Ruthenium Based Catalysts: Catalytic Dehalogenation of Chloroarenes and Syntheses of Bimetallic Carbene Complexes

by

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In Partial Fulfillment of the Requirements

for the Degree of

Master of Science

California Institute of Technology

Pasadena, California

1999

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Acknowledgements

I would like to thank Bob Grubbs for his support and guidance, but also for the freedom he left me in developing this thesis. I have learned a great deal from being part of his group.

I would also like to extend my thanks to all of the people without whose help this report would not have been possible: Michael Wagaman, for helping me to get started; Thomas Belderrain for many interesting discussions and ideas for the research presented in chapter 2; Tom Wilhelm, for lots of helpful discussions and computer assistance; and Marcus Weck, who has been a great resource person and a great person to work with in lab.

Synthesis of Barrelene Derivatives

1. Introduction

The interest in utilizing organic materials in the development of electroluminescent (EL) devices stems from the various properties afforded by these materials such as an extremely high photoluminescence quantum efficiency in the visible spectrum.[1] The discovery of the electromluminescence of poly(1,4-phenylene vinylene) (PPV) shown in Figure 1 attracted much interest in investigating conjugated polymers for the fabrication of light emmitting diodes (LEDs).[2] With its excellent thermal and chemical stabilities PPV can be used as the emissive layer in light emitting diodes.
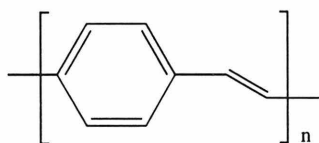

Figure 1. Poly(1,4-phenylene vinylene) (PPV)

This finding has fueled research in investigating other polymers which might exhibit electroluminescence. Another advantage of using polymer materials is that they can synthesized to form conjugated block copolymers. Block copolymers are predicted in comparison to homopolymers to have better luminescence efficiencies. Yet in spite of this there are few conjugated block copolymers reported. This is likely due to the difficulty in obtaining polymers with narrow weight distributions by methods such as step-growth polymerizations or condensation polymerizations.[3] However, ring-opening metathesis polymerization (ROMP) can polymerize block copolymers in a living manner and allow thus an effective means of synthesizing block copolymers. One of the monomers that has been used for producing PPV by ROMP is barrelene.

Since Zimmerman first reported the synthesis of barrelene, bicyclo[2.2.2]octatriene, [4,5] there has been considerable interest in the synthesis and study of this compound and its derivatives.[6] Although other syntheses of barrelene have been reported which allow this compound to be prepared by shorter routes than the original procedure,[7-13] these routes have generally not been applied to the synthesis of substituted barrelenes. Conversely, methods employed for the synthesis of substituted barrelenes[14-23] have generally not been applied to the synthesis of the parent unsubstituted barrelene.[24] One reason for this is that barrlenes such as dicyano- and bistrifluoromethylbarrelene are

synthesized by the Diels-Alder reaction of benzene with highly activated acetylenes, dicyanoacetylene and hexafluoro-2-butyne.[14-16,18] This same procedure has not be used to prepare unsubstituted barrelenes since acetylene is not sufficiently activated to undergo an efficient Diels-Alder reaction with benzene. In fact, while dicyanobarrelene[18] is obtained in 63% yield by this procedure, bistrifluoromethylbarrelene[14-16] is produced in yields of only 8-10%.[25] Following this trend further, Diels-Alder addition of the less activated, diester substituted acetylenes to benzene produces barrlene products only when the benzene derivative employed is also activated.[23,26,27]
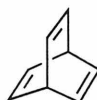

Figure 2. Barrelene

Recently the synthesis of 2,3-diester substituted barrelenes and the ring-opening metathesis polymerization (ROMP) of these molecules was reported from our group.[28] The synthesis developed for those barrelenes can now be extended to the synthesis of unsubstituted barrelene and other disubstituted barrelenes. Since benzene is a poor diene for most dienophiles *cis*-3,5-cyclohexadiene-1,2-diol was utilized. This route allows the preparation of a variety of barrelenes in as few as three steps from commercially available starting materials.

2. Results

2.1 Monomer Syntheses: All syntheses were carried out in a similar manner with the Diels-Alder addition of an acetylene bearing electron withdrawing groups to the benzene equivalent *cis*-3,5-cyclohexadiene-1,2-diol, (**1**). The barrelenes were then obtained by conversion of the diol to the olefin. In cases where protection of the diol was not necessary, the Diels-Alder reaction was followed by conversion of the diol (**3**) to the thiocarbonate (**4**), using thiocarbonyldiimidazole (TCDI) as shown in Scheme 1. Conversion of **4** to barrelene was then accomplished using 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine (DPD).[29,30] Purification of **5a-c** can be accomplished by column chromatography or by a combination of column chromatography and recrystallization.[28,30]

Scheme 1.

a: X = COOCH$_3$
b: X = COOC(CH$_3$)$_3$
c: X = COOCH$_2$CH(CH$_2$CH$_3$)(CH$_2$)$_3$CH$_3$
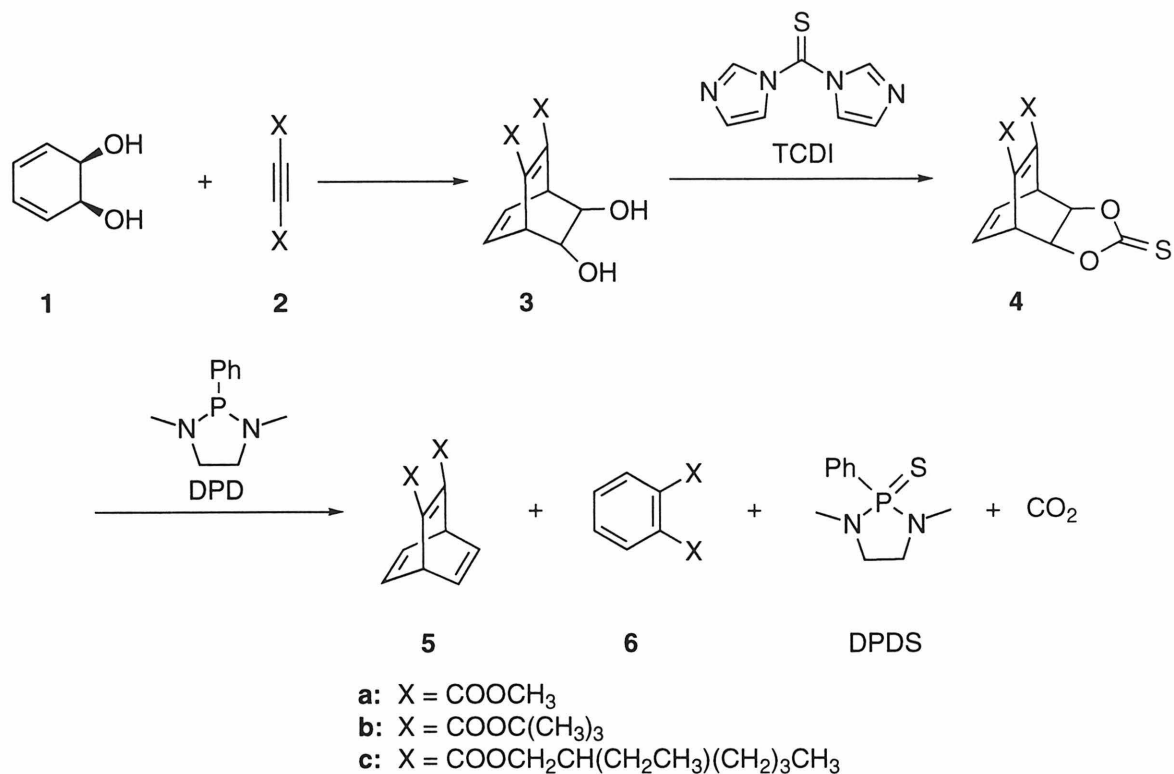
Other methods to generate the final double bond either directly from the diol,[31,32] or by base initiated thermal fragmentation of the benzaldehyde acetal as previously reported for benzobarrelene,[33,34] failed. Fragmentation of the acetal using KDA led to complete decomposition of the starting material, and as previously observed for the synthesis of benzobarrelene, no reaction occurred when LDA was employed. In the case of direct reduction of the diol, only decomposition was observed when Ti^0 reagents were employed[32] and the method reported by Barua et. al[31] produced only recovered starting material.

3.   Conclusion

The synthesis presented here affords an efficient route to several substituted barrelenes in as few as three steps from commercially available starting materials. Reaction of activated acetylenes with *cis*-3,5-cyclohexadiene-1,2-diol generally afforded the Diels-Alder adduct in high yield. This intermediate was then converted to barrelene by formation of the thiocarbonate followed by elimination of this moiety to yield the final olefin bond. In addition to the barrelenes synthesized here, the route presented should allow the preparation

of other related barrelenes and benzobarrelenes by using other dienophiles and/or any of the wide variety of substituted benzene equivalents similar to **1**.[38] This possibility is currently being explored. Efforts to polymerize these monomers types are ongoing.

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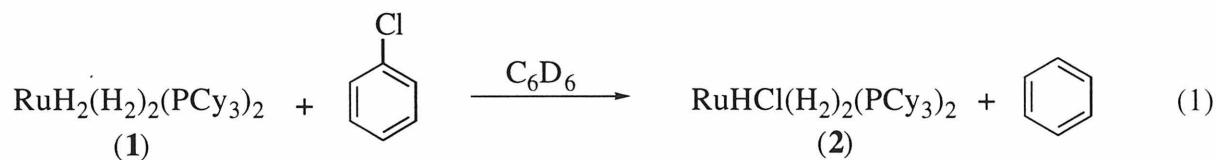
Chapter 2

Catalytic Dehalogenation of Aryl Chlorides Mediated by Ruthenium (II) Phosphine Complexes

1. Introduction

Chloroarenes are of particular interest because of their deleterious environmental and health impact[1] as well as their importance in organic synthesis.[2] Environmental concerns have driven researchers to examine practical and effective processes for the reduction of highly toxic chloroarenes into less toxic arenes. The high stability of the aryl carbon-chlorine bond renders it less reactive compared to other aryl-halogen bonds in many organic transformations and reactions.[2] It is with this chemical resiliency and potential carcinogenicity in mind that we directed our efforts towards the transformation of C-Cl bonds.

Several methods for hydrogenolysis of chloroarenes, using either stoichiometric and/or catalytic reagents, have been developed by Imai (Pd),[3] Carfagna (Ni),[4] Qian (La),[5] Horváth (Rh)[6] and Alper (Rh)[7] among others.[8] However, these systems can still be improved as most suffer from incomplete dechlorination, low catalytic activity, low substrate/catalyst ratio, extreme conditions (high H_2 pressure, long reaction times) or narrow functional group tolerance.

Ruthenium hydride complexes are useful as precursors to ruthenium carbenes[9,10] as well as active hydrogenation catalysts.[11-14] Interest in ruthenium complexes has grown due to their tolerance towards oxygen, protic solvents and a variety of functional groups. During earlier work in our group,[9] the formation of $RuHCl(H_2)_2(PCy_3)_2$ (**2**) by reaction of $RuH_2(H_2)_2(PCy_3)_2$ (**1**) and chlorobenzene was observed (Equation 1):

$$RuH_2(H_2)_2(PCy_3)_2 \ + \ \underset{\textstyle(\text{PhCl})}{\text{Cl}} \ \xrightarrow{\ C_6D_6\ } \ RuHCl(H_2)_2(PCy_3)_2 \ + \ \text{Ph} \qquad (1)$$
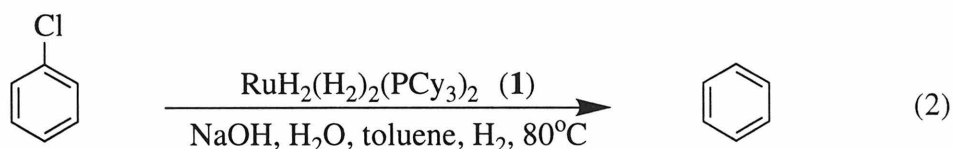
$$(\mathbf{1}) \hspace{9cm} (\mathbf{2})$$

A similar reaction reported by Chaudret and co-workers was the observation by NMR that **1** readily reacted with dichloromethane leading to the formation of **2**.[15] These reactions prompted interest in investigating the catalytic activity of **1** with chloroarenes. We have

recently reported convenient synthetic routes leading to the isolation of $RuH_2(H_2)_2(PCy_3)_2$ (**1**)[9] and $RuHCl(H_2)_2(PCy_3)_2$ (**2**)[10] from readily available materials in high yields and were interested in exploring the potential use of these ruthenium hydride complexes as dechlorination catalysts. We now report the rapid and complete catalytic reduction of chloroarenes to arenes using Ru(II) catalysts without a need for hydrogen gas.
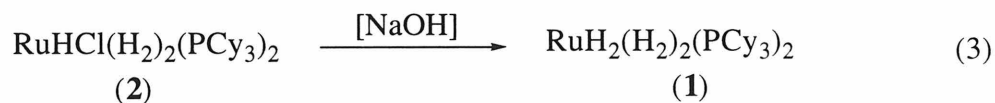
2.   Results and Discussion

2.1 Dechlorination with $Ru(H)(X)(H_2)_2(PCy_3)_2$ (X = H, Cl) under H_2: Similar conditions employed for the synthesis of **1** were used as a starting point in the dechlorination studies with complex **1** as the catalyst precursor.   More specifically, the conversion of chlorobenzene to benzene was performed using 1 mol % of catalyst **1**, 30 % (by weight) aqueous sodium hydroxide solution, under 3 atm H_2 at 80°C in toluene. Under these conditions, GC analysis showed that conversion to benzene was efficient but not complete.
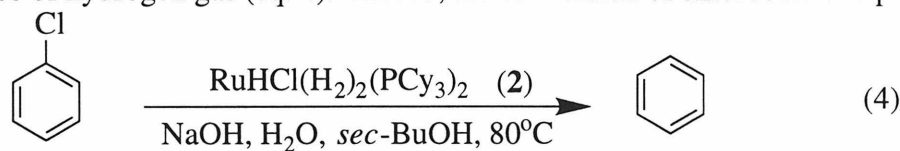

$$\text{Cl-C}_6\text{H}_5 \xrightarrow[\text{NaOH, H}_2\text{O, toluene, H}_2, 80°C]{\text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2 \ (\textbf{1})} \text{C}_6\text{H}_6 \tag{2}$$

Further studies showed that **1** could be prepared from **2** under strong basic conditions (Equation 3).

$$\text{RuHCl(H}_2)_2(\text{PCy}_3)_2 \xrightarrow{\text{[NaOH]}} \text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2 \tag{3}$$
$$(\textbf{2}) \qquad\qquad\qquad\qquad (\textbf{1})$$

This result lead us to consider the use of **2** as a catalyst for the dechlorination of arylchlorides. This would provide a number of synthetic advantages since **2** is easier to isolate and is more stable than **1**. In fact, complex **2** can also convert chlorobenzene to benzene using the same conditions as those described in Equation 2. Complex **2** was subsequently used as the catalyst precursor.

2.2 Dechlorination with $Ru(H)(X)(H_2)_2(PCy_3)_2$ (X = H, Cl) without H_2: In an effort to improve/ simplify catalytic conditions, solvent effects on catalytic conversions were investigated. Since the system utilizes biphasic conditions, it was important to examine whether changing the solvent or using a phase transfer catalyst could improve conversions by enhancing the interaction between the aqueous and organic phases.
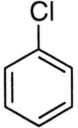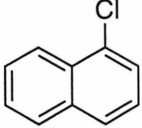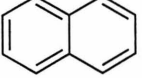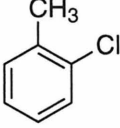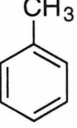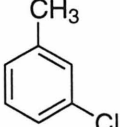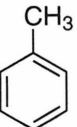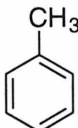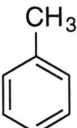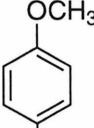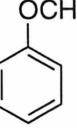
Changing the solvent from toluene to sec-butyl alcohol resulted in improved catalytic activity under hydrogen atmosphere. Simultaneously in our group, efforts directed toward the syntheses of ruthenium-hydride complexes showed that a secondary alcohol could provide an efficient hydrogen source and that molecular hydrogen was not needed and was often an impediment to the isolation of ruthenium hydride complexes.[16] Transfer hydrogenation mediated by transition metal centers (including ruthenium) has been reported by other groups.[17-22] This prompted investigation of the use of a secondary alcohol, sec-butyl alcohol, as the solvent used in the dechlorination of chloroarenes in the absence of hydrogen gas (eq. 4). Indeed, the conversion of chlorobenzene proceeds

$$\text{C}_6\text{H}_5\text{Cl} \quad \xrightarrow[\text{NaOH, H}_2\text{O, } sec\text{-BuOH, 80}^\circ\text{C}]{\text{RuHCl(H}_2)_2(\text{PCy}_3)_2 \quad (\mathbf{2})} \quad \text{C}_6\text{H}_6 \qquad (4)$$

efficiently and cleanly in the absence of hydrogen gas. In fact, the conversion efficiency is significantly higher in the absence of H_2. It appears that H_2 has a retarding effect on catalytic activity as has been reported in other hydrogen-transfer systems.[23]
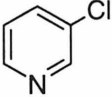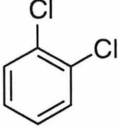
The concentration of the base and catalyst loading on catalytic activity were also investigated to determine whether more basic conditions would improve conversions. Only a modest improvement in conversions was observed when increasing the base concentration from 30% to 50% .[24] In an effort to futher optimize catalytic conditions, the catalyst loading was increased from 1% to 2.5%. As expected, the conversion efficiency greatly improved with the higher catalyst loading from 49% (with 1% catalyst) to 100% (with 2.5% catalyst) under identical conditions. After determining optimum catalytic conditions, a variety of chloroarene substrates were investigated. All are quantitatively converted to dechlorinated products after one hour at 80°C. The dechlorination results are summarized in Table 1.

Table 1. Catalytic Dehalogenation with RuHCl(PCy$_3$)$_2$(H$_2$)$_2$ in *sec*-Butyl Alcohol

Substrate	Product	Cat. mol %	Time (h)	% Converted[a]
		2.5	1	100
		2.5	1	100
		2.5	1	100
		2.5	1	100
		2.5	1	100
		2.5	1	100
		2.5	1	100
		2.5	1	100

[a]Percent conversions determined by GC

9

Importantly, the catalytic system displays tolerance towards substrates bearing functional groups such as ketones, ethers and pyridines. Moreover, multichlorinated arenes are completely dechlorinated.[25]

   2.3 In situ Catalyst Generation from [RuCl$_2$(COD)]$_x$: Since **1** and **2** can be synthesized from the air-stable [RuCl$_2$(COD)]$_x$ (**3**), hydrogenolysis of chloroarenes was examined by *in situ* generation of the catalyst precursor. This methodology is advantageous as it does not require the isolation of the catalyst precursor, enabling dechlorination to be carried out in a "one pot" reaction. To verify the need of dihydrogen in the generation of the *in situ* catalyst complex, side by side reactions were conducted in the absence and presence of dihydrogen.

$$[RuCl_2(COD)]_x + 2PCy_3 \quad \xrightarrow[\text{2. R-Cl addition under Ar, 80°C}]{\text{1. NaOH, H}_2\text{O, }sec\text{-BuOH, 80°C}} \quad \text{dark red solution} \qquad (5)$$
                (**3**)

$$[RuCl_2(COD)]_x + 2PCy_3 \quad \xrightarrow[\text{2. R-Cl addition under Ar, 80°C}]{\text{1. NaOH, H}_2\text{O, }sec\text{-BuOH, }\mathbf{H_2}\text{, 80°C, 2h}} \quad \text{orange solution} \qquad (6)$$
                (**3**)
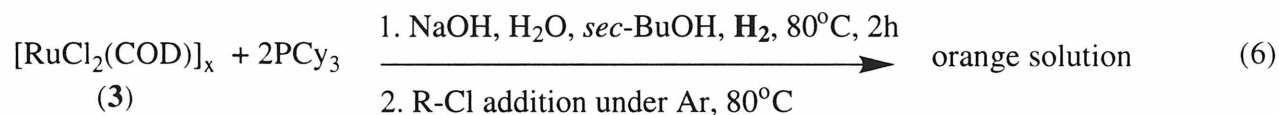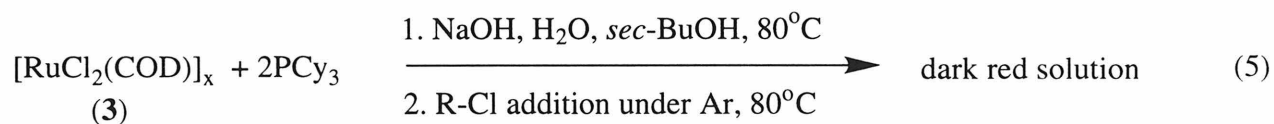
In the absence of hydrogen (eq.5), the species generated is neither **1** nor **2** but a close parent Ru(η^3-C$_6$H$_8$-PCy$_2$)(PCy$_3$)Cl (**4**) which has been reported to hydrogenate nitrile substrates.[26] Since complex **4** can be readily converted to complex **2**,[26] it follows that both **2** and **4** are likely entrypoints into the catalytic cycle.

   The effect of temperature on percent conversion was investigated for chlorobenzene with the *in situ* generated catalyst **4** in the absence of H$_2$ (results shown in Figure 1).

Percent Conversion vs Temperature
with In Situ Generated Catalyst in the Absence of H$_2$
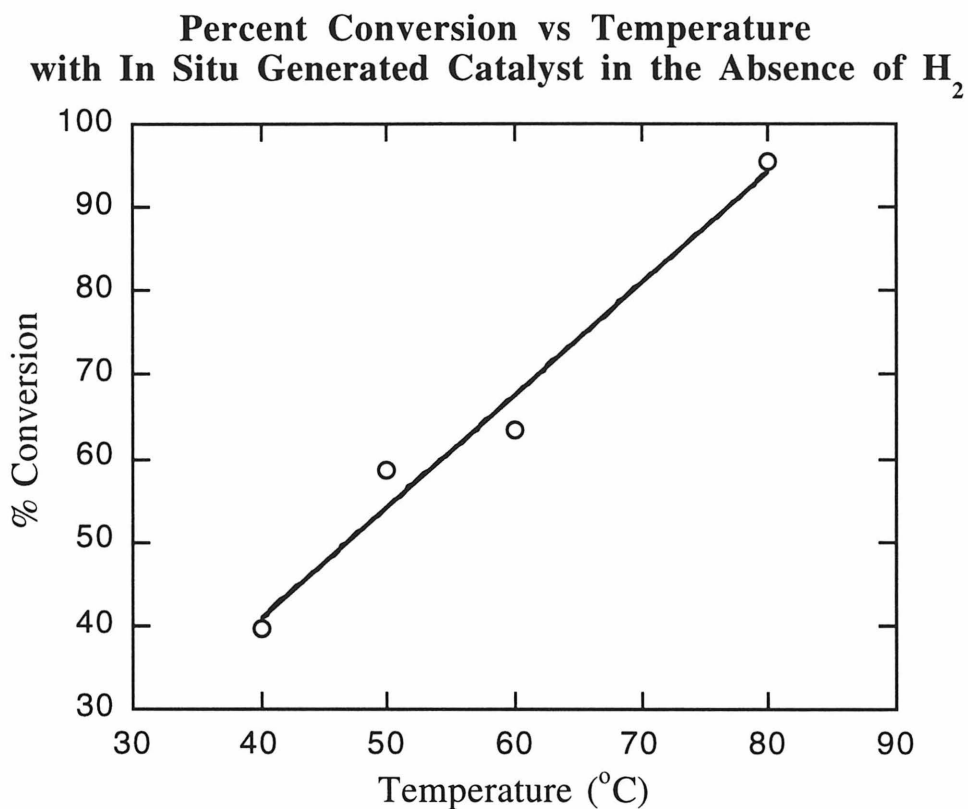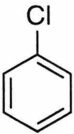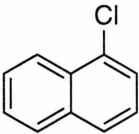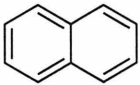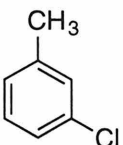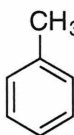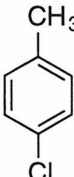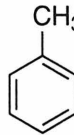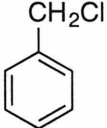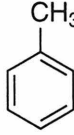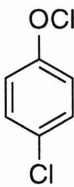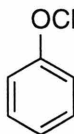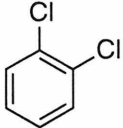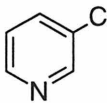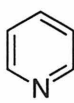
Figure 1.   Conversion of Chlorobenzene to Benzene vs Reaction Temperature using
in situ Generated Catalyst Without Dihydrogen.   Slope = 1.34; R = 0.99.

Increasing the temperatures leads to greater conversion efficiency with a maximum reached at 80°C. However, above this temperature, the homogeneous solution displays signs of catalyst decomposition (Figure 1). The reactivity of the catalytic species formed from **3** is comparable to that displayed by the isolated catalysts **1** or **2**. The catalytic results involving **3** are presented in Table 2.

Table 2. Catalytic Dehalogenation with [RuCl$_2$(COD)]$_x$ +2PCy$_3$ in sec-Butyl Alcohol and H$_2$.

Substrate	Product	Cat. mol %	Time (h)	% Converted[a]
Cl (chlorobenzene)	(benzene)	2.5	1	99
Cl (1-chloronaphthalene)	(naphthalene)	2.5	1	96
CH$_3$ / Cl (3-chlorotoluene)	CH$_3$ (toluene)	2.5	1	95
CH$_3$ / Cl (4-chlorotoluene)	CH$_3$ (toluene)	2.5	1	89
CH$_2$Cl (benzyl chloride)	CH$_3$ (toluene)	2.5	1	92
OCH$_3$ / Cl (4-chloroanisole)	OCH$_3$ (anisole)	2.5	1	95
Cl, Cl (1,2-dichlorobenzene)	(benzene)	2.5	1	81
Cl (3-chloropyridine)	(pyridine)	2.5	1	35

[a]Percent conversions determined by GC

The isolated catalysts **1** and **2** give slightly better conversions suggesting that a small percentage of the starting material may not be converted into active catalytic species. The rate of dechlorination of chlorobenzene using **2** was monitored by GC analysis of aliquots taken from the reaction mixture at known time intervals. A first order rate constant of 1.8×10^{-3} (sec^{-1}) can be calculated for the conversion which corresponds to a $t_{1/2} = 6.4$ min. The kinetic plot is presented in Figure 2.

y = 0.72326 + -0.0018207x R= 0.99629
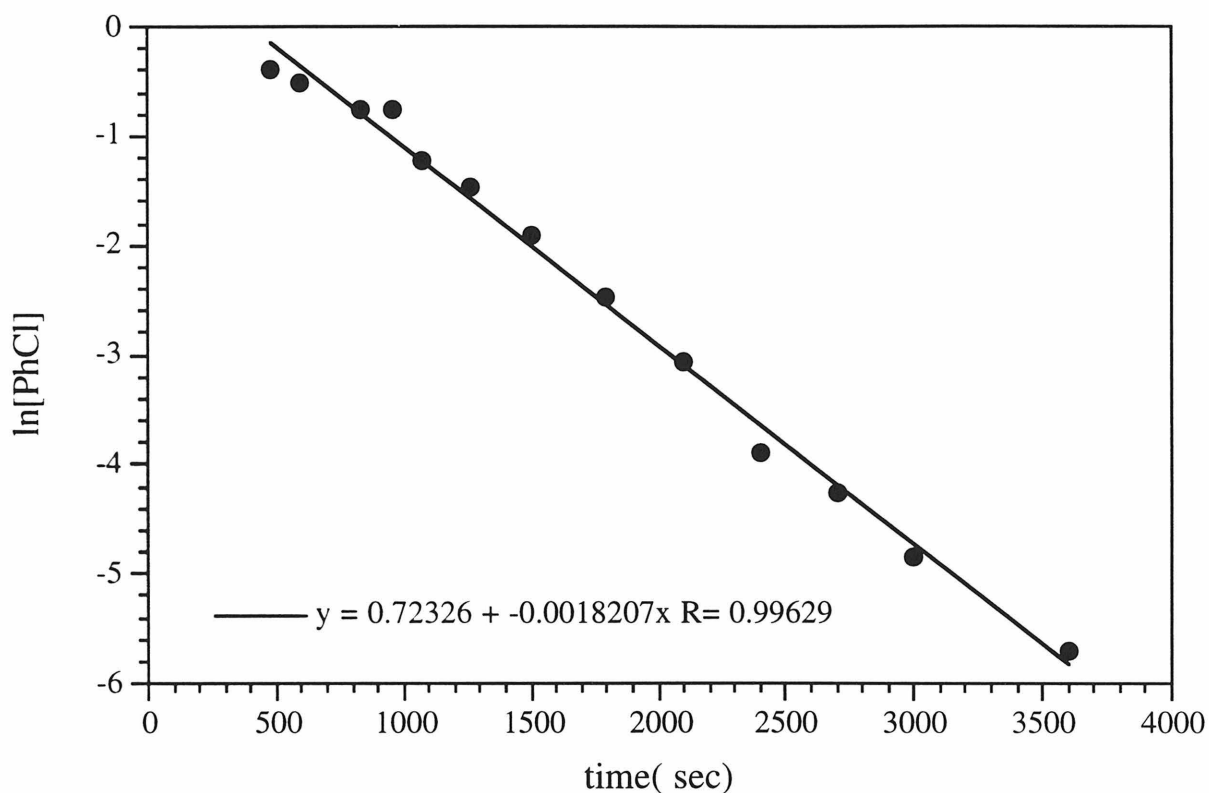
Figure 2. ln[PhCl] vs time (sec) for dehalogenation using catalyst **2** (2.5 mM) and [PhCl]$_0$ = 0.100 M. Slope = -0.0018 ± 0.0002; R = 0.996.

2.4 Dechlorination with Ru(H)Cl(H$_2$)$_2$(P^{i}Pr$_3$)$_2$: The efficiency and activity of the dechlorination reaction was tested as a function of the nature of the phosphine ligand bound to the ruthenium center. Using identical experimental reaction conditions as Equation 7, reaction of [RuCl$_2$(COD)]$_x$ (3) with two equivalents of P^{i}Pr$_3$ leads to the formation of RuHCl(H$_2$)$_2$(P^{i}Pr$_3$)$_2$ (5).[10]

$$[RuCl_2(COD)]_x + 2\ P^iPr_3 \ + \ NEt_3 \xrightarrow[\ H_2\ ]{sec\text{-}BuOH}$$

$$[Ru(H)(Cl)(H_2)_2(P^iPr_3)_2] \quad + HNEt_3Cl \ + C_8H_{16} \qquad (7)$$
$$\mathbf{5}$$
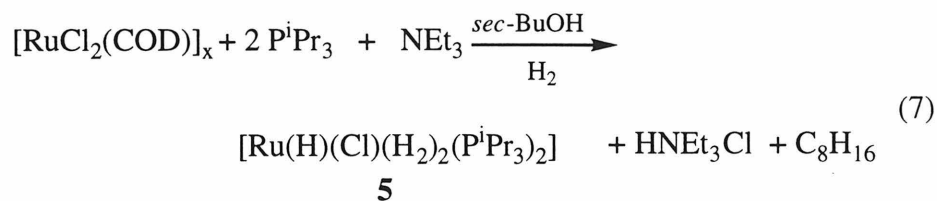
Utilization of 5 in catalytic dechlorination experiments leads to complete conversion of chlorobenzene to benzene. Catalytic conversions are the same as those performed using 1 or 2.

2.5 Proposed Mechanism : From the available experimental evidence, a simple mechanism based on transfer hydrogenation chemistry is proposed. The catalytic cycle is illustrated in Scheme 1.

Scheme 1. Proposed Mechanism for Ruthenium -Mediated Catalytic Dehalogenation

S = Solvent

PR_3 = P^iPr_3 and PCy_3
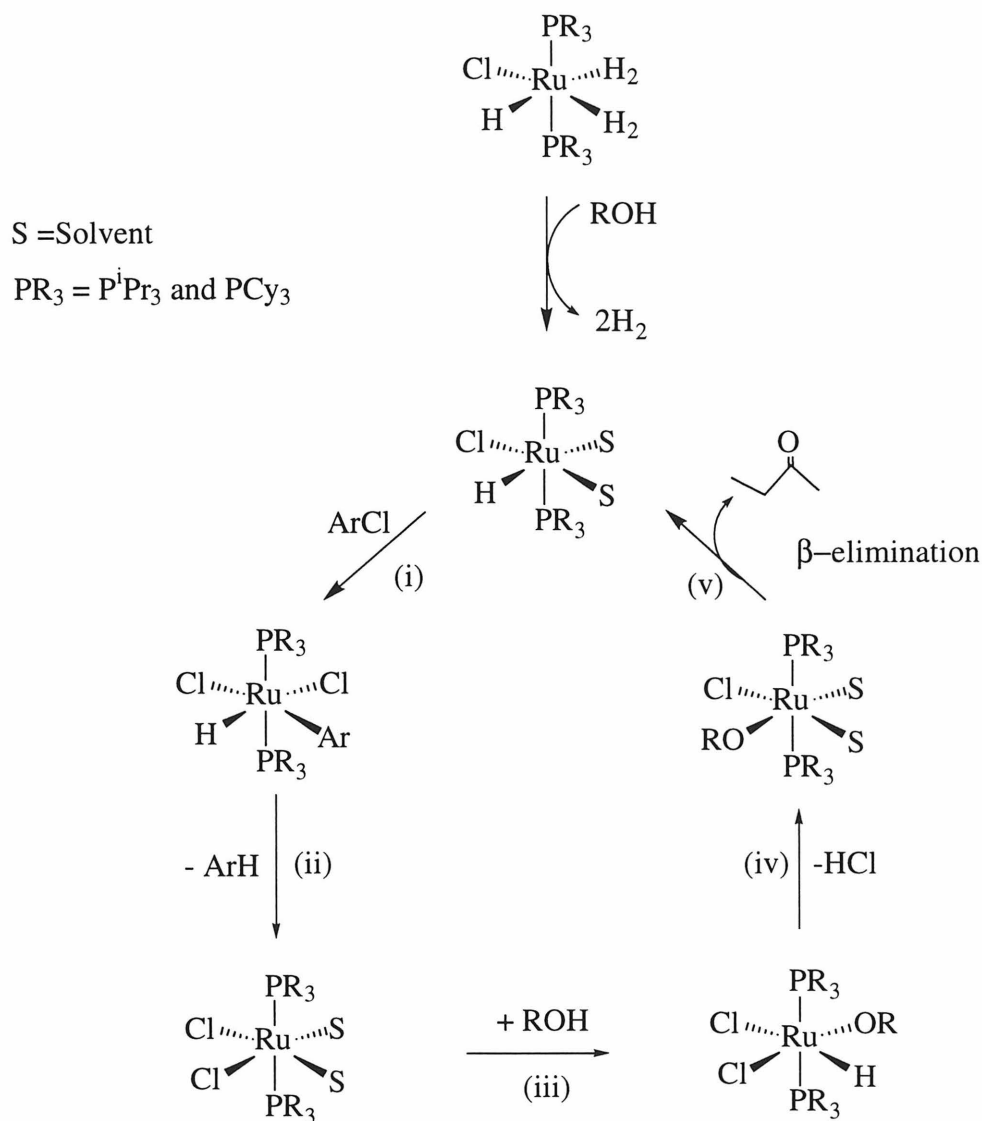
In a first step (i), a ruthenium (II) species oxidatively adds the aryl chloride leading to the formation of a ruthenium (IV) complex. In a second step (ii), the arene is reductively eliminated from the coordination sphere of the metal leading to the formation of a ruthenium dichloro species which then undergoes oxidative addition of the alcohol to form a ruthenium (IV) complex (step iii). This species then releases HCl (driven by the presence of the base) leading to an alkoxy chloro ruthenium species. β - Hydride elimination from the alkoxy ligand, liberating the ketone, regenerates the initial catalytic species.

Hydrogen transfer reactions of alkoxides, or alcohols in presence of NaOH, with ruthenium halide complexes are a well-known method for the preparation of ruthenium hydrides.[27] 2-butanone, the ketone generated in step (iv), was detected by GC in every dechlorination experiment carried out in *sec*- butyl alcohol. If a nonsecondary alcohol is used, such as methanol or *tert*-butanol, no conversion occurs. The formation of ruthenium carbonyl complexes via decarbonylation of methanol has previously been reported. This specific need for a secondary alcohol was tested by using 2-propanol as the solvent. Efficient conversions are observed, as in experiments involving *sec*-butyl alcohol .

A number of entry ways into the catalytic cycle are possible. It has already been stated that complexes **1** and **2** can be interconverted. We therefore consider them as a single entry point. Simple loss of its dihydrogen ligands in the presence of alcohol solvent converts **2** into the initial catalytic species.

$$
\begin{array}{ccc}
\underset{\textbf{(2)}}{\underset{\underset{PCy_3}{|}}{\overset{\overset{PCy_3}{|}}{Cl_{\prime\prime\prime}\cdots\underset{H}{\overset{}{Ru}}\cdots^{\prime\prime}\overset{H_2}{\underset{H_2}{}}}}} & \xrightarrow[-2H_2]{S\ =\ ROH} & \underset{PCy_3}{\overset{\overset{PCy_3}{|}}{Cl_{\prime\prime\prime}\cdots\underset{H}{\overset{}{Ru}}\cdots^{\prime\prime}\overset{S}{\underset{S}{}}}} & (7)
\end{array}
$$
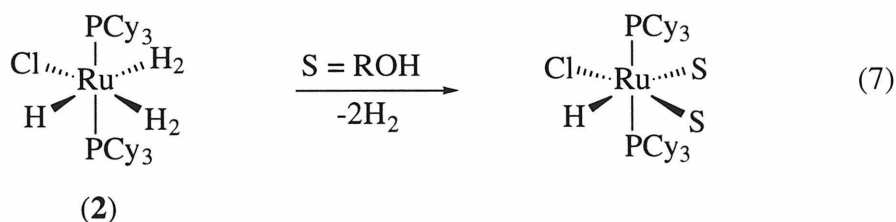
The *in situ* catalyst generation reaction leads to **1** or **2** if dihydrogen is used in the precatalyst formation reaction. The independently synthesized complex Ru $(\eta^3\text{-}C_6H_8\text{-}PCy_2)(PCy_3)Cl$ (**4**) can also be used as a catalyst precursor and may be one of the intermediates involved in the course of the *in situ* catalyst generation. Since **4** is easily converted into **1** under hydrogen in basic media, we consider it as an alternative entry way into the catalytic cycle.

Cy$_2$P / Ru—Cl / PCy$_3$ **(4)** → ROH, −HCl → Cy$_2$P / S—Ru—O / H, PCy$_3$ (8)

Cl,,, / S — Ru—(C$_6$H$_5$) / PCy$_3$, PCy$_3$ ←   S—Ru—O= / PCy$_3$, PCy$_3$ + C$_6$H$_5$Cl
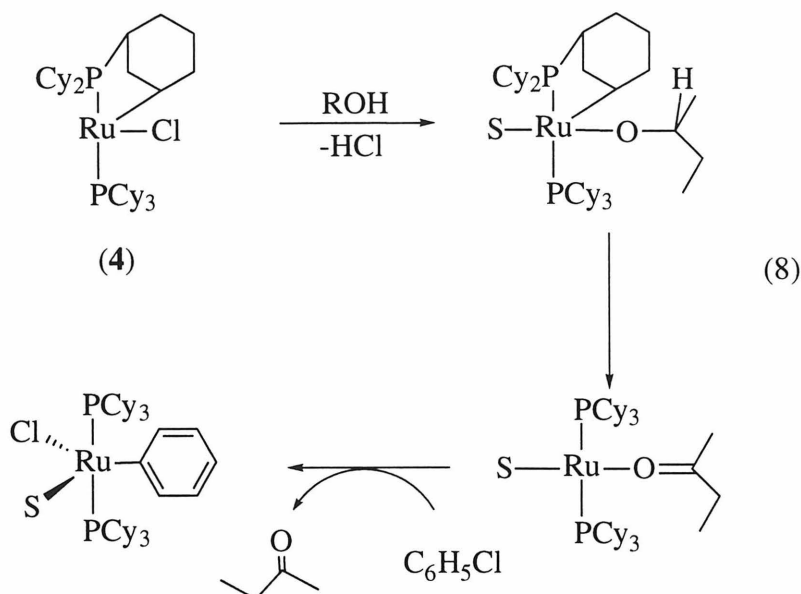
Although the entry way is illustrated with **4**, complexes bearing either PCy$_3$ and P^{i}Pr$_3$ ligands in the η^3 binding mode have been reported.[28,29] Their stability is surprising in view of the considerable strain present in such five-membered cyclic systems.[30]

3. Conclusion

RuH$_2$(H$_2$)$_2$(PCy$_3$)$_2$ (**1**) and RuHCl(H$_2$)$_2$(PCy$_3$)$_2$ (**2**) prove to be excellent catalysts for the dechlorination of chloroarenes. The reactions are complete after one hour.   Most notably the reactions are performed in the absence of dihydrogen. The dechlorination proceeds via transfer hydrogenation. The catalysts are tolerant of a variety of functional groups and are efficient in dechlorinating multichlorinated arenes. The catalytic species may be generated *in situ* from the air-stable precursor [RuCl$_2$(COD)]$_x$ (**3**) and conversions obtained using **3** are comparable to those obtained using the isolated catalyst **2**. The catalyst lifetime/ activity was tested by subsequent addition of substrate and showed constant conversion efficiency. The experimental results, especially the identification of the ketone generated in the course of the reaction[31], lend support to the proposed mechanism which involves transfer hydrogenation using secondary alcohols as the hydrogen source.

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Li, C.; Cucullu, M. E.; McIntyre, R. A.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1994**, *13*, 3621-3627 and references cited.

31. Since Rh complexes have been shown to perform transfer hydrogenations[22], we found that the Rh system, $[RhL_2(H)Cl_2]$, (L = PCy_3 or P^iPr_3) gave complete dechlorination of aromatic chlorides without dihydrogen when a secondary alcohol was used as the solvent.

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Chapter 3

Binuclear Ruthenium Carbene Complexes

1. Introduction

Two basic metathesis transformations are ring-closing metathesis (RCM) and ring-opening metathesis polymerization (ROMP) both of which have become increasingly important in organic and polymer synthesis.
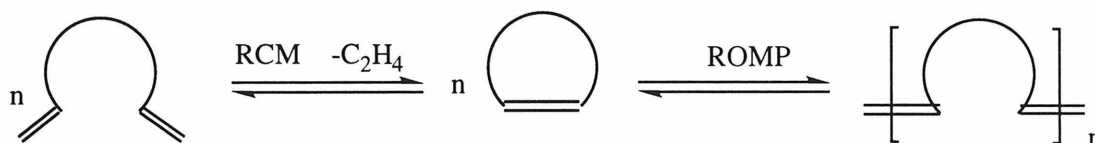
Scheme 1.

Cyclic olefins can be produced by RCM of α,ω-dienes to form five, six, seven and even eight membered rings.[1] RCM has also been successfully applied to produce macrocyclic and solid-supported compounds.[1] In the case of ROMP, polylolefins can be obtained starting from strained cyclic alkenes and it is the release of the monomer's ring strain that overcomes the entropically disfavored polymerization and is the driving force for the polymerization. ROMP has facilitated the synthesis of a large variety of functionalized polymers and its success is evident in a number of applications such as electroluminescent and conducting polymers[2], sidechain liquid-crystalline polymers[3] and internally and terminally functionalized polymers.[4]

Many recent advances in catalyst research as applied to olefin metathesis reactions have led to some of these tremendous developments in organic and polymer chemistry. In the past, the catalysts specifically for ROMP were multicomponent mixtures, ill- defined and were not able to polymerize strained olefins in a living manner. Further developments lead to the next generation of catalysts based on Ti, Ta, Mo, W and Re metal carbenes.[5] While these single component catalysts were an improvement, they still lacked tolerance towards polar functional groups, protic media and air. There was clearly a need for well-defined single component catalysts that would be easier to synthesize and stable to more conditions. Tremendous progress has been made in the development of new catalysts by

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Grubbs and co-workers. One of the first examples of a single-component, late transition metal catalyst system was ruthenium diphenylvinly alkylidene **1a**. This lead to futher investigations in the search for more active single component catalysts and the development of catalyst **1b**. Both catalysts are remarkably stable towards functional groups and much less sensitive to air and protic media.

1a: R = CHCPh$_2$
1b: R = Ph
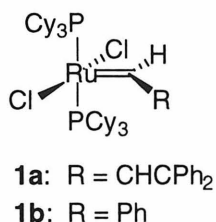
Further studies on catalysts 1a and 1b has lead to a new generation of single-component ruthenium catalysts.

2. Background: bimetallic synthesis, reactivity and trends

Mechanistic studies of ruthenium carbenes 1a and 1b in the interests of designing a more active catalyst revealed that for a system to be first-order in catalyst concentration it should have only one phosphine and a hemilabile chelating ligand. These dimeric bridging chloride species are well known to react with phosphines,[6] and were found to react cleanly and quickly with catalysts **1a** and **1b** (Scheme 2).

1a: R = CHCPh$_2$
1b: R = Ph

M = Ru   M = Os
2a: R = CHCPh$_2$ **3a**: R = CHCPh$_2$
2b: R = Ph   **3b**: R = Ph
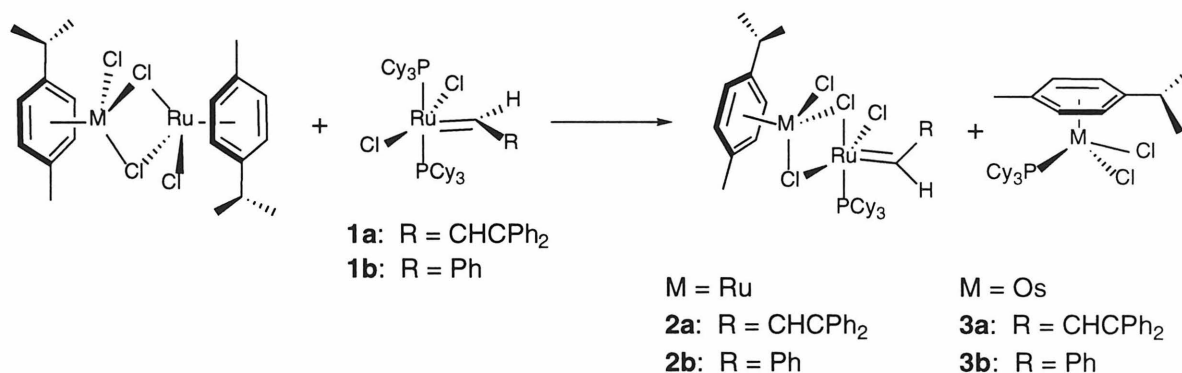
Scheme 2. Synthesis of binuclear complex starting from a bridging chloride dimer

Reaction of [Os(*p*-cymene)Cl$_2$]$_2$ was shown to react in an analogous fashion to yield the bimetallic species **3a** and **3b**. The dimer [Ru(benzene)Cl$_2$]$_2$ was also investigated with catalysts **1a** and **1b** and although a bimetallic alkylidene species was detected by ^{1}H NMR it was not stable and rapidly decomposed.

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In a similar fashion the dimer [Rh(^tBu₂Cp)Cl₂]₂ was reacted with catalysts **1a** and **1b** and was found to proceed cleanly and quantitatively to form products **4a** and **4b** respectively.

1a: R = CHCPh$_2$
1b: R = Ph

4a: R = CHCPh$_2$
4b: R = Ph
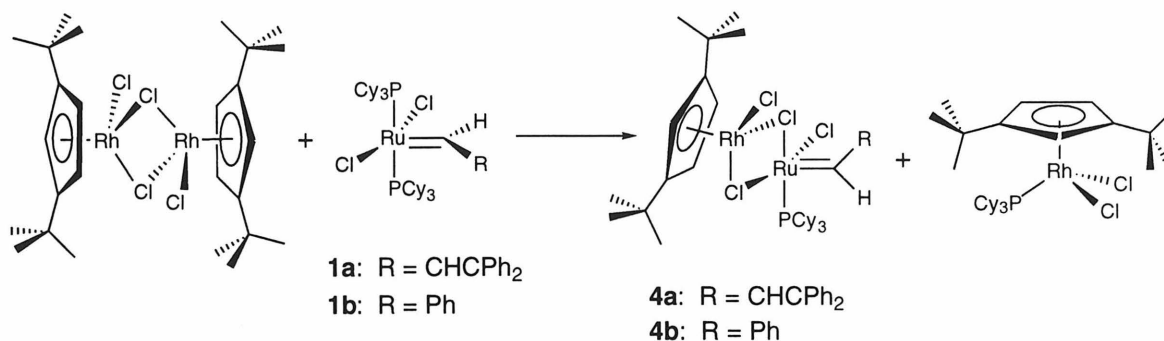
Scheme 3. Synthesis of rhodium-ruthenium alkylidene

The stability of a series of other rhodium chloride dimers was also investigated with catalyst **1a** and **1b**. The reactions of these dimers [RhCp*Cl$_2$]$_2$ and [Rh(^tBuCp)Cl$_2$]$_2$ with catalyst **1a** and **1b** were shown to initially form a bimetallic alkylidene species but this was followed by decomposition.

A comparison of the activity of the three types of binuclear catalyst in the ROMP of 1,5-cyclooctadiene with catalysts **1a** and **1b** revealed all three bimetallic catalysts: **2a,b**; **3a,b** and **4a,b** had significantly greater activities. In fact the rhodium displayed the largest increase in catalyst activity with rates almost 80 times that of catalyst **1a**. The order of increasing activity for the bimetallic catalysts was Ru<Os<<Rh. The reactivity increases as the bridging chloride becomes more electron withdrawing. A metal with ancillary ligation which will enhance this effect would also enhance reactivity of the carbene species.

Thus, two important trends in these bimetallic systems have been observed: significant steric bulk is required in order to minimize bimolecular carbene decomposition and electron withdrawing effects of the ancillary metal center helps stabilize the carbene fragment. Both effects appear important and a fine balance of both is surely needed in order to achieve carbene stability yet increased reactivity. These bimetallic systems have provided a better understanding of the reactivity and stability of ruthenium catalysts. Yet, even though the bimetallic catalysts have proven to be more reactive than the parent catalysts **1a** and **1b** there is still much to learn in the development of more reactive and stable ruthenium catalysts.

3. Preliminary Results and Future Goals

3.1 Electronic Effect : The nature of the second metal in the previous discussion was shown to be important in the reactivity of the catalyst. An extensive study is essential to understand how catalyst activity might be controlled by altering the electronics of the system. A survey of dimers substituted with electron withdrawing groups will be performed. An example of a dimer bearing electron withdrawing groups is [Ru(CO)3Cl2]2.[7] The dimer will be investigated with the benzilydene to determine whether a carbene will be formed.
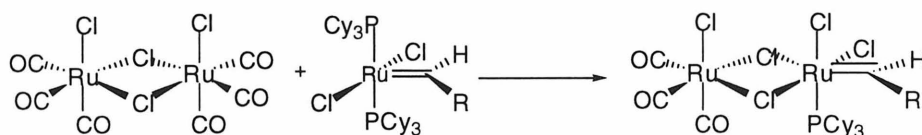
Scheme 4.

Other dimers bearing both bulky and electron withdrawing substituents will be investigated. Trispyrazolylborate ligands might be ideal for this system, as they generally form more stable compounds than their Cp analogues. As discussed (vide infra), it is possible to synthesize a wide variety of sterically demanding trispyrazolylborate ligands. Furthermore, a systematic study of electronic effects with this ligand system should also be possible.

To further our understanding of the binuclear systems, a series of metal carbonyl dimers: [CpM(CO)3]2, M = Mo, W, Cr; [CpM(CO)2]2, M = Fe, Ru were considered which can be readily transformed into the anionic species by reacting the dimer with Na/K alloy.[8] These systems were of interest because they would potentially afford a direct metal - metal bond to the parent carbene by salt elimination route and modifications could be easily made to the ancillarly metal complex to tune the electronics of the system, a limitation of the binuclear systems thus far investigated. Since the basicity of these anions has been evaluated extensively by Norton and co-workers[9r] whether or not the binuclear species formed would provide information about the basicity of the parent carbene. The pK$_a$ values of the metal hydrides are shown in Table 1.

Table 1. The pK$_a$ values of hydrides in acetonitrile

hydride	pK$_a$
HCl	8.9
CpCr(CO)$_3$H	13.3
CpMo(CO)$_3$H	13.9
CpW(CO)$_3$H	16.1
CpFe(CO)$_2$H	19.4
CpRu(CO)$_2$H	20.2

Reaction of the parent carbene with two of the metal anions, [CpMo(CO)$_3$]$^-$ and [CpFe(CO)$_2$]$^-$, by NMR showed no change in either species. This suggests these anions are too basic to react with the ruthenium carbene species.

3.2 Steric contribution :   The nature of the second metal as well as the steric demand of the capping ligand were shown to be very important in the initial studies. It was demonstrated that the stability of the bimetallic carbenes is strongly effected by the steric bulk present on the ancillary metal. Rapid decomposition of the bimetallic species results when a less sterically hindered ligand sphere is used for the ancillary metal. The trend observed from changing the arene from benzene to *p*-cymene in the [Ru(arene)Cl$_2$]$_2$ resulted in a dramatic improvement in stability. Thus analogous more sterically demanding arene systems, such as [Ru(hexamethylbenzene)Cl$_2$]$_2$[10] (Scheme 5) will be investigated to understand where the stability of bimetallic carbene species is relative to the others.
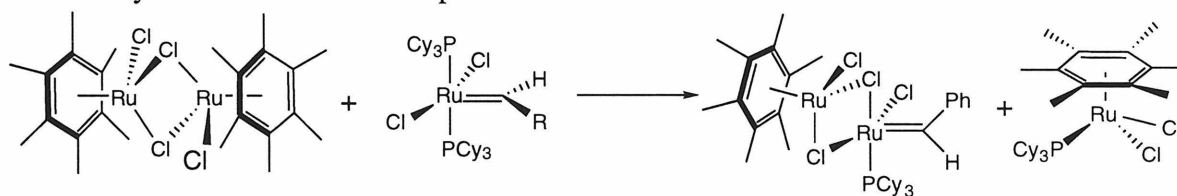
Scheme 5.

 The [Ru(hexamethylbenzene)Cl$_2$]$_2$ should react in a similar fashion as in the *p*-cymene case. Another ruthenium dimer which bears an even more sterically bulky ligand sphere, [Ru(trindane)Cl$_2$]$_2$[11,12] will also be investigated as shown in Scheme 6. This ancillary metal ligand sphere would afford even greater shielding thereby potentially yielding more stable bimetallic alkylidenes.
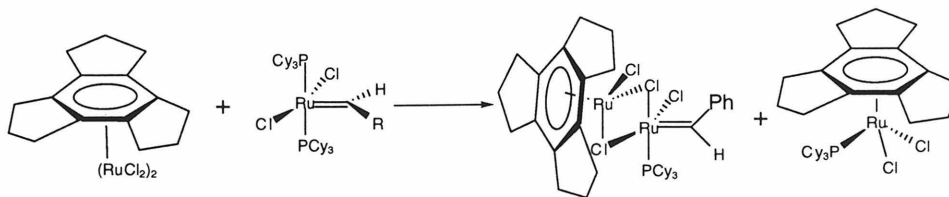
Scheme 6.

The Lewis acidity of the second metal could also be important in the opening of the required coordination site. We will build on an observation made in earlier Tebbe chemistry[13] where it was found that a tungsten oxo complex formed a very stable bridging species.
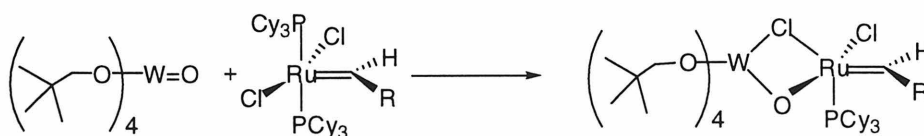
Scheme 7.

With the W(IV) metal in a high oxidation state and with the presence of the neopentoxy groups, this would provide both an electron withdrawing ancillarly metal center and a sterically bulky environment. Thus this system will be rigorously studied. The abundance of metal oxo complexes, such as Re and Os, would extend the investigation to include other analogous Lewis acidic metal oxo complexes.

3.3 Conclusion: New stratigies for synthesizing potentially more stable and/or reactive bimetallic carbenes have been presented. The steric effect on the stability will be investigated. Efforts will also be directed towards considering systems which might make the ruthenium-bound chloride more electron withdrawing. This may be accomplished by making the ancillary metal more electron withdrawing and/or the ligands coordinated to the ancillarly metal more electron withdrawing. In addition to these studies, systems which encompass both the electronic and steric effects will be synthesized and investigated. An example of such a system is the Lewis acid tungsten oxo complex. This could potentially lead to the development and exploration of other metal oxo systems where the possibilities of fine-tuning of the electronics and/or sterics is accessible.

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Appendix I

Experimental Section:

Chapter 1:

General Procedures. NMR spectra were recorded on a QE Plus-300 MHz (300.1 MHz
^{1}H; 75.49 MHz ^{13}C) spectrometer. Argon was purified by passage through columns of
BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). Elemental analyses
were performed by Caltech Analytical Labs or Mid-West Microlab. High resolution mass
spectra were obtained from UC Riverside Mass Spectrometry Facility.

Materials. THF and toluene were dried by passing through activated alumina columns.
Acetylene **2c**,[34] was prepared according to literature procedures.
Hexamethylphosphoramide (HMPA) was purchased from Aldrich and dried over calcium
hydride and then distilled under reduced pressure prior to use. *Cis*-3,5-cyclohexadiene-
1,2-diol was obtained from ICI. Thiocarbonyldiimidazole (TCDI), 1,3-dimethyl-2-phenyl-
1,3,2-diazaphospholidine (DPD) and acetylenedicarboxylic acid were purchased from
Aldrich and used without further purification except where noted otherwise.
**5,6-Bis(2-ethylhexyl)-2,3-dihydroxy-5,7-bicyclo[2.2.2]octa-5,7-diene-
5,6-dicarboxylate (3c).** A 100 mL round bottom flask was charged with 10.43 g
(30.81 mmol) of 2-ethylhexyl acetylenedicarboxylate and 15.00 g (150 mmol) of CaCO$_3$.
After stirring for 30 minutes under a flow of argon, 1.73 g (15.43 mmol) of *cis* -3,5-
cyclohexadiene-1,2-diol and 2.13 mL of dry THF was added to the flask. The reaction
was heated at 60 °C for 3 days and then filtered to remove CaCO$_3$. After rinsing the
CaCO$_3$ with CHCl$_3$, solvent was removed under vacuum to yield a yellow oil . The
yellow oil was loaded onto a column of silica gel and eluted with 10% ethyl acetate/hexane.
Following removal of solvent, 5.03 g (11.16 mmol, 71.20%) of a mixture of syn and anti
product isomers was obtained as a yellow oil. Note: Calcium carbonate was added to this
reaction to decrease formation of phenol. ^{1}H NMR (300 MHz, C$_6$D$_6$) anti δ 6.21 (m, 2H),
syn δ 5.72 (dd, *J* = 4.2, 3.3 Hz, 2H), 4.21 (m, 2H) 4.19 - 4.02 (m, 6H), 3.73 (bs, 2H).
2.37 (bs, *J* = 2H), 1.53 (m, 2H), 1.40 - 1.02 (m, 16H) 0.89 - 0.79 (m, 12H); ^{13}C NMR
(75 MHz, C$_6$D$_6$) anti δ 166.1, 141.0, 132.3, 68.5, 67.8, 47.9, 39.5, 31.1, 29.6, 24.5,
23.7, 14.6, 11.5; syn δ 167.35, 140.3, 132.4, 68.3, 67.2, 47.3, 39.5, 31.1, 29.6, 24.5,

23.7, 14.6, 11.5; HRMS calcd for $C_{26}H_{42}O_6$ (M+H)$^+$ 451.30594, found 451.3070. Anal. Calcd for $C_{26}H_{42}O_6$: C, 69.30; H, 9.39. Found: C, 68.91; H, 9.34.

5,6-Bis(2-ethylhexyl)-2,3-thiocarbonate-5,7-bicyclo[2.2.2]octa-5,7-diene-5,6-dicarboxylate (4c). Compound **3c** (3.98 g, 8.84 mmol) and 1.93 g (90% pure, 9.72 mmol) of thiocarbonyldiimidazole (TCDI) were loaded into a 50 mL flask purged with argon. 30 mL of dry toluene was added to yield a solution containing undissolved TCDI. The solution was heated in an oil bath, which had been preheated to 135 °C, for 20 minutes. An additional 0.913g of TCDI was loaded into the flask and the reaction was heated for 15 minutes. After cooling to room temperature, the yellow solution was poured onto a plug of silica gel and eluted with 50% ethyl acetate/hexane. Removal of solvent under vacuum yielded 4.01 g (8.15 mmol, 92.12%) of **4c** as a yellow oil. ^{1}H NMR (300 MHz, CDCl$_3$) anti δ 6.55 (dd, J = 4.2, 3.3 Hz, 2H), 5.00 (m, 2H), 4.55 (m, 2H), 4.12 (m, 4H), 1.60 (m, 2H), 1.4 - 1.29 (m, 16H), 0.90 (t, J = 7.2, 12H); syn δ 6.40 (dd, J = 4.5, 3.0 Hz, 2H), 4.91 (m, 2H), 4.55 (m, 2H), 4.14 (m, 4H), 1.64 (m, 2H), 1.46 - 1.23 (m, 16H), 0.90 (m, 12H); ^{13}C NMR (75 MHz, CDCl$_3$) anti δ 191.5, 164.3, 139.4, 131.3 81.4, 69.1, 43.0, 38.9, 30.8, 29.1, 24.0, 23.9, 14.3, 11.1; syn δ 191.6, 165.5, 139.6, 132.4, 80.7, 68.5, 43.4, 39.6, 31.0, 29.7, 24.4, 23.8, 14.6, 11.6; HRMS Calcd. for $C_{27}H_{40}O_6S$ (M+H)$^+$ 493.2624, found 493.2620. Anal. Calcd for $C_{27}H_{40}O_6S$: C, 65.82; H, 8.18. Found: C, 65.87; H, 8.21.

2,3-Bis(2-ethylhexyl)bicyclo[2.2.2]octa-2,5,7-triene-2,3-dicarboxylate (5c). A 50 mL round bottom flask was charged with 4.013g (8.15 mmol) of compound **4c** and 4.50 mL of 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine (DPD) to yield a brown mixture. The mixture was heated under argon in an oil bath at 40 °C for 7 days. The brown solution was then loaded onto a silica gel column and eluted with 10% ethyl acetate/hexane. After evaporation of solvent, 1.78 g (4.27 mmol, 52.5%) of the product was obtained as a yellow oil. ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.87 (m, 4H), 5.08 (m, 2H), 4.06 (dd, J = 6.0, 3.0 Hz, 4H), 1.59 (m, 2H), 1.39 - 1.28 (m, 16H), 0.88 (m, 12H); ^{13}C NMR (75 MHz, C$_6$D$_6$) δ 167.5, 149.7, 140.9, 68.2, 50.7, 39.5, 31.1, 29.6, 24.5, 23.7, 14.6, 11.5; HRMS calcd for $C_{26}H_{40}O_4$ M$^+$ 416.2926, found 416.2920. Anal. Calcd for $C_{26}H_{40}O_4$: C, 74.95; H, 9.68. Found: C, 74.87; H, 9.86.

Chapter 2:

General Considerations. All manipulations were carried out using standard high vacuum or Schlenk techniques under an atmosphere of argon. Argon was purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4-Å molecular sieves. Solids were transferred and stored in a nitrogen-filled Vacuum Atmospheres drybox. ^{1}H

and ^{31}P NMR spectra were recorded on a JEOL GX-400 MHz (399.1 MHz ^{1}H, 161.9 MHz ^{31}P) spectrometer at 20°C. Gas Chromatography analyses were performed on a Hewlett-Packard model 5890 series II GC equipped with an SE 30 capillary column. Identity of reaction components were determined by comparison with commercial samples by gas chromatography.

Materials. Chloroarenes, arene products and 2-butanone were purchased from Aldrich. Organometallic complexes $RuH_2(H_2)_2(PCy_3)_2$ (**1**)[9,10] , $RuHCl(H_2)_2(PCy_3)_2$ (**2**)[10], $[RuCl_2(COD)]_x$ (**3**)[32] , $RuHCl(H_2)_2(P^iPr_3)_2$ (**5**)[10] and $Rh(H)Cl_2(PCy_3)_2$ (**6**)[7] were synthesized according to literature procedures. *Sec*-butyl alcohol, methanol, 2-propanol and *t*-butyl alcohol were purchased from Aldrich as anhydrous grade (99.5%) and purged with Ar prior to use. Toluene and deuterated benzene were purified using procedures previously reported.[33] $RuCl_3 \cdot xH_2O$, $RhCl_3 \cdot xH_2O$, PCy_3 and P^iPr_3 were purchased from Strem and used as received.

General Procedure for the $Ru(H)(Cl)(H_2)_2(PCy_3)_2$ Catalyzed Dehalogenations of Chloroarenes. A 500 mL Fisher-Porter bottle was charged with $Ru(H)(Cl)(H_2)_2(PCy_3)_2$ (**2**) (100 mg, 1.4 mmol). Degassed *sec*-butyl alcohol (40 mL) and 50% NaOH solution (15 mL) were then cannula transferred in the reaction vessel. The chloroarene substrate (56 mmol) was then added by syringe and the reaction vessel was then closed and heated to 80°C for 1 hour. After cooling to room temperature, an aliquot was removed from the organic phase and filtered through a silica gel-glass wool plug loaded in a disposable pipette. The filtrate was then analyzed by GC using an internal standard.

General Procedure for the *in situ* Catalyzed Dehalogenations of Chloroarenes from $[RuCl_2(COD)]_x$ A 500 mL Fisher-Porter bottle was charged with $[RuCl_2(COD)]_x$ (**3**) (100 mg, 2.5 mmol) and two equivalents of PR_3 [R = cyclohexyl or isopropyl]. Degassed *sec*-butyl alcohol (40 mL) and 50% NaOH solution (15 mL) were cannula transferred into the reaction container. The reaction mixture was then pressurized to 3 atm of H_2. The reaction vessel was then closed and heated to 80°C for 3 hours. Prior to addition of the chloroarene substrate, the reaction vessel was cooled to room temperature and was purged for 20 minutes under a flow of argon. Next, the chloroarene substrate was added (100 mmol) and the reaction vessel was again heated to 80°C for 1 hour. After cooling, an aliquot, taken from the organic phase, was filtered

through a silica gel-glass wool plug in a disposable pipette. The filtrate was analyzed by GC with an internal standard.