H_6BrI$: C, 36.07; H, 1.82. Found: C, 36.07; H, 1.65.

Procedure for the preparation of brominobiaryls.

Synthesis of 2-bromo-(4-nitrobenzene)anisole.

A dry sealable Schlenk flask was charged with zirconocene(methyl)chloride (0.272 g, 1 mmol) in a glove box. The flask was removed from the glove box and attached to a Schlenk line. The zirconocene(methyl)chloride was dissolved in THF (10 mL) and the mixture was cooled to -78 °C. A round bottom Schlenk flask was charged with 2-bromoanisole (0.13 mL, 1 mmol) and cooled to -78 °C. Using a gas-tight syringe, *n*-butyllithium (0.63 mL, 1 mmol, 1.6 M in hexane) was added. After 30 min, the contents of the round bottom flask were added to the sealable Schlenk flask containing the zirconocene(methyl)chloride using a cannula (all at -78 °C). The reaction was allowed to proceed for 15 min at -78 °C after which time the flask was removed from the -78 °C bath and allowed to warm to room temperature over 1 h. Diethyl methylborinate (0.26 mL, 2 mmol) was added *via* syringe and the flask was sealed and then heated in an oil bath for 18 h at 80 °C. After allowing the reaction mixture to cool to room temperature, the volatiles were removed *in vacuo* and the yellowish boron-zirconium complex was dissolved in THF (10 mL). A dry round bottom Schlenk flask equipped with a stirbar was attached to the Schlenk line. The round bottom flask was charged with bromine (72 µL, 1.4 mmol) and THF (5 mL). The boron-zirconium complex was added quickly to the halogen solution *via* cannula at room temperature with vigorous stirring. After this addition was complete, the cannula was removed and the flask was heated to 50 °C for 1 h. Oxygen was bubbled through the solution for one hour using a gas dispersion tube while additional THF was added to compensate for evaporation. Volatiles were removed under vacuum and the crude aryl boronate compound was redissolved in THF (6 mL). A sealable Schlenk tube equipped with a stir bar was charged with 1-iodo-4-nitrobenzene (0.249 g, 1 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol) and sodium carbonate (0.212g, 2 mmol), then purged with argon. The aryl boronate solution was transferred to the sealable tube using a cannula. Water (2 mL), degassed with an argon purge, was added to the mixture using a syringe, the tube was sealed and the solution stirred while heating at 80 °C for 12 hours. The tube was removed from the heating bath and left to cool to room temperature. Brine (50 mL) was added to the crude product mixture and which was then extracted with methylene chloride (3 X 75 mL). The organic extracts were dried over magnesium sulfate and the volatiles were removed under vacuum. The product was purified using preparative flash chromatography with hexane/ether (90:10) as eluent. Removal of solvent under vacuum gave a clean white crystalline product in 45 % yield from the starting 2-bromoanisole.

Spectral data for 2-bromo-3-(4-nitrobenzene)anisole. The product was a yellow solid. ^{1}H NMR (300 MHz, C_6D_6): δ 3.28 (s, 3H), 6.34 (d, *J*=8.3 Hz, 1H), 6.52 (d, *J*=8.0, 1H), 6.91 (t, *J*=7.8, 1H), 6.96 (d, *J*=8.8, 1H), 7.82 (d, *J*=8.8, 1H); ^{13}C

NMR (300 MHz, THF-d_8): δ 56.90, 112.64, 112.78, 123.65, 124,03, 129.30, 131.60, 143.43, 148.58, 148.89, 157.89; mp 140-141 °C; IR (KBr, cm^{-1}): 698, 791, 857, 1031, 1118, 1348, 1462, 1515, 1587, 3072; Anal. Calcd for $C_{13}H_{10}BrNO_3$: C, 50.67; H, 3.27. Found: C, 50.43; H, 3.14.

Synthesis of 1-bromo-2 (4-nitrobenzene)benzene.

In the case of the synthesis of 1-bromo-2 (4-nitrobenzene)benzene, diphenyl zirconocene was used instead of the zirconocene(methyl)chloride and an aryl bromide substrate. Either Et_2BOMe or $(EtO)_3B$ could be used as the boron reagent. In the case where $(EtO)_3B$ was used, the oxygenation step was omitted. The product was purified using flash chromatography with hexane as the eluent. Removal of the solvent under vacuum gave a white crystalline product in 44 % yield. The yields were the same for the procedures using either boron reagent.

*Spectral data for 2-bromo-3-(4-nitrobenzene)benzene.*The product was a white solid. ^1H NMR (300 MHz, C_6D_6): 6.72 (m, 2H), 6.87 (m,, 3H), 7.38 (d, J=8.5, 1H), 7.79 (d, J=8.6, 2H); ^{13}C NMR (300 MHz, THF-d_8): δ 122.85, 124.13, 128.87,130.99, 131.62, 132.14, 134.41, 141.78, 148.46, 148.65; mp 76-77 °C; IR (KBr, cm^{-1}): 697, 756, 856, 1004, 1108, 1348, 1428, 1463, 1514, 1599; Anal. Calcd for $C_{12}H_8BrNO_2$: C, 51.83; H, 2.90 Found: C, 51.99; H, 3.13.

Synthesis of Triphenylene. The procedure used for the synthesis of triphenylene is exactly the same as for the synthesis of α-bromoiodoarenes where $(EtO)_3B$ is used as the boron reagent except that 1-iodo-4-nitrobenzene is not added in the Suzuki coupling step. The product was isolated in 33 % yield using flash chromatography with hexane as the eluent. The product was characterized by ^1H NMR which was consistent with triphenylene.

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CHAPTER 3

THE SYNTHESIS OF (LnO)CuS IN A SODIUM POLYSULFIDE FLUX:

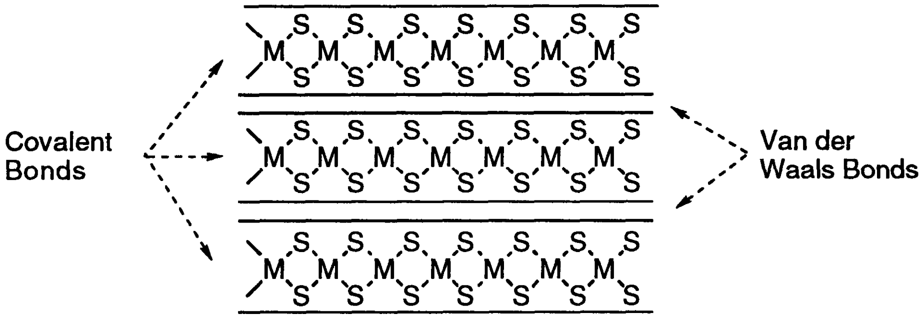
Ln = La, Nd, Sm and Eu

Introduction

The synthesis and characterization of low-dimensional materials have been a major area of research in the field of solid state chemistry. This interest stems from the interesting anisotropic electronic, magnetic and mechanical properties of these compounds. This chapter will deal mainly with the synthesis and characterization of a of a series of Lanthanide copper oxysulfides which exhibit a layered structure. Although some of these compounds have been made, a novel method, synthesis in a sodium polysulfide flux, is presented here.

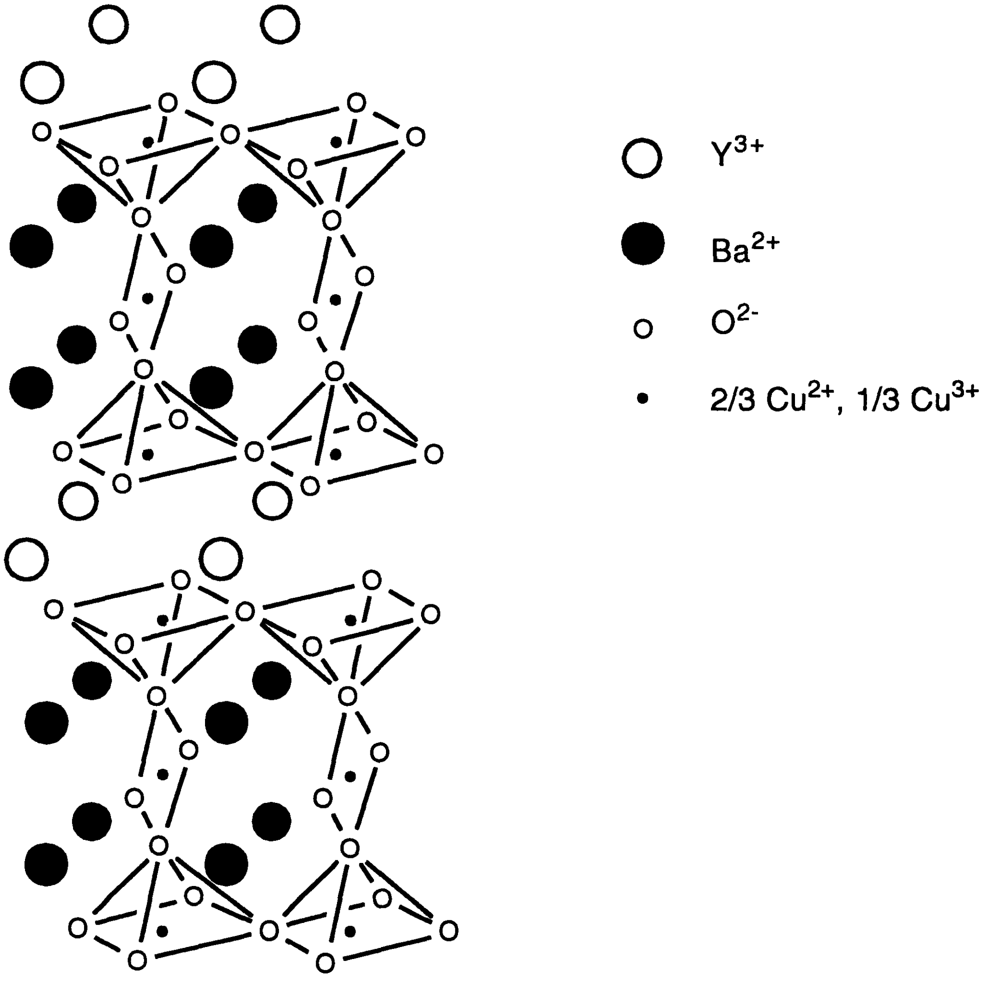
Transition metal sulfides are a class of materials which often form structures with two-dimensional slabs or one-dimensional chains in the solid state.[1] Figure 3.1 shows schematically a metal sulfide of composition $[MS_2]_n$ with a two-dimensional structure. The structure consists of $[MS_2]_n$ slabs where the bonding between the metal and sulfur is primarily covalent. The coordination geometry around the metal center is octahedral or trigonal prismatic, depending upon the metal.[2] The slabs are held together by Van der Waals bonds. The layered nature of these compounds leads to some interesting properties. For example, the Van der Waals gap leads to materials that are useful as high temperature lubricants[3] and as hosts for intercalation of atoms and small molecules.[2] The two-dimensional array of metals leads to interesting electronic properties such as the development of charge density waves[4] and superconductivity.[5]

Figure 3.1: Schematic Structure of $[MS_2]_n$ Two Dimensional Structure.



Layered oxides are of great current interest as high temperature superconductors.[6] The 90 K superconductor $YBa_2Cu_3O_7$ (Figure 3.2) can be described as an ordered, oxygen deficient perovskite where the A sites are occupied by barium and ytterbium cations. The copper atoms, in B sites, form a triple layer of $[Cu_3O_7]_\infty$ corner sharing polyhedra. The structure is considered layered since the barium cations reside in sites within the $[Cu_3O_7]_\infty$ slabs while the ytterbium cations are found between the slabs.

Figure 3.2: Structure of 90 K $YBa_2Cu_3O_7$ Superconductor.[a]



[a]Reproduced form reference 6.

Due to the interesting structures and properties of layered oxides and sulfides, it is intriguing to consider the possible properties and structures of compounds containing both metal-oxygen and metal-sulfur bonds. Kanatzidis defines these compounds, which contain metal-oxygen and metal-chalcogenide bonds, as oxychalcogenides.[7] There are numerous examples of ternary and quaternary oxychalcogenides,[7-17] but quaternary oxychalcogenides containing a lanthanide and a transition metal are rarer.[18-22]

The synthesis of solid state compounds is a challenging problem due to lack of general synthetic methods and little understanding of the mechanisms involved in solid state reactions.[23] As basic a parameter as the final stoichiometry of a solid state reaction is often difficult to predict. Structural prediction remains an important and difficult problem although some elegant methods have been developed.[24] One very successful and common practice towards rational synthesis is the substitution of an atom in a structure with similar atoms. This substitution is a way of tuning the properties of a material and gives a degree of predictive power to the chemist. The goal of this atom substitution is not a new structure type and leads to derivatives of a known material. Another practical problem in solid state chemistry is the purification and characterization of products, which is much less routine than for molecular synthetic chemistry. A molecular chemist would have to consider trying to do synthetic molecular chemistry without chromatography and NMR to understand some of the difficulties encountered. For the above reasons, solid state chemists rely heavily on the empirical knowledge gathered through the many different compounds synthesized as extended solids. It is therefore a current and important problem to explore methods for making solid state compounds as single phases.

Traditional methods[25] of solid state synthesis involve grinding starting materials together, pressing these into pellets and heating the pellets at temperatures in excess of 500 °C for days or even weeks. The grinding and heating stages are often repeated several times before obtaining a single phase product. This harsh treatment is required for diffusion between the solid starting material to occur and for homogeneous products to be formed. Although the ceramic method is a very fruitful method of synthesis, it is not always conducive to single crystal growth and leads to thermodynamically stable phases. Since there may be a spectrum of metastable phases of similar stoichiometry formed at different temperatures, it is desirable to find ways to react compounds at lower temperatures.[26] Use of low melting salts as solvents often can lead to the growth of single crystals and synthesis of materials at lower temperatures.[27] The idea is to find the appropriate flux that can dissolve at least some components of the starting materials to speed up diffusion, much as a solvent is used in molecular chemistry to dissolve starting materials.

It has been known for some time that chalcogenides could be reduced in liquid ammonia to form linear polynuclear or Zintl ions.[28] The alkali-metal chalcogenides form amorphous Zintl phase[29] with chacogenides of varied composition M_2E_n (M = alkali-metal, E = chalcogenide, n = 2 - 6). These can be made by several methods. For example, the alkali metal and chalcogenide can be reacted in liquid ammonia followed by removal of the ammonia. Another method involves the reduction of the chalcogenide using borohydrides.[30] A third method, is by simply fusing the alkali metal and chalcogenide.[27] The third method can be used to add on elemental chalcogenide to a preformed M_2E, as seen in Equation 3.1. Addition of chalcogenide to M_2E_n drastically lowers the melting point. Table 3.1 shows several M_2E_n phases and their corresponding melting points. Several of the M_2E_n compositions have melting points that approach the maximum boiling ranges of organic solvents. Thus in theory these solvents open up the possibility of synthesizing solid state compounds in temperature ranges usually associated with molecular synthesis.

$$3.1)\quad Na_2S \; + \; S \xrightarrow{\sim 490\ ^\circ C} Na_2S_2 \; + \; S \xrightarrow{\sim 230\ ^\circ C} Na_2S_3$$

Table 3.1: Melting Points (°C) of some M_2E_n.[a]

Li_2S 900-975	Li_2S_2 370				
Na_2S 1180	Na_2S_2 490	Na_2S_3 229	Na_2S_4 275	Na_2S_5 252	
Na_2Se >875	Na_2Se_2 490	Na_2Se_3 490	Na_2Se_4 490		Na_2Se_6 258
Na_2Te 953	Na_2Te_2 348				Na_2Te_6 436
K_2S 840	K_2S_2 470	K_2S_3 252	K_2S_4 145	K_2S_5 206	K_2S_6 189
	K_2Se_2 460	K_2Se_3 380	K_2Se_4 205	K_2Se_5 190	
Rb_2S 530	Rb_2S_2 420	Rb_2S_3 213	Rb_2S_4 160	Rb_2S_5 225	Rb_2S_6 201
	Cs_2S_2 460	Cs_2S_3 217	Cs_2S_4 160	Cs_2S_5 210	Cs_2S_6 186

[a] Reproduced from reference 27.

The earliest work with molten chalcogenide fluxes was for the growth of sulfide crystals.[31, 32] More recently, polychalcogenide fluxes have been used as solvents for the synthesis of new chalcogenide materials.[3,27] In these cases the solvent is a reactive flux, since it works as both solvent and reagent. For the synthesis of molecular compounds, the polychalcogenides have been used as reagents, since they are soluble in polar organic solvents and form stable solvated ions.[32]

High temperature methods dominate the synthesis of oxychalcogenides, probably because of the difficulty in finding a suitable flux to dissolve both oxide and sulfide components of the material. This stems from the hard nature of the oxide anion and soft nature of the sulfide anion.[7] The reports of the synthesis of oxychalcogenides using the alkali-metal chalcogenide fluxes are rare.[7] Since these fluxes should help dissolve at least the sulfide components it seems reasonable to attempt to widen the scope of synthesis in the alkali metal fluxes for the synthesis of novel of oxysulfides. Another incentive for our interest in using the polychalcogenides as a flux is that the structures of many materials obtained using this flux are usually low-dimensional.[7,27]

Although as noted previously there was no a priori way of determining the structure and stoichiometry for the synthesis of a new solid state material, the background presented here indicated that a lanthanide copper oxychalcogenide made in a polysulfide flux would form a layered type structure. Since it is difficult to predict the exact structure of a new compound, it would be misleading to imply that a particular electronic or magnetic property was sought for. Rather, the goal was to explore the new synthetic method in hopes of discovering new compounds with a general layered structure . To this end, synthesis of lanthanide transition metal oxysulfides was initiated and a novel synthesis of lanthanide copper oxysulfides using a sodium polysulfide flux was discovered. A new high temperature method for the same products was also explored. Finally, and serendipitously, the synthesis of the known conductor $Na_3Cu_4S_4$ in the polysulfide flux was discovered.

Results and Discussion

The compound (LaO)CuS was first synthesized in powder form by Palazzi using the steam oxidation of $LaCuS_2$ in nitrogen at 800 °C.[34] In addition, Palazzi was able to obtain single crystals by heating the (LnO)CuS to 1300 °C and then slowly cooling the sample. Following this work, Isikawa synthesized the series from lanthanum to neodymium as powders by the solid state reactions of Ln_2O_2S and Cu_2S *in vacuo* at 580 to 1100 °C.[18]

We were able to synthesize the series (LnO)CuS with La, Nd, Sm and Eu by reacting two equivalents of CuS and one equivalent of the appropriate Ln_2O_3 in a molten polysulfide flux. A combination of anhydrous Na_2S and S to give a nominal composition "Na_2S_3" was used as the flux for the reaction. The "Na_2S_3" forms the amorphous Na_2S_3 flux at about 230 °C after which at least partial dissolution of the starting materials is presumed to occur. The reactions were carried out in a sealed quartz tube at 400 °C for four days for the lanthanum and neodymium analogs and 300 °C for eight days for the samarium and europium derivatives. The flux presumably acts as a reducing agent for the copper although the mechanism is not clear. This may change the composition and properties of the flux as the reaction proceeds.

Attempts to grow single crystals of the (LnO)CuS materials by including a slow temperature cooling gradient to the reaction conditions were unsuccessful. Instead, single crystals of the know compound,[35] $Na_3Cu_4S_4$, formed. The compound $Na_3Cu_4S_4$ is a mixed-valent one-dimensional metal. Its structure and electronic properties have been studied. This compound could be synthesized by starting with CuO in "Na_2S_3", heating the mixture to 400 °C and then cooling the mixture slowly. The experiment yielded long blue black needles of $Na_3Cu_4S_4$ and emphasizes the reducing nature of the Na_2S_3 flux.

A new ceramic method for synthesis of (LnO)CuS (Ln = La, Pr and Nd) was also discovered. In this ceramic method, a well ground mixture of CuS and La_2O_3 in the appropriate ratio was sealed in a graphite coated quartz tube and heated at 1000 °C for several days. The carbon acts as a reducing agent in this method. The heating and regrinding steps were repeated several times in an attempt to obtain single phases. A single phase of (LaO)CuS was obtained but unfortunately the praseodymium and neodymium compounds always contained some unidentified impurity phases as evidenced by Powder X-Ray Diffraction (XRD).

The samarium and europium analogs of (LnO)CuS could not be made by solid state methods. Ishikawa's attempts at forming (SmO)CuS led to the formation of Sm_2O_2S and Cu_2S. This demonstrates the usefulness of synthesis in a low temperature flux, where a metastable phase can be formed. High temperature sintering (above 1150 °C) of the pre-formed (LaO)CuS to try and grow single crystals lead to a similar decomposition to La_2O_2S and unidentified copper phases. The observation of impurities from the solid state reactions between Ln_2O_3 and CuS in the presence of carbon also demonstrates the usefulness of the Na_2S_3 flux synthesis of these compounds.

The oxysulfides (LnO)CuS form an isostructural series. The lanthanum, praseodymium and neodymium compounds crystallize in the tetragonal space group P4/nmm.[18,34] The XRD pattern of the lanthanum and neodymium compounds made by the sodium sulfide flux method match those of the corresponding (LnO)CuS reported by Palazzi and Ishikawa. The samarium and europium compounds were also analyzed by XRD and were indexed in the P4/nmm space group. The refinement gave probable errors in the 10^{-3} Å range.

The unit cell parameters of the series are listed in Table 2.3. The unit cells change as expected by the lanthanide contraction.

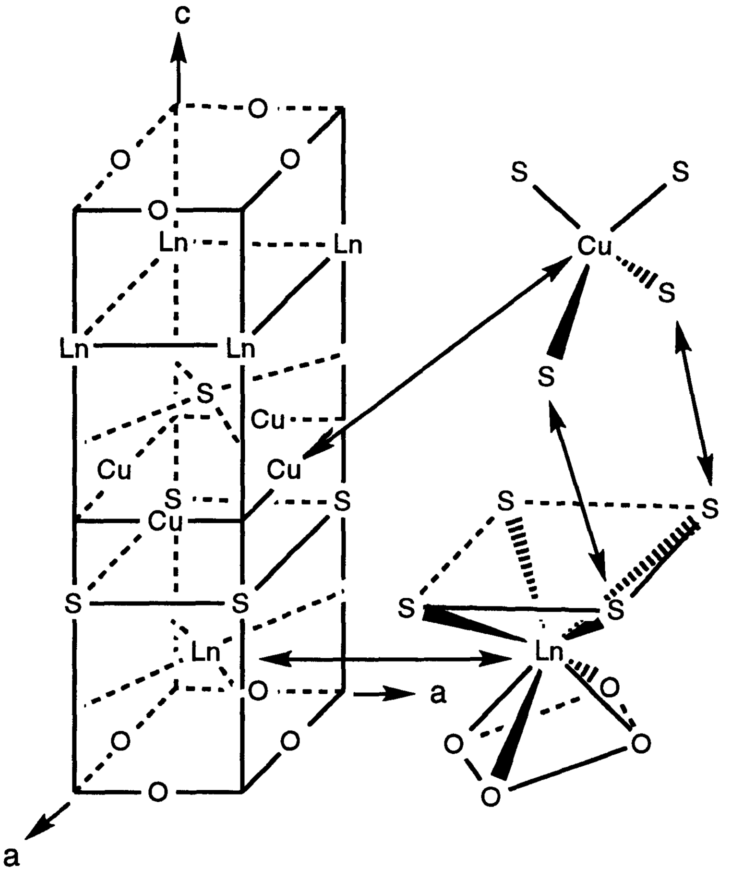
Table 3.2: Lattice Parameters of the (LnO)CuS Series

Compound	System	Lattice constants **a** (Å)	**c** (Å)
(LaO)CuS[a]	Tetragonal	4.000	8.521
(PrO)CuS[a]	Tetragonal	3.946	8.441
(NdO)CuS[a]	Tetragonal	3.921	8.435
(SmO)CuS	Tetragonal	3.885(1)	8.392(2)
(EuO)CuS	Tetragonal	3.870(1)	8.385(2)

[a]From reference 18.

The structures of (LnO)CuS consist of CuS layers alternating with LnO layers. The copper is tetrahedrally coordinated to four sulfur atoms. The lanthanide atoms are coordinated on one side to four oxygen atoms and the other to four sulfur atoms forming an eclipsed square anti-prism. Figure 3.3 shows the structure and coordination polyhedra of the lanthanide and copper. There are no S_n chains in the structure. This is surprising since most sulfides made below 500 °C in polychalcogenide fluxes generally show Zintl anions in the structure. The compounds are more consistent with observed structures crystallized at higher temperatures where simple sulfides are isolated.[31, 32] The layering in the structure evidently is associated with the high affinity of copper for the sulfide and lanthanide for the oxide.

Figure 3.3: The (LnO)CuS Structure.[a]



Note: double headed arrows indicate equivalent atoms.

[a]Partially reproduced from 18.

The synthesis of $Na_3Cu_4S_4$ demonstrates one of the problems facing synthetic solid state chemistry, the difficulty in predicting the products of new reaction conditions. However, the synthesis of a layered oxychalcogenide in the polysulfide flux demonstrates that some features of a structure can be predicted, in this case the layering of the atoms. A second principle for rational synthesis is demonstrated in accommodation of several different lanthanides in the same site and structure. The synthesis of (LnO)CuS at low temperatures using a sodium polysulfide flux is a novel approach. The method allows for the isolation of the samarium and europium analogs, phases that cannot be formed by ceramic methods due to the stability of other phases at high temperatures. Thus the method demonstrates one of the important features of synthesis in molten salts; the isolation of metastable or kinetic phases. The synthesis also widens the scope of synthesis in alkali metal polychalcogenides with this first synthesis of a quaternary oxysulfide in a polysulfide flux.

Experimental Section

General Considerations. Transfer and storage of air sensitive, moisture sensitive or hygroscopic materials were performed in a Vacuum Atmospheres Co. dry box under an atmosphere of nitrogen. Characterization of the compounds was done primarily by Powder X-Ray Diffraction (XRD) on a Rigaku 300 Powder Diffractometer with Cu Kα radiation. Least squares refinement was done using the software of the Rigaku instrument. Sodium sulfide nonahydrate(98 %) was purchased from the Aldrich chemical company. Copper(II)sulfide(99.5%), Sm_2O_3 (99.9 %), Eu_2O_3 (99.9 %), Pr_2O_3(99.9 %) and Copper(II)oxide were from Cerac. The La_2O_3 (99.99 %) and Nd_2O_3 (99.9 %) were purchased from Aesar.

Preparation of Na_2S_3. The nonahydrate was dried in a quartz reaction chamber under a flow of dry nitrogen using gentle heating (~ 200 °C). A large batch of "Na_2S_3" was prepared by mixing the anhydrous sodium sulfide with pure sulfur and was used as the flux for synthetic reactions. The mixture consists of sodium sulfide and sulfur until heated to approximately 250 °C after which the amorphous Na_2S_3 phase forms.

Caution: the anhydrous sodium sulfide must be stored in an inert dry atmosphere as it is extremely hyrgroscopic and reacts with air to give off H_2S and SO_2.

Preparation of (LnO)CuO in Na_2S_3 (Ln = La, Nd, Sm and Eu). Copper(II)sulfide and La_2O_3 , Nd_2O_3, Sm_2O_3 or Eu_2O_3 were combined in a molar ratio of two to one with a total mass of 0.5 g. The reactants and "Na_2S" (3 g) were sealed *in vacuo* (~ 10^{-4} Torr) in a quartz tube. For the synthesis of the lanthanum and neodymium derivatives, the tubes were heated at 400 °C for four days. In the case of the samarium and europium derivatives, the tubes were heated at 300 °C for eight days. The tubes were opened in a fume hood, and the flux removed by washing with distilled water. The (LnO)CuS products were light to dark grey powders and were characterized using XRD with silicon as an internal standard.

Preparation of (LnO)CuS using ceramic methods (Ln = La, Pr and Nd). Copper(II)sulfide and the appropriate lanthanide oxides were combined in a molar ratio of two to one respectively, where the total mass was 3 g. The two components were ground together using a mortar and pestle, loaded into a graphite coated quart tube and heated to 1000 °C for several days. The products of the reactions were removed from the tube, reground, resealed in a graphite coated quartz tube and heated as before. Cycles of heating and regrinding were repeated several times. A single phase of LaO(CuS) was obtained as evidenced by XRD. Some unidentified phases that could not be removed were found in the cases of (PrO)CuS and (NdO)CuS. The (LaO)CuS compound decomposes above 1150 °C to La_2O_2S and unidentified copper phases.

Preparation of $Na_3Cu_4S_4$ in Na_2S_3. Copper(II)oxide(0.5 g) and Na_2S_3 (3 g) were sealed in a quartz tube at about 10^{-4} Torr. The tube was heated to 400 °C for one day and then slowly cooled to room temperature over four days. The flux was removed in a fume hood by washing with water. The products were shiny blue-black crystals of up to 50 mm in length and typically 0.1 mm in the other two dimensions. The high conductivity of the crystals could be readily confirmed using a hand held Ohm meter. The crystals were ground and the powder analyzed by XRD.

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