Easier and More Efficient Methods for the Generation of Metathesis Catalysts: Investigations into Group VI and VIII

Thesis by

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to my family,

to Anne and Henry,

and to Harold

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Abstract:

Chapter 1:

A high yield procedure for generating the ruthenium hydride complexes $Ru(H)(H_2)Cl(PR_3)_2$ (R=Cyclohexyl, cyclopentyl, isopropyl) in very high yield is presented. Following a novel insertion-elimination pathway, these hydrides can react with propargyl or vinyl halides to make metathesis active vinyl and alkyl carbene species with the general formulas $(PR_3)_2Cl_2Ru=CH-CH=CR'_2$ and $(PR_3)_2Cl_2Ru=CHR'$, respectively. Tertiary propargyl chlorides like 3-chloro-3-methyl-1-butyne work best, yielding Ru-vinyl carbenes in extremely high yield. An alternate route is to first add an alkyne, and then add HCl to give similar species.

In attempting to learn about the insertion-elimination mechanism, the compounds $M(H)Cl(CO)(PR_3)_2$ (M=Ru, Os; R=cyclohexyl, isopropyl) were found to react with 3-chloro-3-methyl-1-butyne to produce the metathesis inactive carbenes with general formula *cis*-Cl_2-*trans*$(PCy_3)_2(CO)M=CHCH=CMe_2$. Kinetics of $Ru(H)Cl(CO)(P^iPr_3)_2$ can only be analyzed qualitatively, but from all of the available data a mechanism is proposed for the insertion of hydrides into alkynes and rearrangement to give carbenes. The compounds $M(H)Cl(CO)_2(PR_3)_2$ (M=Ru, Os; R=cyclohexyl, isopropyl) show no alkyne insertion.

The osmium analogs $Os(H)_3Cl(PCy_3)_2$ and $(PCy_3)_2Cl_2Os=CH=CH=CMe_2$ were investigated for the ability to generate carbenes. The osmium carbene, however, rapidly transforms to the hydrido-carbyne species $(PCy_3)_2Cl_2Os(H)(\equiv C-CH=CMe_2)$. It appears that additional stabilization of the osmium system will be necessary to prevent such rearrangement.

It is also presented that $(PCy_3)_2Cl_2Ru=CHR'$ reacts with dihydrogen to

Abstract (continued)

give H_3CR', $Ru(H)_2(Cl)_2(PCy_3)_2$, and $Ru(H)(H_2)Cl(PCy_3)_2$. Theoretically, all $Ru(H)_2(Cl)_2(PCy_3)_2$ can be converted to $Ru(H)(H_2)Cl(PCy_3)_2$. It is thus possible to go from hydrides to carbenes, and back to hydrides.

Chapter 2:

Complexes of the type $M(O)Cl_2(PR_3)_3$ (M=W, Mo; R_3=$PMePh_2$, PMe_2Ph) were synthesized using literature procedures, and shown to react with 3,3-diphenylcyclopropene to give the η^2-olefin complexes $M(O)Cl_2(PR_3)_2(\eta^2$-diphenylcyclopropene). Spectroscopic data suggest a distorted octahedral structure for both, with the oxo ligand in the axial position with the olefin cis to it and the two mutually trans phosphines in the equatorial plane, which was confirmed for M=W with an x-ray diffraction study. The olefin complexes react with suitable alkoxides to give the oxo-carbene species $M(O)(OR)_2(PR_3)(=CH-CH=CPh_2)$, the first known single component tungsten and molybdenum oxo-alkylidene metathesis catalysts, in which the phosphine is readily displaced with THF. For these complexes, spectroscopic data suggest a distorted trigonal bipyramid with the oxo, alkylidene, and one alkoxide ligand in the equatorial plane, which was confirmed for M=W by a diffraction experiment. These alkylidene species are active in olefin metathesis reactions, showing comparable activity to similar arylimido complexes previously described; polymerization data is presented for norbornene and cyclooctene. In addition, the olefin complexes were shown to be active in olefin metathesis at elevated temperatures.

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Chapter 1:

New Methods for the Generation of Group VIII Carbenes: Active Metathesis Catalysts from Insertion into Metal Hydrides

Abstract:

A high yield procedure for generating the ruthenium hydride complexes $Ru(H)(H_2)Cl(PR_3)_2$ (R=Cyclohexyl, cyclopentyl, isopropyl) in very high yield is presented. Following a novel insertion-elimination pathway, these hydrides can react with propargyl or vinyl halides to make metathesis active vinyl and alkyl carbene species with the general formulas $(PR_3)_2Cl_2Ru=CH-CH=CR'_2$ and $(PR_3)_2Cl_2Ru=CHR'$, respectively. Tertiary propargyl chlorides like 3-chloro-3-methyl-1-butyne work best, yielding Ru-vinyl carbenes in extremely high yield. An alternate route is to first add an alkyne, and then add HCl to give similar species.

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The osmium analogs $Os(H)_3Cl(PCy_3)_2$ and $(PCy_3)_2Cl_2Os{=}CH{=}CH{=}CMe_2$ were investigated for the ability to generate carbenes. The osmium carbene, however, rapidly transforms to the hydrido-carbyne species $(PCy_3)_2Cl_2Os(H)(\equiv C\text{-}CH{=}CMe_2)$. It appears that additional stabilization of the osmium system will be necessary to prevent such rearrangement.

It is also presented that $(PCy_3)_2Cl_2Ru{=}CHR'$ reacts with dihydrogen to give H_3CR', $Ru(H)_2(Cl)_2(PCy_3)_2$, and $Ru(H)(H_2)Cl(PCy_3)_2$. Theoretically, all $Ru(H)_2(Cl)_2(PCy_3)_2$ can be converted to $Ru(H)(H_2)Cl(PCy_3)_2$. It is thus possible to go from hydrides to carbenes, and back to hydrides.

List of Compounds and Abbreviations

$(PMe_3)_2Cl_2W(O)(=CHC(Me)_3)$	**A**	$(PCy_3)_2Cl_2Ru(=CH\text{-}CH=C(CH_2)_5)$	**11**
$Br_2(OR)_2W(=CHC(Me_3))$	**B**	$(PCy_3)_2Cl_2Ru=CH\text{-}CH=CHPh$	**12**
$(OR)_2(ArN=)M(=CHC(Me)_2)$ M=W, Mo	**C**	$(PCy_3)_2Cl_2Ru=CH\text{-}CH=CHMe$	**13**
$(OR)_2(THF)ArN=W=CH(2\text{-}OMe\text{-}C_6H_4)$	**D**	$(PCy_3)_2Cl_2Ru=CH\text{-}CH=CH_2$	**14**
$(OR)_2(P(OMe)_3)ArN=W=CH\text{-}CH=CPh_2$	**E**	$(PCy_3)_2ClBrRu=CH\text{-}CH=CMe_2$	**15**
$(PR_3)_2Cl_2Ru=CHR$	**F**	$Ru(H)_2ClBr(PCy_3)_2$	**16**
$(PPh_3)_2Cl_2Ru(=CH\text{-}CH=CPh_2)$	**G**	$(PCy_3)_2Br_2Ru(=CH\text{-}CH=CMe_2)$	**17**
$(PPh_3)_2Cl_2Ru(=CHPh)$	**H**	$(PCy_3)_2Cl_2Ru(=C(CH_3)\text{-}CH=C(CH_2)_5)$	**18**
$(PCy_3)_2Cl_2Ru(=CH_2)$	**I**	$(PCy_3)_2Cl_2Ru(=CH\text{-}CH=CPh_2)$	**19**
$(PCy_3)_2Cl_2Ru(=CHPh)$	**J**		
$LMCl\text{-}\mu\text{-}(Cl)_2\text{-}Ru(Cl)(PR_3)(=CHR)$	**K**	"$(PCy_3)_2(X)(Y)Ru=CH\text{-}CH=CMe_2$)"	**20**
salicylaldehydeimine-$ClRu=CHR(PR_3)$	**L**	X=Cl, Y=OAc	**a**
[*trans*-$Cl(CO)(P^iPr_3)_2M=CHCH=CR_2]BF_4$	**M**	X=Cl, Y=$OCOCF_3$	**b**
(M=Ru,Os)		X=Y=OAc	**c**
		X=OAc, Y=$OCOCF_3$	**d**
$Os(H)_3Cl(P^iPr_3)_2$	**N**		
$Os(H)_2Cl_2(P^iPr_3)_2$	**O**	$Ru(H)(H_2)(acac)(PCy_3)_2$	**21**
$(P^iPr_3)_2Cl_2Os(H)(\equiv C\text{-}CH_2R)$	**P**	$(PCy_3)_2(acac)ClRu=CH\text{-}CH=CMe_2$"	**22**
$Ru(H)(H_2)Cl(PCy_3)_2$	**1**	$(PCy_3)_2Cl_2Ru=CHCH_2CH_3$	**23**
$Ru(H)(H_2)Cl(P^iPr_3)_2$	**2**	"$(PCy_3)_2Cl_2Ru(=CH\text{-}CH(CH_3)_2)$"	**24**
$Ru(H)(H_2)Cl(PCp_3)_2$	**3**	$(PCy_3)_2Cl_2Ru(=C(CH_3)_2)$	**25**
$Ru(H)_2(H_2)_2(PCy_3)_2$	**4**	"$(PCy_3)_2Cl_2Ru(=CH\text{-}CH_2Cl)$"	**26**
$Ru(H)_2Cl_2(PCy_3)_2$	**5**	$(PCy_3)_2Cl_2Ru(=CHCH_2Ph)$	**27**
$(PPh_3)_2Cl_2Ru(=CH\text{-}CH=CMe_2)$	**6**	$(PCy_3)_2Cl_2Ru(=CHCH_2CH(CH_3)_2)$	**28**
$(PCy_3)_2Cl_2Ru(=CH\text{-}CH=CMe_2)$	**7**	$(PCy_3)_2Cl_2Ru(=CHCH_2C(CH_3)_3)$	**29**
$(P^iPr_3)_2Cl_2Ru(=CH\text{-}CH=CMe_2)$	**8**	$(PCy_3)_2Cl_2Ru(=CH(CH_3)\text{-}CH_2CH_2CH_3)$	**30**
$(PCp_3)_2Cl_2Ru(=CH\text{-}CH=CMe_2)$	**9**	$(PCy_3)_2Cl(H)Ru(=C=CHPh)$	**31**
$(PCy_3)_2Cl_2Ru(=CHCH_3)$	**10**	$(PCy_3)_2Cl_2Ru(=C=CHPh)$	**32**

List of Compounds (continued)

$(PCy_3)_2Cl_2Ru(=C=CHtBu)$	**33**	$MHCl(CO)(PCy_3)_2$ M=Ru (**a**), Os (**b**)	**42**
$(PCy_3)_2Cl_2Ru(=C=CHC_4H_9)$	**34**	*cis*-Cl_2-*trans*$(P^iPr_3)_2(CO)M=CHCH=CMe_2$ M=Ru (**a**), Os (**b**)	**43**
cis-$(PPh_3)_2Cl_2Ru(=CH\text{-}CH=CMe_2)$	**35**	*cis*-Cl_2-*trans*$(PCy_3)_2(CO)M=CHCH=CMe_2$ M=Ru (**a**), Os (**b**)	**44**
$(PPh_3)_2Cl_2Ru(=CHCH_2Ph)$	**36**	$MHCl(CO)_2(P^iPr_3)_2$ M=Ru (**a**), Os (**b**)	**45**
$(PPh_3)_2Cl_2Ru(=CHCH_2C(CH_3)_3)$	**37**	$MHCl(CO)_2(PCy_3)_2$ M=Ru (**a**), Os (**b**)	**46**
$(PCy_3)_2Cl_2Ru(=C=CH\text{-}C(=CH_2)CH_3)$	**38**	$Os(H)_3Cl(PCy_3)_2$	**47**
$(PCy_3)_2Cl_2Ru(=CH(CH_2)_4CH_3)$	**39**	$(PCy_3)_2Cl_2Os(=CH\text{-}CH=CMe_2)$	**48**
$(PCy_3)_2Cl_2Ru(=C=CH\text{-}(CH_2)_3CH_3)$	**40**	$(PCy_3)_2Cl_2Os(H)(\equiv C\text{-}CH=CMe_2)$	**49**
$MHCl(CO)(P^iPr_3)_2$ M=Ru (**a**), Os (**b**)	**41**	$Os(H)_6(PCy_3)_2$	**50**

PCy_3=tricyclohexylphosphine

PCp_3=tricyclopentylphosphine

P^iPr_3=triisopropylphosphine

Introduction

The development of well-defined, alkylidene based olefin metathesis catalysts has been the focus of much research since it was shown that metal carbenes play a central role in catalyzing olefin metathesis reactions.[1] The olefin metathesis reaction is generally catalyzed by complexes of titanium,[2] tantalum,[3] tungsten,[4-8] molybdenum,[9,10] ruthenium,[11] or rhenium.[12] Metal alkylidene complexes have been found to be active in acyclic olefin metathesis,[13-16] ring-opening metathesis polymerization (ROMP),[13] acyclic diene-[17] and alkyne-[18] polymerizations, carbonyl olefinations,[19] and ring-closing metathesis (RCM).[20] Recently, the use of olefin metathesis has expanded tremendously with applications including the construction of macrocycles in peptides and other systems,[21-24] tandem ring opening/ring closing and construction of fused ring systems,[25-27], olefin metathesis in compressed carbon dioxide,[28] and ring opening metathesis polymerization in aqueous media.[29,30] In particular, the role of olefin metathesis in organic synthesis has recently received much attention.[31-33] The generalized metathesis pathway, first proposed by Chauvin[34] is shown in Figure 1, and a series of representative catalysts is shown in Figure 2. During

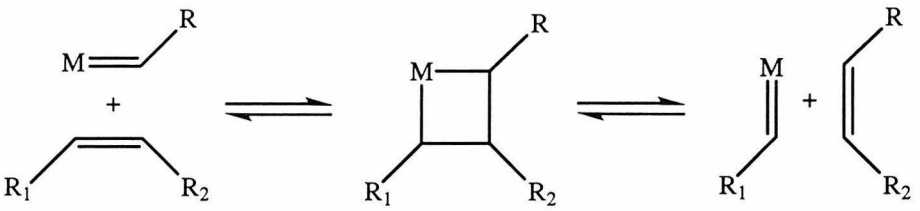
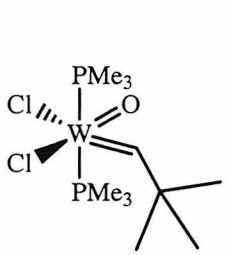


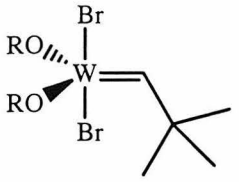
Figure 1-Generalized Metathesis Pathway

transition metal catalyzed olefin metathesis, a metal carbon double bond forms a metallacyclobutane with an olefin. This metallacycle can either unproductively cleave to give starting materials, or productively cleave to give a new metal carbon double bond and a new olefin.

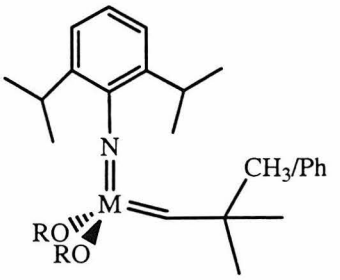
Especially useful are metathesis catalysts based on ruthenium (like **F**)



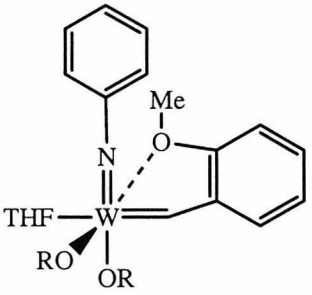
A
R.R. Schrock



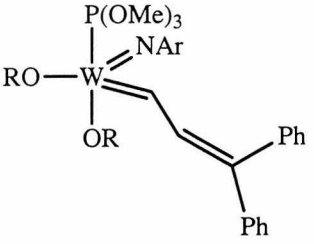
B
J.A. Osborn



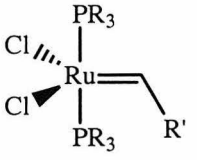
C
R.R. Schrock
M=Mo, W
OR=$OC(CH_3)_x(CF_3)_{3-x}$, x=0,1,2



D
R.H. Grubbs
OR=$OC(CH_3)_x(CF_3)_{3-x}$, x=0,1,2



E
R.H. Grubbs
OR=$OC(CH_3)(CF_3)_2$



F
R.H. Grubbs
R'=H, Ph, Me, diphenylvinyl

Figure 2-Well defined Tungsten, Molybdenum, and Ruthenium carbenes

which have demonstrated remarkable stability towards oxygen, protic solvents, and many functional groups.[11,29,35] While these compounds can be prepared in moderate to high yields, existing syntheses rely on relatively inaccessible or unstable organic compounds such as 3,3-diphenylcyclopropene[11] or phenyl diazomethane.[35] In addition, all synthetic methods for carbene generation center on triphenylphosphine containing starting materials. The triphenylphosphine is then exchanged with a more basic phosphine to give more active systems.

Increasing the accessibility, availability, and yields of such catalytic compounds will always be a goal, especially when relatively expensive late transition metals are used. Procedures and methods for synthetic generation and use should be easily and safely accomplished, and accessible to non-organometallic

specialists in order to reach a larger part of the chemistry community and expand the scope of the olefin metathesis reaction itself. It is the focus of this work to present a simpler, easier, and more accessible route to active ruthenium and osmium carbene systems based on the insertion of alkynes and alkenes into metal hydride bonds. Ideally, this synthesis should be from commercially available stable starting materials, require no triphenylphosphine, no unstable or explosive organic fragments, and proceed in as high yield as possible.

Background

Discussed in the next few sections is a significant quantity of background information on metathesis catalysts, condensed into a relatively small space. For more or more general information on metathesis, there are several books and quite a few reviews mentioned in the introduction. Presented first in the background section is the development of metathesis catalysts, describing evolution from a heterogeneous to the more recent single component homogeneous catalysts, and some of the problems with these systems. Following that is the background of ruthenium catalysts in particular, from the very beginnings of metathesis with ruthenium to the most recent advances from our labs. Synthetic methods, activity trends, and the proposed mechanism for these catalysts is examined. Finally, the idea to exploit the stability of the ruthenium catalysts in order to investigate new synthetic methods is presented.

Development of Metathesis Catalysts

The evolution of metathesis catalysts has been in three stages or phases. First were heterogeneous metathesis catalysts, also called classical or multicomponent catalysts. These are easily prepared by mixing several reagents, usually a metal-halide, an alkyl-aluminum, and a proton source. They are ill-defined, but generally show high activity, though it has been estimated that at any time only a few percent of the mixture is active. Some representative heterogeneous systems are: $Mo(NO)_2L_2Cl_2/RAlCl_2$, $WCl_6/EtOH/EtAlCl_2$, $WOCl_4/EtAlCl_2$, and $Re_2O_7/Al_2O_3/Me_4Sn$.[14]

A major advancement in catalyst design came with the second stage in development, based on the realization that the two most important catalytic intermediates were a metal carbon double bond and a metallacyclobutane.[34] Second generation catalysts contain well characterized metal carbene or

metallacyclobutane compounds which, although not catalytically active themselves, do show activity upon the addition of a second component (usually a strong Lewis Acid). These catalysts can be designated as well defined multi-component systems. Two examples of this type of catalyst are **A** and **B**, both requiring a Lewis Acid to show activity.

By convention, the carbene moiety is considered to be either electrophilic or nucleophilic, and the first examples of well-defined systems are electrophilic carbenes, also known as Fischer carbenes. Identified by the presence of an electron donating group on the carbene, some of these complexes are active for alkyne polymerization, as well as polymerization of strained cyclic olefins. However, they are not active in metathesis of low-strain olefins. A typical carbene of this type is $(CO)_5W{=}C(Ph)(OMe)$.[36]

Homogeneous systems which do not require further activation or co-catalyst to show activity represent the third stage of catalyst development, and nucleophilic carbenes, also known as Schrock carbenes, dominate this category. Nucleophilic carbenes have been shown to be active in a much broader scope of metathesis reactions than Fischer carbenes, and are the main focus of recent research on metathesis catalysts. A ruthenium carbene (**F**) and several typical nucleophilic molybdenum and tungsten carbenes (**C, D,** and **E**) are shown in Figure 2. Single component catalysts, however, are generally much more difficult to prepare than previous generations of catalysts, but are that much more amenable to detailed study. The ability to make single component systems has lead to detailed mechanistic investigations, the possibility of stereochemical control, and variation of activity by controlled modification of ligand environments.[13,14,37,38]

Since the mid 1980's there have been continuing developments into the generation of single component metathesis catalysts, and until recently the most

widely used was certainly **C**. Available with both W and Mo, catalyst **C** contains features which are amenable to detailed study and controlled activity. While the tungsten containing **C** shows higher activity, the Mo catalyst is more tolerant of functionalities and for that reason has seen wider use. High oxidation state four-coordinate complexes like **C** are stabilized by the steric bulk of the arylimido, alkylidene, and alkoxide ligands. Both can incorporate arylimido units of differing steric bulk, and alkoxide ligands with different steric and electronic properties.[37,38] It has been shown that the activity of these systems can be drastically affected by the basicity of the alkoxide functionalities,[39] which is easily accomplished by varying the number of fluorinated methyl groups on the alkoxide in the last synthetic step.

Not surprisingly, the high oxidation state of catalyst **C** makes it incredibly sensitive to air, water, and many functional groups, which is the case with many if not all of the early metal systems. In addition, the difficult synthetic regimens necessary for its production render the catalyst inaccessible to the vast majority of chemists who could expand its applications. [Synthetic schemes for the generation of catalyst **C** can be found in Chapter 2.] Synthesis of **C** requires an inert atmosphere glove box, rigorously dried and oxygen free solvents and reagents, and a considerable knowledge of inert-atmosphere chemistry, some of which is more art than science. In recent years, though, catalyst **C** has become commercially available. In theory, this should extend its use in the chemistry community. However, storage and use requires a glove box or an extremely good glove bag, equipment which many groups do not have. The same requirements remain for rigorously purified reagents and solvents for reactions with **C**, and the low temperature which **C** (M=Mo) requires to remain stable in storage makes shipping and storage of this system very difficult. Stories have been told of groups attempting reactions with purchased **C** only to

have all their reactions fail; upon investigation their catalysts were brown sludge instead of the yellow-orange crystalline powders of the non-decomposed catalyst.

While development of early transition metal systems seems to dominate the literature, late metal systems have also been described. While often less active and more expensive than their early metal counterparts, the late metal systems are unparalleled for stability to functionalities, air, and water. Shown in Figure 3 are the relative reactivities of different metal carbenes towards

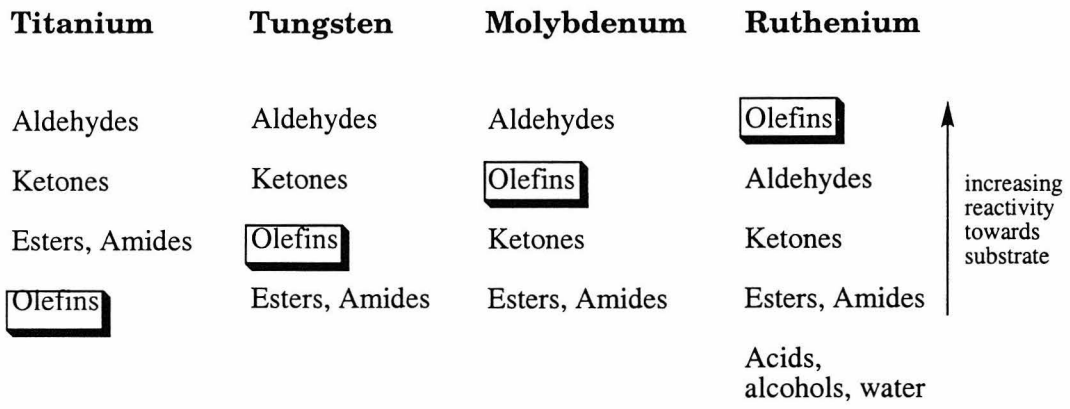


Figure 3-Relative reactivities of different metal carbenes

different substrates. In particular for the topic at hand, simple compounds of the Group VIII metals have been shown to have high metathesis activity and tolerance of air, water, many functionalities, and even acid, which none of the earlier systems can tolerate even in trace amounts.

General Characteristics and Synthetic Methods of Ru Systems

Quite early in the area of catalyst development, it was found that $RuCl_3*H_2O$ polymerized cyclobutenes[40,41] and norbornene[42,43] by ring-opening metathesis in alcoholic and aqueous emulsions. Later, in the Grubbs group, it was shown that aqueous solutions of Ru(II) olefin complexes had high activ-

ity for the polymerization of functionalized norbornenes.[44-48] These observations eventually gave the now well known Ru(II) systems: $(PR_3)_2Cl_2Ru{=}CHR$ (**F**).[11,35,49]

The first report of a well defined Ru metathesis catalyst was in 1993. Following the general idea that metal carbenes had been implicated in several transformations of cyclopropenes by transition metals,[50-52] diphenylcyclopropene was used as a carbene precursor. The first use of ring opening of cyclopropenes to generate a metal carbene was in 1989 when Binger reported the vinylcarbene complex $Cp_2(PMe_3)M{=}CH{-}CH{=}CR_2$ (M=Ti, Zr).[53] Shown in Figure 4, the reac-

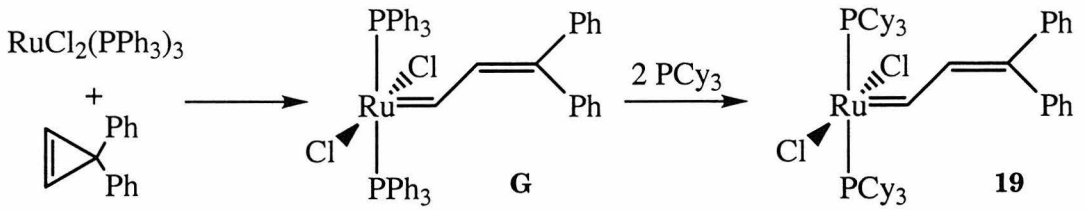


Figure 4-Reaction of Ru(II) with diphenylcyclopropene

tion of a Ru(II) starting material, $RuCl_2(PPh_3)_3$, and diphenylcyclopropene gives $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ (**G**).[11] Diphenylcyclopropene, however, is a synthetic challenge (especially for an inorganic chemist) and decomposes over time in storage. In addition, if the catalyst generated by this route is active enough, ROMP of the cyclopropene could occur (see Chapter 2). Phosphine exchange to a more basic phosphine, such as tricyclohexylphosphine, is a required step in order to achieve more active catalysts.

A major advancement in the generation of Ru carbenes came in 1995, when the same Ru(II) starting material was reacted with diazoalkane and diazoaryl compounds, to give $(PPh_3)_2Cl_2Ru(=CHPh)$ (**H**) shown in Figure 5.[35,49] With this breakthrough, a wide variety of carbenes can be made, from alkyl to substituted aryl, including the first ever isolated metathesis active methylidene

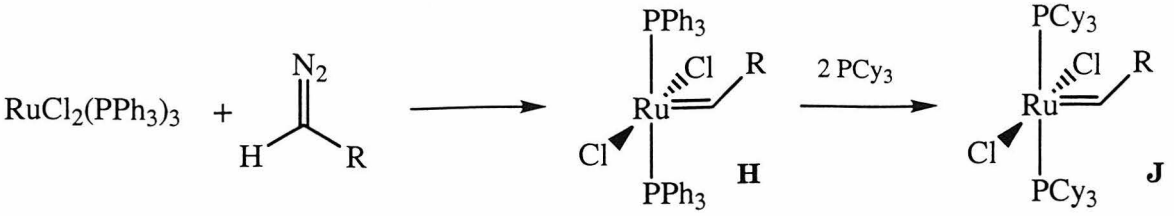


Figure 5-Reaction of Ru(II) with diazo compounds

complex$(PCy_3)_2Cl_2Ru{=}CH_2$ (**I**). The most active and stable of these, the benzylidene $(PCy_3)_2Cl_2Ru{=}CHPh$, was a more efficient initiator than previous vinylcarbenes, and applications for these catalysts grew. The only drawbacks besides the sometimes moderate yield are the use of diazo- compounds, which can be explosive, and the continuing need for a phosphine exchange to give $(PCy_3)_2Cl_2Ru(=CHPh)$ (**J**), because tricyclohexylphosphine starting materials are not available.

In general, all of the Ru systems show the same activity trends, and similar stabilities. The ligand sphere is identical: two phosphines, two halides or anionic ligands, and one carbene. Each ligand, in turn, affects the activity of the entire complex. Structurally, all complexes are five coordinate distorted square pyramidal geometry with the carbene in the axial position and the *trans*-phosphines and chlorides in the equatorial plane.[11,35] Interestingly, in most cases the carbene is located in the Cl-Ru-Cl plane, that is perpendicular to the phosphines and showing no H-P coupling for the carbene proton (following the Karplus relationship). Notable exceptions to this geometry are most if not all triphenylphosphine compounds, where the carbene is in the P-Ru-P plane and does present H-P coupling of the carbene proton. The geometry of the carbene ligand, then, can be determined by observation of the splitting of the proton signal, which is generally in the 18-21ppm range. In terms of stability, these complexes in the solid state are stable in air for extended periods of time (at least months, if not more), and indefinitely under an inert atmosphere. They

can be used in air, though over time begin to decompose in solution.

As mentioned above triphenylphosphine ruthenium carbenes show limited activity, reacting with highly strained cyclic and exocyclic olefins.[11,54] A simple phosphine exchange to a more basic phosphine increases activity, the larger and more basic the phosphine the higher the activity seen (trend: PPh_3 << P^iPr_3 < PCy_3).[11,55] This is in direct contrast to earlier systems (W and Mo based) where switching to a more basic phosphine dramatically slows the reaction. In contrast to the trend observed for the phosphine, the anionic ligands show that a more electron withdrawing halide gives a dramatically more active catalyst (trend: I << Br < Cl).[55] These trends are quantitatively illustrated by examining a series of complexes with identical carbenes but different phosphines and halides, in the ring closing metathesis of diethyl-diallylmalonate by $(PR_3)_2X_2Ru$=CH-CH=CPh_2, shown in Table 1 (a similar trend is observed for several polymerization reactions).[55] Under similar conditions the parent catalyst $(PPh_3)_2Cl_2Ru$=CH-CH=CPh_2 shows no measurable activity.

Two pathways considered most likely representative of the catalytic cycle have been proposed (shown in Figure 6, for clarity the starting olefin substituent is underlined), one termed "associative" (not in the classical sense) the other

Table 1-Activity of $(PR_3)_2Cl_2Ru$=CH-CH=CPh_2 in the RCM of Diethyl-diallylmalonate[a]

PR_3	X	Activity (turnovers/hr)
PCy_3	Cl	19.4
	Br	15.4
	I	1.4
PCy_2Ph	Cl	8.0
	Br	4.5
	I	—[b]
P^iPr_3	Cl	17.5
	Br	13.9
	I	1.1
P^iPr_2Ph	Cl	5.5
	Br	2.3
	I	—[b]

Conditions: [monomer]=0.2 M, [catalyst]=0.10M, temp=20°C; [b]No activity seen over several hours

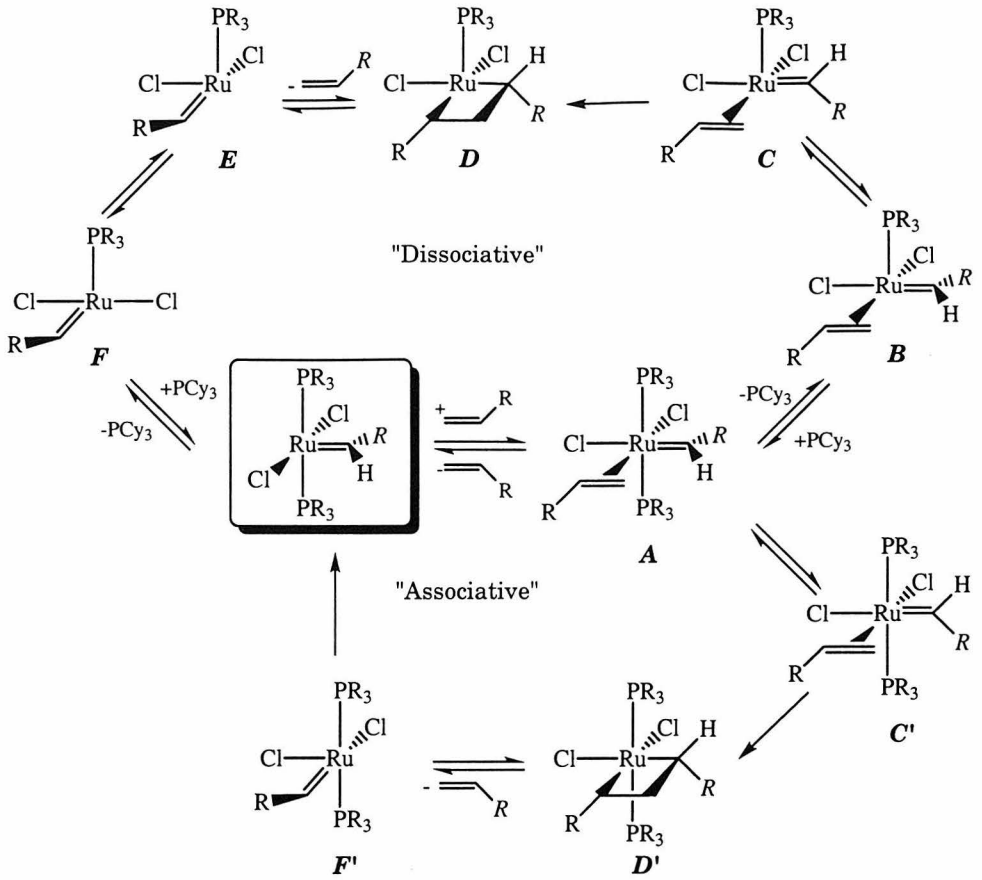


Figure 6-Proposed mechanism of Ru metathesis catalysts

"dissociative."[55] In both pathways the first step is coordination of the olefin (*A*), *cis* to the carbene and *trans* to a halide. In the dissociative pathway (upper cycle in Figure 6), after the olefin coordinates (*A*), a phosphine dissociates (*B*). This is followed by rotation of the carbene to the P-Ru-P plane (*C*), formation of the metallacycle (*D*), elimination of the new olefin (*E*), reorientation of the carbene and halides (*F*), and finally phosphine addition. In the associative pathway (depicted in the bottom cycle in Figure 6) the carbene first rotates (*C'*), so that it may form the metallacycle (*D'*), which then productively eliminates the new olefin (*F'*), and reorients to give the starting catalyst. The rotation of the carbene is necessary for proper orbital overlap, while reorientation of the halides is necessary for microscopic reversibility.

At first glance, the associative pathway seems much more likely, as all

species and intermediates have 16 or 18 electrons, while the dissociative pathway has the 14 electron metallacyclobutane. Detailed kinetics, however, support the fact that both pathways are active, with the dissociative pathway accounting for >90-95% of catalyst activity.[55] One important detail obtained by kinetic analysis is that addition of phosphine dramatically reduces the reaction rate. If the dominant pathway is "associative" there should be no rate depression.

Combining the proposed pathways and kinetic data the observed activity trends can be explained.[55] The higher activity of catalysts with more electron withdrawing halides is rationalized by the fact that when the olefin binds to the ruthenium center, a more electron withdrawing halide will result in a stronger ruthenium-olefin bond trans to it. In addition, the size of the halides should dramatically affect the reaction rate, as they must during the reaction become *cis* to each other. The phosphine dependence can be rationalized for two reasons. First, as the steric bulk of the phosphine increases, phosphine dissociation from the crowded 18 electron olefin complex becomes more favored, increasing the availability of the dissociative pathway. Second, as the electron donating ability of the phosphine increases so does its *trans* influence and the stabilization of a vacant coordination site *trans* to it. These proposed mechanistic ideas have been recently supported by theoretical calculations.[56]

In attempts to increase reactivity of these ruthenium carbenes, knowing that the loss of phosphine accounts for the more active species, several phosphine sponges were added. It was found that CuCl dramatically increases the reaction rate, up to twenty times faster. It was proposed that rather than simply scavenging a phosphine CuCl actually formed a chloride bridged bimetallic system,[55] which led to the examination of other additives to increase reaction rates. Even more dramatically increased reaction rates (up to 80 times) were

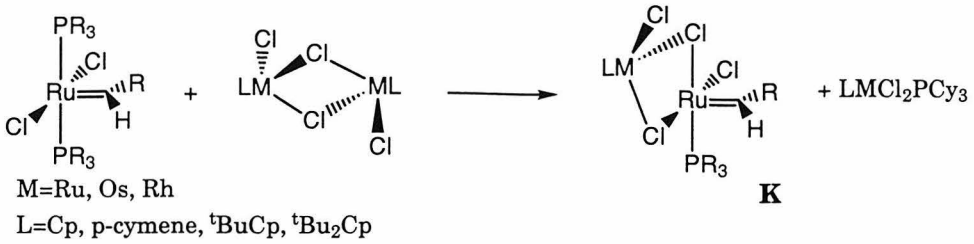


Figure 7-Generation of bimetallic metathesis catalysts

obtained by mixing the parent catalyst with chloride bridged metal dimers, shown in Figure 7, to give complexes like LMCl-μ-$(Cl)_2$-Ru(Cl)(PR_3)(=CHR) (**K**).[57] It appears that the steric bulk of the second metal center affects the bimetallic complex's stability (Cp* < tBuCp < tBu_2Cp) and the metal center itself play a role in this rate enhancement (general trend: Ru < Os < Rh).[57] Interestingly, the bimetallic systems seem to favor the "associative" mechanism described above. Further investigations of bimetallic systems are currently underway.

Another attempt at rate or stability enhancement has been by altering the ligand sphere. One way in which this has been accomplished is by using a Schiff-base ligand.[58] By preparing a series of ligands from substituted salicylaldehydes and substituted amines, a library of Schiff-base complexes, (salicylaldehydeimine)-Ru(Cl)(PR_3)(=CHR) (**L**), can easily be prepared by ligand exchange with a parent catalyst (Figure 8). While an increase in activity at

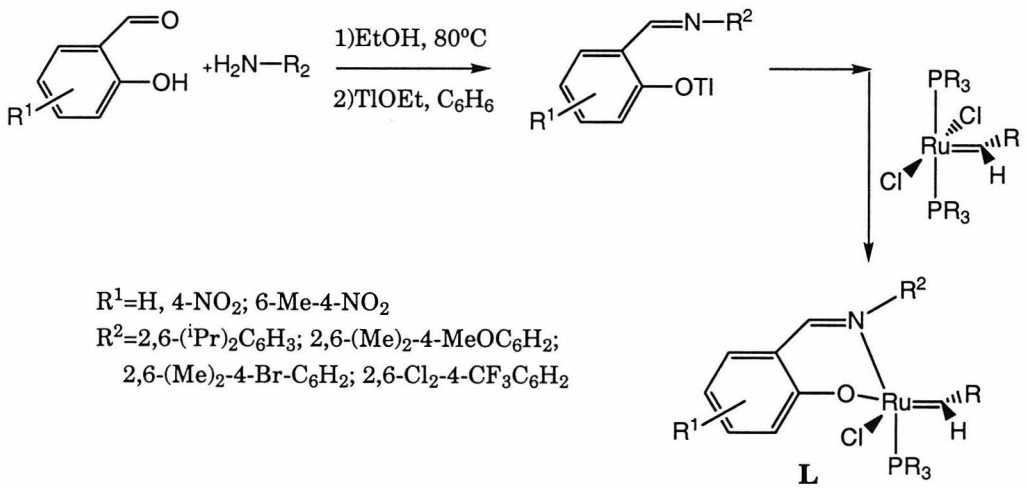


Figure 8-Generation of Schiff-Base Ru systems

room temperature was not realized, stability and reaction rates at higher temperatures are dramatically improved with these ligands, as is stability to oxygen. Since the parent catalyst is not particularly stable at higher temperatures, an increase in thermal stability is a major accomplishment. The current proposed mechanism for these catalysts is based on the idea that the phosphine remains bound to the metal, and the imine dissociates. This is supported by the observation that the triphenylphosphine system shows no metathesis activity while the tricyclohexylphosphine system is active.[59] If the phosphines in each case dissociated from the metal, the remaining fragments would be identical.

Although the phosphines and halides have a great impact on the relative reactivity, catalyst initiation also depends on the structure of the carbene. It is important, though, to note that the propagating species for any given reaction will be the same (or virtually the same in the case of making polymers) after initiation. While the vinyl-carbenes afford added stability, their initiation rates are only moderate in most cases.[11] Switching to the (now more common) benzylidene increased initiation greatly, while still maintaining stability.[35] Most recently, alkyl and even ester[60] carbenes have been synthesized, showing the same or better initiation than the benzylidene. In the case of $(PCy_3)_2Cl_2Ru{=}CHCO_2R$ (R=Me, *p*-tolyl, *t*-butyl, *i*-propyl, cyclohexyl, 1-adamantyl) *ring opening of cyclohexene is observed.* In general, then, initiation rates follow the trend $(PPh_3)_2Cl_2Ru{=}CHR << (PCy_3)_2Cl_2Ru{=}CH\text{-}CH{=}CR_2 < (PCy_3)_2Cl_2Ru{=}CHPh \leq (PCy_3)_2Cl_2Ru{=}CHR < (PCy_3)_2Cl_2Ru{=}CHCO_2R$. This is not to say, however, that the vinyl carbenes are not efficient metathesis catalysts. Until very recently *all* of the many and varied applications of Ru carbenes utilized the parent vinylcarbene, and in some cases "apparent activity" is virtually identical to the benzylidene.

The insertion idea

The demonstration that osmium[61-64] and ruthenium[65-67] hydride systems could be used to generate carbenes (mostly with metal carbonyls; no carbonyl containing carbene species has shown metathesis activity) suggested to us that metal hydrides might be an efficient system for the generation of metathesis active carbene complexes. With an appropriate choice of starting materials, active Ru systems might be generated.

As discussed above, the Ru catalyst system is extremely stable, especially compared to most other metathesis catalysts. In exploration of new methods of catalyst generation, it was thought that the remarkable thermodynamic stability of these systems might be exploited; a compound or intermediate very close to the catalyst might spontaneously rearrange to give the desired product. For example a Ru-alkyl species with an α-chloro substituent, [Ru]-CCl(HR) might α-chloro eliminate to give the carbene Cl-[Ru]=CHR. One way in which such a compound or intermediate could be obtained is insertion of a metal-hydride into an unsaturated organic fragment containing the appropriate substitution,

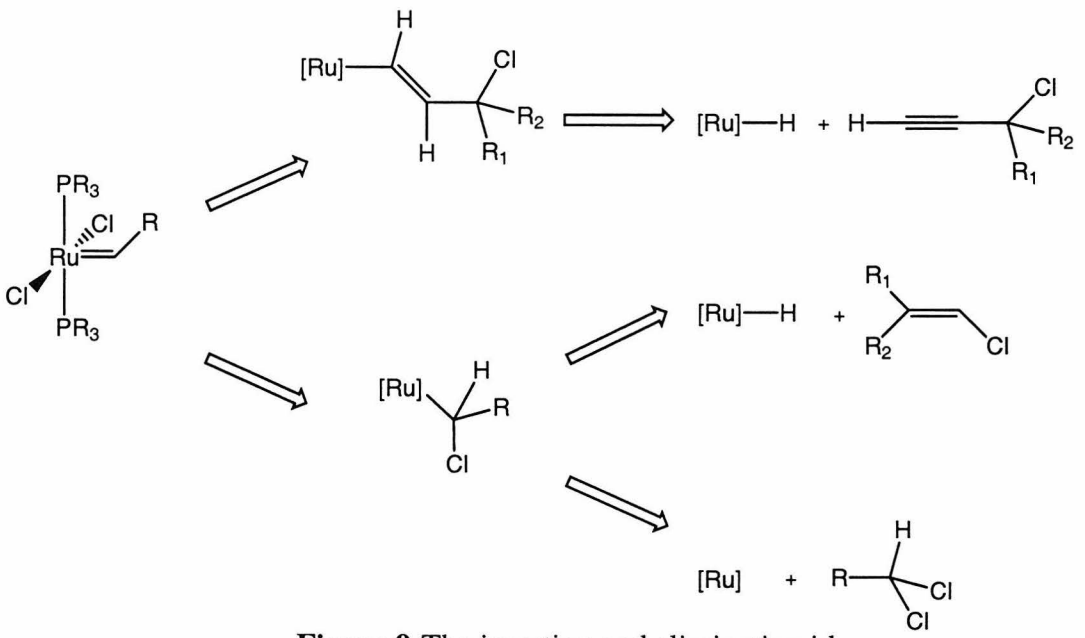


Figure 9-The insertion and elimination idea

another would be to generate a more reduced Ru species and oxidatively add one or more C-Cl bond(s).

Given all these ideas, a series of insertion reactions with metal hydrides were considered, and are depicted in Figure 9. The first two pathways center on Ru-hydride insertions into propargyl-chlorides and vinyl-chlorides. It was thought that vinyl chlorides might insert into the metal hydride to yield the Ru-α-chloro-alkyl compound, while insertion with propargyl halides might lead to a Ru-γ-chloro-alkenyl species.[68] In both cases, relocation of the chloride to the metal center would give the desired carbene. The final pathway consists of a nominally Ru^0 species which first oxidatively adds a $C(Cl)_2HR$ species to give a compound similar to the Ru-alkyl compound with α-chloro substitution, which could then α-chloro eliminate.[60] The most clever pathway would involve starting materials which, in addition to being commercially available or easy to make, were already very close to the desired catalyst in composition so that all which was necessary would be addition of the carbene generating organic fragment. Since the inception of this idea, all three of these pathways have been successfully employed for carbene generation.

Results and Discussion:[69,70]

Starting Materials and Initial Investigations

The first barrier to this chemistry involves the appropriate choice of starting material. The best choices for inorganic starting materials would contain only the metal center, phosphines, and halides (plus, of course, the hydride if a hydride insertion is being considered). Previous examples of Ru and Os-hydrides which eventually gave carbenes involved metal-hydrido-carbonyl complexes. Shown in Figure 10 are $MHCl(CO)(PiPr_3)_2$ (M=Ru (**41a**), Os (**41b**))[62,65,71,72] inserting into an alkyne-1-ol triple bond to give a γ-hydroxyvinyl complex *trans*-$Cl(CO)(PiPr_3)_2M\text{-}CH{=}CH\text{-}C(OH)R_2$ (M=Ru, Os).[62,65] Ionization

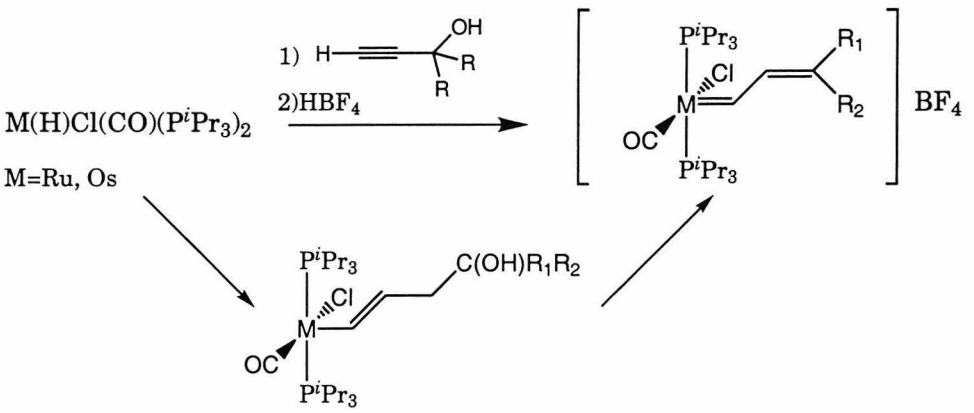


Figure 10-Insertions into alkyne-1-ol

at the γ-carbon is accomplished by addition of an acid with a non-coordinating counter ion such as HBF_4 to give [*trans*-$Cl(CO)(PiPr_3)_2M{=}CHCH{=}CR_2]BF_4$ (M=Ru, Os).[62,65] Later, a similar reaction was reported with $Ru(H)Cl(CO)(PPh_3)_3$ and alkyne-1-ols.[73] It is important to note that although the lack of metathesis activity for these compounds was not discussed in the literature, they were verified to show no activity in our labs.

The first supporting evidence that the insertion-elimination idea might be a successful way to generate ruthenium carbenes involved Wilkinson's com-

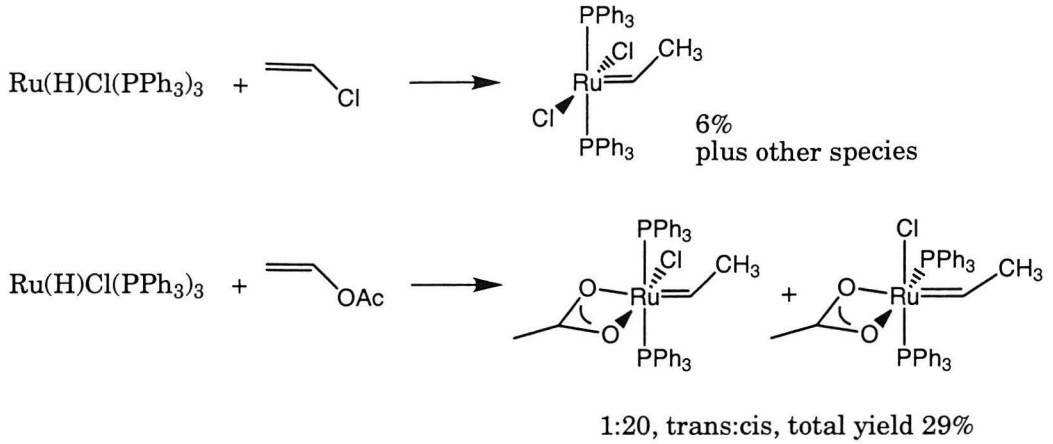


Figure 11-Initial investigations of insertion/elimination

plex, $RuHCl(PPh_3)_3$ and vinyl-chlorides and -acetates.[74] Depicted in Figure 11, addition of vinyl-chloride to the above hydride gave approximately 6% of the desired carbene $(PPh_3)_2Cl_2Ru{=}CHCH_3$. Insertion into vinyl-acetates proved more successful, but more problematic: *cis* and *trans* isomers were formed, in addition to several other species which could not be separated. The proposed mechanism for this insertion and elimination considers two pathways, differing in whether the insertion places the Ru on the same carbon with the chloride (call this α-insertion) or on the other carbon in the vinyl chloride (β-insertion) (Figure 12). In the first case, α-chloro elimination affords the desired product, while in the second case it is expected that β-chloro elimination would give free ethylene and $RuCl_2(PPh_3)_3$. Insertion with propargylic halides was also attempted, shown in Figure 13 with $RuHCl(PPh_3)_3$ and 3-chloro-3-methyl-1-

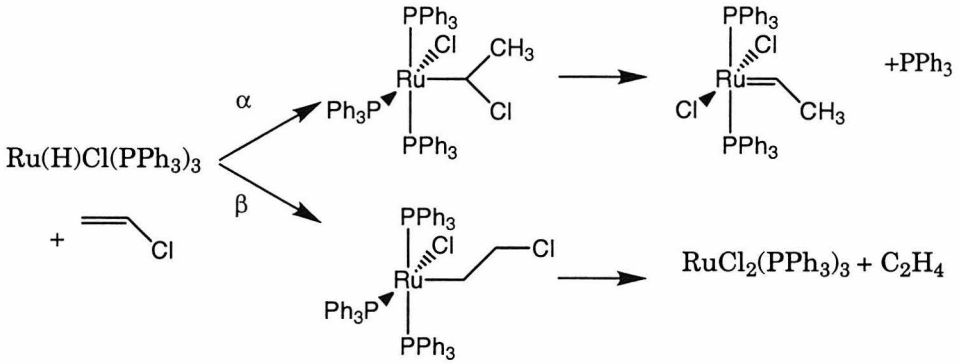


Figure 12-Proposed mechanism for vinyl insertion and elimination

butyne, and proceeded to give the desired carbene, $(PPh_3)_2Cl_2Ru=CH-CH=CMe_2$ (**6**) in moderate yields. This procedure was later revisited, and it was observed that if the reaction is kept at low temperature **6** can be isolated in high yields. An insertion-elimination mechanism is proposed, similar to that shown in Figure 10. In order to obtain the much more active compound with tricyclohexylphosphine ligands (**7**) a phosphine exchange must be accomplished (Figure 13).

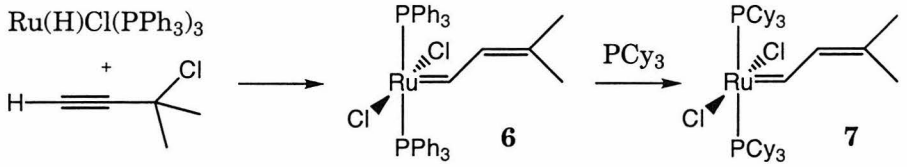


Figure 13-Initial investigations with propargylic halides

A second suitable starting material was then chosen: $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**),[75-77] one previous use of **1** has been as an active hydrogenation catalyst,[77] Seemingly ideal for the insertion and elimination pathway to give Ru-carbenes this hydride contains only tricyclohexylphosphine, one chloride (the other will come from an appropriately chosen organic fragment) and hydrogen. Previous low yield multistep syntheses of **1** focused on transformation from Ru(1,3,5-cyclooctatriene)(1,5-cyclooctadiene) either directly or through isolation of $Ru(H)_2(H_2)_2(PCy_3)_2$ (**4**).[75,76,78] Recently, in the preparation of $Ru(H)_2(Cl)_2(PiPr_3)_2$, the similar species $Ru(H)(H_2)Cl(PiPr_3)_2$ (**2**) was proposed as an intermediate in a reaction with $[RuCl_2(COD)]_x$, excess $PiPr_3$, and H_2 in sec-butanol.[66] Further, it was demonstrated that a solution of **2** could be reacted with terminal acetylenes to give ruthenium carbene species in moderate yields.[66]

Attempts to make **1** from $[RuCl_2(COD)]_x$ following the above method were promising, giving **1** in 40% yield along with a large amount of a Ru(IV) species

presumed to be $Ru(H)_2(Cl)_2(PCy_3)_2$ (**5**) from ^1H and ^{31}P NMR data. Interestingly, the Ru(IV) species is diamagnetic, and the structure of $Ru(H)_2(Cl)_2(PiPr_3)_2$, best described as a distorted D_{4d} square antiprism with the two vacant sites in alternate positions at one square base of the polyhedron, has been confirmed by x-ray diffraction.[66] Since the reaction between isolated **1** and HCl was found to give the same Ru(IV) species, and since HCl is produced in the reaction that forms **1**, it was surmised that the addition of base to the reaction mixture would improve the yield of **1**. Reacting $[RuCl_2(COD)]_x$, two equivalents of PCy_3, 1.5 atmospheres of H_2, and one equivalent of NEt_3 in sec-butanol for 8 hours at 80°C gives the desired orange, air-sensitive hydride $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) in 94% yield.[69] In this case, the use of triphenylphosphine is completely avoided, only the phosphine required for the products is used, another dramatic improvement. Since the orange solid precipitates from the reaction mixture, simple filtration and washing with methanol gives **1**.

The first reactions attempted with **1** were with propargylic halides, assuming that they would again react more cleanly and productively than vinyl halides. The hydrido chloride complex $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) reacts rapidly with a variety of propargylic halides to yield ruthenium vinylcarbene complexes. For example, **1** reacts immediately with commercially available 3-choro-3-methyl-1-butyne in methylene chloride to give the dimethylvinylcarbene complex $(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}CMe_2$ (**7**), in 96% isolated yield (Figure 14). Monitoring the reaction by ^1H NMR indicates that it is complete in less than one minute even at -30 °C, evidenced by the instantaneous dramatic color change, and inte-

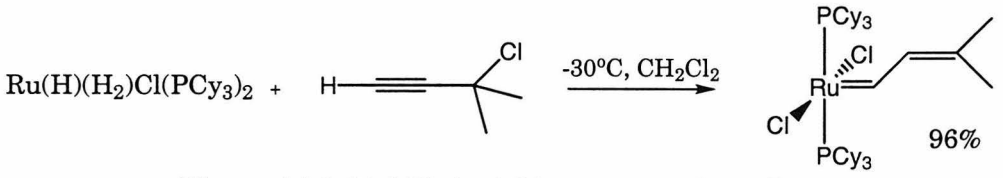


Figure 14-Initial High yield route to carbene **7**

gration against an internal standard shows that the actual yield is ~99.5%. Again, the isolation is extremely simple: remove the methylene chloride (or simply reduce the volume), add excess methanol to precipitate a purple solid, filter and wash with methanol to give the analytically pure solid. The proposed mechanism for this transformation involves insertion of the metal hydride into the alkyne, to give something resembling the metal-alkenyl species seen in Figure 10, followed by rearrangement of the chloride to give the carbene. As will be discussed below, along with a more detailed investigation of the mechanism of this and similar hydrides, it was extremely fortuitous to begin these investigations with 3-chloro-3-methyl-1-butyne. Tertiary propargyl halides work the best of all systems explored, and 3-chloro-3-methyl-1-butyne is the only commercially available propargyl chloride other than the parent 3-chloro-1-propyne (propargyl chloride).

Since compound **1** is slightly soluble in sec-butanol, the idea arose to perform a one-pot procedure for the generation of catalyst **7** (Figure 15). After the generation of compound **1** by the above route, the reaction is cooled to room temperature, then to 0°C. Excess hydrogen is removed, and 3-chloro-3-methyl-1-butyne is added over a few minutes. After stirring for half an hour the reaction is virtually complete, evidenced by the orange precipitate becoming a purple precipitate, which is isolated in greater than 95% yield. The use of the one-pot

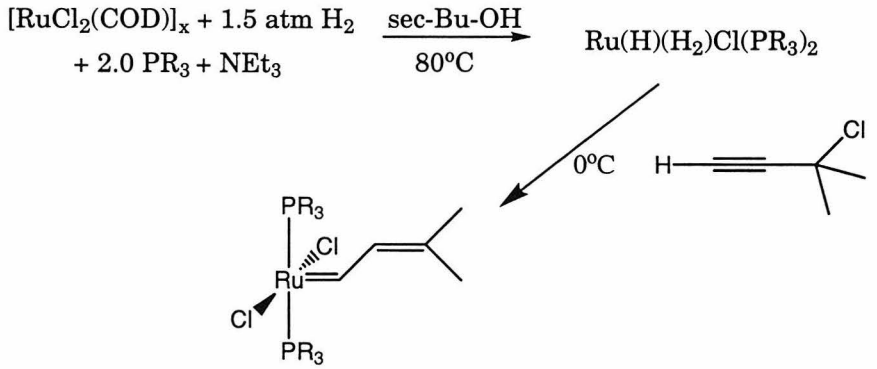


Figure 15-One pot synthesis of carbenes via propargyl halides

procedure expands this synthetic method to the use of other phosphines for which the isolation of the hydrides is problematic. For example, it was mentioned above that $Ru(H)(H_2)Cl(P^iPr_3)_2$ (**2**) was proposed as an intermediate but could not be isolated.[66] Generation of **2** via the above method (only two equivalents of phosphine used) followed by cooling and slow, careful addition of 3-chloro-3-methyl-1-butyne (the reaction is quite a bit more vigorous due to the total solubility of **2**) gives the corresponding carbene $(P^iPr_3)_2Cl_2Ru(=CH-CH=CMe_2)$ (**8**) in 93% yield. The tricyclopentylphosphine analog $Ru(H)(H_2)Cl(PCp_3)_2$ (**3**) and $(PCp_3)_2Cl_2Ru(=CH-CH=CMe_2)$ (**9**) can also be made via this route, but surprisingly both are also totally soluble in sec-butanol. By changing to isopropanol, and cooling to 0°C for one hour, micro-crystalline **3** can be obtained but most of the material passes through a frit. Likewise, in order to isolate any **9** the reaction must be cooled to between 0°C and -30°C for at least one hour before filtration is attempted. The high yield of **3** is evident, though, from NMR experiments between isolated **3** and 3-chloro-3-methyl-1-butyne, as well as the one pot reaction to give **9**, both of which proceed in high yield (very clean by NMR, > 90%; isolated yields >70% hampered by solubility issues). Both **8** and **9** are very brightly colored purple solids, much more vibrant in color than **7**. In addition, **9** has a pronounced tendency towards microcrystallinity.

Attempts to further simplify the one-pot procedure were not successful. It is clear that the higher pressure (1.5 atm) of H_2 is absolutely necessary to the successful generation of **3** and **7**. Attempts with a bubbler or a series of hydrogen balloons did allow preparation of both **3** and **7**, but produced along with **3** is an extremely fine white insoluble solid, presumed to be some sort of bridged hydride species. While this white solid is not particularly stable (the internal H_2 pressure routinely dips below one atmosphere during the reaction, as long as the vessel is repressurized and allowed to react further there is no trace of

this insoluble solid) it does not separate from either **3** or **7**. In addition, attempts to prepare the corresponding dinitrogen-hydride $Ru(H)(N_2)Cl(PCy_3)_2$ by conducting the reaction under dinitrogen also failed (for this reaction to proceed it is necessary to assume that the original hydride comes from the alcohol under transfer hydrogenation conditions).

$Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) also reacts with a variety of vinyl chlorides to give low to moderate yields of the corresponding carbenes. For example, **1** reacts with vinyl chloride to give the expected carbene, $(PCy_3)_2Cl_2Ru{=}CHCH_3$ (**10**), the methylidene, $(PCy_3)_2Cl_2Ru{=}CH_2$,[35] and the Ru(IV) species $Ru(H)_2(Cl)_2(PCy_3)_2$ (**5**). The methylidene is from the generation of **10** followed by the metathesis of vinylchloride, which can be confirmed by adding more vinyl chloride to the generated mixture of **10** and the methylidene. The proposed mechanism for this transformation is identical to that proposed in Figure 12 for the $RuHCl(PPh_3)_3$ insertion. In this case, however, it could be the β-elimination pathway which leads to the Ru(IV) species. More mechanistic investigations will be discussed below.

The increased yield in the preparation of $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) led us to consider the production of other hydrides. By simply changing the base to excess sodium hydroxide, $Ru(H)_2(H_2)_2(PCy_3)_2$ (**4**) is produced in high yields. Completing the insertion pathways to carbenes shown in Figure 9, **4** reacts with gem-dichloro compounds to give carbenes presumably by first oxidatively adding one C-Cl bond, and then α-chloro eliminating to give the carbene. For example, reacting **4** with α,α-dichlorotoluene produces the benzylidene $(PCy_3)_2Cl_2Ru(=CHPh)$ (**J**) in good yields.[60]

Mechanistic Investigations: Propargyl halides

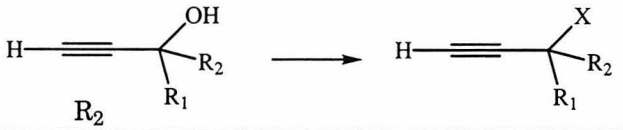
The fact that $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) has been shown to react with both propargylic and vinyl chlorides to give, at least in one case, extremely high yield of the carbene product, led us to attempt to answer the questions of how and why. A variety of both propargyl halides and vinyl chlorides were examined for effect on product yields, reactivity, and overall breadth of the reactions.

Being able to propose a mechanism for any of these transformations is hindered on several fronts and proved to be the most difficult part of the entire project. First, any successful reactions with **1** are incredibly fast, even at -30°C (clearly evidenced by the dramatic color change). This means that by the time one could inject the organic fragment into an NMR tube and insert it into the instrument the reaction is already done. At -30°C compound **1** is no longer completely soluble, which means that if any kinetic data could be obtained it could only be examined in a qualitative way. As will be discussed, any attempt at labeling experiments, say a deuterium on the alkyne and a bromine instead of a chlorine, is useless because *in solution the halides on the catalyst exchange*. These three facts meant that the best hope at being able to at least rule out some mechanisms is to look for reactivity trends, or to look at the reaction "sideways," in as many ways as possible. Three different routes for this were chosen: (1) a series of propargylic and vinylic halides with different halogens and steric configurations, (2) attempts to extend the methodology to the carbonyl complexes discussed above in attempts to obtain greater insight into the general mechanism, and (3) various kinetic experiments which could be measured from either of the two other routes.

One factor not examined above in the generation of $(PCy_3)_2Cl_2Ru{=}CH\text{-}CH{=}CMe_2$ (**7**) is the observation that a small quantity of the Ru(IV) species $Ru(H)_2(Cl)_2(PCy_3)_2$ (**5**) is also generated. When examining this reaction by NMR

no **5** is observed. From later observations with other propargylic halides it can be concluded that this means the ratio of **7**:**5** is greater than 200:1. When preparing **7** on a larger scale, however, it is clearly evident from the brown washings that **5** is generated. Compound **5** is highly colored and it takes very little for the initial washings to be dark brown.

A series of reactions with different propargylic halides was examined by ^{1}H and ^{31}P NMR to see if different carbene to Ru(IV) ratios are observed. A simplified version of the synthetic methods used to generate the propargyl halides is shown in Figure 16, and complete details can be found in *Preparative*

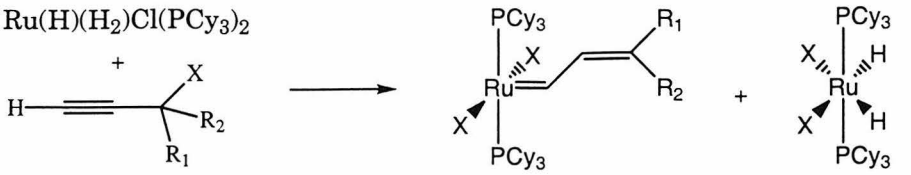


	R_1	R_2	
X=Cl	CH_3	CH_3	commercially available
	CH_3	H	limited commercial availibility, alcohol to tosylate, then LiCl
	H	H	commercially available
	$(CH_2)_5$		alcohol + Cu/CuCl, conc. HCl, NH_4Cl, HCl gas
	Ph	H	alcohol + $SOCl_2$
	Ph	Ph	forms allene instead
X=Br	CH_3	CH_3	alcohol + PBr_3

Figure 16-Synthesis of propargyl halides

Acetylenic Chemistry.[79] Alkynes with tertiary (in addition to 3-chloro-3-methyl-1-butyne to give $(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}CMe_2$ (**7**), 1-ethynyl-1-chlorocyclohexane, to form $(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}C(CH_2)_5$ (**11**)) or benzylic ($HC{\equiv}CCH(Ph)Cl$, to form $(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}CHPh$ (**12**)) chlorides react essentially quantitatively, although a trace of the ruthenium(IV) complex **5** is seen as a byproduct. The amount of **5** formed increases as the steric bulk of the propargyl group decreases, with the monomethyl-substituted $HC{\equiv}CCH(CH_3)Cl$ giving $(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}CHMe$ (**13**) and **5** in an 8:1 ratio and the parent propargyl chloride $HC{\equiv}CCH_2Cl$ giving $(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}CH_2$ (**14**) and **5**

Table 2-Product ratios for a variety of propargyl halides



7, 11-15 **5, 16**

	carbene	R_1	R_2	CD_2Cl_2 carbene	CD_2Cl_2 Ru(IV)	C_6D_6 carbene	C_6D_6 Ru(IV)
X=Cl	**7**	CH_3	CH_3	1	*	1	*
	11	$(CH_2)_5$		100	1	1	*
	12	Ph	H	166	1	1	*
	13	CH_3	H	8	1	37	1
	14	H	H	0.8	1	30	1
X=Br	**15**	CH_3	CH_3	30	1	1	*

*=not observed

in a 0.8:1 ratio. All of these results, summarized in Table 2, were in CD_2Cl_2. Not surprisingly, all of the compounds with secondary propargylic carbons generate two isomers, representing the *cis-* and *trans-* isomers of the terminal vinyl group. Reported above are the sum of the two isomeric carbenes in ratio to the Ru(IV). It is important to note that the diphenylpropargyl chloride could not be synthesized, due to its tendency to rearrange to the allene.

Changing the halogen from chlorine to bromine also increases the amount of **5** formed: the dimethyl-substituted propargyl bromide, $HC{\equiv}CC(Me)_2Br$, gives 30:1 of the expected mixed halogen carbene $(PCy_3)_2ClBrRu{=}CH\text{-}CH{=}CMe_2$ (**15**) to the mixed halogen Ru(IV) species $Ru(H)_2ClBr(PCy_3)_2$ (**16**) which is substantially different from the >200:1 ratio seen with the corresponding chloride; more Ru(IV) is generated with the better leaving group. The mixed halide species is initially the dominant species, but immediately begins to equilibrate to the statistical 1:2:1 mixture of the dichloro, mixed halo, and dibromo species. This equilibration is faster in methylene chloride than in toluene or benzene. As the

mixed halo species can never be isolated from the mixture compounds, **15** is more properly designated as $(PCy_3)_2Br_xCl_{2-x}Ru(=CH\text{-}CH=CMe_2)$ (x=0, 1, 2), and **16** as $Ru(H)_2Br_xCl_{2-x}(PCy_3)_2$ (x=0, 1, 2). To confirm the identity of the peaks assigned to **15**, the dibromo species can be made independently by reacting **7** with excess of LiBr to quantitatively give $(PCy_3)_2Br_2Ru(=CH\text{-}CH=CMe_2)$ (**17**). A mixture of **7** and **17** in an NMR solvent then gives the same mixture of carbene species identified as **15**.

The ratios of carbene to **5** can be improved dramatically if the solvent is changed from dichloromethane to benzene or toluene: from 0.8:1 to 30:1 for **14**, from 8:1 to 37:1 for **13**, and to no detectable Ru(IV) in the generation of **11**, **12**, and **15** (Table 2). It can now be concluded that the ratio of carbene:Ru(IV) is dependent on solvent polarity, leaving group, and sterics of the propargylic carbon. Suprisingly, a mechanism as simple as nucleophilic substitution with the Ru-hydride as the nucleophile fits this data. A similar mechanism has been proposed for $Ni(PR_3)_4$ and substitution with simple alkyl-halides.[80]

To further expand the reaction between **1** and propargyl halides, a non-terminal α-halo-alkyne was examined. Due to its relatively easy synthesis, 1-(propynyl)-1-chlorocyclohexane ($CH_3C{\equiv}C(Cl)(CH_2)_5$) was prepared from propynyl-lithium and cyclohexanone, followed by PCl_3. From ^{31}P NMR, the expected carbene, $(PCy_3)_2Cl_2Ru(=C(CH_3)\text{-}CH=C(CH_2)_5)$ (**18**), is identified upon addition of this alkyne to **1**. Further identification can be accomplished by reacting **18** with excess styrene to give the more easily identifiable benzylidene $(PCy_3)_2Cl_2Ru(=CHPh)$ (**J**).

To try and observe an intermediate, the reaction between $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) and 3-chloro-3-methyl-1-butyne was investigated at low temperature. Though the reaction was slower from -30°C to -60°C, only starting material (**1**) and product (**7**) were observed. As mentioned above, **1** is not

completely soluble at or below -30°C, so monitoring the appearance of carbene or disappearance of hydride would have no meaning. Addition of phosphine, hoping to take advantage of the possibility that the first step or even a later step would require dissociation of phosphine, showed no measurable decrease in reaction rate from 0.25 to 20 equivalents of phosphine added. It could be that a rather dramatic effect does occur, but fails to bring the reaction rate into a measurable time scale.

A concentration study was undertaken to determine if the carbene forming part of the reaction involved a bimolecular intermediate. Presumably, if the reaction is bimolecular a higher percentage of carbene is expected to form at higher concentrations. In two separate NMR tubes, $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) and propargyl chloride were combined in C_6D_5Cl. Tube A was set to be 0.119M, while tube B was 0.0048M. These concentrations reach the limit of solubility of **1**, and the limit of accurate measurement and dispersion of propargyl chloride. Sample spectra were taken before propargyl chloride was added, and directly after (approximately five minutes), comparing the ratio of carbene $(PCy_3)_2Cl_2Ru(=CH\text{-}CH=CH_2)$ (**14**) generated to $Ru(H)_2Cl_2(PCy_3)_2$ (**5**) generated. For tube A the resulting ratio of carbenes to Ru(IV) was 1.11:1, while for tube B the ratio was 1.73:1. It was presumed from this relatively small change in product ratio over such a large change in concentration that the carbene forming reaction is unlikely to be bimolecular.

The mechanism of formation for the Ru(IV) species **5** is as elusive as that for the carbene. Pictured in Figure 17 are two pathways in which the Ru(IV) might be generated. Pathway *a* shows how "proper" insertion leads to the carbene. If the insertion geometry is reversed, shown in pathway *b*, β-chloro elimination would likely yield Ru(IV) and the allene product pictured. Finally, in pathway *c* a mechanism akin to S_N2 or possibly even a direct oxidative addi-

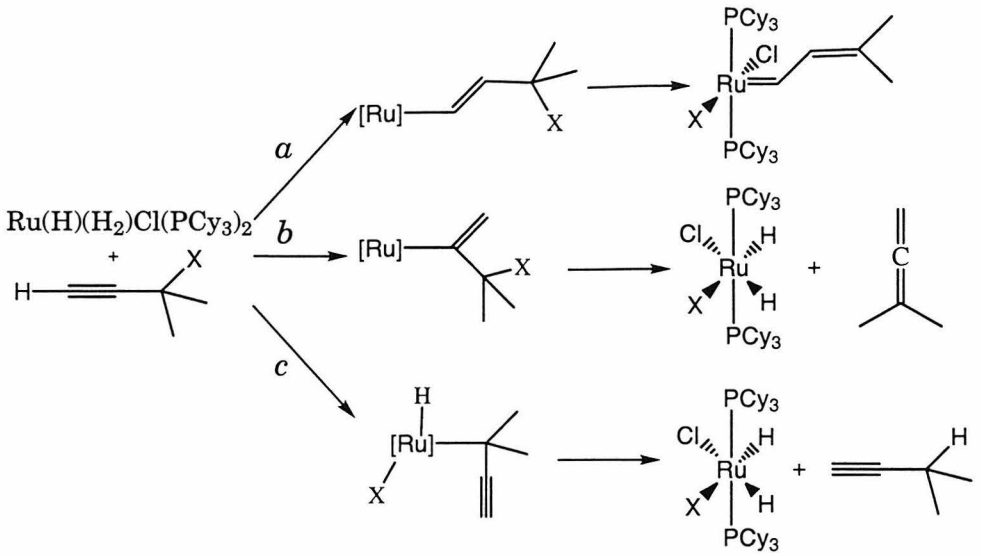


Figure 17-Some possible mechanisms for Ru(IV) generation

tion of the C-Cl bond would first give a metal-alkyl species, which could then reductively eliminate to give a dechlorinated alkyne.

Unfortunately, attempts to identify *in-situ* the organic compound(s) generated in the production of **5** failed due to the large section of the ^1H NMR blocked by the cyclohexyl rings of the phosphine (approximately 0.5 to 3 ppm). Attempts were made to isolate the organic products from the reaction with the parent propargyl chloride, which generates the most Ru(IV). Regardless of the mechanism of formation, a low boiling point compound would be generated. In an attempt to isolate this organic compound, the reaction was setup like a vacuum transfer, with a J-Young NMR tube in the receiving end. Propargyl chloride was added to the hydride, which was in a solution of CD_2Cl_2, allowed to stir, and then vacuum transferred to the NMR tube in an attempt to avoid tricyclohexylphosphine. Nothing conclusive could be identified from the transferred products.

Reactions with Alkyne-1-ol

Looking back at the original methods used to generate carbenes from $MHCl(CO)(PiPr_3)_2$ (M=Os, Ru)[62,65,72] and alkyne-1-ols, the reactions of **1** with propargyl alcohols and HCl were investigated, as depicted in Figure 18.

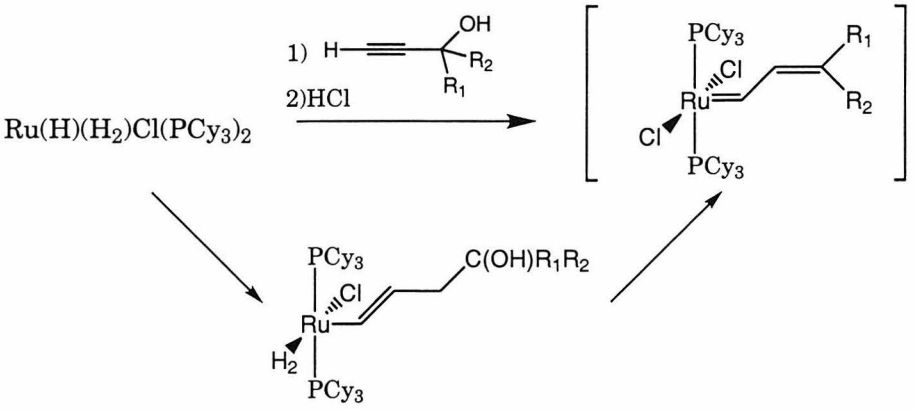


Figure 18-Insertions into alkyne-1-ol

After addition of HCl, reactions between **1** and 3-methyl-3-hydroxy-1-butyne gives $(PCy_3)_2Cl_2Ru(=CH\text{-}CH=CMe_2)$ (**7**), 1-ethynl-cyclohexan-1-ol gives $(PCy_3)_2Cl_2Ru(=CH\text{-}CH=C(CH_2)_5)$ (**11**), and 1,1-diphenyl-1-hydroxy-2-propyne gives $(PCy_3)_2Cl_2Ru(=CH\text{-}CH=CPh_2)$ (**19**) all in moderate yields (50-70%), presumably through the same insertion pathway previously proposed. All reactions were done by adding the alkyne-1-ol to a solution of **1** and allowing the reaction to sit at -30°C for thirty minutes before HCl was added. The parent propargyl alcohol ($HC{\equiv}CCH_2OH$) did not give any observable **14**.

Not surprisingly, NMR scale reactions showed a significant quantity of **5** generated in all cases with alkyne-1-ol and HCl. Presumably the insertion reaction is incomplete, which leaves some **1** in solution, which easily and quantitatively reacts with HCl to give **5**. With the propargyl-chloride systems it is the combination of insertion and elimination steps which drive the reaction to such high yields.

Acetate Based systems

The leaving group can further be expanded to include acetate based compounds. An acetate version of 3-chloro-3-methyl-1-butyne is made by reacting 3-hydroxy-3-methyl-1-butyne with triethylamine and acetylchloride (Figure 19).[79] Reactions between this propargyl-acetate and **1** give a mixture of carbenes, of which after one hour only $(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}CMe_2$ (**7**) remains. It is presumed, though, that one of the carbenes generated is "$(PCy_3)_2Cl(OAc)Ru{=}CH{-}CH{=}CMe_2$)" (**20a**).

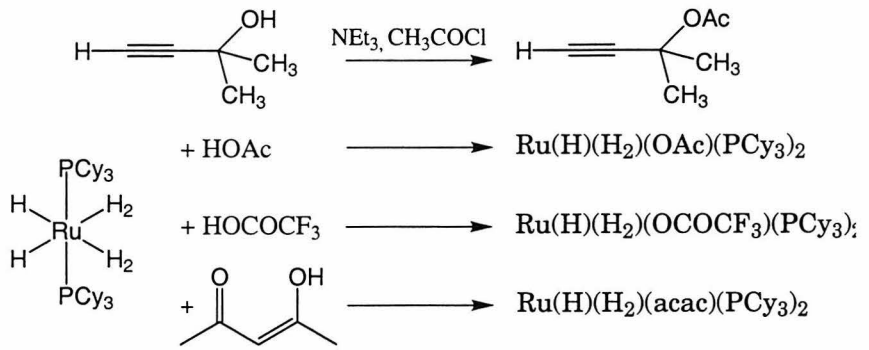


Figure 19-Generation of acetate based starting materials

To further investigate this phenomenon, the corresponding hydrido-acetate complexes of Ru can be made, by simple addition of the corresponding acid to $Ru(H)_2(H_2)_2(PCy_3)_2$. In this manner the previously described complexes $Ru(H)(H_2)(OCOCH_3)(PCy_3)_2$ and $Ru(H)(H_2)(OCOCF_3)(PCy_3)_2$,[82,83] and the new complex $Ru(H)(H_2)(acac)(PCy_3)_2$ (**21**) were made (Figure 19). Reaction of $Ru(H)(H_2)(OCOCH_3)(PCy_3)_2$ or $Ru(H)(H_2)(OCOCF_3)(PCy_3)_2$ with 3-chloro-3-methyl-1-buytne results in a mixture of carbenes of which **7** is the dominant species, and after one hour only **7** remains. It is presumed that in each case the appropriate halo-acetate carbene is generated: "$(PCy_3)_2(X)(Y)Ru{=}CH{-}CH{=}CMe_2$" (X=Cl, Y=OAc (**20a**); X=Cl, Y=$OCOCF_3$ (**20b**)). Reacting $Ru(H)(H_2)(OCOCH_3)(PCy_3)_2$ or $Ru(H)(H_2)(OCOCF_3)(PCy_3)_2$ with the propargyl acetate gave a mixture of several carbenes, and since there was no chloride

present there was no **7** generated. All of the other carbenes decompose in less than thirty minutes. Again, it is presumed that one of the carbenes generated is the appropriate bis-acetate carbene "$(PCy_3)_2(X)(Y)Ru{=}CH\text{-}CH{=}CMe_2$" (X=Y=OAc (**20c**); X=OAc, Y=$OCOCF_3$ (**20d**)).

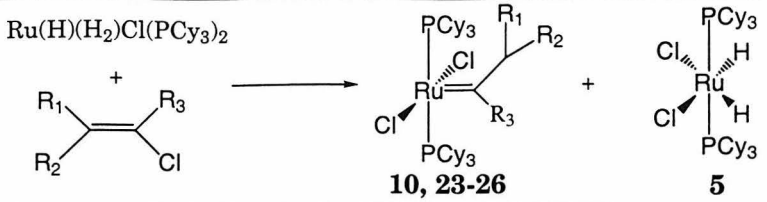
The new compound, $Ru(H)(H_2)(acac)(PCy_3)_2$, shows only a slight reaction with 3-chloro-3-methyl-1-butyne over several days (to give **7**), and no reaction with the propargyl-acetate. The expected product, "$(PCy_3)_2(acac)ClRu{=}CH\text{-}CH{=}CMe_2$" (**22**), was never observed.

Mechanistic Investigations: Vinyl chlorides

Described above are reactions between $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) and propargyl halides and some of the methods employed in attempts to understand the mechanism of their transformation into carbenes. Similar experiments were performed with vinyl chlorides, albeit with much less success. Steric constraints were applied with commercially available alkene-chlorides, in hopes of obtaining the proper regiochemistry so that α-halide elimination to give carbenes is favored (β-halogen elimination can yield only ruthenium halide and dehalogenated alkene, the same pathways as shown in Figure 12).

Consistent with the insertion-elimination mechanism, the ruthenium hydride complex **1** does react with alkenyl halides to give carbene products, but the reactions are significantly less clean than those observed with propargyl halides. For example, **1** reacts with vinyl chloride to give the expected carbene $(PCy_3)_2Cl_2Ru{=}CH\text{-}CH_3$ (**10**),[35] the methylidene complex $(PCy_3)_2Cl_2Ru{=}CH_2$,[35] (arising from cross-metathesis of **10** with vinylchloride), and the Ru(IV) species **5**. The ratio of total carbenes:Ru(IV) is a modest 2.1:1 in methylene chloride, 10:1 in benzene (Table 3). Increasing the steric bulk at the β-carbon (to suppress β-addition) does not improve the yield of carbene; **1** and a mixture of cis-

Table 3-Product Ratios for a variety of vinyl chlorides



10, 23-26 **5**

				CD_2Cl_2		C_6D_6	
	R_1	R_2	R_3	**carbene**	**Ru(IV)**	**carbene**	**Ru(IV)**
10	H	H	H	2.1†	1	10†	1
23	CH_3	H	H	0.8	1	1	0.34
24	CH_3	CH_3	H	*	1	*	1
25	H	H	CH_3	0.5	1	nd	nd
26	Cl	H	H	1†	4.5	nd	nd

*=not observed; †=mixture of carbenes

and trans-1-chloro-1-propene react to give the propylidene complex $(PCy_3)_2Cl_2Ru{=}CHCH_2CH_3$ (**23**)[35] and **5** in a ratio of 0.8:1 in methylene chloride, 1:0.34 in benzene. The even more bulky β-disubstituted olefin 1-chloro-2-methyl-1-propene produces none of the expected carbene "$(PCy_3)_2Cl_2Ru(=CH\text{-}CH(CH_3)_2)$" (**24**), and only gives **5** very slowly (several days vs. <10 min for all other reactions). Since attempts to block β-addition failed, these results suggests that β-addition is not the dominant pathway in the generation of **5** from **1** and vinyl chlorides.

Altering the location of the chloride by using 2-chloro-propene gave what is identified by ^{31}P NMR as $(PCy_3)_2Cl_2Ru(=C(CH_3)_2)$ (**25**) plus some of the methylidene complex $(PCy_3)_2Cl_2Ru{=}CH_2$ (**I**). Since there is no observable carbene proton, **25** was reacted with an excess of styrene to give the more identifiable benzylidene (**J**), at which point the ratio of total carbenes to Ru(IV) is 0.5:1. Finally, reaction of **1** with 1,2-dichloroethylene gave some products which are carbenes (^1H and ^{31}P resonances which are very broad but in characteristic regions) but could not be identified before decomposition. The expected carbene

in this case would be "$(PCy_3)_2Cl_2Ru(=CH\text{-}CH_2Cl)$" (**26**), which is not expected to be stable.

Expansion of Insertion methodology: Alkyne + HCl route, Ru(IV)

The preparation of $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) based on the proposal of $Ru(H)(H_2)Cl(PiPr_3)_2$ (**2**) is described above. It was also noted that a solution of what was assumed to be **2** reacts with terminal acetylenes to give ruthenium carbene species in moderate yields,[66] and that HCl was generated in the reaction to make both **1** and **2**. It is this combination of metal-hydride, alkyne, and HCl which allow the formation of carbenes.

Made in this fashion are $(PCy_3)_2Cl_2Ru(=CHCH_2Ph)$ (**27**) from phenylacetylene, $(PCy_3)_2Cl_2Ru(=CHCH_2CH(CH_3)_2)$ (**28**) from 3-methyl-1-butyne, $(PCy_3)_2Cl_2Ru(=CHCH_2C(CH_3)_3)$ (**29**) from *t*-butylacetylene, $(PCy_3)_2Cl_2Ru(=C(CH_3)\text{-}CH_2CH_2CH_3)$ (**30**) from 2-pentyne, and $(PCy_3)_2Cl_2Ru{=}CH\text{-}CH{=}CMe_2$ (**7**) from 2-methyl-1-butene-3-yne,[64,81] all in moderate yields (<75%). There are no apparent trends in the amount of Ru(IV) generated, but it is clear that it is necessary to attempt to remove as much hydrogen as possible from the system before adding alkyne. As mentioned before, **1** is a well known hydrogenation catalyst. When the reactions to make **27-30** are allowed to stir for too long before the addition of HCl, a fraction of the alkyne is hydrogenated to the olefin. Since the alkyl carbenes are very reactive, they will react with the olefin to give a mixture of carbenes. Each carbene **27-30** reacts with an excess of styrene to quantitatively give the benzylidene (**J**) in less than fifteen minutes. The presence of multiple carbene species can be reduced by carefully degassing the solution of **1** to remove any dihydrogen before addition of the alkyne, carefully measuring the alkyne so that there is no excess to be easily hydrogenated, and by keeping the reaction cold.

Originally, it was thought that reactions between **1**, alkynes, and HCl would proceed via a similar insertion mechanism to that for that seen with an alkyne-1-ol. The resulting metal-alkenyl species could then add a proton to the end of the alkene and the chloride (both from the HCl) to the metal center directly. Later, it was concluded from spectroscopic observations that the intermediate was more likely to be a hydrido-vinylidene species, for example $(PCy_3)_2Cl(H)Ru(=C=CHPh)$ (**31**) from **1** and phenylacetylene, because a peak characteristic of a vinylidene has the same integration as a new hydride, both of which disappeared after HCl addition. This fact was recently confirmed in the literature by isolation of the hydrido-vinylidene, $(PCy_3)_2Cl(H)Ru=C=CHR$,[84,85] followed by reaction with HCl to give the carbene $(PCy_3)_2Cl(H)Ru=CH\text{-}CH_2R$, shown in Figure 20.[84] The mechanism proposed by Werner for this transformation first adds the HCl across the terminal vinylidene C=C bond, placing the chloride on carbon α to the ruthenium (Figure 20). The hydride still on the metal center then migrates to the α-carbon, and the chloride α-chloro eliminates.

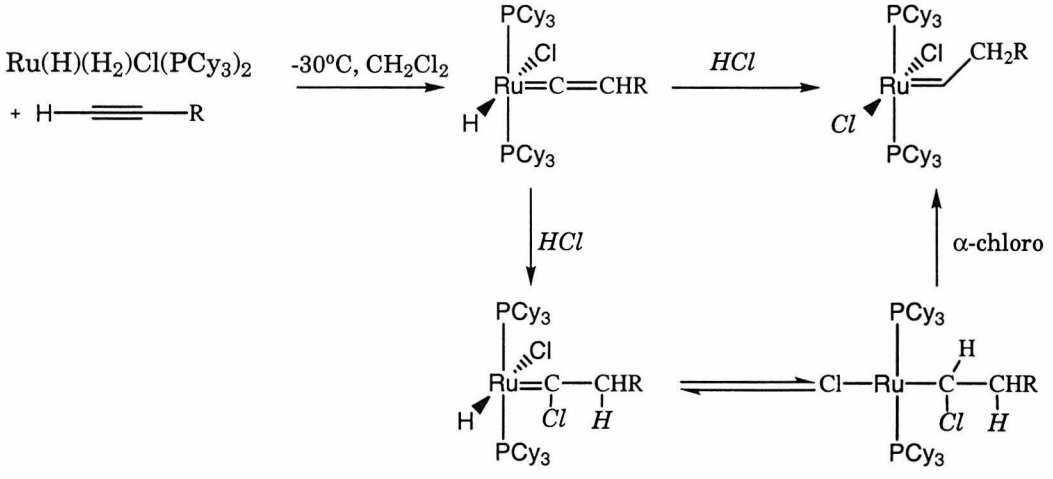


Figure 20-Alkyne + HCl Route

In contrast to the literature description, however, another vinylidene which cannot be separated from the carbene is often observed after the addition

of HCl, with the general formula $(PCy_3)_2Cl_2Ru{=}C{=}CHR$. Also in contrast to the literature preparation, which uses PCy_3HCl as an acid source, it was found that NEt_3HCl does not complete the reaction, and a one pot procedure from $[RuCl_2(COD)]_x$ requires addition of HCl. Confirmation of the vinylidene ($(PCy_3)_2Cl_2Ru{=}C{=}CHR$) identity is accomplished by independently making the vinylidenes: $(PCy_3)_2Cl_2Ru(=C=CHPh)$ (**32**), $(PCy_3)_2Cl_2Ru(=C=CHtBu)$ (**33**), and $(PCy_3)_2Cl_2Ru(=C=CHC_4H_9)$ (**34**). These vinylidenes are made by reacting either $[(p\text{-cymene})RuCl_2]_2$ or $[(benzene)RuCl_2]_2$ with tricyclohexylphosphine and phenylacetylene, *t*-butylacetylene, and 1-hexyne respectively, in procedures similar to those previously described.[86]

The triphenylphosphine starting material $Ru(H)Cl(PPh_3)_3$ was also investigated for insertion into alkynes. It was thought that the triphenylphosphine analogs would not hydrogenate the alkyne, and thus eliminate the possibility of multiple carbenes. Unfortunately, reactions with $RuHCl(PPh_3)_3$ and alkynes, followed by HCl, met with much more limited success. Generated were *cis*-$(PPh_3)_2Cl_2Ru(=CH\text{-}CH=CMe_2)$ (**35**) from 2-methyl-1-butene-3-yne (the *cis*- designation is from the upfield shift of the carbene proton at 15.75), $(PPh_3)_2Cl_2Ru(=CHCH_2Ph)$ (**36**) from phenylacetylene, and $(PPh_3)_2Cl_2Ru(=CHCH_2C(CH_3)_3)$ (**37**) from *t*-butylacetylene. The carbenes **35**-**37** were observed only in trace amounts by NMR, and were not isolated.

In determining whether the order and timing of the addition was important, it was realized once again that adding HCl to **1** gives the Ru(IV) compound $Ru(H)_2Cl_2(PCy_3)_2$ (**5**). Compound **5** can be isolated in high yield from **1** and allylchloride in methylene chloride (in benzene there is no reaction).[87] Isolated **5** reacts with alkynes to give a mixture of carbenes and vinylidenes. This is in direct contrast to the osmium complex $Os(H)_2Cl_2(P^iPr_3)_2$, which reacts with alkynes to give hydrido-carbyne complexes.[61] Complex **5** reacts with 2-

methyl-1-butene-3-yne to give only two phosphorous containing products by NMR, identified as $(PCy_3)_2Cl_2Ru(=CH\text{-}CH=CMe_2)$ (**7**) and what is presumed to be $(PCy_3)_2Cl_2Ru(=C=CH\text{-}C(=CH_2)CH_3)$ (**38**), in an approximate ratio of 1:3. Likewise, 1-hexyne and **5** give what is identified by NMR as $(PCy_3)_2Cl_2Ru(=CH(CH_2)_4CH_3)$ (**39**) and $(PCy_3)_2Cl_2Ru(=C=CH\text{-}(CH_2)_3CH_3)$ (**40**), in an approximate ratio of 1:8.

Attempts at Making Fluorine containing complexes

As discussed in the introduction, the activity trend in terms of halide substituent is I << Br < Cl: the more electronegative and small the halide, the more active the carbene. It seems appropriate, then, to expect that the trend would continue with fluorine, but no fluorine containing carbenes have been previously synthesized–simple halide exchange does not occur. The hydride approach appeared to be a likely candidate for fluorine incorporation, especially the alkyne and acid route where HF could be substituted for HCl.

All attempts to incorporate fluorine via the hydride insertion chemistry failed. In all cases either no carbene at all is observed or no fluoride is detected. It was previously reported that $Ru(H)Cl(CO)(PR_3)_2$ complexes would exchange F for Cl by treatment with CsF in acetone.[88,89] In our hands, however, all attempts to treat $Ru(H)Cl(CO)(P^iPr_3)_2$ with CsF failed to show fluorine incorporation, as did all reactions with **1** and CsF. In situ experiments with **1** and CsF followed by addition of 3-chloro-3-methyl-1-butyne gave only $(PCy_3)_2Cl_2Ru(=CH\text{-}CH=CMe_2)$ (**7**).

Reactions between **1**, alkyne, and either some F^- source (CsF, NaF, N(*t*-Bu)$_4$F) followed by a non-coordinating acid like HBF_4 or by using aqueous HF directly fail to give carbenes. One final attempt involved trifluoromethyl acetylene ($HC\equiv CCF_3$). Although the electronic character of this propargyl halide is

completely different than the previously explored propargylic chlorides there was the possibility it would at least insert into the metal hydride. Trifluoromethyl acetylene gives no carbenes with **1**.

Further Mechanistic Investigations: Carbonyl Complexes

One of the starting points for this project was the report in the literature that $MHCl(CO)(PiPr_3)_2$ (M=Os, Ru)[62,65,72] reacts with alkyne-1-ols, which can then be converted to carbenes (Figure 10). With hopes of uncovering some mechanistic details of the hydride insertion-elimination reaction between **1** and propargyl chlorides, these complexes were examined for reactivity with 3-chloro-3-methyl-1-butyne.

First, a variety of hydrido carbonyl complexes were synthesized. $MHCl(CO)(PiPr_3)_2$ (M=Ru (**41a**) and Os (**41b**)) was prepared according to literature procedures.[62,65,72] The corresponding tricyclohexylphosphine complexes, $MHCl(CO)(PCy_3)_2$ (M=Ru (**42a**) and Os (**42b**)), was prepared using procedures similar to those for **41**. Though not able to prepare **42** pure enough for elemental analysis, only one hydride resonance is seen in the NMR spectrum, and only one CO stretch in the IR and as such was sufficiently pure for the purposes of this investigation. Previous preparations of **42** are from $RuCl_3$ and K_2OsCl_4 respectively.[90,91]

Initially it was thought that loss of H_2 was essential in the steps leading to carbene formation from compound **1** and propargyl chlorides. If this was the case, by replacing H_2 with CO carbene formation would be completely blocked. Surprisingly, **41** and **42** both react with 3-chloro-3-methyl-1-butyne to give *cis*-Cl_2-*trans*-$(PR_3)_2(CO)M{=}CH\text{-}CH{=}CMe_2$ (P^iPr_3-Ru (**43a**); P^iPr_3-Os (**43b**); PCy_3-Ru (**44a**), PCy_3-Os (**44b**)), shown in Figure 21 (pathway *b*). Structure of these carbenes was established by making the identical carbenes via the previously

established route shown in Figure 21 (pathway *a*). In all cases the pathway (*a*) gives complexes with *trans* phosphines, *cis* chlorides, and the CO *cis* to the carbene and *trans* to one chloride. In particular **43b**,[64] and two complexes extremely similar to **43a** differing only in the functionality on the terminal vinyl

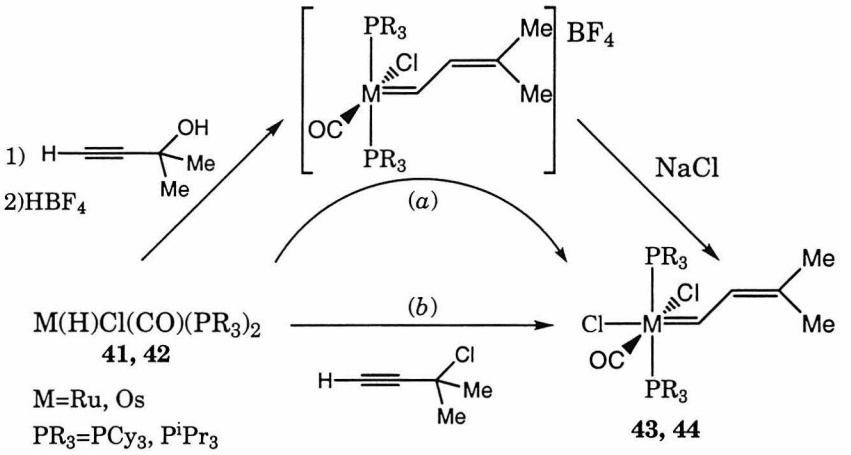


Figure 21-New route to CO carbenes

group, *trans*-$(P^iPr_3)_2$-*cis*-$Cl_2(CO)Ru(=CH\text{-}CH=CPh_2)$ and *trans*-$(PiPr_3)_2$-*cis*-$Cl_2(CO)Ru(=CH\text{-}CH=CHPh)$ [65] have been previously made and described with x-ray structures. Identical spectral data (NMR and IR) is obtained for the propargyl chloride route to **43b**, and the characterization of **43a** is extremely similar to the previously reported complexes.

Continuing to change the coordination sphere of the metal, reactivity with alkynes is blocked by addition of CO to the hydrides. Compounds **41** and **42** react with CO to yield $MHCl(CO)_2(PiPr_3)_2$ (M=Ru (**45a**), Os (**45b**)) and $MHCl(CO)_2(PCy_3)_2$ (M=Ru (**46a**), Os (**46b**)).[75,90,91] Unlike the mono-carbonyl complexes **41** and **42**, the bis-carbonyl compounds show no reactivity towards propargyl chlorides over several days.

Incredibly, $RuHCl(CO)(PCy_3)_2$ (**42a**) gives not only the expected CO containing carbene, but the parent non-CO containing $(PCy_3)_2Cl_2Ru(=CH\text{-}CH=CMe_2)$ (**7**) in an approximate ratio of 1:2. This means that somewhere in

the reaction of **42a** and 3-chloro-3-methyl-1-butyne, CO is released from the metal. It is possible that **42b** gives similar reactivity, but because of complications arising with osmium carbenes the non-CO species is never observed. Nothing more could be ascertained about how or when the CO dissociates from the metal: when allowed to sit in solution immediately after generation, **7** eventually decomposes because of the presence of free CO (see below), when isolated in the solid state the ratio does not change over a relatively short time, and when dissolved after being isolated shows no sign of further isomerization (even for 15 minutes under UV).

Because of the generation of multiple species when dealing with tricyclohexylphosphine carbonyl hydrides, triisopropylphosphine systems were used for kinetic analysis, and in particular the reaction of **41a** with 3-chloro-3-methyl-1-butyne and with 3-hydroxy-3-methyl-1-butyne were examined. Although **41a** reacts slower than $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) with propargyl chlorides, the reaction is still complete in minutes. It was thought that addition of phosphine might inhibit one or more steps in the reaction, and thus give some mechanistic clues. To further complicate the issue, addition of CO to any carbene which does not contain CO already causes instant and total decomposition. All attempts at analyzing the mixture of compounds generated from the addition of CO to any of the non-CO carbenes met only with frustration. Adding excess CO gives a white solid which could not be identified by NMR, but contains no carbenes. Adding less than one equivalent of CO only starting material is observed, while addition of CO in portions gives the white solid.

In considering the mechanism of the transformation from hydride to carbene, it is easier to consider the reaction in two halves. Three observed requirements help in the construction of possible reaction pathways: (1) the hydride and the alkyne must be *cis* to each other for insertion to occur,[92,93] (2)

the ruthenium must be bound to the terminal alkyne carbon, (3) the geometry of the final compound is *cis* phosphines and *cis* chlorides, with the CO *trans* to a chloride and *cis* to the carbene. First, let the possible ways in which insertion of the metal hydride into the alkyne bond be considered, and then how the insertion product might rearrange to yield carbene.

In path *1*, the alkyne coordinates in the empty coordination site. In order for the alkyne to become *cis* to the hydride, a phosphine then dissociates, and the alkyne migrates and inserts. Although generally considered the appropriate place for coordination, to the best of our knowledge the only evidence of addition to that site is the reaction between $OsHCl(CO)_2(PiPr_3)_2$ (**41b**) and $RHCN_2$, which generates a stable carbene trans to the hydride.[94] In this case

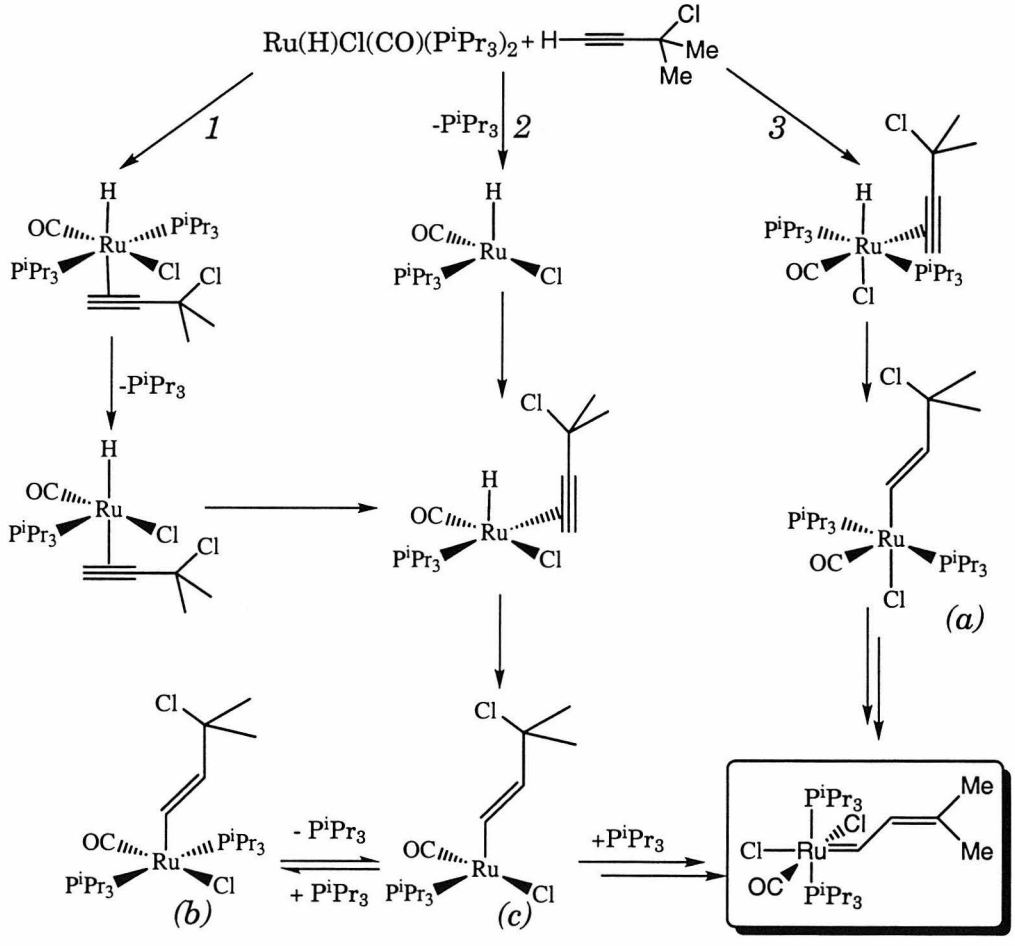


Figure 22-Hydride insertion pathways

no phosphine dissociation and no insertion of the carbene into the hydride, to give an osmium alkyl species, is observed.[94]

Pathway *2* is similar to pathway *1*, except that the first step is dissociation of a phosphine. The alkyne then coordinates in the newly vacant site, and inserts. Sometime after insertion, before or after rearrangement, the phosphine coordinates to the metal center again (intermediates *(b)* and *(c)* and product).

It is possible, however, that due to the geometry of the hydride there is sufficient room for the alkyne to squeeze in above the equatorial plane of the distorted square pyramid of **41a**, and insertion occurs without ligand dissociation. This would then place the alkyne essentially *cis* to the hydride, ready for insertion. The extreme of this idea is shown in pathway *3* (Figure 22), where one of the ligands (here the chloride) is "pushed" by the alkyne into the axial location opposite the hydride to give intermediate *(a)*. This would then allow insertion with no ligand dissociation. Though the chloride is depicted as the ligand which moves, it is possible that either of the phosphines or the CO could also move. The fact that CO never appears *trans* to the carbene in an isolated compound might be considered as supporting evidence that it does not migrate to the axial position, but having CO in this position could also be the origin of the loss of CO described with **42a**. It seems unlikely that the bulky phosphines would be stable *cis* to each other, but depicted in pathway *3* is the extreme case. It is possible that an octahedral species as such is never formed, and the square bipyramid becomes distorted just enough to allow coordination of the alkyne and insertion.

Next, consider the second half of the reaction, and pathways available to give a carbene once insertion has occurred. Again, there are several facts which help in the construction of pathways. If the same mechanism is operating for **1**

as for the carbonyl complexes, the bimolecular pathway for carbene formation can be eliminated, but unfortunately there is no side product to compare ratios of carbene at different concentrations so this cannot be measured. Since the reaction works equally well in benzene as in methylene chloride or sec-butanol, there is no great separation of charge, no free floating chloride ions. In fact, it seems most likely that the chloride (from the propargyl chloride) remains in the coordination sphere of the metal, or at least the chloride and the alkyne add to the same metal center.

From the insertion pathways presented in Figure 22 there are three possible intermediates after the insertion has occurred, designated *(a), (b),* and *(c)* in Figure 23. Intermediate *a* is from the "push" pathway (*3*), in which no ligand dissociates from the metal. If the chloride, or whichever ligand is "pushed," relocates to its original position intermediate *(b)* is formed, which is the same intermediate from either pathway *(1)* or *(2)* with phosphine re-coordinated. Compound (*b*) can be isolated if reactions are carried out with propargyl alcohols instead of propargyl chlorides. Finally, intermediate *(c)* is again from either pathway *(1)* or *(2)* without the phosphine re-coordination. Intermediates *(b)*

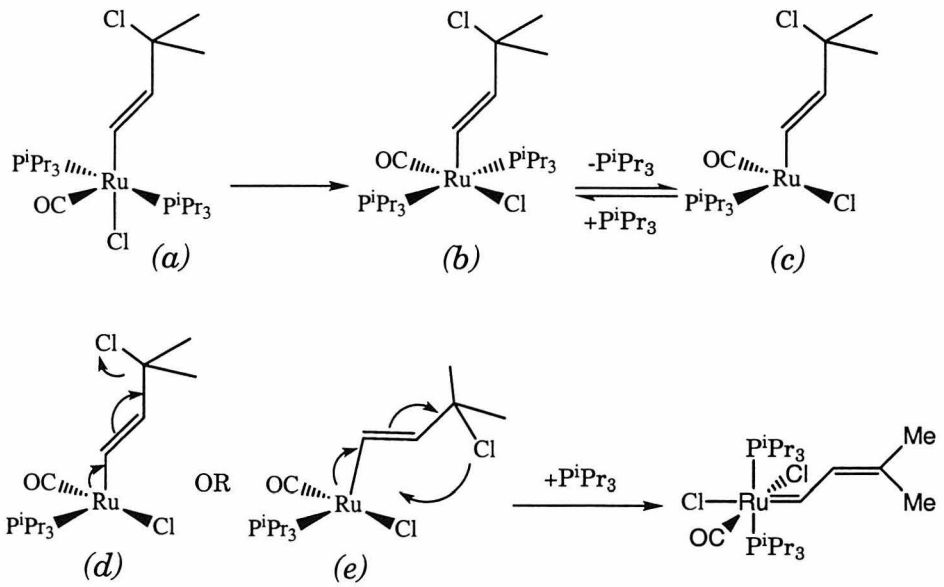


Figure 23-Possible carbene formation intermediates and pathways

and *(c)*, of course, are interchangeable with addition of phosphine.

An arrow pushing diagram illustrates the rearrangement pathways from the insertion intermediates very well, though the arrows are not necessarily indicative of how the reaction proceeds (Figure 23). The geometry of insertion, placing the Ru and the hydride on the same side of the double bond, means that at three atoms away the chloride is relatively inaccessible to the metal unless the alkene bends significantly. In the first case, the carbene forms by pushing the chloride out (intermediates (*d*) or (*b*)). Because there is no great charge separation, the chloride stays very near the metal before coordination. Intermediate (*d*) has one phosphine dissociated, which means that the chloride could coordinate either *trans* to the carbene, or *trans* to the remaining phosphine. If intermediate (*b*) rearranges to form the carbene, the only open coordination site is trans to the carbene. The chloride must then either transfer to the other side of the molecule, or push the other chloride *trans* to the carbene. In the second case, the alkene bends around such that something resembling a cyclic rearrangement occurs (intermediates (*e*) and (*a*)). Intermediate (*e*) suggests that the chloride on the alkene would end up in the open coordination site *trans* to the phosphine. Since this species is never observed nor isolated, it must then add phosphine to "push" the chloride into the position *trans* to the carbene. Finally, intermediate (*a*) could also rearrange to give carbene by having the alkene bend around to place the chloride in the open coordination site, which would yield the final product.

Kinetic studies were performed between $RuHCl(CO)_2(PiPr_3)_2$ (**41a**) and either 3-chloro-3-methyl-1-butyne or 3-hydroxy-3-methyl-1-butyne, with 0.25, 0.5, and 1.0 equivalents of added triisopropylphosphine. Unfortunately, quantitative kinetic data could not be sufficiently obtained. Qualitatively, though, several conclusions can be drawn. Reaction of **41a** with 3-chloro-3-methyl-1-

butyne shows a *dramatic inhibition with addition of phosphine*, with the estimated half life of the reaction going from 180 seconds at 0.25 equivalents of phosphine to 536 seconds for 1 equivalent of phosphine. Interestingly, reaction of **41a** and 3-hydroxy-3-methyl-1-butyne, which cannot rearrange to give the carbene without the addition of acid (see the alkyne-1-ol section described above) *shows no phosphine dependence.* Estimated half lives for this reaction are 95 seconds for 0.25 equivalents of phosphine to 97 seconds for 1 equivalent of phosphine. This can be interpreted as (1) the rate determining step for insertion of the alkyne into the metal hydride *does not* involve phosphine dissociation (2) the rate determining step for rearrangement of the alkene chloride to the carbene after insertion *does* depends on phosphine dissociation.

To monitor the activity of the phosphines bound to the metal in $RuHCl(CO)_2(PiPr_3)_2$ (**41a**), tricyclohexylphosphine is added to the reaction. While not an energetically neutral exchange (tricyclohexyl versus triisopropyl), it is also expected that sterics might be a problem. The bis-tricyclohexylphosphine analogs of the hydride (**42a**) and insertion product (compound *b* in Figure 22-23, where the vinyl-Cl is replaced by OH) have been characterized and isolated, though, so clearly sterics is not that much of an issue. Ideally, of course, a deuterated version of triisopropyl phosphine should be used, and the integration of the isopropyl hydrogen monitored (there is a significant shift in this peak when coordinated to the metal), but if exchange is occurring, it will be easier to follow with tricyclohexylphosphine. First, starting materials were examined. Compound **41a** and tricyclohexylphosphine were dissolved in CD_2Cl_2, and it was apparent that the phosphines do indeed exchange. After thirty minutes the exchange to give mixed phosphine species was approximately 13% complete, after one hour about 18% (equilibrium is not achieved after half an hour). Next, the reaction itself was examined to see if either the insertion

product or an intermediate in the reaction dissociates phosphine. Compound **41a** and 3-hydroxy-3-methyl-1-butyne were reacted (giving compound *b* in Figure 22-23, where the vinyl-Cl is replaced by OH) either in the presence of tricyclohexylphosphine or adding the tricyclohexylphosphine after the insertion reaction was complete. In both cases the exchange to give the mixed phosphine species was approximately 12% complete in half an hour. The fact that the phosphine exchanges at all means that phosphines are dissociating from the metal hydride compound and the insertion product. All three exchange reactions are at approximately the same level of completion after thirty minutes, which is not the equilibrium point for phosphine exchange. In all three cases, phosphine exchange of this type is much slower than the reaction to give the insertion product.

From this qualitative kinetic analysis, a final mechanistic proposal can be made, presented in Figure 24. Since there is no phosphine inhibition in the insertion step, pathway *(3)* from Figure 22 is chosen because either of pathways *(1)* or *(2)* would show phosphine inhibition. Because insertion is extremely fast, and no intermediates are ever observed (except compound *b* in Figure 22-23, where the vinyl-Cl is replaced by OH), it seems likely that in either of these cases loss of phosphine would be a rate determining step. The result of this insertion are such that, intermediate *(a)*, rearranges to produce *(b)* which then forms *(c)*. At this point the phosphine inhibition takes place. With added phosphine the equilibrium between (*b)* and (*c)* would be shifted towards (*b)*, and no further rearrangement would take place. The alkene in intermediate *(c)* can bend towards the metal (*e*), and rearrange to produce a carbene with two chlorides and one phosphine (*f*). The chloride *trans* to the phosphine is then "pushed" again to yield the final product. It seems equally as likely that intermediate (*d*) is involved in the rearrangement to produce carbene. Although it is possible for

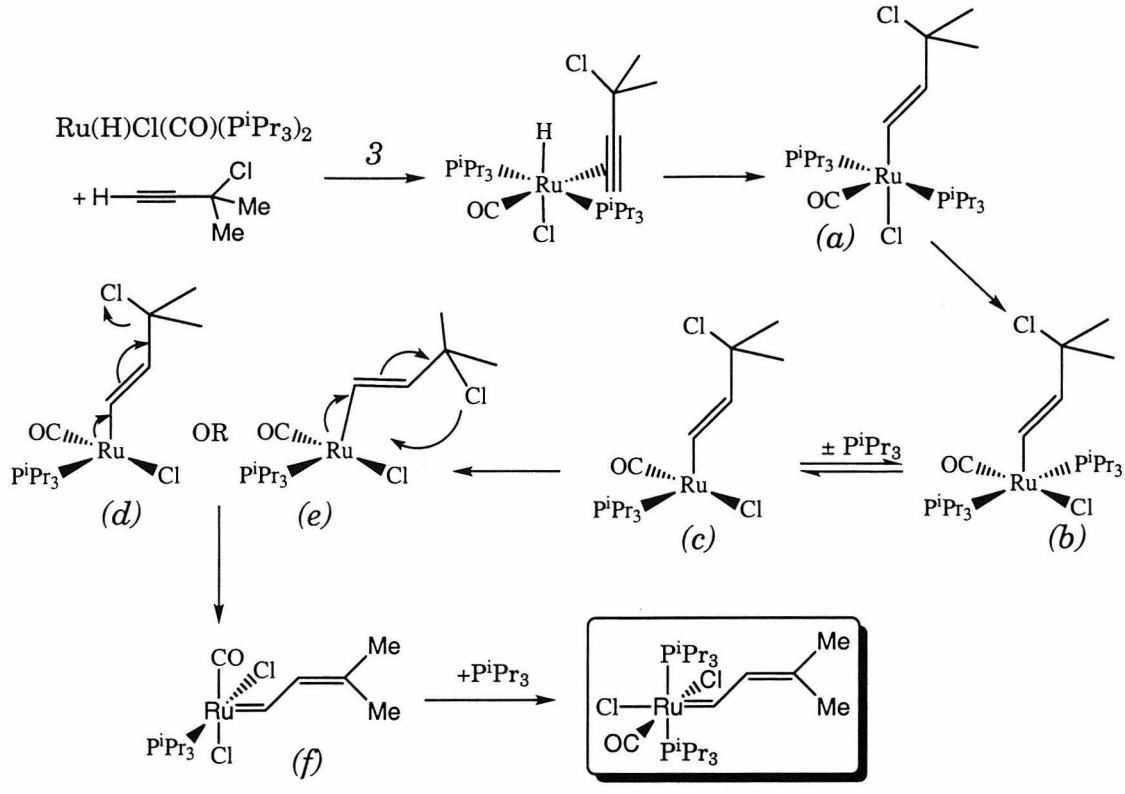


Figure 24-Proposed Mechanism for insertion and rearrangement

the intermediate *(b)* to rearrange to produce a carbene and a closely held chloride ion, intermediate *(f)* still seems the likely product since phosphine would have to dissociate in order to explain the phosphine dependence.

It would be of particular interest to compare this mechanistic proposal with some useful data for the transformation from $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) to $(PCy_3)_2Cl_2Ru(=CH\text{-}CH=CMe_2)$ (**7**), but no such data could be acquired (as discussed in a previous section). It is clear, however, that there are several instances in Figure 24 where replacement of CO with H_2 would facilitate the reaction. For example, it would be expected that the alkyne could immediately displace the dihydrogen, and hence eliminate several steps from the pathway. If the alkyne coordinates to the bottom of the molecule, it could then displace the H_2 whereas CO would not be displaced. Another possibility would be that the dihydrogen remains until something resembling *(b)* is generated, and is then displaced in the rearrangement.

Osmium

It is a goal of this project to extend the chemistry explored above to include osmium. To our knowledge, there is very little information about metathesis active osmium carbene complexes present in the literature. Most osmium carbenes are stabilized by either CO or NO attached to the metal.[95] Previous reports from the Grubbs group were based on observation by NMR of what was assigned to be the osmium analog of the reaction with diphenylcyclopropene to produce $(PPh_3)_2Cl_2Os{=}CH\text{-}CH{=}CPh_2$.[86] Recently, attempts at duplicating this chemistry as well as extending the chemistry involving phenyldiazomethane have been undertaken.[96] In all cases, the carbene is observed, but decomposes rapidly. It was hoped that the hydride insertion reactions would lead to the generation of osmium carbenes.

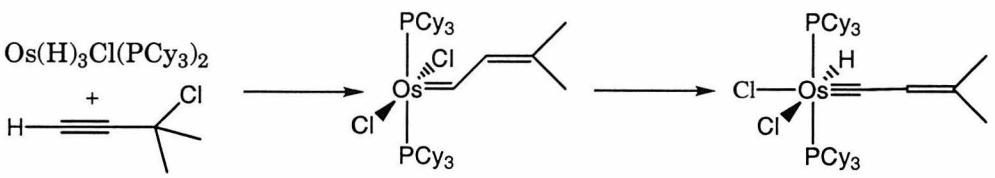
There is, however, a qualitative difference between known hydride systems of ruthenium and osmium. Osmium hydrides tend to be classical hydrides (all $M(H)_n$), while ruthenium tends to have at least one dihydrogen ($M(H)_n(H_2)_m$).[97] In the preparation of $Os(H)_3Cl(P^iPr_3)_2$ (**N**), however, it was proposed that $Os(H)(H_2)Cl(P^iPr_3)_2$ is a realistic intermediate or transition state for the intramolecular hydride site exchange observed above -80°C.[97] If this intermediate actually occurs, it would greatly facilitate the generation of osmium carbenes via the insertion-elimination route with unsaturated organic halides.

The first task of such a project is again the generation of starting materials. Many osmium hydrides are known, including those described in the previous section: $OsHCl(CO)(P^iPr_3)_2$ (**41b**). Also well characterized are analogs of the Ru(IV) compound, $Os(H)_2Cl_2(P^iPr_3)_2$ (**O**), and a compound with a similar formula to **1**, $Os(H)_3Cl(P^iPr_3)_2$ (**N**).[97] Unknown in the literature were tricyclohexylphosphine complexes. If the trend for ruthenium carbenes is the

same for osmium carbenes, the tricyclohexylphosphine systems will be more active. Hence the first osmium compound to be prepared was $Os(H)_3Cl(PCy_3)_2$ (**47**).

Compound **47** is equally as easy to prepare as the ruthenium analog $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**). A mixture of $OsCl_3$ hydrate, and either excess tricyclohexylphosphine or two equivalents of phosphine and one of triethylamine are mixed in sec-butanol and heated under a hydrogen atmosphere. A brown solid precipitates, and is spectroscopically similar to $Os(H)_3Cl(P^iPr_3)_2$ (**N**).[97] Attempts, however, to make the tricyclohexylphosphine analog of the Os(IV) complex $Os(H)_2Cl_2(P^iPr_3)_2$ (**O**) produce only **47**. This is notably easier than the preparation of **N**, which involves first making **O**, treating it with TMS-Cl, followed by reaction with dihydrogen and water, and finally purification in toluene to remove excess dihydrogen.[97]

The osmium hydride $Os(H)_3Cl(PCy_3)_2$ (**47**) does in fact react with 3-chloro-3-methyl-1-butyne to give the appropriate osmium carbene, $(PCy_3)_2Cl_2Os(=CH-CH=CMe_2)$ (**48**), in moderate yields by NMR. The only way this carbene could be generated would be to have dihydrogen leave the molecule. Another major product is also observed, and has been identified as the hydrido-alkylidyne complex $(PCy_3)_2Cl_2Os(H)(\equiv C-CH=CMe_2)$ (**49**) (Figure 25). While the carbene is the initial product, over approximately one hour it has completely converted to **49**



48 **49**

Figure 25-Generation and decomposition of osmium carbenes

and some minor decomposition products. Supporting evidence for this assignment comes from the literature reaction between $Os(H)_2Cl_2(P^iPr_3)_2$ (**O**) and

terminal alkynes (HC≡CR) to give the hydrido-alkylidyne complexes $(P^iPr_3)_2Cl_2Os(H)(\equiv C\text{-}CH_2R)$ (**P**).[61] Another way to confirm these structural assignments would be to react $Os(H)_2Cl_2(PCy_3)$ with a suitable alkyne, but the osmium complex could not be synthesized.

Recent work by the group of Caulton has shown that the differences in reactivity between osmium and ruthenium manifest themselves in the stability of the corresponding carbene[98] and hydrido-vinylidene[99,100] species. Of particular relevance here is comparing the stabilities of the carbene and hydrido-carbyne species: calculations show that the energy difference between the carbene and hydrido-carbyne complex is 21.4 kcal/mol less for Os than for Ru, and for Os the two species are almost isoenergetic (Figure 26).[98] Lacking in this report is the observation of either the osmium carbene or the ruthenium

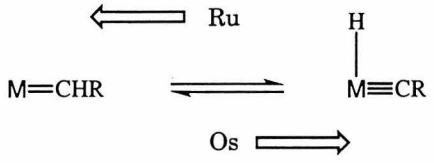


Figure 26-Relative stabilities of metal carbene and hydrido-carbyne

hydrido-carbyne. For osmium, complex $(P^iPr_3)_2Cl_2Os(H)(\equiv C\text{-}CH_2R)$ (**P**) is made from $Os(H)_2Cl_2(P^iPr_3)_2$ (**O**) and alkynes, and no carbene is observed. Likewise, the ruthenium carbene $(PCy_3)_2Cl_2Ru(=CHPh)$ (**J**) cannot be interconverted to the hydrido-carbyne.[98] With the insertion-elimination chemistry, the osmium carbene can actually be generated and observed to transform into the hydrido-carbyne $(PCy_3)_2Cl_2Os(H)(\equiv C\text{-}CH=CMe_2)$ (**49**). It is presumed that the earlier routes (diphenylcyclopropene and phenyldiazomethane) were successful in generating osmium carbenes, but they too rearranged to give the hydrido-carbyne complexes.

The hydride $Os(H)_3Cl(PCy_3)_2$ (**47**) failed to produce carbenes with 1-chloro-1-propene, 1-chloro-2-methyl-1-propene, or 1-pentyne and HCl, although in some

cases it appeared to yield some of the hydrido-alkylidyne complex. Another hydride, $Os(H)_6(PCy_3)_2$ (**50**), the analog of $Ru(H)_2(H_2)_2(PCy_3)_2$ (**4**), was made following the preparation of $Os(H)_6(P^iPr_3)_2$.[101] Compound **50** shows no reaction with excess styrene, α,α-dichlorotoluene, or 3-chloro-3-methyl-1-butyne.

Full Circle

It was observed in our labs over the past several years that hydrogenated polymers could be made simply by doing the polymerization with any of the ruthenium catalysts, for example, $(PCy_3)_2Cl_2Ru(=CHPh)$ (**J**), and heating the reaction mixture under H_2.[102] Presumably the carbene is somehow acting as a hydrogenation catalyst after being heated under dihydrogen. In an attempt to explain this phenomenon, the reaction was investigated by NMR.

A solution of $(PCy_3)_2Cl_2Ru(=CHPh)$ (**J**) was either placed under one atmosphere of dihydrogen in either a J-Young NMR tube via a vacuum line or an NMR tube was sealed with a rubber septum and H_2 was bubbled through for one minute. At room temperature the reaction is slow, but it is markedly faster at 50°C. Nevertheless, after one hour all reactions show the presence of toluene, $Ru(H)_2Cl_2(PCy_3)_2$ (**5**) , $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) and the starting carbene, as well as small amounts of unidentified decomposition products. After one hour at 50°C the ratio of (**5**):(**1**):(**J**), is approximately 1:1:8, the reaction is only twenty percent complete. The presence of **5** is clearly from the splitting of dihydrogen and the generation of toluene. The presence of **1** can be explained by the fact that the starting carbene, **J**, always generates a small amount of free phosphine. This phosphine is basic enough to turn **5** into **1** under H_2. By adding an equivalent of phosphine to a preparative scale reaction, it is observed that after six hours at 55°C the ratio of (**5**):(**1**):(**J**) is approximately 2:1:5, the

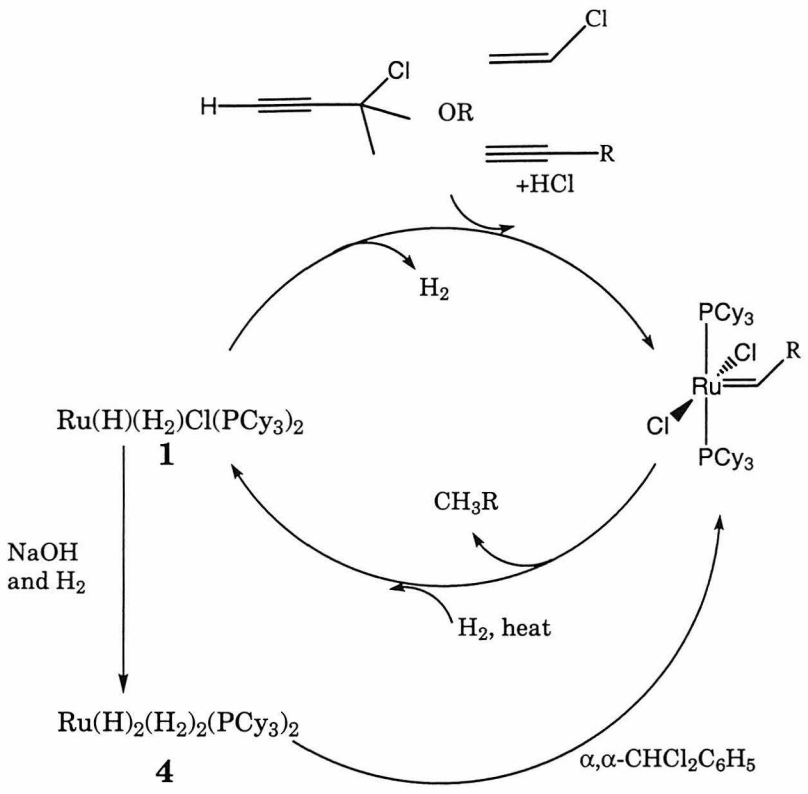


Figure 27-Full Circle: Carbenes to hydrides and back again

reaction is forty percent complete. Presumably under higher pressures and temperatures more of the carbene is converted to the hydrides. The remarkable stability of the ruthenium carbene catalysts has been exploited for their generation, with the above observations, however, we can now theoretically go full circle from hydrides to carbenes and back again (Figure 27).

Conclusions

A new procedure for the generation of the ruthenium hydride-dihydrogen species $Ru(H)(H_2)Cl(PR_3)_2$ has been presented, with all reactions proceeding in very high yield. The tricyclohexylphosphine complex can be isolated in 95+% yield, but the tricyclopentylphosphine and triisopropylphosphine analogs are much more soluble, hindering or preventing isolation. The high yields of these complexes is demonstrated by reacting *in-situ* with 3-chloro-3-methyl-1-butyne to yield the metathesis active carbenes $(PR_3)_2Cl_2Ru(=CH\text{-}CH=CMe_2)$ in very high isolated yield. Wilkinson's Complex, $RuHCl(PPh_3)_3$ reacts in a similar manner to produce the triphenylphosphine analog of the carbene.

These hydrides, like $Ru(H)(H_2)Cl(PCy_3)_2$, react with propargyl and vinyl halides to give carbenes via an insertion-elimination pathway, with a side product of $Ru(H)_2Cl_2(PCy_3)_2$. Tertiary propargyl halides work best, with the ratio of carbene:side product depending on sterics at the propargyl carbon, solvent polarity, and leaving group. Vinyl chlorides present no general reactivity trend. An alternate method for carbene generation is to take $Ru(H)(H_2)Cl(PCy_3)_2$ and react with an alkyne, which produces a hydrido-vinylidene product which then rearranges to yield a carbene upon the addition of HCl.

Surprisingly, the carbonyl-hyrdides, $MHCl(CO)_2(PR_3)_2$ also react with 3-chloro-3-methyl-1-butyne to give carbenes with the structure *cis*-Cl_2-*trans*-$(PR_3)_2(CO)M=CH\text{-}CH=CMe_2$, which are not active for metathesis. From qualitative kinetic data of the reaction of these hydrides with 3-chloro-3-methyl-1-butyne, 3-hydroxy-3-methyl-1-butyne, and various quantities of phosphine, a mechanism for the insertion and elimination pathway is proposed.

Osmium hydrides were also examined for reactivity. $OsH_3Cl(PCy_3)_2$ does react to give the carbene $(PCy_3)_2Cl_2Os(=CH\text{-}CH=CMe_2)$, which unfortunately rearranges quite rapidly to give $(PCy_3)_2Cl_2Os(H)(\equiv C\text{-}CH=CMe_2)$. Recently in

the literature it has been proposed that the hydrido-carbyne species is more stable than the carbene for Osmium. Undoubtedly it has been this rearrangement which has hampered previous investigations of osmium carbenes.

Finally, is was shown that the Ru carbenes, $(PCy_3)_2Cl_2Ru{=}CHR$ react with hydrogen to give H_3CR', $Ru(H)_2Cl_2(PCy_3)_2$, and $Ru(H)(H_2)Cl(PCy_3)_2$. Theoretically all $Ru(H)_2Cl_2(PCy_3)_2$ can be converted to $Ru(H)(H_2)Cl(PCy_3)_2$. It is thus possible to go from hydrides to carbenes, and back to hydrides.

Experimental:

General Considerations.

Unless otherwise specified, all manipulations were performed in a nitrogen-filled Vac-Atmospheres drybox or by using standard Schlenk techniques under an atmosphere of argon. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a JEOL GX-400 spectrometer (399.1 MHz ^{1}H, 140 MHz ^{13}C, 161.9 MHz ^{31}P), or a QE-300 Plus (300.10 MHz ^{1}H, 75.49 MHz ^{13}C) at 25 °C. All chemical shift values are given in ppm (δ) and are referenced with respect to residual protons in the solvent for proton spectra, or referenced with respect to phosphoric acid for phosphorus spectra. All coupling constants are reported in Hz. For the ^{1}H and ^{13}C NMR virtual triplet resonances of *trans* phosphine ligands, the coupling constant $N=|{}^{2}J_{HP} + {}^{4}J_{HP}|$ is given, where N is the separation of the outer lines of the triplet. Polymer molecular weights are referenced to polystyrene standards. Elemental analyses were performed on a Perkin Elmer 2400 CHNN Series 2.

Materials:

Solvents: Toluene, benzene, pentane, hexanes, diethyl ether, benzene-d_6, methylene chloride and tetrahydrofuran were purified by methods developed in our research group.[103] Olefin-free pentane was made by stirring stock pentane over concentrated H_2SO_4. It was then washed with bicarbonate solution, dried over $MgSO_4$, CaH_2, vacuum transferred from a sodium-benzophenone ketyl solution and degassed with several freeze-pump-thaw cycles. THF-d_8 and toluene-d_8 were dried over sodium-benzophenone, CD_2Cl_2 over CaH_2, and degassed using the freeze-pump-thaw method.

$[RuCl_2(COD)]_x$,[104] $Ru(H)Cl(PPh_3)_3$,[105]
$RuCl[E\text{-}CH{=}CHC(OH)R^1R^2](CO)(P^iPr_3)_2$ and
$[RuCl(=CH\text{-}CH{=}CR^1R^2)(CO)(P^iPr_3)_2]BF_4$,[65]
$OsCl[E\text{-}CH{=}CHC(OH)R^1R^2](CO)(P^iPr_3)_2$ and
$[OsCl(=CH\text{-}CH{=}CR^1R^2)(CO)(P^iPr_3)_2]BF_4$,[62]
$RuCl[E\text{-}CH{=}CHC(OH)R^1R^2](CO)(P^iPr_3)_2$ and
$[RuCl(=CH\text{-}CH{=}CR^1R^2)(CO)(P^iPr_3)_2]BF_4$,[81]
$Os(H)(CO)Cl(P^iPr_3)_2$, $Ru(H)(CO)Cl(P^iPr_3)_2$, $Os(H)(CO)_2Cl(P^iPr_3)_2$ and
$Ru(H)(CO)_2Cl(P^iPr_3)_2$,[71] $Os(H_2)Cl_2(P^iPr_3)_2$,[101] $Ru(H)(H_2)(OCOCF_3)(PCy_3)_2$ and
$Ru(H)(H_2)(OCOCH_3)(PCy_3)_2$,[82] were made by literature methods.

Acetylenes and acetylene derivatives not commercially available were prepared following methods in *Preparative Acetylenic Chemistry*.[79] Propargyl halides were passed through a plug of silica gel immediately before use.

All other reagents were used without further purification unless otherwise noted.

Unless otherwise specified, Ru(IV) refers to $Ru(H)_2(Cl)_2(PR_3)_2$,[66] where the phosphine is the same as that described in the starting materials of the experiment being described.

In many cases only selected ^1H NMR data is presented. For trialkylphosphines with saturated ring systems, such as tricyclohexyl- or tricyclopentyl-phosphine, the section of the spectra from 0-3 ppm is completely covered with the signals from the rings on the phosphines. In many cases this obscures any other alkyl signals which might be present in the system. Also, the signals from these phosphines have a tendency to be broad, which makes it very difficult to assign specific peaks. Where possible, a listing of the observed multiplets is presented.

Compounds presented in quotation marks were never successfully syn-

thesized (for example, "CH_6"). Methods attempted are provided in hopes that they might be useful in the future.

Procedures:

$Ru(H)(H_2)Cl(PCy_3)_2$ (1)[66,75,76] $[RuCl_2(COD)]_x$ (4.00 g, 14.28 mmol) and tricyclohexylphosphine (Strem, 97% pure, 8.46 g, 29.26 mmol) are placed in a 500 mL high pressure system equipped with a pressure gauge. To this system, 200 mL of degassed sec-butanol and triethylamine (1.99 mL, 14.28 mmol) is added. After purging with hydrogen, the system is pressurized with 1.5 atm of hydrogen and heated to 80°C for a total of 20 hours, repressurizing as needed. Generation of **(1)** can also be accomplished in a suitably sized, thick walled teflon-valved Strauss flask. The air-sensitive orange solid is isolated by cooling the system to room temperature and adding a volume (200mL) of degassed methanol to insure complete precipitation before filtering. The solid is filtered, washed with methanol until the washings are colorless, and dried in vacuo to give 9.26g, 94% of **(1)**. The pressure of H_2 is necessary, as attempts to make the same compound using an oil bubbler or hydrogen filled balloons gave reduced yields and an insoluble white solid as an additional product.

Attempts at making the analogous N_2 complex, $Ru(H)(N_2)Cl(PCy_3)_2$ failed under all similar conditions.

Selected NMR data: (CD_2Cl_2):^{1}H: -16.9 (br s, Ru*H*(H_2), 3H), 2.4-1 (RuP*Cy*$_3$, 54H); ^{31}P: 53.64 (s, Ru*P*Cy_3).

$Ru(H)(H_2)Cl(P^iPr_3)_2$ (2)[66] Following the literature procedure, $[RuCl_2(COD)]_x$ (1.00g, 3.57 mmol) and triisopropylphosphine (1.14 g, 7.14 mmol), 50 mL of degassed sec-butanol, and triethylamine (0.497 mL, 3.57 mmol) were added as

described in the preparation of **1**. Unlike the previous example, **2** is completely soluble and could not be isolated. All reactions with **2** were done *in-situ*.

$Ru(H)(H_2)Cl(PCp_3)_2$ (**3**) $[RuCl_2(COD)]_x$ (1.00 g, 3.57 mmol) and tricyclopentyphosphine (1.7g, 7.14 mmol), 50mL of degassed isopropanol, and triethylamine (0.497 mL, 3.57 mmol) were added. After purging with hydrogen, the system was pressurized with 1.5 atm of hydrogen and heated to 80°C for a total of 20 hours, repressurizing as needed. After cooling to room temperature, the reaction is then placed in an ice bath for one hour and an orange microcrystalline solid is observed. Attempts at filtration are poor, as the very fine solid goes through the fine frit, and only a small amount of the solid is isolated and washed with cold (0°C) degassed isopropanol. Isolated 0.310 g, 14%, though it is clear the yield is actually much higher (from the solid which went through the frit and the reactions done below).

Selected NMR data (CD_2Cl_2):^{1}H: -16.77 (br s, Ru*H*(H_2), 3H), 2.19, 1.79, 1.68, 1.59, 1.51 (m, P*C*p_3, 54H total); ^{31}P: 54.88 (s, Ru*P*Cp_3).

$Ru(H)_2(H_2)_2(PCy_3)_2$ (**4**) Following the new literature procedure[60] $[RuCl_2(COD)]$ (6.0 g, 21.43 mmol), sodium hydroxide (7.2 g), and tricyclohexylphosphine (12.0 g, 42.86 mmol) are placed in a Fisher Porter Bottle. Degassed *sec*-butanol (250 mL) is added, the reaction pressurized with 2 atmospheres of H_2, and heated to 90°C for 18 hours. After cooling, a pale yellow precipitate was obtained. Under H_2, 30 mL of water is added, and the solid filtered, washed with water (2x30 mL) and methanol (2x20 mL), and dried in a stream of H_2. Isolated 11.8 g, 83%. For characterization see the above reference.

$Ru(H)_2Cl_2(PCy_3)_2$ (**5**) To a solution of $Ru(H)(H)_2Cl(PCy_3)_2$ (**1**) (0.300 g, 0.43 mmol) in methylene chloride is added allylchloride (0.14 mL, 1.72 mmol). The solution changes from orange to red, and is allowed to stir for fifteen minutes. The solvent is removed, to give quantitative product.

Similar reactions in benzene give only decomposition. Ru(IV) is completely soluble in methanol, and is stable under inert atmosphere over a period of days, after which decomposition begins to occur.

Selected NMR data: (CD_2Cl_2):^{1}H -12.49 (t, J=31.5 Hz); ^{31}P: 92.1.

(C_6D_6) ^{1}H: -11.93 (t, J=31.5 Hz); ^{31}P: 91.05.

$(PPh_3)_2Cl_2Ru(=CH\text{-}CH=CMe_2)$ (**6**) $Ru(H)Cl(PPh_3)_2$ (21.00 g, 22.25 mmol) is dissolved in 300 mL of degassed dry methylene chloride and cooled to -30°C. 3-chloro-3-methyl-1-butyne (3.8 mL, 33.7 mmol) is added and allowed to stir for 1 hour at -30°C and then another hour at 0°C. Solvent is then removed, and pentane is added (100 mL). The brown-red solid is isolated and washed with pentane to yield 17.0 g, 98%.

Selected NMR data (CD_2Cl_2): ^{1}H: 18.10 (dd, RuC*H*, J_{HH}=9.5 Hz, J_{HP}=19.7 Hz), 8.01-6.99 (RuCHC*H* and P*Ph*$_3$, 31 H), 1.24 and 0.98 (s (each), RuCHCHC*Me*$_2$, 6H total); ^{31}P: 30.64 (s, Ru*P*Ph$_3$).

$(PCy_3)_2Cl_2Ru(=CH\text{-}CH=CMe_2)$ (7)

Method A: $Ru(H)(H_2)_2Cl(PCy_3)_2$ (**1**) (1.00 g,1.43 mmol) under an inert atmosphere is dissolved in 30mL of dichloromethane, cooled to -30°C and 3-chloro-3-methyl-1-butyne (170 μL, 1.5 mmol) is added. The solution instantly turns dark red-purple, and is allowed to stir for fifteen minutes before removing the flask from the cooling bath and concentrating to a viscous oil. Degassed methanol (20 mL) is added to precipitate the purple solid, which is then washed

with methanol until the washings are colorless and dried to give 1.09 g, 95.2% of the carbene (**7**).

Method B: $[RuCl_2(COD)]_x$ (0.500 g, 1.78 mmol) and tricyclohexylphosphine (1.050 g, 3.75 mmol) were placed in a 250 mL thick walled teflon-valved Strauss flask. To this system, 20mL of degassed sec-butanol is added. The system is purged with hydrogen, sealed, and heated to 80°C, re-pressurizing with hydrogen every four hours, for a total of twenty hours. The system is then cooled to room temperature and one volume of toluene is added. The resulting solution is cooled to -30°C and 2-methyl-1-butene-3-yne (254 μL, 2.66 mmol) is added. After stirring for one hour the solution is concentrated by half and 50mL of degassed methanol is added to give a purple solid, isolated as above to give 0.590 g, 41% of (**7**).

Method C: $[RuCl_2(COD)]_x$ (5.0 g, 17.85 mmol), tricyclohexylphosphine (10.01 g, 35.7 mmol), 200 mL of degassed sec-butanol, and triethylamine (2.54 mL, 17.85 mmol) were added. After purging with hydrogen, the system was pressurized with 1.5 atm of hydrogen and heated to 80°C for a total of 20 hours, repressurizing as needed. After cooling to room temperature, an orange microcrystalline solid is observed, previously identified as $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**). To this slurry 3-chloro-3-methyl-1-butyne (3 mL, 26.7 mmol) is added, and the reaction is left to stir for 30 minutes, at which point the solution is slightly darkened and the solid is purple. 200 mL of degassed methanol is added, and the solid isolated on a frit and washed with degassed methanol until the washings are colorless. Isolated 13.61 g, 95.2%.

Method D: To a solution of $Ru(H)(H_2)_2Cl(PCy_3)_2$ (**1**) (0.020 g, 0.029 mmol) in 0.5 mL of CD_2Cl_2 was added 3-hydroxy-3-methyl-1-butyne (3.1 μL, 0.029 mmol). After ten minutes HCl (28 μL, 1M solution, 0.029 mmol) is added, after ten more minutes the NMR was taken. Observed was the appropriate carbene

and the Ru(IV) species, in a ratio of 3:1.

Method E: To a solution of $Ru(H)(H_2)_2Cl(PCy_3)_2$ (**1**) (0.500 g, 0.71 mmol) in 10 mL of methylene chloride is added 2-methyl-1-butene-3-yne (68 μL, 0.71mmol). After ten minutes HCl (714 μL, 1M solution, 0.71mmol) is added, after ten more minutes the solvent was removed, and methanol added to give a purple precipitate. The solid was filtered and washed with methanol until the washings were colorless, isolate 0.402mg, 71%.

Method F: Two NMR solutions of $Ru(H)(H_2)_2Cl(PCy_3)_2$ (**1**) (0.020 g, 0.029 mmol) in 0.5 mL of CD_2Cl_2 with triphenylphosphine (1 equivalent) are made, and the ^{31}P NMR is taken and referenced to PPh_3. One is cooled to -30°C, the other left at room temperature. 3-chloro-3-methyl-1-butyne (3.2 μL, 0.029 mmol) is added to each, and allowed to mix for ten minutes, after which the NMR is taken. Comparison of integration shows that the reaction at low temperature gave a yield of 99.5%, the room temperature reaction a yield of 98.5%. Neither NMR showed observable amounts of Ru(IV). It is then assumed that the carbene:Ru(IV) ratio is >200:1.

Method G: To a solution of $RuH_6(PCy_3)_2$ (30 mg, 0.05 mmol) in 0.5mL of C_6D_6 is added 3-chloro-3-methyl-1-butyne (5 μL, 0.05 mmol). **5** is seen as the major (approximately 50%) product, presumably from first dechlorination of 3-chloro-3-methyl-1-butyne to give **1** followed by insertion into a second 3-chloro-3-methyl-1-butyne to give **7**.

Selected NMR data (CD_2Cl_2):^1H: 19.26 (d, RuC*H*, J=11.7 Hz), 7.81 (d, RuCHC*H*, J=11.7 Hz), 2.55, 1.83, 1.75, 1.68, 1.49, 1.22 (RuP*Cy*$_3$, 66H total), end methyl groups are buried in 2.5-1.2; ^{31}P: 36.4 (s, Ru*P*Cy_3); ^{13}C: 288.4 (t, Ru*C*H, J_{CP}=9.6Hz), 146.9 (s), 133.5 (s).

(C_6D_6):^1H 19.88 (d, RuC*H*, J=11.7 Hz), 8.34 (d, RuCHC*H*, J=11.7 Hz), 2.83, 2.05, 1.79, 1.67, 1.32, 1.28 (RuP*Cy*$_3$, 66H total), 1.38, 1.05 (s (each),

RuCHCHC*Me*$_2$, 3H each); ^{31}P: 36.3 (s, Ru*P*Cy$_3$)

Analysis Calculated for $RuP_2Cl_2C_{41}H_{74}$: C, 61.48; H, 9.31. Found C, 61.42; H, 9.61.

(P^iPr_3)$_2$Cl$_2$Ru(=CH-CH=CMe$_2$) (**8**) in a procedure identical to that for **7**, using [RuCl$_2$(COD)]$_x$ (1.00 g, 3.57 mmol), triisopropylphosphine (1.00 g, 3.57 mmol), 50 mL of degassed sec-butanol, and triethylamine (0.498 mL, 3.57 mmol) were added. In this case the intermediate Ru(H)(H$_2$)Cl(P^iPr_3)$_2$ is completely soluble, giving a red-brown solution which is then cooled to 0°C and 3-chloro-3-methyl-1-butyne (0.402 mL 3.57 mmol) is added dropwise. The reaction is quite vigorous, with gas evolved immediately and a deep purple precipitate observed. The solid is isolated as above to give 1.85 g, 92.5% of the carbene.

Selected NMR data (CD_2Cl_2):^{1}H: 19.38 (d, RuC*H*, J=11 Hz), 7.95 (d, RuCHC*H*, J=11 Hz), 2.80 (m, RuPC*H*(CH_3)$_2$, 6H), 1.23 (q, J=6.6 Hz, RuPCH(*C*H_3)$_2$, 36H), 1.53 and 1.30 (s (each), RuCHCHC*Me*$_2$, 6H total); ^{31}P: 45.78 (s, Ru*P*^{i}Pr$_3$).

(C_6D_6):^{1}H: 19.88 (d, RuC*H*, J=11 Hz), 8.37 (d, RuCHC*H*, J=11 Hz), 2.89 (m, RuPC*H*(CH_3)$_2$, 6H), 1.24 (q, J=6.6 Hz, RuPCH(*C*H_3)$_2$, 36H), 1.28 and 0.956 (s (each), RuCHCHC*Me*$_2$, 6H total); ^{31}P: 46.45 (s, Ru*P*^{i}Pr$_3$).

Analysis Calculated for $RuP_2Cl_2C_{23}H_{50}$: C, 49.28; H, 8.99. Found C, 49.48; H, 9.33.

(PCp$_3$)$_2$Cl$_2$Ru(=CH-CH=CMe$_2$) (9) In a procedure identical to that for the generation of **5**, [RuCl$_2$(COD)]$_x$ (10.00 g, 35.7 mmol), tricyclopentyphosphine (17.01 g, 71.4 mmol), and triethylamine (4.98 mL, 35.7mmol) are combined in 400mL of degassed isopropanol, and reacted under 1.5 atm of hydrogen at 80°C for a total of 20 hours. After cooling to room temperature, the reaction is stirred

at 0°C for 1 hour, at which point the orange microcrystalline $Ru(H)(H_2)Cl(PCp_3)_2$ (**3**) is observed in the flask. 3-chloro-3-methyl-1-butyne (4.02 mL, 35.7 mmol) is added dropwise over a period of several minutes, as the reaction and release of H_2 is quite vigorous. After addition, the reaction is allowed to stir for one hour at 0°C, and a dark purple microcrystalline solid is observed. This is filtered (at 0°C), and washed with cold degassed methanol (3x15 mL). Since **9** is soluble in methanol, the washings will always be colored, and washing decreases the yield. It is important, though, to remove all NEt_3HCl which is generated in the reaction. Isolated 18.3 g, 71.5%.

Selected NMR data: (CD_2Cl_2): ^1H: 19.46 (d, RuC*H*, J=10.98 Hz), 7.88 (d, RuCHC*H*, J=10.98 Hz), 2.61, 1.82, 1.78, 1.65 ,1.51 (RuPCp_3, 54H total), 1.5 and 1.26 (s, RuCHCHCMe_2, 3H) ; ^{31}P: 30.56 (s, Ru*P*Cp_3).

(C_6D_6) ^1H: 20.03 (d, RuC*H*, J=10.98 Hz), 8.32 (d, RuCHC*H*, J=10.98 Hz), 2.73, 2.03, 1.91, 1.70, 1.49 (m, RuPCp_3, 54H total), 1.27 and 0.95 (s (each), RuCHCHCMe_2, 3H each)); ^{31}P: 31.15 (s, Ru*P*Cp_3).

Analysis Calculated for $RuP_2Cl_2C_{35}H_{62}$: C, 58.65; H, 8.72. Found C, 58.64; H, 9.05.

$(PCy_3)_2Cl_2Ru(=CHCH_3)$ (**10**) A solution is made from $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) (0.02 g, 0.029 mmol) in 0.5 mL of C_6D_6 or CD_2Cl_2, and placed in a -30°C cold bath. Vinylchloride is added by condensing into a Schlenk flask and using a cold syringe, or simply adding via a needle and purging the atmosphere above the solution. NMR shows the presence of $(PCy_3)_2Cl_2Ru(=CHCH_3)$, $(PCy_3)_2Cl_2Ru(=CH_2)$, and $Ru(H)_2Cl_2(PCy_3)_2$ in a ratio of 10:1 with benzene, 2.1:1 with methylene chloride (ratios are total carbenes:Ru(IV). $(PCy_3)_2Cl_2Ru(=CH_2)$ arises from generation of the carbene followed by metathesis of vinylchloride.

Selected NMR data: (CD_2Cl_2): 19.21 (q, RuC*H*, J=5.9 Hz); ^{31}P: 35.8 (s,

Ru*P*Cy_3).

(C_6D_6) ^{1}H: 19.63 (q, RuC*H*, J= 5.9 Hz); ^{31}P: 36.3 (s, Ru*P*Cy_3)

(PCy_3)$_2$$Cl_2$Ru(=CH-CH=C($CH_2$)$_5$) (11)

Method A: To a solution of Ru(H)(H_2)$_2$Cl(PCy_3)$_2$ (**1**) (0.500 g, 0.71 mmol) in 10 mL of methylene chloride is added 1-ethynl-1-chlorocyclohexane (69 μL, approximately 0.71 mmol). The reaction is allowed to stir for 30 minutes, after which the solvent is removed and methanol is added to precipitate a purple solid. This solid is filtered and washed with methanol until the washings are colorless. Isolated 0.542 g, 90%.

Method B: To a solution of Ru(H)(H_2)$_2$Cl(PCy_3)$_2$ (**1**) (0.300 g, 0.43 mmol) in 10 mL of methylene chloride is added 1-ethynl-1-cyclohexanol (55 μL, 0.43 mmol). The reaction was allowed to stir for fifteen minutes, after which HCl (0.429 mL, 1M solution, 0.43 mmol) is added. The reaction is allowed to stir for fifteen minutes, solvents are removed, and methanol is added to precipitate a purple powder. The solid is filtered and washed with methanol until the washings are colorless. Isolated 0.125 g, 33%.

Method C: To a solution of Ru(H)(H_2)$_2$Cl(PCy_3)$_2$ (**1**) (0.015 g, 0.021 mmol) in 0.5 mL of either C_6D_6 or CD_2Cl_2 was added 1-ethynl-1-chlorocyclohexane (3.3 μL, approximately 0.021 mmol). After ten minutes the NMR is taken. Observed are the appropriate carbene and the Ru(IV) species. In CD_2Cl_2 the ratio is 100:1, while in C_6D_6 there is no Ru(IV) observed (assume, then, a ratio of >200:1).

Method D: To a solution of Ru(H)(H_2)$_2$Cl(PCy_3)$_2$ (**1**) (0.020 g, 0.029 mmol) in 0.5 mL of CD_2Cl_2 is added 1-ethynl-1-cyclohexanol (3.6 μL, 0.029 mmol). After ten minutes HCl (28 μL, 1M solution, 0.029 mmol) is added, after ten more minutes the NMR is taken. Observed are the appropriate carbene and

the Ru(IV) species, in a ratio of 3.8:1.

Selected NMR data:(CD_2Cl_2):^{1}H: 19.34 (d, RuC*H*, J=11.7 Hz), 7.81 (d, RuCHC*H*, J=11.7 Hz), 2.55, 1.84, 1.81, 1.78, 1.47, 1.22 (P*Cy*$_3$, 66H total), 2.28, 1.75, 1.64, 1.56, 1.3 (RuCHCHC(C*H*$_2$)$_5$) ^{31}P: 35.7; ^{13}C: 288.3 (t, Ru*C*, J=7.7 Hz).

(PCy_3)$_2$$Cl_2$Ru(=CH-CH=CHPh) (**12**) To a solution of Ru(H)(H_2)$_2$Cl(PCy_3)$_2$ (**1**) (0.015 g, 0.021 mmol) in 0.5 mL of either C_6D_6 or CD_2Cl_2 is added 3-chloro-3-phenyl-1-propyne (3.3 μL, approximately 0.021 mmol). After ten minutes the NMR is taken. In both solvents two carbenes are observed, representing the *cis-* and *trans-* isomers on the vinyl group. In CD_2Cl_2 this ratio is 1:13 (based on the H-H coupling constant), and in a ratio of carbenes:Ru(IV) of 166:1. In C_6D_6 only the carbenes are observed in a *cis-:trans-* ratio of 1:36 (assume, then, a ratio of >200:1 carbenes:Ru(IV)).

Selected NMR data (CD_2Cl_2): ^{1}H *cis-* carbene: ^{1}H 19.86 (d, RuC*H*, J=11.7 Hz), 8.01 (m, RuCHC*H*, J=11.7 Hz); ^{31}P: 37.1. *trans-* carbene: ^{1}H 19.04 (d, RuC*H*, J=10.3 Hz), 8.53 (m, RuCHC*H*, J=10.3, 15.4 Hz); ^{31}P: 36.95.

(C_6D_6): ^{1}H *cis-* carbene: ^{1}H 20.62 (d, RuC*H*, J=11.7 Hz), 8.45 (m, RuCHC*H*); ^{31}P: 37.2. *trans-* carbene: ^{1}H 19.71 (d, RuC*H*, J=10.3 Hz), 9.08 (m, RuCHC*H*, J=10.3, 15.4 Hz); ^{31}P: 36.8.

(PCy_3)$_2$$Cl_2$Ru(=CH-CH=CH$CH_3$) (**13**) To a solution of Ru(H)(H_2)$_2$Cl(PCy_3)$_2$ (**1**) (0.015 g, 0.021 mmol) in 0.5mL of either C_6D_6 or CD_2Cl_2 is added 3-chloro-1-butyne (1.97 μL, 0.021 mmol). After ten minutes the NMR is taken. In both solvents two carbenes are observed, representing the *cis-* and *trans-* isomers of the vinyl group. In CD_2Cl_2 a ratio of 1:2 is observed (based on the H-H coupling constant) with a ratio of carbenes:Ru(IV) of 8:1, while in C_6D_6 the *cis-:trans-* ratio is 1:3, and the carbene:Ru(IV) ratio is 37:1.

Selected NMR data (CD_2Cl_2): *cis-* carbene: ^1H 19.6 (d, RuC*H*, J=11.7 Hz), 7.84 (m, RuCHC*H*, J=11.7 Hz), 6.27 (m, RuCHCHC*H*); ^{31}P: 36.6. *trans-* carbene: ^1H 18.69 (d, RuC*H*, J=10.24 Hz), 7.98 (m, RuCHC*H*, J=10.24 Hz), 6.6 (m, RuCHCHC*H*, J=8 Hz); ^{31}P: 36.0.

(C_6D_6): *cis-* carbene: ^1H 20.21 (d, RuC*H*, J=11.7 Hz), 8.27 (m, RuCHC*H*), 6.09 (m, RuCHCHC*H*); ^{31}P: 37.08. *trans-* carbene: ^1H 19.25 (d, RuC*H*, J=10.24 Hz), 8.37 (m, RuCHC*H*), 6.46 (m, RuCHCHC*H*, J=8 Hz); ^{31}P: 36.47.

$(PCy_3)_2Cl_2Ru(=CH\text{-}CH=CH_2)$ (**14**) To a solution of $Ru(H)(H_2)_2Cl(PCy_3)_2$ (**1**) (0.015 g, 0.021 mmol) in 0.5mL of either C_6D_6 or CD_2Cl_2 is added propargyl-chloride (1.55 μL, 0.021 mmol). After ten minutes the NMR is taken. In CD_2Cl_2 the ratio carbenes:Ru(IV) is 0.8:1, while in C_6D_6 the ratio is 30:1.

Selected NMR data (CD_2Cl_2): ^1H 19.04 (d, RuC*H*, J=11 Hz), 8.08 (m, RuCHC*H*), 6.00 and 6.23 (m, RuCHCHCH_2, 2H); ^{31}P: 36.5.

(C_6D_6): ^1H 19.63 (d, RuC*H*, J=11 Hz), 8.54 (m, RuCHC*H*, J=11 Hz), 5.98 and 5.84 (m, RuCHCHCH_2, 2H); ^{31}P: 36.81.

$(PCy_3)_2Br_xCl_{2-x}Ru(=CH\text{-}CH=CMe_2)$ (x=0, 1, 2) (**15**)

Method A: To a solution of $Ru(H)(H_2)_2Cl(PCy_3)_2$ (**1**) (0.015 g, 0.021 mmol) in 0.5 mL of either C_6D_6 or CD_2Cl_2 is added 3-bromo-3-methyl-1-butyne (3.2 μL, approximately 0.021 mmol) After ten minutes the NMR is taken. In CD_2Cl_2 three carbenes $(PCy_3)_2Br_xCl_{2-x}Ru(=CH\text{-}CH=CMe_2)$ (x=0, 1, 2) and three Ru(IV) species $(PCy_3)_2Br_xCl_{2-x}RuH_2$ (x=0, 1, 2) (**16**) are observed in a ratio of 29:1 (total carbenes:total Ru(IV)). The ratios of carbenes themselves quickly becomes the expected statistical mixture 1:2:1 (x=0,1,2 respectively). In C_6D_6 only the carbenes are observed (assume, then, a ratio of >200:1 carbenes:Ru(IV)), and the halide exchange process is much slower.

Method B: A mixture of $(PCy_3)_2Br_2Ru(=CH\text{-}CH=CMe_2)$ and $(PCy_3)_2Cl_2Ru(=CH\text{-}CH=CMe_2)$ (0.025 g each) are placed in an NMR tube and dissolved in 1 mL of either C_6D_6 or CD_2Cl_2. The mixture quickly equilibrates to a 1:2:1 (x=0,1,2 respectively) ratio of carbenes in CD_2Cl_2 (complete in <30 minutes), less rapidly in C_6D_6 (after 1 hour approximately 10% of the x=1 species is observed).

Selected NMR data (CD_2Cl_2): ^1H 19.26 (d, Cl_2RuCH), 19.22 (d, BrClRuC*H*, J=11Hz), 19.15 (d, Br_2RuCH, J=11.7 Hz), 7.83-7.93 (overlap of beta protons $X_2RuCHCH$), -12.48 (t, Cl_2H_2Ru, J= 31.48 Hz), -11.96 (t, $ClBrH_2Ru$, J=31.52 Hz), -11.51 (t, Br_2H_2Ru, J= 32.2 Hz). ^{31}P: 36.52 (Br_2RuP_2), 36.4 ($ClBrRuP_2$), 36.31 (Cl_2RuP).

(C_6D_6): ^1H 19.88 (d, Cl_2RuCH, J=11.7 Hz), 19.80 (d, ClBrRuC*H*, J=11 Hz), 19.70 (d, Br_2RuCH, J=11.7 Hz), 8.3-8.4 (overlap of beta protons $X_2RuCHCH$); ^{31}P: 37.07 (Br_2RuP_2), 36.90 ($ClBrRuP_2$), 36.3 (Cl_2RuP).

$(PCy_3)_2Br_2Ru(=CH\text{-}CH=CMe_2)$ (17) $(PCy_3)_2Cl_2Ru(=CH\text{-}CH=CMe_2)$ (0.500 g, 0.624 mmol) (**7**) and LiBr (1 g, approximately 20 equivalents) are dissolved in 15 mL of tetrahydrofuran, and allowed to stir for 3 hours. The THF is then removed, and the residue dissolved in benzene and passed through a plug of celite. Washes are done until the solution is colorless, and the benzene is freeze dried to give a quantitative yield of the purple solid.

Selected NMR: (CD_2Cl_2): ^1H 19.16 (d, RuC*H*, J=11.7 Hz), 7.93 (d, RuCHC*H*, J=11.7 Hz), 2.8, 1.84, 1.75, 1.69, 1.45, 1.22 ($RuPCy_3$, 66H total), 1.49 and 1.27 (s, $RuCHCHCMe_2$, 3H each); ^{31}P: 36.52 (Br_2RuP).

(C_6D_6): ^1H 19.70 (d, RuC*H*, J=11.7 Hz), 8.39 (d, RuCHC*H*, J=11.7 Hz), 3.1, 2.08, 1.79, 1.66, 1.36, 1.29 ($RuPCy_3$, 66H total), 1.33 and 1.03 (s, $RuCHCHCMe_2$, 3H each); ^{31}P: 37.07 (Ru*P*).

$(PCy_3)_2Cl_2Ru(=C(CH_3)\text{-}CH=C(CH_2)_5)$ (18) $Ru(H)(H_2)_2Cl(PCy_3)_2$ (**1**) (0.500 g, 0.71 mmol) under an inert atmosphere is dissolved in 15mL of dichloromethane cooled to -30°C, and 1-(methylethynl)-1-chlorocyclohexane (170 μL, approximately 1.5 equivalents) is added. The reaction is allowed to stir for 30 minutes, after which the solvent is removed and methanol is added to precipitate the solid. Isolated 0.36 g, 60%. This carbene can be reacted directly with styrene (excess) to slowly give the more easily identifiable $(PCy_3)_2Cl_2Ru(=CHPh)$.

Selected NMR data (CD_2Cl_2): ^1H: 7.7 (s, $RuC(CH_3)\text{-}C\mathit{H}$), 2.63 (s, RuC(CH3), 3H); 31P: 46.62 (s, RuPCy3).

$(PCy_3)_2Cl_2Ru(=CH\text{-}CH=CPh_2)$ (19) To a solution of $Ru(H)(H_2)_2Cl(PCy_3)_2$ (**1**) (0.036 g, 0.051 mmol) in 0.8mL of CD_2Cl_2 is added 3,3-diphenyl-3-hydroxy-1-propyne (0.0144 mg, approximately 0.051 mmol) which is allowed to mix for twenty minutes before adding HCl (52 μL of a 1M solution, 0.051mmol). Observed in the NMR are the appropriate carbene which has been previously characterized[11] and the Ru(IV) species, in a ratio of 4.5:1.

Selected NMR data (CD_2Cl_2): ^1H 19.05 (d, $RuC\mathit{H}$, J=11 Hz); ^{31}P: 37.38.

Acetate based compounds:

"$(PCy_3)_2(X)(Y)Ru=CH\text{-}CH=CMe_2$)" (X=Cl, Y=OAc (**20a**); X=Cl, Y=$OCOCF_3$ (**20b**); X=Y=OAc (**20c**)

Reactions with $Ru(H)(H_2)(OCOCF_3)(PCy_3)_2$ or $Ru(H)(H_2)(OCOCH_3)(PCy_3)_2$ and 3-chloro-3-methyl-1-butyne, as well as $Ru(H)(H_2)Cl(PCy_3)_2$ and 3-acetato-3-methyl-1-butyne were attempted in a manner similar to that described for the (acac) compound below. In all cases, multiple carbenes are observed, presumed to be mixtures of halide and acetate combinations. In all cases, however, the dominant species after 1 hour is the parent compound $(PCy_3)_2Cl_2Ru(=CH\text{-}$

$CH{=}CMe_2$) (**7**), and all other carbenes have decomposed.

$Ru(H)(H_2)(acac)(PCy_3)_2$ (21) Following the procedures for making both $Ru(H)(H_2)(OCOCF_3)(PCy_3)_2$ and $Ru(H)(H_2)(OCOCH_3)(PCy_3)_2$,[82] to a suspension of $Ru(H)_6(PCy_3)_2$ (400 mg, 0.599 mmol) in degassed acetone (15 mL) at -78°C, acetylacetonate (61.5 μL, 0.599 mmol) is added. The reaction is stirred for two hours and after being brought to room temperature a yellow precipitate is observed. The solid is filtered and washed with acetone until the washings are colorless. Isolated 0.420 g, 92%, which is assigned as $Ru(H)(H_2)(acac)(PCy_3)_2$ based on comparing spectroscopic data to the previously described compounds.

Selected NMR data(CD_2Cl_2): ^{1}H: -13.02 (t, Ru*H*, J= 15.4 Hz, 3H), 5.34 (s, $Ru(CH_3CO)_2C\mathit{H}$, 1H), 1.99 (s,$Ru(C\mathit{H}_3CO)_2CH$, 6H); ^{31}P: 50.44 (s, Ru*P*Cy_3).

"[(acac)$Ru(PCy_3)_2(=CH\text{-}CH{=}C(CH_3)_2)$]Cl" (22) To a solution of $Ru(H)(H_2)(acac)(PCy_3)_2$ (**21**) (15 mg, 0.02 mmol) in CD_2Cl_2, 3-chloro-3-methyl-1-butyne (2.5 μL, 0.02 mmol) is added. No reaction is observed immediately, and only after several hours is there a small amount of carbene, identified as $(PCy_3)_2Cl_2Ru(=CH\text{-}CH{=}CMe_2)$ (**7**). After 24 hours, only a small amount of reaction has occurred, with no products other than **7** visible by NMR.

$(PCy_3)_2Cl_2Ru(=CHCH_2CH_3)$ (23) $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) (0.02 g, 0.029 mmol) is dissolved in 0.5 mL of C_6D_6 or CD_2Cl_2, and a mixture of *cis*- and *trans*-1-chloropropene (2.4 μL, 0.029 mmol) is added. Initially (approximately five minutes) the hydride is still visible, and only after a slightly longer reaction time, about thirty minutes, is the hydride gone. After the disappearance of the hydride, the ratio of $(PCy_3)_2Cl_2Ru(=CHCH_2CH_3)$ and $Ru(H)_2Cl_2(PCy_3)_2$ is 0.8:1 in CD_2Cl_2 and 1:0.34 in C_6D_6.

Selected NMR data: (CD_2Cl_2) ^1H: 19.09 (t, RuC*H*, J=5.9 Hz); ^{31}P: 36.58 (s, Ru*P*Cy_3). (C_6D_6) ^1H: 19.59 (t, RuC*H*, J= 5.9 Hz); ^{31}P: 36.86 (s, Ru*P*Cy_3)

"($PCy_3)_2Cl_2Ru(=CH\text{-}CH(CH_3)_2)$" (**24**) Ru(H)($H_2$)Cl($PCy_3)_2$ (**1**) (0.02 g, 0.029 mmol) is dissolved in 0.5 mL of C_6D_6 or CD_2Cl_2, and 1-chloro-2-methyl-1-propene (2.8 μL, 0.029 mmol) is added. No reaction is observed over several hours.

($PCy_3)_2Cl_2Ru(=C(CH_3)_2)$ (**25**) To a solution of Ru(H)(H_2)Cl($PCy_3)_2$ (**1**) (0.02 g, 0.029 mmol) in 0.5 mL of CD_2Cl_2 is added 2-chloropropene (4.1 μL, 0.029 mmol). Over ten minutes a color change occurs, and the NMR is taken. Observed by ^1H are the product of carbene generation and metathesis with 2-chloropropene ($PCy_3)_2Cl_2Ru(=CH_2)$ in small yield, and Ru(IV). The ^{31}P shows the expected carbene, the methylidene, and Ru(IV). To further identify the products, styrene (10 equivalents) is added and the benzylidene ($PCy_3)_2Cl_2Ru(=CHPh)$ is generated. Ratio of total carbenes:Ru(IV) is then 0.5:1. Selected NMR data (CD_2Cl_2) ^{31}P: 35.88.

"($PCy_3)_2Cl_2Ru(=CH\text{-}CH_2Cl)$" (**26**) To a solution of Ru(H)(H_2)Cl($PCy_3)_2$ (**1**) (0.02 g, 0.029 mmol) was dissolved in 0.5mL of C_6D_6 or CD_2Cl_2, and 1,2-dichloroethylene (2.2 μL, 0.029 mmol) is added. Only broad messy peaks are observed in the ^1H NMR, at 19.23, 19.13, and 18.7, with peaks in the ^{31}P at 37.7, 35.88, and 35.55. These compounds are clearly carbenes, but could not be identified before decomposition. Ru(IV) is also observed.

Alkyne + HCl route

In general, attempts follow this pattern. To a solution of Ru(H)(H_2)Cl($PCy_3)_2$ (**1**) in methylene chloride, which has been degassed after

dissolving **1**, cooled to -30°C, two equivalents of alkyne (HCCR, for example) are added. The reaction is allowed to stir for 30 minutes, at which point 1 equivalent of HCl in diethylether is added. The reaction is allowed to stir for 15 minutes, at which point all solvent is removed, and methanol is added to precipitate the resulting solid, which is then filtered and washed with methanol until washings are colorless. Three possible products are identified, in varying proportions (sometimes not all three are present). The first is the expected carbene, $(PCy_3)_2Cl_2Ru(=CH\text{-}CH_2R)$, the second the vinylidene $(PCy_3)_2Cl_2Ru(=C=CHR)$, and the third the result of first hydrogenating the alkyne to give $CH_2=CHR$, which then reacts with the generated carbene to give $(PCy_3)_2Cl_2Ru(=CHR)$. If all compounds are generated they cannot be easily separated.

$(PCy_3)_2Cl_2Ru(=CHCH_2Ph)$ (27)

Method A: A solution is made with $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) (0.625 g, 0.89 mmol) in methylene chloride, which is further degassed by stirring for thirty minutes and occasionally removing the headspace, by bubbling argon through the solution, or by simply removing solvent and redissolving several times. To this solution, phenylacetylene (194 μL, 1.78 mmol) is added, and allowed to stir for thirty minutes, followed by addition of HCl (0.892 mL, 1M solution, 0.89 mmol). The volume is reduced to 1 mL and 20 mL of methanol are added to precipitate a red-purple solid. Isolate 0.484g, 65%.

Method B: To a solution of $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) (0.02 g, 0.029 mmol) in 0.5 mL of C_6D_6 or CD_2Cl_2, a mixture of *cis*- and *trans*-β-styrene (4.1 μL, 0.029 mmol) is added. Only Ru(IV) is observed by NMR, no carbenes.

Method C: To a solution of $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) (0.02 g, 0.029 mmol) in 0.5mL of C_6D_6 or CD_2Cl_2, phenylacetlyene (3.2 μL, 0.029 mmol) is added.

After ten minutes HCl (29.3 μL, 1M solution, 0.029 mmol) is added, and after ten minutes the NMR is taken. Both the expected product and $(PCy_3)_2Cl_2Ru(=CHPh)$ are observed, along with the Ru(IV) species, in a ratio of 2:1:1.1 respectively, giving a carbenes:Ru(IV) of 3:1.1.

Selected NMR data: (CD_2Cl_2) ^1H: 19.39 (t, RuC*H*, J=5.1 Hz), 3.99 (d, RuCHCH_2, 2H, J=5.1 Hz); ^{31}P: 35.74 (s, Ru*P*Cy_3).

$(PCy_3)_2Cl_2Ru(=CHPh)$ (J)[35,49] This compound can be made by reacting any $(PCy_3)_2Cl_2Ru(=CHCH_2R)$ with styrene. For example, $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) (0.520g, 0.74 mmol), 2-pentyne (68.5 μL, 0.74mmol), and HCl (0.74mL of 1M solution in diethylether) are combined as described above, and allowed to react for twenty minutes. Styrene (0.85 mL, 7.4 mmol) is added, and the reaction allowed to stir for another ten minutes. The solvent is removed, and methanol added to precipitate. Isolate 0.39 g, 64%.

$(PCy_3)_2Cl_2Ru(=CHCH_2CH(CH_3)_2)$ (28)

Method A: To a solution of $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) (0.325 g, 0.46 mmol), 3-methyl-1-butyne (47.4 μL, 0.46 mmol) is added and allowed to stir at -30°C for ten minutes. HCl (0.464 mL of 1M solution, 0.46 mmol) is then added and allowed to stir for an additional ten minutes. Solvents are removed, and methanol is added to give a purple solid. The solid is filtered and washed with methanol until the washings are colorless. Isolate 0.152 g, 41%.

Method B: To a solution of $Ru(H)(H_2)_2Cl(PCy_3)_2$ (**1**) (0.020 g, 0.029 mmol) in 0.5 mL of CD_2Cl_2 was added 3-methyl-1-butyne (3.6 μL, 0.029 mmol). After ten minutes HCl (28 μL, 1M solution, 0.029 mmol) is added, and after ten more minutes the NMR is taken. Observed are the appropriate carbene and the Ru(IV) species, in a ratio of 3:1.

Selected NMR data: (CD_2Cl_2) ^1H: 20.01 (t, RuC*H*, J=4 Hz), 2.35 (br. s, RuCHC*H*$_2$, 2H); ^{31}P: 33.63 (s, Ru*P*Cy$_3$).

($PCy_3)_2Cl_2Ru(=CHCH_2C(CH_3)_3)$ (29)

Method A: To a solution of $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) (0.325 g, 0.46 mmol), *t*-butylacetylene (57.2 μL, 0.46 mmol) is added and allowed to stir at -30°C for ten minutes. HCl (0.464 mL of 1M solution, 0.46 mmol) is then added and allowed to stir for an additional ten minutes. Solvents are removed, and methanol is added to give a purple solid. The solid is filtered and washed with methanol until the washings are colorless. Isolate 0.135g, 36%.

Method B: To a solution of $Ru(H)(H_2)_2Cl(PCy_3)_2$ (**1**) (0.020 g, 0.029 mmol) in 0.5 mL of CD_2Cl_2 is added *t*-butylacetylene (3.5 μL, 0.029 mmol). After ten minutes HCl (28 μL, 1M solution, 0.029 mmol) is added, after ten more minutes the NMR is taken. Observed was the appropriate carbene and the Ru(IV) species, in a ratio of 3.6:1.

Selected NMR data: (CD_2Cl_2): ^1H: 20.02 (t, RuCH, J=4.4 Hz), 2.34 (br. s, $RuCHCH_2$, 2H), 1.03 (s, $RuCHCH_2C(CH_3)_3$, 9H); ^{31}P: 33.58 (s, $RuPCy_3$).

($PCy_3)_2Cl_2Ru(=C(CH_3)$-$CH_2CH_2CH_3)$ (30) $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) (0.250 g, 0.36 mmol), 2-pentyne (68.5 μL, 0.72 mmol), and HCl (0.35 mL of 1M solution in diethylether) are combined as described above. Isolated 0.15 g, 53%. This carbene can be reacted directly with styrene (excess) to give the more easily identifiable $(PCy_3)_2Cl_2Ru(=CHPh)$ (**J**). Selected NMR data (CD_2Cl_2): ^{31}P: 46.67 (s, $RuPCy_3$). (no distinguishing ^1H NMR).

Vinylidenes:

$(PCy_3)_2Cl(H)Ru(=C=CHPh)$ (31) To a solution of $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) (0.020 g, 0.028 mmol) in C_6D_6 (0.5 mL) phenylacetlyene (6.27 μL, 0.057 mmol) is added. NMR shows the presence of what is assigned to be $(PCy_3)_2Cl(H)Ru(=C=CHPh)$ based on spectroscopic information, mainly the vinylidene peak at 4.42 and the hydride at -12.8 of equal integration. This identification was later confirmed in the literature.[84] Selected NMR data: (C_6D_6): ^1H: 4.42 (br, Ru=C=C*H*Ph), -12.88 (t, Ru-H, J=17.6); ^{31}P: 41.73 (s, Ru*P*Cy_3).

$(PCy_3)_2Cl_2Ru(=C=CHPh)$ (32) [(p-cymene)$RuCl_2]_2$ (2.5 g, 8.16 mmol Ru) and tricyclohexylphosphine (4.6 g, 16.33 mmol) are placed in a Fisher Porter bottle as with **7** or in a suitably sized thick walled Schlenk flask (with lots of headspace). Benzene (60 mL) and phenylacetlyene (0.90 mL, 8.16 mmol) are added. The headspace is evacuated, and the reaction heated at 90°C for 18 hours. When the reaction is allowed to cool, a purple-white solid precipitates, filtered, and washed with pentane (3x5 mL). Isolate 6.6 g, 97%.

This reaction can also be done starting with [(benzene)$RuCl_2]_2$ (0.500 g, 2.0 mmol Ru), tricyclohexylphosphine (1.12 g, 4.0 mmol), and phenylacetylene (0.22 mL, 2.0 mmol) to give 1.59 g, 95%.

Selected NMR data: (CD_2Cl_2): ^1H: 7.10 (dd, Ph-H_m, J=8.04, 7.32 Hz, 2H), 6.88 (d, Ph-H_o, J=8.04 Hz, 2H), 6.82 (t, Ph-H_p, J=7.32 Hz, 1H), 4.35 (t, Ru=C=C*H*Ph, J=3.7 Hz) 2.61-1.99 (P*Cy*$_3$, 66H); ^{31}P: 22.41 (s, Ru*P*Cy_3).

$(PCy_3)_2Cl_2Ru(=C=CH$*t*$Bu)$ (33) In a procedure identical to that for (**32**): [(p-cymene)$RuCl_2]_2$ (1 g, 3.28 mmol Ru) and tricyclohexylphosphine (1.84g, 6.56 mmol) are used. Benzene (30 mL) and *t*-butylacetlyene (0.269 mL, 3.28 mmol)

are added. Isolate 2.4 g, 90%.

Selected NMR data: (C_6D_6): ^{1}H: 4.59 (t, Ru=C=C*H*tBu, J=3.7 Hz); ^{31}P: 17.4 (s, Ru*P*Cy$_3$).

($PCy_3)_2Cl_2Ru(=C=CHC_4H_9)$ (34) [(p-cymene)$RuCl_2]_2$ (0.500 g, 1.63 mmol Ru), and tricyclohexylphosphine (0.915 g, 3.27 mmol) are placed in a Fisher Porter bottle as with **7** or in a suitably sized thick walled Schlenk flask (with lots of headspace). Benzene (30 mL) and 1-hexyne (0.0.375 mL, 1.63 mmol) are added, and the headspace is evacuated. The reaction is stirred at 90°C for 18 hours, and after cooling only a small amount of solid has precipitated. The solvent is removed, and methanol is added to give an orange-pink solid, which is filtered and washed with methanol until the washings are colorless. Isolate 1.25 g, 94%.

Selected NMR data: (C_6D_6): ^{1}H: 3.42 (t, Ru=C=C*H*, J=7.3 Hz), 2.58 (m, RuPC*H*$(CH_2)_5$, 6H), 2.35 (q, Ru=C=CH(C*H*$_2$), J=6.6 Hz, 2H), 2.04, 1.78, 1.59, 1.24 (all Ru(PCH(C*H*$_2)_5$), 60H total), 1.63 (br s, Ru=C=CH(CH_2)(C*H*$_2)_2(CH_3)$, 4H), 0.858 (t, Ru=C=CH$(CH_2)_3$(C*H*$_3$), J=7.32 Hz, 3H) ; ^{31}P: 25.84 (s, Ru*P*Cy$_3$).

cis-($PPh_3)_2Cl_2Ru(=CH-CH=CMe_2)$ (35) To a solution of $(PPh_3)_3$RuHCl (0.020 g, 0.02 mmol) in 0.5 mL of CD_2Cl_2 at 0°C is added 2-methyl-1-butene-3-yne (1.9 μL, 0.020 mmol). After ten minutes, HCl (20 μL, 1M solution, 0.020 mmol) is added. The reaction is kept at 0°C for another fifteen minutes, after which the NMR is taken. Observed in small yield in the NMR is a signal assigned to cis-$(PPh_3)_2Cl_2Ru(=CH-CH=CMe_2)$ at 15.75 (m, RuC*H*), with a corresponding ^{31}P peak at 28.46.

$(PPh_3)_2Cl_2Ru(=CHCH_2Ph)$ (36) To a solution of $(PPh_3)_3RuHCl$ (0.020 g, 0.02 mmol) in 0.5 mL of CD_2Cl_2 at 0°C is added phenylacetylene (2.2 μL, 0.020 mmol). After ten minutes, HCl (20 μL, 1M solution, 0.020 mmol) is added. The reaction is kept at 0°C for another fifteen minutes, after which the NMR is taken. Observed in small yield in the NMR is a signal assigned to $(PPh_3)_2Cl_2Ru(=CHCH_2Ph)$ at 16.41 (m, RuCH), with a corresponding ^{31}P peak at 27.64.

$(PPh_3)_2Cl_2Ru(=CHCH_2C(CH_3)_3)$ (37) To a solution of $(PPh_3)_3RuHCl$ (0.020 g, 0.02 mmol) in 0.5mL of CD_2Cl_2 at 0°C is added *t*-butylacetylene (2.4 μL, 0.020 mmol). After ten minutes, HCl (20 μL, 1M solution, 0.020 mmol) is added. The reaction is kept at 0°C for another fifteen minutes, after which the NMR is taken. Observed in small yield in the NMR is a signal assigned to $(PPh_3)_2Cl_2Ru(=CHCH_2(t\text{-}Bu))$ at 18.65 (tt, RuC*H*, J_{HH}=5.12 Hz, J_{HP}=10.3 Hz), with a corresponding ^{31}P peak at 29.49.

Reactions with $Ru(H)_2Cl_2(PCy_3)_2$

(a)To as solution of $Ru(H)_2Cl_2(PCy_3)_2$ (0.01 g, 0.014 mmol) in 0.5 mL C_6D_6 is added 2-methyl-1-butene-3-yne (1.3 μL, 0.014 mmol). Only two phosphorous containing products are seen in the NMR, identified as $(PCy_3)_2Cl_2Ru(=CH\text{-}CH=CMe_2)$ (**7**) and $(PCy_3)_2Cl_2Ru(=C=CH\text{-}C(=CH_2)CH_3)$, in an approximate ratio of 1:3. Selected NMR data for vinylidene **38** (C_6D_6) ^1H: 4.29 (br s, RuC=C*H*); ^{31}P: 21.7 (s, Ru*P*Cy_3).

(b)To a solution of $Ru(H)_2Cl_2(PCy_3)_2$ (0.015 g, 0.021 mmol) in 0.5 mL C_6D_6 is added 1-hexyne (2.1 μL, 0.021 mmol). After ten minutes only two phosphorous containing products are seen in the NMR, identified as $(PCy_3)_2Cl_2Ru(=CH(CH_2)_4CH_3)$ (**39**) and $(PCy_3)_2Cl_2Ru(=C=CH\text{-}(CH_2)_3CH_3)$ (**40**),

in an approximate ratio of 1:8.

Selected NMR data for carbene **39** (C_6D_6) ^{1}H: 19.79 (t, RuC*H*, J=5.1 Hz); ^{31}P: 36.5 (s, Ru*P*Cy$_3$)

Selected NMR data for vinylidene **40** (C_6D_6) ^{1}H: 4.27 (br s, RuC=C*H*); ^{31}P: 23.8 (s, Ru*P*Cy$_3$)

Attempts at making Ru-F carbenes:

"trans-(P^iPr_3)$_2$-cis-ClF(CO)Ru(=CH-CH=CMe$_2$)" To a solution of Ru(H)(CO)Cl(P^iPr_3)$_2$ (40 mg, 0.08 mmol) in benzene (5 mL), 3-chloro-3-methyl-1-butyne (9 μL, 0.08 mmol) is added. The reaction is allowed to stir for 15 minutes, after which the solvent is removed and methanol (5 mL) is added along with of CsF (240 mg, approximately 20 equivalents). This is allowed to stir for 3 hours, after which it is filtered, the solvent removed, and solid isolated. No carbenes were detected by NMR of the isolated solid, or by doing the same sequence all in CD_2Cl_2 on an NMR scale in a J-Young tube."

Ru(H)(CO)F(P^iPr_3)$_2$" To a solution of Ru(H)(CO)Cl(P^iPr_3)$_2$ (250 mg, 0.51 mmol) in degassed dry acetone CsF (1g, excess) is added, and the mixture allowed to stir for 12 hours. The solvent is removed, and the residue extracted with pentane, which was then removed to give a yellow solid. ^{1}H and ^{31}P NMR showed no change from the starting materials, no F incorporation.

"Ru(H)(H$_2$)F(PCy$_3$)$_2$"

Method A: A mixture of Ru(H)(H$_2$)Cl(PCy$_3$)$_2$ (**1**) (0.1 g, 0.14 mmol) and CsF (500 mg, excess) is placed under degassed acetone for 3 hours, after which either the solvent is removed and the residue extracted with benzene to give an orange solid (identified as only **1**) or 3-chloro-3-methyl-1-butyne is added, giv-

ing only a purple solid identified as **7**.

Method B: To a solution of $Ru(H)_2(H_2)_2(PCy_3)_2$ (0.500 g, 0.749 mmol) at -78°C is added NaF (32 mg, 0.76 mmol) and HBF_4 (103 μL of ether solution equal to 122 mg of acid, 0.749 mmol). Alternatively, HF (40.5 μL, 0.749 mmol, of 48 wt% solution in water) is added directly. After approximately 20 minutes the reaction is warmed to room temperature, and allowed to stir for another 20 minutes. A white-yellow solid is obtained, 0.35-0.42 g. Reactions of this solid with 3-chloro-3-methyl-1-butyne show only a carbene identified as **7**, and it was therefore concluded that the fluorinated hydride had not been generated.

"**$(PCy_3)_2Cl_2Ru(=CH\text{-}CH=CF_2)$**" To a solution of $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) (0.020 g, 0.029 mmol) connected to a Schlenk line or sealed with a rubber septa, "some" $HCCCF_3$ is condensed with liquid nitrogen directly into the sample or into a Schlenk flask and added via a cold needle, respectively. No carbene is observed by NMR.

Carbonyl Complexes:

$Ru(H)(CO)Cl(PCy_3)_2$ (**42a**) Following the preparation of $Ru(H)(CO)Cl(P^iPr_3)_2$,[71] $RuCl_3$-hydrate (1.0 g, 4.8 mmol) and tricyclohexylphosphine (6.22 g, 22.2 mmol) are dissolved in dry, degassed methanol (100 mL) and heated to reflux overnight, filtered and washed with pentane. Isolate 3.10 g of an orange-yellow solid, 88.6%.

Selected NMR data (CD_2Cl_2): ^1H: -24.74 (t, Ru*H*, J=18.3 Hz), 2.5-1.2 (RuP*Cy*$_3$, 66H total); ^{31}P: 46.62 (s, Ru*P*Cy_3). IR (cm^{-1}): (nujol) ν-CO: 1904, ν-MH: 2057.

$Os(H)(CO)Cl(PCy_3)_2$ (42b) Following the preparation of $Os(H)(CO)Cl(PiPr_3)_2$,[71] $OsCl_3$-hydrate (1.0 g, 3.37 mmol) and tricyclohexylphosphine (4.35 g, 15.5 mmol) are dissolved in dry, degassed methanol (100 mL) and heated to reflux overnight, filtered and washed with pentane. Isolate 2.15 g of an orange-yellow solid, 78.2%.

Selected NMR data (CD_2Cl_2): ^1H: -33 (br s, OsH), 2.8-1.0 ($OsPCy_3$, 66H total); ^{31}P: 37.1 (s, $OsPCy_3$). IR (cm^{-1}): (nujol) ν-CO: 1945, ν-MH: not observed.

All trans-$(PR_3)_2$-cis-$Cl_2(CO)M(=CH-CH=CMe_2)$ compounds were investigated by IR, by taking the solid isolated below and making a nujol mull on solid NaCl plates. In addition, solutions of the hydrides $M(H)(CO)Cl(PR_3)_2$ were made in methylene chloride, and in the drybox placed in solution IR cells, sealing the openings with NMR size septa. After obtaining a spectra of the hydrides, 3-chloro-3-methyl-1-butyne is added via syringe, and the reactions monitored. In all cases only starting materials and products were observed.

All of the compounds $M(H)(CO)_2Cl(PR_3)_2$ (M=Ru, Os; R=Cy, ^iPr) failed to react at all with 3-chloro-3-methyl-1-butyne.

trans-$(PiPr_3)_2$-cis-$Cl_2(CO)Ru(=CH-CH=CMe_2)$ (43a) To a solution of $Ru(H)(CO)Cl(PiPr_3)_2$ (415 mg, 0.85 mmol) in methylene chloride (10mL), 3-chloro-3-methyl-1-butyne (95.9 μL, 0.85 mmol) is added. The reaction is allowed to stir for 15 minutes, after which the solvent is removed and a puffy oil remains. Pentane is added to precipitate an orange solid, which is then filtered and washed with pentane until the washings are colorless. Isolated 0.486 mg, 97%.

Selected NMR data: (CD_2Cl_2): ^1H: 17.26 (d, RuC*H*, J=13.9 Hz), 8.00 (d, RuCHC*H*, J=13.9 Hz), 2.85 (m, $RuPCH(CH_3)_2$, 6H), 1.45 (m, J=6.6 Hz,

RuPCH(CH_3)$_2$, 36H), 1.30 and 1.04 (s (each), RuCHCHCMe_2, 6H total); ^{31}P: 40.30 (s, RuP^iPr$_3$). IR (cm^{-1}): ν-CO: (nujol) 1935.9; (CH_2Cl_2) 1950. These data are extremely similar to those for similar compounds *trans*-(P^iPr$_3$)$_2$-*cis*-Cl$_2$(CO)Ru(=CH-CH=CPh$_2$) and *trans*-(PiPr$_3$)$_2$-*cis*-Cl$_2$(CO)Ru(=CH-CH=CHPh), which were previously reported.[65]

trans-(PiPr$_3$)$_2$-cis-Cl$_2$(CO)Os(=CH-CH=CMe$_2$) (**43b**) To a solution of Os(H)(CO)Cl(PiPr$_3$)$_2$ (415 mg, 0.56 mmol) in methylene chloride (10 mL), 3-chloro-3-methyl-1-butyne (63.1 μL, 0.56 mmol) is added. The reaction is allowed to stir for 15 minutes, after which the solvent is removed and a puffy oil remains. Pentane is added to precipitate an orange-red solid, which is then filtered and washed with pentane until the washings are colorless. Isolated 0.347 mg, 91%.

Selected NMR data: (CD_2Cl_2): ^{1}H: 18.2 (d, OsC*H*, J=13.8 Hz), 7.7 (d, OsCHC*H*, J=13.8 Hz), 2.87 (m, OsPC*H*(CH_3)$_2$, 6H), 1.43 (q, J=7.32 Hz, OsPCH(CH_3)$_2$, 36H), 1.11 and 0.81 (s (each), OsCHCHCMe_2, 6H total); ^{31}P: 12.9 (s, OsP^iPr$_3$). IR (cm^{-1}): ν-CO: (nujol): 1925; (CH_2Cl_2): 1927. These spectral data match exactly the previous preparations of this compound.[64]

trans-(PCy$_3$)$_2$-cis-Cl$_2$(CO)Ru(=CH-CH=CMe$_2$) (**44a**) To a solution of Ru(H)(CO)Cl(PCy$_3$)$_2$ (0.300 g, 0.42 mmol) in methylene chloride (10 mL), 3-chloro-3-methyl-1-butyne (46.7 μL, 0.42 mmol) is added. The reaction is allowed to stir for 15 minutes, after which the solvent is removed. Pentane is added to precipitate a brown solid, which is then filtered and washed with pentane until the washings are colorless. Isolated 0.335 g, 97% of a mixture of this compound and **7**, in an approximate ratio of 1:2.

Selected NMR data: (CD_2Cl_2): ^{1}H: 17.35 (d, RuCH, J=14.3 Hz), 8.08 (d,

RuCHCH, J=14.3 Hz); ^{31}P: 47.45 (s, RuPCy_3). IR (cm^{-1}): ν-CO: (nujol) 1936; (CH_2Cl_2) 1930.

trans-$(PCy_3)_2$-cis-Cl_2(CO)Os(=CH-CH=CMe_2) (**44b**) To a solution of Os(H)(CO)Cl$(PCy_3)_2$ (0.300 g, 0.37 mmol) in methylene chloride (10 mL), 3-chloro-3-methyl-1-butyne (41.7 μL, 0.37 mmol) is added. The reaction is allowed to stir for 15 minutes, after which the solvent is removed. Pentane is added to precipitate a brown-yellow solid, which is then filtered and washed with pentane until the washings are colorless. Isolated 0.320 g, 94% of slightly impure (**44b**).

Selected NMR data: (CD_2Cl_2): ^{1}H: 18.20 (d, OsC*H*, J=13.9 Hz), 7.76 (d, OsCHC*H*, J=13.9 Hz); ^{31}P: 2.54 (s, Os*P*Cy_3). IR (cm^{-1}): ν-CO: (nujol) 1921; (CH_2Cl_2) 1923.

Ru(H)$(CO)_2$Cl$(PCy_3)_2$ (**46a**) Following the procedure used for Ru(H)$(CO)_2$Cl$(P^iPr_3)_2$,[71] of Ru(H)(CO)Cl$(PCy_3)_2$ (1.0 g) is suspended in 50 mL of methylene chloride, and CO is bubbled through the solution for 5 minutes. The solvent is removed, and a white powder is obtained: 1.01 g, 97% (assumed to be stoichiometric, but all solid could not be removed from the flask).

Selected NMR data: (C_6D_6): ^{1}H: -4.98 (t, Ru*H*, J=19.8 Hz); ^{31}P: 51.5 (s, Ru*P*Cy_3).

Os(H)$(CO)_2$Cl$(PCy_3)_2$ (**46b**) A procedure identical to that for (**46a**) is used, starting with Os(H)(CO)Cl$(PCy_3)_2$, and isolating 0.350g, 85%.

Selected NMR data: (C_6D_6): ^{1}H: -4.38 (t, Os*H*, J=20.5 Hz); ^{31}P: 21.02 (s, Ru*P*Cy_3).

$Os(H)_3Cl(PCy_3)_2$ (**47**) $OsCl_3$*hydrate (0.500 g, 1.69 mmol) and tricyclohexylphosphine (2.5 g, 8.91 mmol) are combined in a Fisher-Porter bottle and isopropanol (50 mL) is added. Triethylamine can be used (0.234 mL, 1.69 mmol) to reduce the amount of tricyclohexylphosphine (0.945 g, 3.38 mmol) to two equivalents with no change in yield. The reaction is heated to 80^0C for 6 hours, and then cooled to room temperature, then 0^oC for 1 hour. The brown-yellow solid which precipitates is filtered, and washed with methanol until the washings are colorless. Isolate 0.913 g, 69%.

$Os(H)_3Cl(PCy_3)_2$ failed to give carbenes with 1-chloro-1-propene, 1-chloro-2-methyl-1-propene, or 1-pentyne and HCl, although in some cases it appeared to give some of the hydrido-alkylidyne complex, like $(P^iPr_3)_2Cl_2Os(H)(\equiv CCH_2Ph)$,[61] manifesting as a triplet in the -6 to -7ppm range.

It is of interest to note that the corresponding Os(IV) compound, $Os(H)_2Cl_2(PCy_3)_2$ could not be made following the preparation for the analogous P^iPr_3 compound. $Os(H)_3Cl(PCy_3)_2$ is always generated instead.

Selected NMR data:(CD_2Cl_2):^{1}H: -19.7 (br, Os*H*, 3H), 3.66-0.79 (OsP*Cy*$_3$, 66H); ^{31}P: 42.5 (s, Os*P*Cy_3).

$(PCy_3)_2Cl_2Os(=CH\text{-}CH=CMe_2)$ (**48**)

Method A: To a solution of $Os(H)_3Cl(PCy_3)_2$ (255 mg, 0.32 mmol) in methylene chloride (10 mL) cooled to -78^oC, 3-chloro-3-methyl-1-butyne (36 μL, 0.32 mmol) is added. After 15 minutes at low temperature, the cold bath is removed and the reaction is allowed to stir for an additional 15 minutes at room temperature. The solvent is removed, and a red-purple solid is observed on the walls of the flask. Methanol is added to precipitate solid, and 0.27 g of a pink solid is isolated. The NMR of this solid shows the carbene along with what has been identified as an osmium-hydrido-alkylidyne, $(PCy_3)_2Cl_2Os(H)(\equiv C$-

$CH{=}CMe_2$) (**49**), by comparison to data from the previously described for $(P^iPr_3)_2Cl_2Os(H)(\equiv CCH_2Ph)$.[61]

Method B: In an NMR tube, $Os(H)_3Cl(PCy_3)_2$ (0.020 g, 0.025 mmol) is dissolved in CD_2Cl_2 (0.5 mL) and, 3-chloro-3-methyl-1-butyne (2.9 μL, 0.025 mmol) is added. Identified in the spectra are the carbene and the hydrido-alkylidyne.

Selected NMR data Carbene: (CD_2Cl_2):^{1}H: 17.23 (d, OsC*H*, J=12.4 Hz), 7.04 (d, OsCHC*H*, J=12.4 Hz); ^{31}P: 9.13 (s, Os*P*Cy_3). (C_6D_6) ^{1}H: 17.92 (d, OsC*H*, J=12.4 Hz), 7.17 (d, OsCHC*H*, J=12.4 Hz), 1.03 and 0.73 (each 3H, OsCHCHC(CH_3)$_2$); ^{31}P: 8.62 (s, Os*P*Cy_3).

Hydride: (CD_2Cl_2):^{1}H: -7.18 (t, OsH, J=16.8 Hz).

$Os(H)_6(PCy_3)_2$ (**50**) Following the preparation of $Os(H)_6(P^iPr_3)_2$,[101] $Os(H)_3Cl(PCy_3)_2$ (0.200 g, 0.25 mmol) is dissolved in benzene (15 mL) and $NaBH_4$ (100mg, excess) is added piecewise over five minutes. After stirring for ten minutes, 1mL of methanol is added dropwise, at which point the solution changes to a light yellow color. This is stirred for ten minutes, then the solution is filtered away from the sodium salts, and the solvent removed. Isolate 0.170g, 88% of a white solid.

$Os(H)_6(PCy_3)_2$ showed no reaction with excess styrene, α,α-dichlorotoluene, or 3-chloro-3-methyl-1-butyne.

Selected NMR data (CD_2Cl_2) ^{1}H: -9.56 (t, Os*H*, J=9.5 Hz, 6H), 2.2-1.1 (P*Cy*$_3$, 66H); ^{31}P: 45.8 (s, Os*P*Cy_3).

Decomposition of carbenes under hydrogen:

Method A: Two NMR solutions are made with $(PCy_3)_2Cl_2Ru(=CHPh)$ (0.030 g, 0.036 mmol) in 0.5 mL of CD_2Cl_2, one in a J-Young tube, the other in

sealed with a septum. The J-Young tube is connected to the Schlenk line, and filled with 1 atm of H_2, after degassing by the freeze-pump-thaw method. H_2 is bubbled through the septum sealed tube with a needle for approximately 30 seconds. The J-Young tube is heated at 50°C for one hour, while the septum sealed tube is left at room temperature. After one hour, both show the presence of toluene. In addition, Ru(IV), $Ru(H)(H_2)Cl(PCy_3)_2$ and the starting carbene in approximately 1:1:8 ratio.

Method B: A solution of $(PCy_3)_2Cl_2Ru(=CH\text{-}CH=CMe_2)$ (1.0g, 1.43mmol) and tricyclohexylphosphine (0.350 g, 1.43 mmol) is made in a Fischer-Porter bottle with 20 mL of sec-butanol with 10 mL methylene chloride. The reaction is stirred at 55°C for 18 hours, after which an aliquot is removed. The ^{31}P of the aliquot shows (given slight differences for the presence of the alcohol) what is assigned to be Ru(IV), $Ru(H)(H_2)Cl(PCy_3)_2$ and the starting carbene in approximately 2:1:5 ratio. The solvent volume is reduced by approximately 10 mL, and 50 mL of methanol is added. The resulting solid is filtered and washed with methanol until the washings are colorless, to give 0.85 g of red-orange solid which is 18% $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**), and 82% $(PCy_3)_2Cl_2Ru(=CH\text{-}CH=CMe_2)$ (**7**).

Generation of "SAL" systems:

$[(2,6\text{-diisopropyl})\text{-}C_6H_3\text{-}N=CH\text{-}(4\text{-}NO_2\text{-}C_6H_3\text{-}2\text{-}O)](PCy_3)ClRu(=CH\text{-}CH=CMe_2)$

Following the literature preparation,[58] $[(2,6\text{-diisopropyl})\text{-}C_6H_3\text{-}N=CH\text{-}(4\text{-}NO_2\text{-}C_6H_3\text{-}2\text{-}O)](PCy_3)ClRu(=CH\text{-}CH=CMe_2)$ is made from the thallium salt of the ligand, which is made from 5-nitrosalicylaldehyde and 2,6-diisopropylaniline. $(PCy_3)_2Cl_2Ru(=CH\text{-}CH=CMe_2)$ (**7**) (12.11 g, 15.1 mmol) and Tl(O-"SAL") (8.41 g, 15.9 mmol) are combined in THF (200 mL) and stirred at room temperature for two hours. THF is removed, and the residue extracted with a minimum

amount of benzene, which is then filtered through celite. The benzene is removed, and pentane added, and cooled to -78°C for 20 hours, and filtered at -78°C to give 12.26 g, 97.5% of the carbene.

Selected NMR data: (CD_2Cl_2): ^1H: 19.28 (dd, RuC*H*, J_{hh}=10.9, J_{HP}=2.9 Hz), 8.19 (d, RuCHC*H*, J=10.9 Hz). ^{31}P: 50.43 (s, Ru*P*Cy_3).

Concentration study:

In two separate NMR tubes, $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) and propargyl chloride are combined in C_6D_5Cl. Tube A is set to be 0.119M (0.05g **1**, 0.6mL C_6D_5Cl, and 5.16 μL propargyl chloride), while tube B is 0.0048M (0.005g **1**, 1.5 mL C_6D_5Cl, 0.52 μL propargyl chloride), both with TMS_2O and PPh_3 as internal standards. Sample spectra were taken before the propargyl chloride is added, and directly after (approximately five minutes), comparing the ratio of carbene $(PCy_3)_2Cl_2Ru(=CH\text{-}CH=CH_2)$ generated to $Ru(H)_2Cl_2(PCy_3)_2$ generated. For tube A the resulting ratio of carbenes to Ru(IV) is 1.11:1, while for tube B the ratio is 1.73:1. It was concluded from this relatively small change in product ratio over such a large change in concentration that the carbene forming reaction is unlikely to be bimolecular.

Reactions with carbenes and carbon monoxide:

Such reactions were attempted in several ways. In all cases the only identifiable compound in the NMR tube was the starting material.

(a) 100 mg of **7** was placed in an NMR tube and 1.5mL of CD_2Cl_2 was added. Outside the box, the septum was removed and CO was blown across the mouth of the tube, which was quickly sealed again with the septum.

(b) 400 mg of **7** is dissolved in methylene chloride (60 mL) and CO is bubbled through, instantly giving a white solid. The solvent is removed, and

the solid isolated. No carbenes or hydrides are observed.

(c) 400 mg of **7** is dissolved in 1.5 mL of CD_2Cl_2, and sealed with a septum. Through the Schlenk line, a large Schlenk flask sealed with a septum was filled with CO, following normal purge-backfill procedures. With a 50 μL gastight syringe, portions of this atmosphere were added to the NMR tube. Although the CO clearly started to disperse into the atmosphere the instant the syringe was removed from the septum, the goal was to attempt to add a small amount of CO at a time, which was surely accomplished using this method.

Typical RCM Experiment:

Solutions are made such that the total concentrations would be 0.2M diethyldiallylmalonate and 0.01M catalyst with a ratio of 20 to 1 monomer:catalyst. Reactions over time are monitored as to degree of completion using the methylene protons on the diallylmalonate (doublet at 2.6ppm) and the corresponding methylene protons on the closed cyclopentene ring (broad singlet at 3ppm). In addition, the propagating carbene species, the methylidene, has a characteristically different shift than the corresponding vinyl carbene α-proton. The vinyl carbene is a doublet (except with triphenylphosphine a quartet is observed), while the methylidene is a singlet (or a doublet for triphenylphosphine systems).

Kinetic studies:

Run 1:Solutions of catalysts $(PCy_3)_2Cl_2Ru(=CH\text{-}CH=CMe_2)$ (**7**), $(P^iPr_3)_2Cl_2Ru(=CH\text{-}CH=CMe_2)$ (**8**), and $(PPh_3)_2Cl_2Ru(=CH\text{-}CH=CMe_2)$ (**6**) are made to follow the typical RCM experiment described above. Diethyldiallylmalonate is added, and kinetics show that over 45 minutes **6** shows no activity distinguishable from the baseline, while with **8** the reaction is 40.8%

done after 4 minutes, 78.9% complete at 20 minutes, 86.7% complete at 35 minutes, and 89.8% complete after 46 minutes; 18.14 turnovers per hour. With catalyst **7** the reaction is 43.5% complete at 5 minutes, 78.9% complete at 20 minutes, 86.7% complete at 35 minutes, and 89.8% complete after 46 minutes, giving 19.2 turnovers per hour. The methylidene is observed with **7**, as well as with **8**, but in neither case is complete initiation observed.

Run 2: A stock solution of $Ru(H)(CO)Cl(P^iPr_3)_2$ (**41a**) is made by dissolving 200 mg in 2.00 mL of CD_2Cl_2, and using 0.400 mL of this stock solution for each sample (equivalent to 40mg). To this P^iPr_3, (16 μL, 8 μL, or 4 μL; 1, 0.5, and 0.25 eq. respectively) is added, and the sample then diluted to a total volume of 0.900mL, to give a total concentration of $Ru(H)(CO)Cl(P^iPr_3)_2$ of 0.0914M. To each sample 9.3 μL of 3-chloro-3-methyl-1-butyne (1 equivalent) is added at t=0. Integration is done of the appearance of the carbene, disappearance of the hydride, and the $P(CH)(CH_3)_2$ total area (both starting materials and products), and standardized to the total integration of the iso-propyl hydrogens. These reactions were done twice, with virtually identical data: Graphing this data is largely unproductive in terms of useful information, as plots of [carbene], -ln[carbene], or 1/[carbene] versus time gave curves, not straight lines. However, graphing -ln[carbene] or 1/[carbene] versus 1/time gave straight lines, from which half lives can be extracted (180s, 189s, and 536s for 0.25, 0.5, and 1.0eq of phosphine). No kinetic profile consistent with this data has been found.

Run 3: A stock solution of $Ru(H)(CO)Cl(P^iPr_3)_2$ (**41a**) is made by dissolving 100 mg in 1.00 mL of CD_2Cl_2, and using 0.400 mL of this stock solution for each sample (equivalent to 40mg). To this P^iPr_3, (16 μL, 8 μL, or 4 μL; 1, 0.5, and 0.25 eq. respectively) is added, and the sample then diluted to a total volume of

0.900mL, to give a total concentration of $Ru(H)(CO)Cl(P^iPr_3)_2$ of 0.0914M. At the NMR 3-hydroxy-3-methyl-1-butyne is added, and integration is done of the appearance of the metal vinyl protons (M-CH=CH), disappearance of hydride, and the $P(CH)(CH_3)_2$ total area (both starting materials and products), and standardized to the total integration of the iso-propyl hydrogens. These reactions were done twice, with virtually identical data. As with Run 2, no linear plots can be made unless 1/time is plotted. Estimated half lives of 95 to 98 seconds were observed, all equivalent within experimental error.

Run 4: A stock solution of $Ru(H)(H_2)Cl(PCy_3)_2$ (**1**) is made by dissolving 200 mg of **1** in 2.00 mL of CD_2Cl_2, using 0.200 mL of this stock solution was used for each sample. Two stock solutions of tricyclohexylphosphine were made 300 mg in 0.3 mL (160 μL, 80 μL, and 40 μL; to give 160 mg, 80 mg, 40 mg; 20, 10, and 5 equivalents) and 50 mg in 1 mL of CD_2Cl_2 (16 μL, 8 μL, and 4 μL; to give 8 mg, 4 mg, 2 mg; 1, 0.5, and 0.25 equivalents) of were added. All solutions were then diluted to a 0.500 mL total volume, giving a $[Ru(H)(H_2)Cl(P^iPr_3)_2]$= 0.057M. To each solution, 3.2 μL of 3-chloro-3-methyl-1-butyne is added. It was intended to examine the appearance of carbene versus disappearance of hydrides, but all reactions were instantaneous at room temperature. A series of reactions was also tried at -30°C, using samples with 10 equivalents of tricyclohexylphosphine. The sample was frozen, and 3-chloro-3-methyl-1-butyne was frozen on the side of the NMR tube at the top. The sample was quickly placed in a pre-cooled NMR probe, but only starting materials and products are observed. Kinetics were not done at -30°C because **1** is not completely soluble at that temperature.

Run 5: A stock solution of $Ru(H)(CO)Cl(P^iPr_3)_2$ (**41a**) is made by dissolving 100 mg in 1.00 mL of CD_2Cl_2, and using 0.300 mL of this stock solution for each

sample (equivalent to 30mg), which is eventually diluted to 0.7 mL. To tube A tricyclohexylphosphine (18 mg, 1 equivalent) is added and the solution diluted. To tube B, tricyclohexylphosphine (18 mg, 1 equivalent) is added and diluted and very quickly 3-hydroxy-3-methyl-1-butyne (6.3 μL, 1 equivalent) is added. To tube C (at 0.7 mL), 3-hydroxy-3-methyl-1-butyne (6.3 μL, 1 equivalent) is added and allowed to react for thirty minutes before adding tricyclohexylphosphine (18 mg, 1 equivalent). All reactions were monitored for phosphine exchange after 30 minutes, and tube A after 1 hour. The mixed phosphine species present an AB quartet, and free isopropyl phosphine is observed in all cases.

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Investigations of Group VI Metathesis Catalysts: Tungsten and Molybdenum Oxo-Alkylidenes

Abstract:

Complexes of the type $M(O)Cl_2(PR_3)_3$ (M=W, Mo; R_3=$PMePh_2$, PMe_2Ph) were synthesized using literature procedures, and shown to react with 3,3-diphenylcyclopropene to give the η^2-olefin complexes $M(O)Cl_2(PR_3)_2(\eta^2$-diphenylcyclopropene). Spectroscopic data suggest a distorted octahedral structure for both, with the oxo ligand in the axial position with the olefin *cis* to it and the two mutually *trans* phosphines in the equatorial plane, which was confirmed for M=W with an x-ray diffraction study. The olefin complexes react with suitable alkoxides to give the oxo-carbene species $M(O)(OR)_2(PR_3)(=CH-CH=CPh_2)$, the first known single component tungsten and molybdenum oxo-alkylidene metathesis catalysts, in which the phosphine is readily displaced with THF. For these complexes, spectroscopic data suggest a distorted trigonal bipyramid with the oxo, alkylidene, and one alkoxide ligand in the equatorial plane, which was confirmed for M=W by a diffraction experiment. These alkylidene species are active in olefin metathesis reactions, showing comparable activity to similar arylimido complexes previously described; polymerization data is presented for norbornene and cyclooctene. In addition, the olefin complexes were shown to be active in olefin metathesis at elevated temperatures.

List of Compounds and their abbreviations:	
1	$WCl_4(PMePh_2)_2$
2	$WCl_2(O)(PMePh_2)_3$
3	$W(O)Cl_2(PMePh_2)_2(\eta^2$-diphenylcyclopropene)
4	$W(O)(=CH\text{-}CH=CPh_2)(PMePh_2)(OR_{F6})_2$
4'	$W(O)(=CH\text{-}CH=CPh_2)(THF)(OR_{F6})_2$
5	3,3-Diphenylcyclopropene
6	$W(NPh)Cl_4$
7	$W(NPh)Cl_2(PMePh_2)_3$
8	$W(NPh)Cl_2(PMePh_2)_2(\eta^2$-diphenylcyclopropene)
9	$WCl_4(PPh_3)_2$
10a	$Mo(O)Cl_2(PMePh_2)_3$
10b	$Mo(O)Cl_2(PMe_2Ph)_3$
11a	$Mo(O)Cl_2(PMePh_2)_2(\eta^2$-diphenylcyclopropene)
11b	$Mo(O)Cl_2(PMe_2Ph)_2(\eta^2$-diphenylcyclopropene)
12	$Mo(O)(=CH\text{-}CH=CPh_2)(PMePh_2)(OR_{F6})_2$
12'	$Mo(O)(=CH\text{-}CH=CPh_2)(THF)(OR_{F6})_2$
A	$W(O)(=CH\textit{t}Bu)Cl_2(PMe_3)_2$
B	$W(=CH\textit{t}Bu)Br_2(OR_2)$
C	$M(=CH\textit{t}Bu)(NAr)(OR_2)$; M=Mo, W
D	$W(NPh)(=CH\text{-}2\text{-}OMe\text{-}C_6H_4)(OR_{F6})_2(THF)$
E	$W(=CH\text{-}CH=CPh_2)(NAr)(P(OMe)_3)(OR_{F6})_2$
F	$Ru(=CHR)Cl_2(PR_3)_2$
G	$W(NPh)(=CH\text{-}CH=CPh_2)(OR_{F6})(PMePh_2)$
H	$W(NPh)(=CHCH=CMe_2)(OR_{F6})(PMePh_2)$
	$OR_{F6}=OC(CH_3)(CF_3)_2$
	NAr=2,6-diisopropyl-C_6H_3

Introduction

The development of well-defined, alkylidene based olefin metathesis catalysts has been the focus of much research since it was shown that metal carbenes play a central role in catalyzing olefin metathesis reactions.[1] The olefin metathesis reaction is generally catalyzed by complexes of titanium,[2] tantalum,[3] tungsten,[4-8] molybdenum,[9;10] ruthenium,[11] or rhenium.[12] Metal alkylidene complexes have been found to be active in acyclic olefin metathesis,[13-16] ring-opening metathesis polymerization (ROMP),[13] acyclic diene-[17] and alkyne-[18] polymerizations, carbonyl olefinations,[19] and ring-closing metathesis (RCM).[20] The generalized metathesis pathway, first proposed by Chauvin[21] is shown in Figure 1.

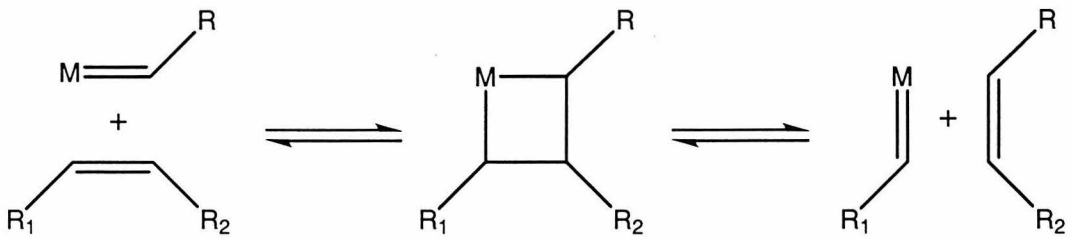


Figure 1-Generalized Metathesis Pathway

In contrast to the large number of arylimido-based metathesis catalysts, the synthesis of active, single-component tungsten- and molybdenum-oxo-alkylidenes was virtually unknown until the beginning of this study,[22] even though these types of compounds were postulated to show activity.[23] For tungsten, only a few oxo-alkylidene complexes were described in the literature,[24-27] and all required Lewis acid activation, while for molybdenum no such complexes have been previously described. Since the initial report of this study, another type of tungsten oxo-alkylidene has been presented in the literature,

based on the use of bulky arylalkoxide ligands.[28]

It has been the focus of this research to create a simple, clear synthetic method for the preparation of single component tungsten and molybdenum-oxo-based compounds. Our goal was to make active metathesis catalysts and the precursors to such catalysts, to characterize such complexes, and to investigate their reactivity. More straightforward synthetic methods were needed because tungsten and molybdenum based systems often show the highest activity, but are considered the most difficult to prepare. It is interesting to directly compare similar oxo and imido complexes, and to show that oxo complexes can be active in metathesis without Lewis Acid activation. The preparation of active molybdenum-oxo catalysts is of special interest, because molybdenum catalysts typically are more tolerant of functional groups than tungsten catalysts.[10]

The Development of Metathesis Catalysts

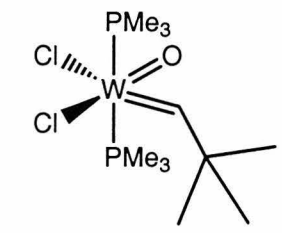
As mentioned above, the utility of well defined metathesis catalysts has been the driving force for a great deal of research. The transition from ill-defined to well-defined catalysts, concurrent with the transition from multi-component to single component catalyst systems has lead to a great deal of understanding of both the metathesis process and catalyst design. Presented below is a brief survey of metathesis catalysts and their development, with a heavy emphasis on tungsten.

Heterogeneous metathesis catalysts, also called classical or multicomponent catalysts, are easily prepared by the mixing of several simple reagents, and these systems generally show high activity. They are ill-defined and present few opportunities for detailed study. Some representative heterogeneous systems are: $Mo(NO)_2L_2Cl_2/RAlCl_2$, $WCl_6/EtOH/EtAlCl_2$, $WOCl_4/EtAlCl_2$, and

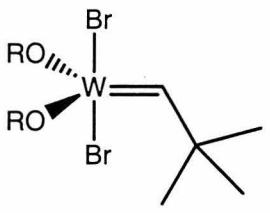
$Re_2O_7/Al_2O_3/Me_4Sn$.[14]

Homogeneous systems, on the other hand, are more difficult to prepare but more amenable to detailed study, such as: mechanistic studies, the possibility of stereochemical control, and variation of activity by modification of ligand environments. All well-defined metathesis catalyst systems have in common a metal-carbon double bond which is considered the "active" part of the molecule. By convention, the carbene moiety in these systems is considered to be either electrophilic or nucleophilic.

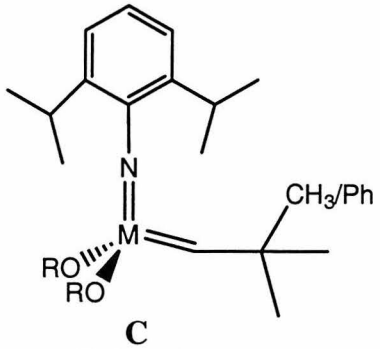
The first examples of well-defined systems belong to the former category, a group of compounds known as Fischer carbenes. While some of these complexes are active for alkyne polymerization, as well as polymerization of strained



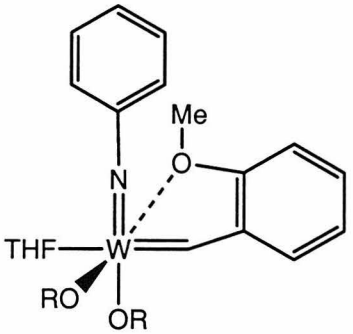
A
R.R. Schrock



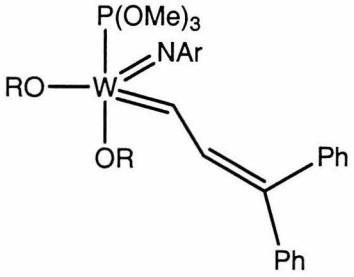
B
J.A. Osborn



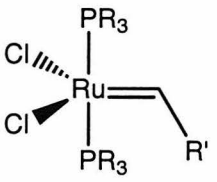
C
R.R. Schrock
M=Mo, W
OR=$OC(CH_3)_x(CF_3)_{3-x}$, x=0,1,2



D
R.H. Grubbs
OR=$OC(CH_3)_x(CF_3)_{3-x}$, x=0,1,2



E
R.H. Grubbs
OR=$OC(CH_3)(CF_3)_2$



F
R.H. Grubbs
R'=H, Ph, Me, diphenylvinyl

Figure 2-Well defined Tungsten, Molybdenum, and Ruthenium carbenes

cyclic olefins, they are not active in metathesis of low-strain olefins. A typical carbene of this type is $(CO)_5W{=}C(Ph)(OMe)$.[29]

Nucleophilic carbenes, also known as Schrock carbenes, have been shown to be active in a much broader scope of metathesis reactions than Fischer carbenes, and are the main focus of recent research of metathesis catalysts. A ruthenium carbene and several typical nucleophilic molybdenum and tungsten carbene catalysts are shown in Figure 2, and will be discussed in the next sections.

Synthetic Methods for Catalyst Preparation

The vast majority of well-defined catalyst systems previously described are variations of tungsten and molybdenum arylimido complexes, and can be divided into three categories. The first two are discussed in some detail below, so direct comparisons can be made with the methods used to make similar oxo complexes. These first two types are representative of a large percentage of known imido complexes. The third type is only described briefly, and is representative of only a small number of compounds.

The first category of imido complexes are neopentyl based, such as compound **C**[4] (Figure 2). These are typically prepared by α-H abstraction from a metal alkyl, or by transfer of a proton to a carbyne ligand. A synthesis of compound **C,** probably the best known single-component metathesis catalyst system, for M=W is shown in Figure 3,[4] and for M=Mo in Figure 4.[30]

High oxidation state four-coordinate complexes like **C** are stabilized by the steric bulk of the arylimido, alkylidene, and alkoxide ligands. Both can incorporate arylimido units of differing steric bulk, and alkoxide ligands with different steric and electronic properties. It has been shown that the activity of these systems can be drastically affected by the bascicity of the alkoxide

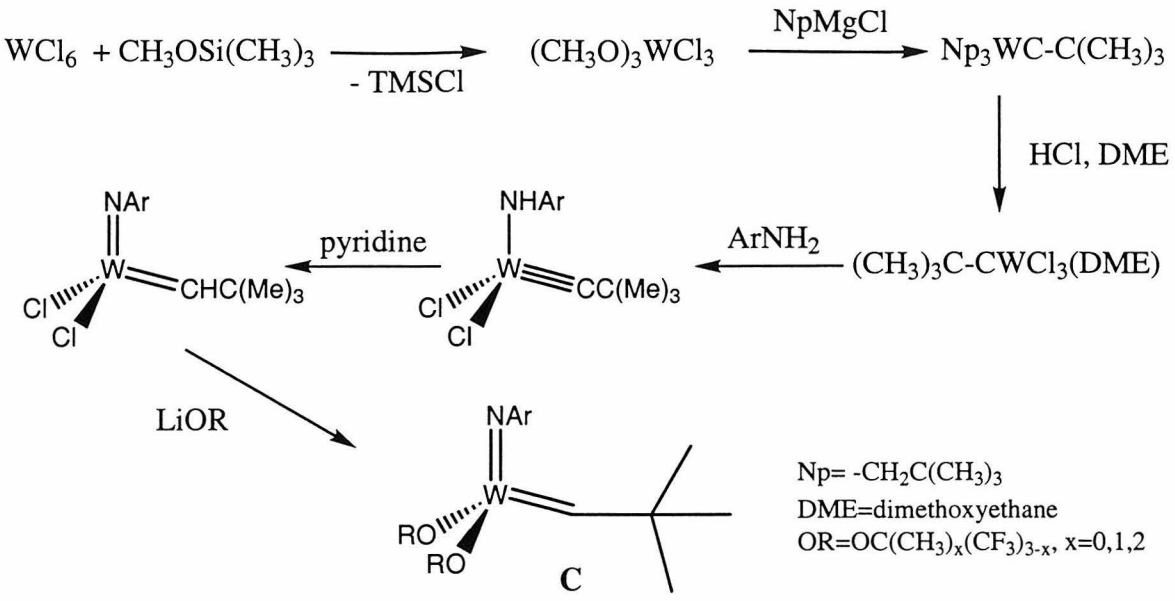


Figure 3-Synthesis of catalyst **C**, M=W

functionalities,[30] which is easily accomplished by varying the number of fluorinated methyl groups on the alkoxide. With the addition of the alkoxide in the last step, both systems present one method for an easy entry into this kind of activity variation. There are drawbacks to these compounds, however. The preparation of neopentyl-Grignard and the use of TfOH can be problematic, and like most early metal systems these compounds are extremely sensitive to air, water, temperature, and some functionalities. More importantly, since the nature of α-H abstraction requires a bulky ligand environment (and absence of β-pro-

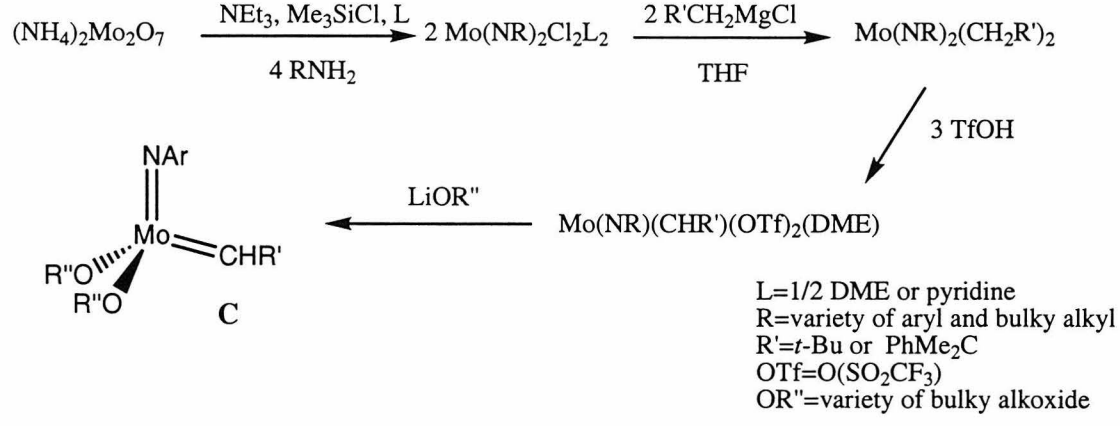


Figure 4-Synthesis of catalyst **C**, M=Mo

tons), only bulky carbenes can be prepared using these methods. As a result, though the catalysts show high activity they generally initiate reactions poorly– a concern especially for polymerization reactions where a narrow molecular weight distribution of polymers is desired. This problem can sometimes be overcome by the addition of a base, such as phosphine or quinuclidine, which slows the propagation step, relative to initiation, by coordinating to the metal.[31]

A second type of known imido complexes incorporate vinyl alkylidenes. The smaller steric bulk of the alkylidene moiety requires additional stabilization by a donor ligand, commonly THF or a phosphine/phosphite. Activity most likely requires the dissociation of this donor. The complexes **D**[32] and **E**[5] (Figure 2) are both active metathesis catalysts, and were prepared by ylide transfer and ring opening of a cyclopropene[33] respectively. A synthesis of **D** is shown in Figure 5, and the synthesis of **E** is similar: replacement of the halide with alkoxide is the second step, and the resultant compound is reduced with sodium-mercury amalgam in the presence of a phosphorous ylide.

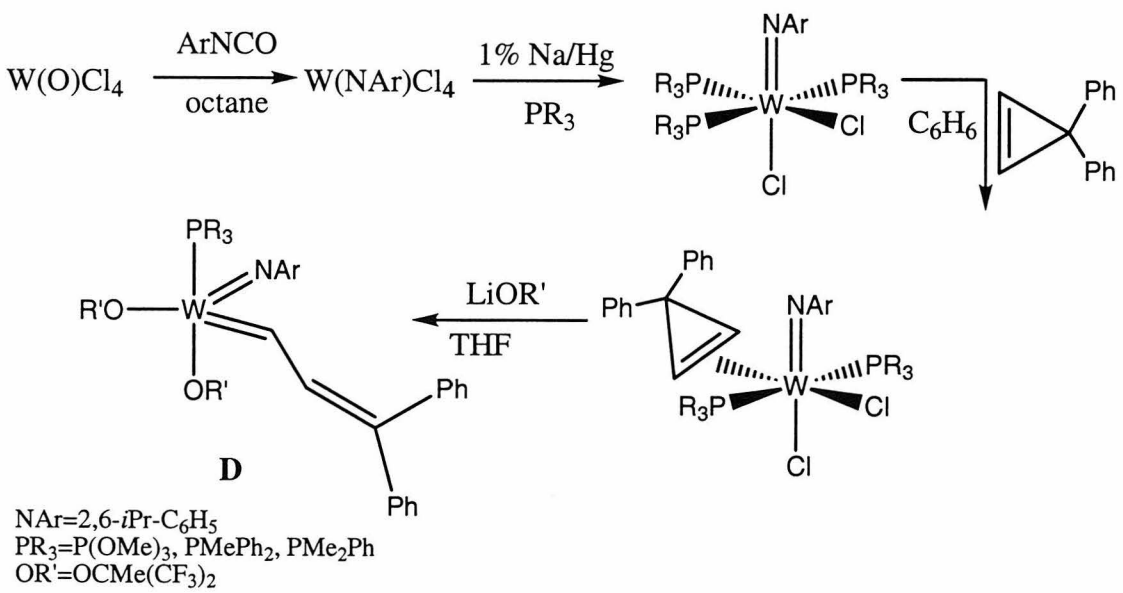


Figure 5-Synthesis of catalyst **D**

These systems (**D** and **E**) present much easier syntheses of tungsten catalysts compared to that for compound **C**. However, a major drawback of these systems is the need to perform a sodium amalgam reduction. Because the concentration of sodium in the amalgam must be small, a large (several gram) scale preparation requires a large amount of mercury, easily greater than a kilogram. An alternate reduction method has been found, and will be discussed later. To prepare compound **D**, one must first make 3,3-diphenylcyclopropene (**5**) which is relatively unstable in the conditions necessary for these reactions (neat and completely dry). Finally, while there are many transition metal complexes with an ylide donor,[34] elimination of the phosphonium functionality to give a carbene is rarely observed,[35-37] which drastically limits the utility of that method.

The third type of imido-alkylidene complex has been made recently by VanKoten and co-workers, and contains bidentate arylamine or phenoxide ligands.[38] These compounds are again formed by α-H elimination, the driving force apparently being the chelation of the bidentate ligand. An example of this kind of complex is $W(\eta^2\text{-}C_6H_4\text{-}o\text{-}CH_2NMe_2)(=NPh)(=CHSiMe_3)(CH_2SiMe_3)$.

As expected, high-oxidation state tungsten complexes are generally very air and moisture sensitive, and some are thermally unstable as well. Compound **F**[11] (Figure 2), developed in our group, represents a new class of active catalysts based on ruthenium that are stable to air and protic solvents. Complexes of this type can be formed by the ring opening of a cyclopropene, alkylidene transfer from a diazoalkane, or reactions involving ruthenium hydrides and organic fragments (see the previous chapter). The phosphine ligands can be exchanged in solution, and a variety of carbene ligands can be made. Variation of either the phosphine or the alkylidene can drastically alter the properties of the catalyst.[39]

Results and Discussion

Oxo Complexes of Tungsten and Molybdenum: Synthesis

In contrast to the methods used above to make imido complexes, oxo compound **A**[24;40] was prepared by the unexpected transfer of the alkylidene, halide, and phosphine ligands from a similar tantalum alkylidene complex and $W(O)(OR)_4$. A variety of similar compounds can be made, with varying phosphines and halides. Compound **B**[6] was formed very slowly in solution from $W(O)(CHR)_2(OR')_2$ and AlX_3. Both **A** and **B** require the presence of a Lewis Acid to show metathesis activity and are thus considered multicomponent catalysts.

The first single-component oxo catalyst was developed in our group by J. de la Mata, and the synthesis of this new catalyst was identical to that for the imido complex **D**, omitting the first step.[22] The problem remained, however, that a sodium amalgam reduction was necessary, so alternate reduction pathways were sought. Since the initial publication of complex **D**, Schrock has presented another series of tungsten oxo-alkylidene compounds similar in structure to **A**.[28] These catalysts are five coordinate (one less phosphine is present) and the chlorides have been replaced by bulky aryl-alkoxide ligands (O-2,6-$Ph_2C_3H_3$), and are active for the polymerization of norbornadienes, giving high *cis* isotactic polymer.

The use of amalgam in the preparation of **D** has been avoided by using phosphine as a reductant, as illustrated separately by Wilkinson[41] and Carmona.[42] W(VI) can be reduced to W(IV) with trimethylphosphine, methyldiphenylphosphine, or dimethylphenylphosphine (Figure 6). Phosphites and triphenylphosphine do not directly reduce W(VI), but W(IV) complexes with these donors can be made by using another reducing agent; the

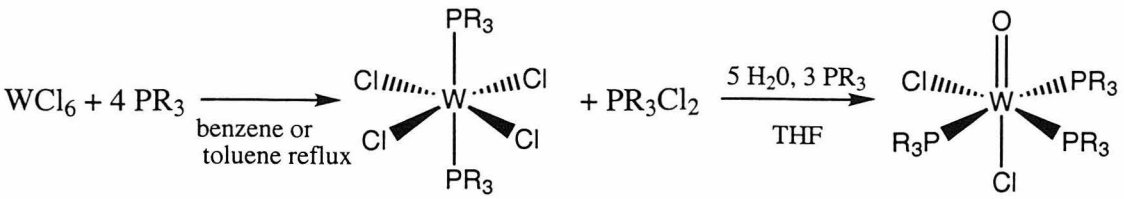


Figure 6-Preparation of W(IV) Starting materials

triphenylphosphine analogue can also be prepared by using a large mesh magnesium powder. [43] The orange $WCl_4(PR_3)_2$ powders can be handled for brief periods of time in air, and isolated by washing (in air) with reagent grade acetone. [44] In a slight modification to this procedure, the powder was then washed with hexane to afford less residual phosphine in the remaining product. These W(IV) compounds are all paramagnetic, but have surprisingly sharp ^1H NMR signals in the 20 to -10 ppm range.

Published procedures for the reduction of WCl_6 in benzene with dimethylphenylphosphine gave ~60% of $WCl_4(PR_3)_2$, while reduction with methyldiphenylphosphine gave only 20%. It was thought that a solubility problem hindered isolation of $WCl_4(PMePh_2)_2$, but switching to refluxing toluene and using the same procedures gave a yield comparable to that for the dimethylphenylphosphine complex, around 65%.[44]

The $WCl_4(PR_3)_2$ complexes (where PR_3=PMe_xPh_{3-x} (x=1,2)) can then be hydrolyzed in hot THF in the presence of three equivalents of phosphine to yield the corresponding meridonal oxo-dichloro-trisphosphine complexes, like $W(O)Cl_2(PMePh_2)_3$ (**2**), in high yield.[42] These 18-electron complexes are bright purple, diamagnetic, and air stable. Two alternative methods of preparation were found, the first of which avoids the isolation of $WCl_4(PR_3)_2$. Instead THF, water, and phosphine are added to the solution from the reduction reaction (shown in Figure 6). The second new method is the use of a different base; while the presence of one phosphine is necessary to make the tris-phosphine

complex in the hydrolysis procedure, the other two act as a base, giving $(HPR_3)Cl$. In place of using phosphine as a base, triethylamine was used with phosphine and water in THF, and $(HNEt_3)Cl$ was eliminated. The only problem with this method is that the triethylamine salt is slightly soluble in THF, and thus requires the use of different solvents to completely separate the salt from the product. Yields for both these process are comparable to the literature methods.

With hopes of using a cheaper, less volatile phosphine, and at the same time hoping to change the reactivity or initiation properties of the resulting complexes, the triphenylphospine complex, $WCl_4(PPh_3)_2$, was also investigated. This oxo-dichloro-trisphosphine complex has not been prepared in the literature, and it could not be prepared using methods similar to those for the other compounds. One possible explanation is that the steric bulk of triphenylphosphine versus mono- or diphenylalkylphosphine prevents placing three phosphines in a meridonal arrangement on one metal center.

Molybdenum starting materials can be prepared using a multistep process involving reduction of $MoCl_5$ with nitriles[43] affords $MoCl_4(NCR)_2$. Replacement of the nitriles with phosphines, followed by deoxygenation of ethylene oxide to give $Mo(O)Cl_2(PR_3)_2$.[45] A more elegant and much simpler method was found,[46] however, and is shown in Figure 7. In this procedure, ethanol is added dropwise to solid $MoCl_5$. After the first several milliliters are added, a brown oil is formed and the remaining amount of ethanol can be added rapidly to give a brightly colored green solution. Addition of phosphine gives several color

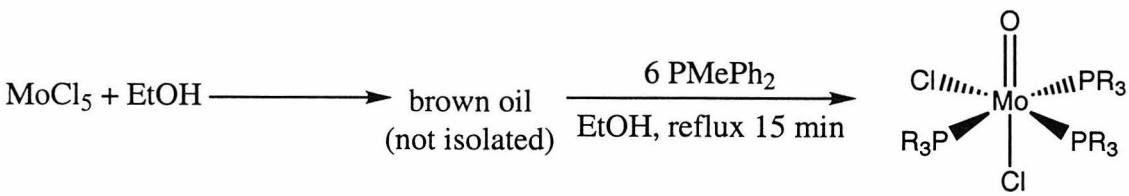


Figure 7-Simple Preparation of Mo(IV) Starting materials

changes, and after refluxing this mixture for between fifteen and thirty minutes the green microcrystalline solid $Mo(O)Cl_2(PR_3)_3$ (**10a**=$PMePh_2$, **10b**=PMe_2Ph) is isolated in good yields.

Both tungsten (**2**) and molybdenum (**10**) complexes react with 3,3-diphenylcyclopropene (**5**) in a manner similar to that used in the preparation of the tungsten-imido complex **E** (Figure 8) to give the η^2-diphenylcyclopropene complexes **3** and **11**. Compounds **2** and **10** are sparingly soluble in benzene, and a mixture of each complex with 1.1 equivalents of the cyclopropene produce the soluble olefin complex. Reactions to make this type of complex are known:

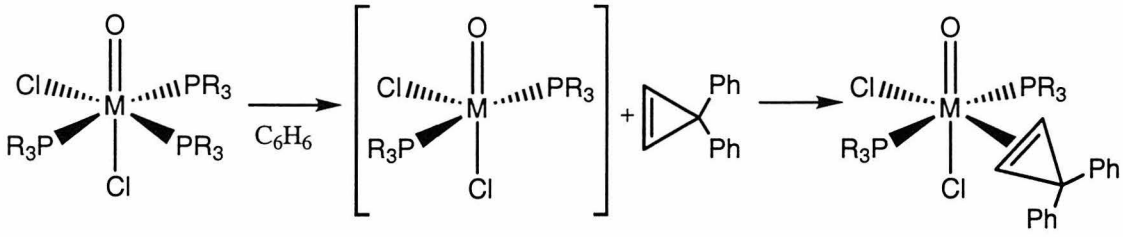


Figure 8-Presumed reaction pathway to make **3** (M=W) and **11** (M=Mo)

displacement of the phosphine with a variety of olefins has been used to make similar η^2-complexes,[47] including the unusual reaction of $WCl_2(PR_3)_4$ with ethylene oxide to give the oxo-ethylene complex.[45] If the reaction is carried out in methylene chloride instead of benzene, slightly shorter reaction times and temperatures can be used, but purification of the product is more difficult due to the much greater solubility of both **2** and **10** in CH_2Cl_2. One point of difficulty with this reaction is its extreme sensitivity to oxygen, giving blue decomposition products in the presence of traces of air. For these reactions a rubber septum sealed flask is not sufficient–a teflon needle valve Strauss flask must be used, and the reaction must be setup in the drybox. If oxygen is rigorously excluded, the reactions proceed in high yield (80% or greater). Since the starting material is air-stable, and the product is only moderately air-sensitive, the

extreme oxygen sensitivity is presumably due to the reactive intermediates. Due to the steric bulk of the phosphine ligands and the fact that only the *cis* meridonal phosphine is exchanged with the cyclopropene, the reaction most likely follows a dissociative pathway as depicted in Figure 8. No mechanistic studies have been done with **3** or **11**, but studies have been done with a compound similar to **10**, in which trimethylphosphine is replaced with ethylene. It was shown that the phosphines exchange in solution, and variation of the concentration of free phosphine had no effect on the rate of ethylene incorporation. Other experiments performed were also more consistent with a dissociative pathway.[45]

It is at this point that the differences between Mo and W begin to manifest themselves. Preparation of the tungsten complex requires 12 to 16 hours at 55°C, while formation of the molybdenum complex is as complete in 2 hours. With tungsten the unreacted starting material can be removed by filtration through glass wool, and any decomposed or dimerized cyclopropene is removed by washing the precipitated solid with pentane. Compound **3** is stable at room temperature under an atmosphere of an inert gas. With molybdenum, the substitution reaction is much more dynamic than with tungsten, as previously demonstrated with ethylene.[45] With tungsten (**10**) the reaction is firmly shifted to the products but the reaction to make **11** is never actually complete, and is always (in solid state or in solution) slowly liberating the cyclopropene and unidentified Mo decomposition products. This causes much more serious complications when the carbene is generated, and will be discussed below. This is not to say, however, that the molybdenum complexes cannot be made, isolated, and identified. Interestingly, compound **11b** $Mo(O)Cl_2(PMe_2Ph)_2(\eta^2$-diphenylcyclopropene) shows strange NMR behavior. In benzene the methyl groups on the phosphine are all equivalent, presenting a single triplet. In me-

thylene chloride, however, the methyl groups appear inequivalent, presenting two triplets of equal integration. Cycling of one sample in different solvents (dissolve, observe NMR, remove solvent and observe again) shows no free phosphine and that this alteration is completely reversible and simply due to the different solvents.

The geometry suggested by the spectroscopic data for **3** and **11** (selected spectroscopic data is summarized in Table 1) is analogous to that of imidodiphenylcyclopropene complexes prepared earlier:[5] a distorted octahedral structure in which the oxo ligand and a chloride occupy the axial positions, and the olefin carbons occupy one position in the equatorial plane, with the olefinic C-C perpendicular to the oxo ligand. On either side of the position with the olefin carbons are the two mutually *trans* phosphine ligands, with the remaining equatorial position (*trans* to the olefin) occupied by the remaining chloride. For complex **3**, crystals suitable for X-ray diffraction studies were grown, and the structure confirms these details. Two views of an ORTEP plot of **3** are shown in Figure 9, and selected bond lengths and angles in Table 2, along with data from a similar structure: $W(O)(PMePh_2)_2Cl_2(\eta^2$-ethylene).[47]

There is nothing surprising about the structure of **3**. The terminal oxo ligand is a typical length (W-oxo terminal average=1.692Å[48]), but it is clear

Table 1-Selected NMR data for η^2-diphenylcyclopropene complexes.[a]

		^{1}H		^{13}C		^{31}P
Cyclopropene complex (C_6D_6)		δ	J_{HP}	δ	J_{CP}	δ
$W(O)(PMePh_2)_2Cl_2(\eta^2$cyclopropene)	**3**	4.35	6.0	76.8	7.0	13
$Mo(O)(PMePh_2)_2Cl_2(\eta^2$cyclopropene)	**11a**	4.33	7.2	80.1	10.1	22.6
$Mo(O)(PMe_2Ph)_2Cl_2(\eta^2$cyclopropene)	**11b**	4.41	7.3	nd	nd	6.59
$W(NPh)(PMePh_2)_2Cl_2(\eta^2$cyclopropene)	**E**	4.19	5.7	72.4	9.0	5
[a]Uncomplexed (CD_2Cl_2)		7.54		113.8		

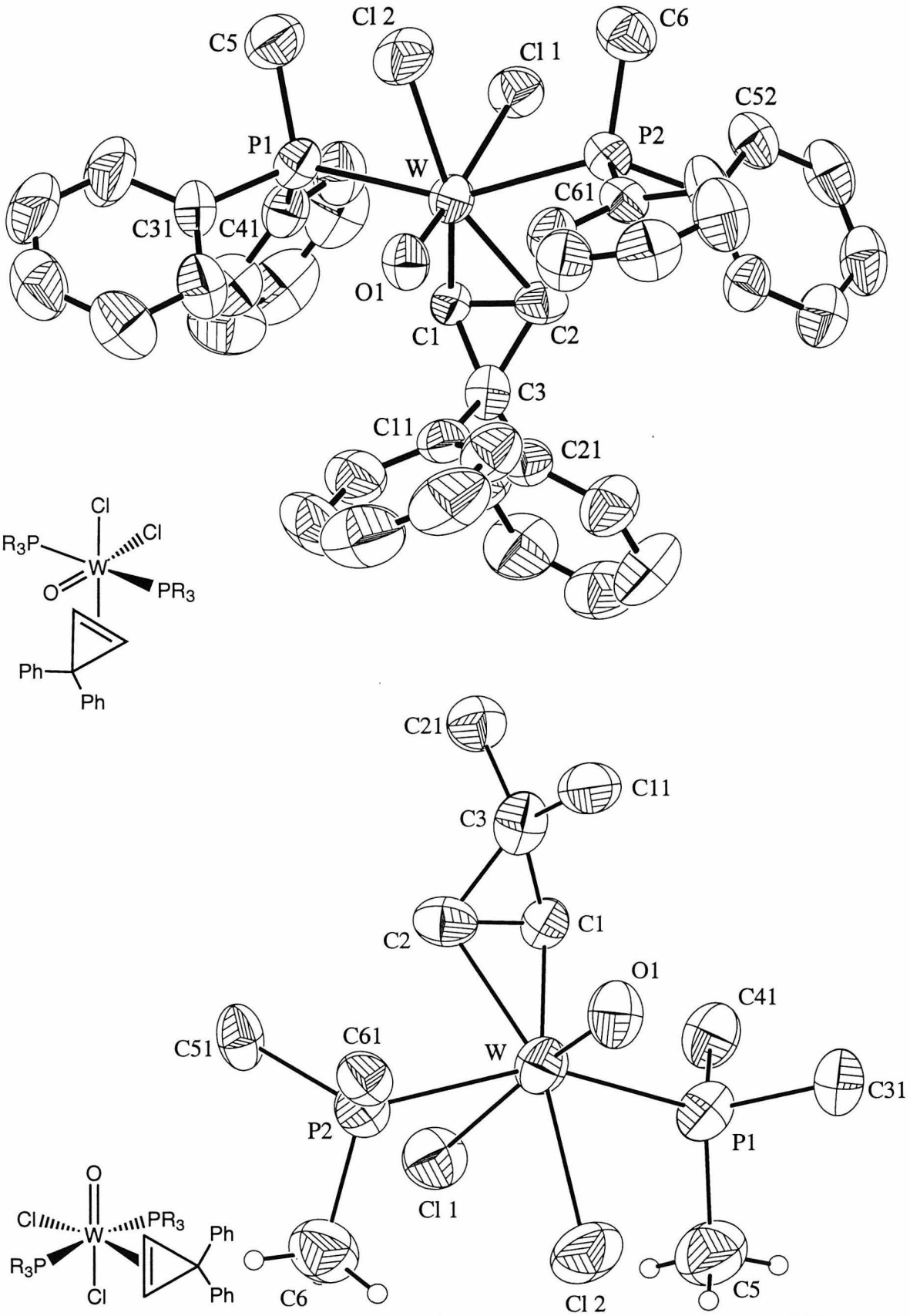


Figure 9-ORTEP Drawing of Compound **3,** drawn at 50% probability level

Table 2:Selected structural data for **3**, and a comparison structure[a]

$W(O)(PMePh_2)_2Cl_2(\eta^2$cyclopropene) **3**		$W(O)(PMePh_2)_2Cl_2(\eta^2$ethylene)	
bond	distance (Å)	bond	distance (Å)
W-O	1.692(4)	W-O	1.714(6)
W-C(1)	2.131(7)	W-C(1)	2.218(12)
W-C(2)	2.133(7)	W-C(2)	2.221(12)
W-P(1)	2.590(2)	W-P(1)	2.594(3)
W-P(2)	2.598(2)	W-P(2)	2.575(3)
W-Cl(1)	2.487(2)	W-Cl(1)	2.495(3)
W-Cl(2)	2.471(2)	W-Cl(2)	2.444(3)
C(1)-C(2)	1.477(8)	C(1)-C(2)	1.404(17)
C(1)-C(3)	1.505(9)		
C(2)-C(3)	1.497(9)		
angle	degrees	angle	degrees
O-W-C(1)	97.8(2)	O-W-C(1)	90.6(4)
O-W-C(2)	97.5(2)	O-W-C(2)	90.7(4)
O-W-Cl(1)	174.35(15)	O-W-Cl(1)	176.1(2)
O-W-P(1)	97.37(15)	O-W-P(1)	98.3(2)
O-W-P(2)	97.74(15)	O-W-P(2)	98.8(2)
P(1)-W-P(2)	154.99(6)	P(1)-W-P(2)	154.7(1)
O-W-Cl(2)	88.66(16)	O-W-Cl(2)	94.2(2)
Cl(1)-W-Cl(2)	85.76(7)	Cl(1)-W-Cl(2)	89.6(1)
P(1)-W-Cl(2)	79.59(7)	P(1)-W-Cl(2)	80.4(1)
P(2)-W-Cl(2)	80.96(7)	P(2)-W-Cl(2)	79.8(1)
C(1)-C(2)-C(3)	61.5(4)		
C(2)-C(3)-C(1)	57.6(4)		
C(3)-C(1)-C(2)	60.9(4)		

[a]Free ethylene C-C:1.337(2) Å; Free **5** C=C:1.294(10)

from the virtually identical C-C bond lengths in the cyclopropene ring that the description of **3** as an olefin complex is not as accurate as describing it as a metalla-bicyclo[1,1,0]butane (for simplicity, however, in this report these complexes will be referred to as η^2-olefin complexes). The steric bulk of the oxo ligand is significantly less than an arylimido ligand, which is reflected in the location of the olefinic C-C bond in the equatorial plane. With a similar imido complex $W(NPh)(P(OMe_3)_2)Cl_2(\eta^2$diphenylcyclopropene),[5] the steric bulk of the imido ligand is invoked to describe the 12.5° displacement of the olefinic carbons below the equatorial plane. Strong pi-back donation by tungsten to the

olefin bond is also found in the structure, evidenced by the lengthening of the olefinic bond and in the relief of strain in the apical cyclopropene angle. These two pieces of information can be used as a gauge of the electron density at the metal center: the more electron rich the metal, the longer the bond and larger the angle. If structures differing in only the axial pi-donor substituent were compared, the donating abilities of that ligand could be directly analyzed.

A solution of **3** can be heated to decomposition (70°C, 5-6 hours), to give unidentified tungsten species and the dimerization product of diphenylcyclopropene (1,1,6,6-tetraphenyl-1,3,5-hexatriene).[22] However, an intermediate decomposition product is observed: an alkylidene species presumed to be $W(O)(=CH\text{-}CH=CPh_2)Cl_2(PMePh_2)_2$ (**3'**) from spectroscopic data. The existence of this compound is not surprising, as similar compounds have been prepared,[24;47] though it has eluded isolation, most likely due to instability at the temperatures used in its generation.

The detection of vinylalkylidene species in solutions of **3** suggested that stable oxo-vinyl-alkylidene species could be generated with increased steric or electronic stabilization. Exchange of the chlorides with the bulkier alkoxides was a way to provide increased steric bulk, which could aid in preventing decomposition. In addition, the use of hexafluoro-*t*-butoxide in previous syntheses gave active, stable catalysts, and could also provide the electronic stabilization necessary to make a stable, active complex. This electronic "stabilization" is actually a change in the difference in energy between the carbene and the intermediate metallacycle. If the difference is too great, as in the case of metallacycles which have been isolated and fully characterized,[10] little or no reactivity is observed–the barrier between the metallacycle and carbene is too great. With electron withdrawing alkoxides, this energy difference is smaller, and therefore more easily overcome. This leads, in effect, to a destabilization of

the metallacycle, and a more active catalyst.

Reaction of **3** or **11** with 2.1 equivalents of $Li(OC(CH_3)(CF_3)_2)$, ($LiOR_{F6}$), in benzene gives the corresponding vinyl-alkylidene species $M(O)(=CH-CH=CPh_2)(OR_{F6})_2(PR_3)$, (M=W:**4**; M=Mo:**12**), as illustrated in Figure 10. Reaction times, temperatures, and yields vary as in the generation of **3** and **11**. For

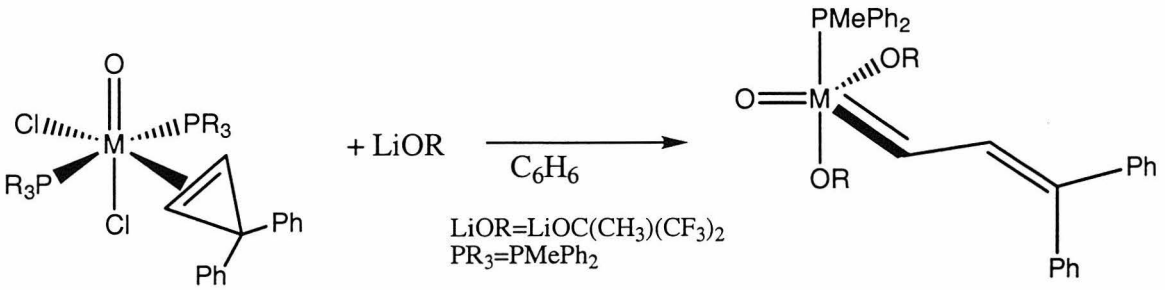


Figure 10-Generation of stable vinylalkylidene species M=W:**4**, M=Mo:**12**

the tungsten complex, a 14 hour reaction time is needed, while for the molybdenum complex two hours is sufficient. The tungsten reaction is further divided into two hours at room temperature and then twelve hours at 55°C. It is presumed that the two hours at room temperature provide the first alkoxide exchange, which has been observed;[22] the elimination of the room temperature step affords a decrease in yield.

Isolation of complexes **4** and **12** is consistently a problem, and any solid isolated is only stable for extended periods if stored in the freezer (-30°C or lower). Complexes **4** and **12** are soluble in aromatic hydrocarbons and chlorinated solvents, while THF displaces the phosphine to form the less bulky THF adduct (**4'** and **12'**), in neat THF and in benzene/THF mixtures. In comparison, compound **E** only exchanges phosphite to bind THF in the presence of a phosphite sponge, even in neat solution. It has been proposed that pi-bound oxo ligands in metal carbene species could be more electron donating than pi-bound arylimido ligands, even though imido ligands are generally considered to be

more pi-donating.[23] In these types of complexes (**4**, **12**, **E**, etc.) it is assumed that a more electron deficient metal center gives a stronger metal-phosphine/ phosphite bond. This has been demonstrated for an imido complex: if the hexafluoro-*t*-butoxides in **E** are replaced with t-butoxides, the phosphite is completely displaced by a small amount of THF.[49] Of course, the steric effects of phosphine versus phosphite are certainly also a factor, as bulky phosphines (such as methyldiphenylphosphine) are more easily displaced than phosphites.

Complexes such as **4** and **12** , as well as **4'** and **12'**, are present as two isomers in solution, consisting of rotamers of the carbene moiety, which can sometimes interchange in solution. The designation of syn and anti is based on similar compounds: with the β-carbon pointed towards the oxo ligand the compounds is designated syn, when it is pointed away it is called anti. The spectroscopic designations of the rotamers are based on comparison of the J_{HH} coupling constants from analogous imido complexes;[5;31] the coupling constant for the anti rotamer is larger. A characteristic alkylidene region of a ^{1}H NMR spec-

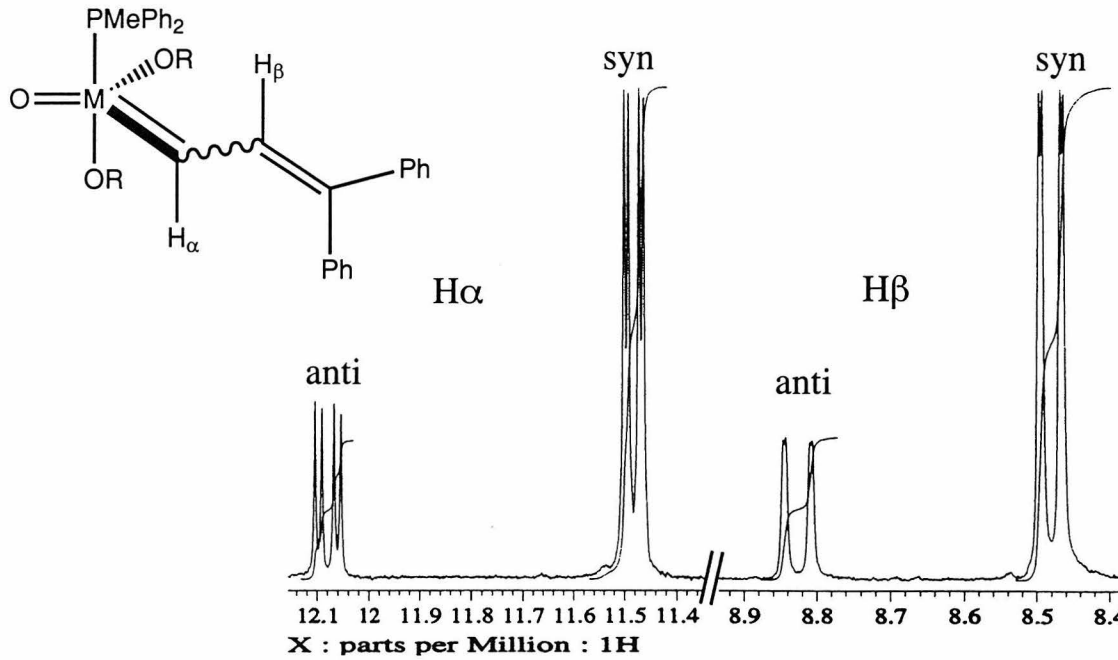


Figure 11-Characteristic ^{1}H NMR in the alkylidene region

Table 3-Selected NMR data for vinyl alkylidene species.[a]

Vinylalkylidene complex		H_α δ	H_α J_{HH}	H_α J_{HP}	H_β δ	H_β J_{HH}	H_β J_{HP}
$W(O)(PR_3)(OR_{F6})_2(=CHCH=CPh_2)$	syn-**4**	11.48	11.4	3.3	8.48	11.4	1.8
	anti-**4**	12.07	14.7	5.4	8.83	14.7	2.1
$W(O)(THF)(OR_{F6})_2(=CHCH=CPh_2)$	syn-**4'**	10.25	10.8	-	9.32	10.8	-
	anti-**4'**	11.83	12.9	-	9.28	12.9	-
$Mo(O)(PR_3)(OR_{F6})_2(=CHCH=CPh_2)$	syn-**12a**	13.22	11.7	5.5	8.51	11.7	0.9
	anti-**12a**	13.58	14.6	6.7	8.88	14.5	1.5
$Mo(O)(THF)(OR_{F6})_2(=CHCH=CPh_2)$	syn-**12'**	13.47	11.5	-	9.45	11.5	-
	anti-**12'**	13.08	14.0	-	9.29	14.0	-
$W(NPh)(=CHCHCMe_2)(OR_{F6})(PMePh_2)$	syn[b]	12.27	10.6	3.3	7.49	10.6	1.0
$W(NAr)(PR_3)(OR_{F6})_2(=CHCH=CPh_2)$	syn[c]	12.32	10.5	3.3	7.52	10.5	-

[a]All spectra were taken in C_6D_6 ; PR_3=$PMePh_2$; OR_{F6}=$OC(CH_3)(CF_3)_2$
[b]Only the syn isomer is present in isolated crystalline samples
[c]NAr=N-2,6-C_6H_3(*i*-Pr), only syn isomer observed

tra is shown in Figure 11, and selected spectroscopic data for these compounds are presented in Table 3. Spectroscopic data for **4**,**12**, **4'**, and **12'** are very similar to those for the analogous imido complexes such as **E**, W(NPh)(=CH-CH=CPh_2)(OR_{F6})($PMePh_2$) (**G**)[50] or W(NPh)(=CHCH=CMe_2)(OR_{F6})($PMePh_2$) (**H**).[49] Therefore, a structure analogous to that for the X-ray structure of compounds **E** and **H** is suggested for both **4** and **12**: a distorted trigonal bipyramid where the equatorial plane consists of the oxo and alkylidene ligands plus one of the alkoxides, while the apical positions are occupied by the phosphine and the remaining alkoxide. The two alkoxide ligands are therefore inequivalent, which can be detected by ^{1}H NMR. For **4**, this structure is confirmed by a low temperature X-ray diffraction study (necessitated by the fact that the crystalline **4** turns into an oil, and then decomposes if left at room temperature): an account of this structure is shown in Figure 12, with selected X-ray data in Table 4. The structure of **4** is consistent with the spectroscopic data. The smaller steric bulk of the oxo ligand compared to an arylimido ligand is again demon-

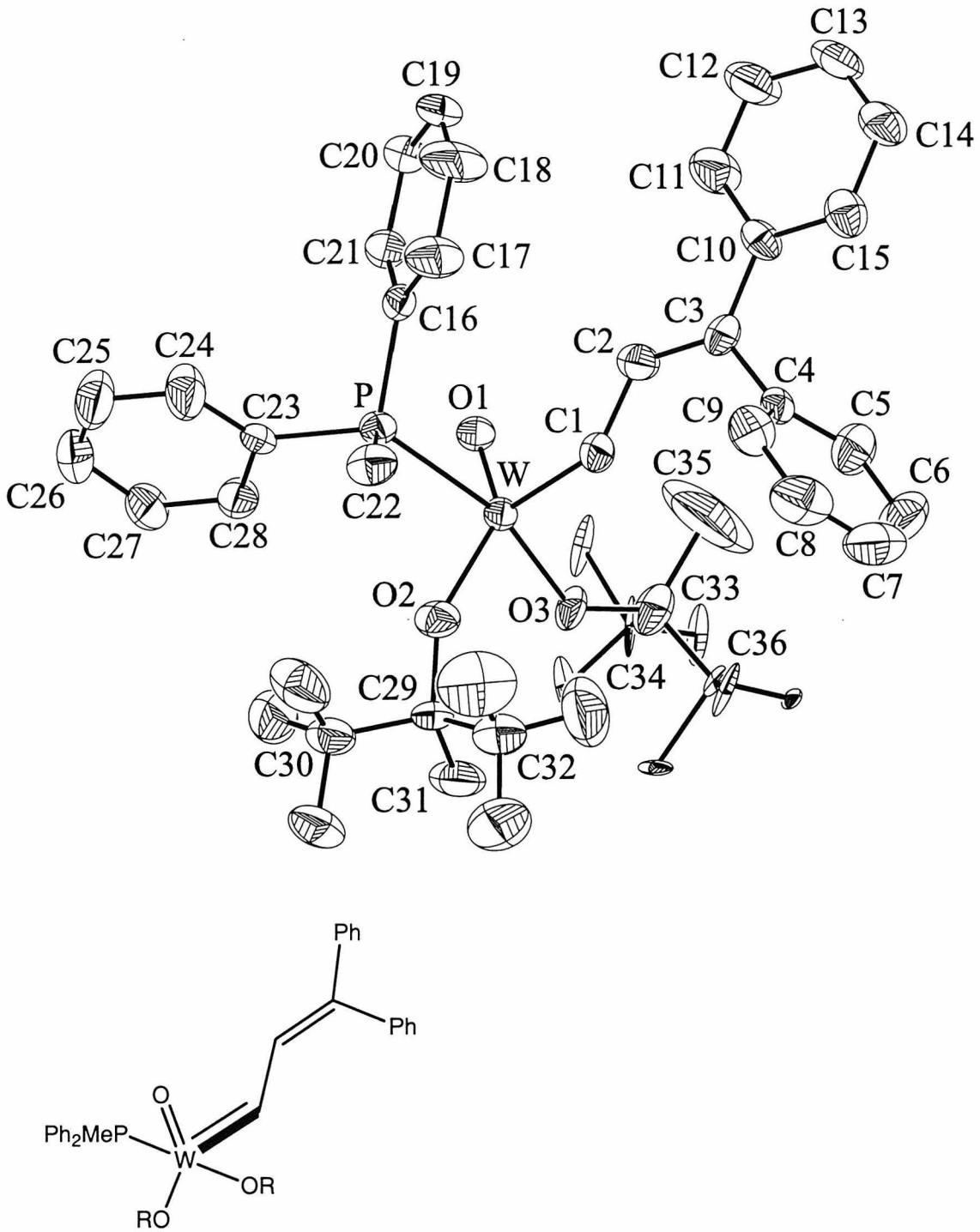


Figure 12-ORTEP drawing of compound **4**, OR=OC(CH_3)(CF_3)$_2$, with 50% probability ellipsoids; the U_{ij} for C34, F34(a-c), C36, and F36(a-c) have been divided by 10 and hydrogens have been omitted for clarity.

Table 4:Selected x-ray data for **4**, and a comparison structure

$W(O)(PMePh_2)(OR_{F6})_2(=CHCH=CPh_2)$ **4**		$W(NPh)(OR_{F6})_2(PMePh_2)(=CHCH=CMe_2)$ **H**	
bond	distance (Å)	bond	distance (Å)
W-O(1)	1.677(5)	W-N	1.753(2)
W-C(1)	1.927(7)	W-C(1)	1.911(3)
C(1)-C(2)	1.416(10)	C(1)-C(2)	1.446(5)
C(2)-C(3)	1.365(10)	C(2)-C(3)	1.341(5)
W-P	2.544(2)	W-P	2.531(1)
W-O(2)	1.950(5)	W-O(1)	1.998(3)
W-O(3)	1.965(5)	W-O(2)	1.984(2)
angle	degrees	angle	degrees
O(1)-W-C(1)	103.0(3)	N-W-C(1)	101.6(1)
O(1)-W-O(2)	137.5(2)	N-W-O(1)	143.9(1)
O(1)-W-O(3)	101.7(2)	N-W-O(2)	99.8(1)
O(1)-W-P	85.11(17)	N-W-P	87.9(1)
O(2)-W-O(3)	86.9(2)	O(1)-W-O(2)	85.2(1)
O(2)-W-C(1)	115.7(3)	O(1)-W-C(1)	111.8(1)
O(3)-W-C(1)	102.8(3)	O(2)-W-C(1)	104.3(1)
W-C(1)-C(2)	131.7(6)	W-C(1)-C(2)	136.3(1)
C(1)-C(2)-C(3)	125.6(7)		
C(1)-W-P	88.9(2)	C(1)-W-P	86.7(1)

strated: the angle between the terminal oxo and the alkoxide in the equatorial plane (O3) is less than that for the same angle in the imido complex. The W=C bond is slightly shorter than typical, similar complexes have given bond lengths in the 1.8-2.1 Å range.[51]

Reactions to make complex **12** give another species, and thus have proven extremely difficult for several reasons. As discussed above, the dynamic nature of the equilibrium between complexes $Mo(O)Cl_2(PR_3)_3$ (**10**) and $Mo(O)Cl_2(PR_3)_2(\eta^2$-diphenylcyclopropene) (**11**) means that at any time there is always free diphenylcyclopropene in solution, generated by **11**. Metathesis of strained cyclic olefins is one of the most traditional types of metathesis chemistry, and it is not surprising that a highly active carbene would initiate metathesis of a highly strained three membered ring. In the ^1H NMR, in addition to the easily identifiable syn and anti isomers of the vinyl alkylidene moiety, a singlet

is seen downfield of the other alkylidene peaks (δ 13.93). Closer inspection of the products show that a single metathesis of the cyclopropene would give a new carbene which does not have a beta proton, and which, if in the proper orientation, will not show coupling to the metal bound phosphine. The identity of this peak can be confirmed by generating the species **12a** in the presence of excess diphenylcyclopropene. Unfortunately attempts to cleave the carbene fragments with common reagents (like benzaldehyde) failed to react with the carbenes, and all other attempts to ascertain directly the nature of the carbenes were inconclusive. All activity measurements described below are done with the solutions of freshly generated **12**.

Unfortunately, the generation of complex **12b** proved too difficult for even in-situ activity determinations. Several carbene species were always generated, and all in small amounts. Most of the carbene peaks were broad (such as 48 Hz), and none particularly distinguishing, while the alkyl region became a forest. To further complicate the situation, it also appears that there is some alkoxide exchange before generation of the carbene(s), as at least one additional bound olefin peak (triplet slightly downfield of the starting material) is observed.

Imido Complexes of Tungsten

The tungsten imido complex $W(NPh)Cl_2(PMePh_2)_2(\eta^2$-diphenylcyclopropene) (**8**) was made previously in the synthesis of **E**, but no X-ray structure was obtained. It is of interest to directly compare the olefin binding between compounds that differ only in the apical multiply bonded ligand, to shed light on the donating ability of imido versus oxo ligands in this kind of complex. Unfortunately, no suitable crystals have yet been grown; attempts

with methods similar to those used to obtain crystals for the oxo compound, **3**, did not give single crystals or crystals which could be broken to give suitable single crystals. Upon analysis of the previously made material, which had been stored in the drybox for the past few years, it was found to have rearranged to give a large percentage of what is presumed to be $W(NPh)Cl_2(=CHCH=CPh_2)(PMePh_2)_2$ on the basis of spectroscopic data. Published procedures to make the starting material $W(NPh)Cl_2(PMePh_2)_3$ (**7**), as mentioned above, utilize a sodium amalgam reduction. In an effort to eliminate this step, alternate preparations were investigated. The first alternate method, which was the only one successful in preparing **7**, gave yields comparable to those of the sodium reduction. This method involved utilizing magnesium powder to reduce $W(NPh)Cl_4$ in the presence of $PMePh_2$ in THF, and to isolate the product in a similar manner to that of the sodium reduction.

Another alternate reduction method investigated was an attempt to duplicate procedures used to make the oxo complex as shown in Figure 6: reactions with $WCl_4(PMePh_2)_2$ (**1**), anilines, and $PMePh_2$ in THF. The reaction type is similar: react $WCl_4(PR_3)_2$ and H_2X to give $W(=X)Cl_2(PMePh_2)_3$. Since initial reactions with the sterically demanding 2,6-di-isopropylphenylaniline failed, it was hoped that the use of a less sterically demanding amine such as aniline would encourage the formation of the product. After heating for over two weeks at 45°C, the slurry/solution was still the characteristic orange color (the imido complex is dark brown) and showed no reaction with aniline by ^1H NMR. The addition of water after the two week reaction time, however, gave the previously described oxo complex **2** in good yield.

The third alternate method examined was a procedure similar to the first step used to make compound **D** (as illustrated in Figure 5): react an isocyanate with an already reduced tungsten(IV)-oxo to give the tungsten-imido and

carbon-dioxide. Reactions with **2** and various phenylisocyanates failed, but it is possible that this method may still show some utility with phosphines of differing steric or electronic properties.

Activity Measurements

In order to compare the activity of the new oxo-alkylidene complexes to that of the previously described imido complexes, various ring-opening metathesis polymerizations (ROMP, shown in Figure 13) and ring closing metathesis (RCM, shown in Figure 14) experiments were performed. Both the tungsten and molybdenum oxo carbenes, **4** and **12**, were found to be active, single component catalysts for both processes. As mentioned above, the isolation of **4** and **12**

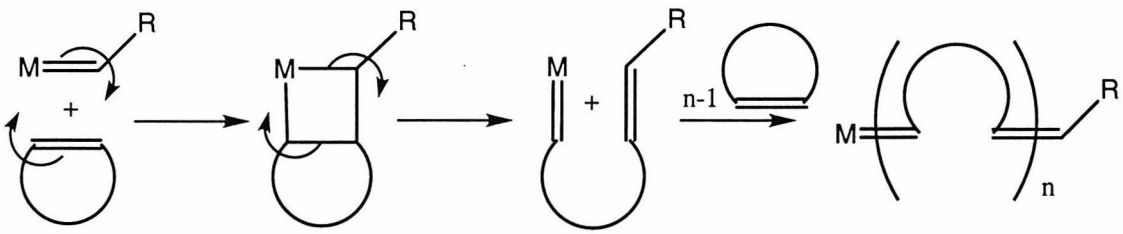


Figure 13-Generalized ROMP Pathway

remains a problem; the polymerization data presented in Table 5 (along with comparison data for **C** (M=W[52], M=Mo[53]), **E** and **H**[49]) were obtained by the use of solutions of catalyst directly after generation. RCM activity was tested with diethyldiallylmalonate, and further activity is currently being investigated.

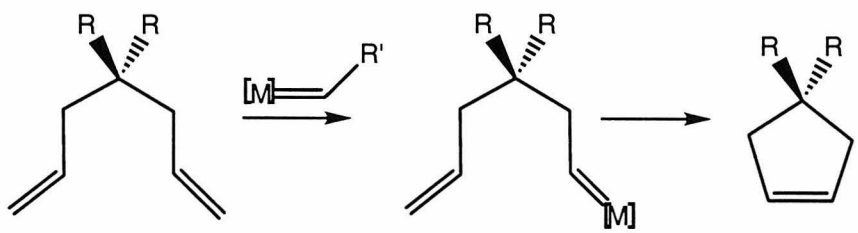


Figure 14-Generalized RCM

Norbornene is one of the classical tests for olefin metathesis–the highly strained monomer gives polynorbornene, which is well characterized in the literature. In addition, the polymerization of cyclooctene can be used to investigate the activity of a catalyst because it is less strained than norbornene, and therefore more difficult to polymerize.

In addition to the activity found for the metal-oxo-carbene complexes, it was found that both the tungsten and molybdenum olefin complexes, **3** and **11**, could be used as temperature-dependent catalysts. While the olefin complexes are not active metathesis catalysts at room temperature, it was found that raising the temperature of a solution of an olefin complex to 65°C in the presence of a cyclic monomer (like norbornene or cyclooctene), gave the corresponding polymer. It is presumed that the active species is generated from the thermal ring-opening of cyclopropene to give the chloro carbene complex described above, and then a related complex with a dissociated phosphine or phosphines. The dissociation of one or both phosphines makes sense not only electronically (16 or 14 electron species for the mono- and di-dissociated species versus 18 electrons for the parent), but also fits the following observations: (a) the thermally activated chloro carbene complex can be generated in solution and can be observed spectroscopically to have two phosphines on the metal, (b) only at elevated temperatures is a species in this mixture an active metathesis catalyst, (c) after cooling, a new species is observed (propagating carbene, which for norbornene δ=12.2), which does not incorporate more monomer until again heating to elevated temperature. Polymerization of norbornene was rapidly accomplished with both **3** and **11**, but the polymerization of cyclooctene was only observed with **3** after 30 hours, at which point no polymer could be precipitated from the reaction with **11**.

In a qualitative manner, it is clear from both the norbornene and

cyclooctene data (Table 5) that propagation is faster than initiation with these catalysts, because the molecular weights of the resulting polymers made are high, and the polydispersities relatively broad. With 100 equivalents of either monomer, a completely initiated amount of catalyst (where propagation is slower than initiation) would give an M_n of approximately 10000. It is hoped that this molecular weight difference, as well as the polydispersity index, will be controllable by a change of phosphine, or addition of a different donor ligand to slow propagation.[31]

Table 5-Polymerization data for various catalysts

Catalyst	Monomer	Equiv. Mon.	M_n*10^3 g/mol	PDI
3	Norbornene	100	108.6	1.53
4	Norbornene	10	4.1	1.83
11a	Norbornene	100	86.6	1.62
12a	Norbornene	130	342.5	1.45
C (M=W)	Norbornene	288	400	1.63
C (M=Mo)	Norbornene	100	22.1	1.06
E	Norbornene	92	11.3	1.14
H	Norbornene	118	11.7	1.9
3	Cyclooctene	110	166.4	1.72
4	Cyclooctene	100	125.5	1.93
12a	Cyclooctene	~150	413.3	1.73
E	Cyclooctene	not active		

Conclusions

It has been demonstrated that well defined, single component metathesis catalysts based on tungsten- and molybdenum-oxo species can be made, and that their syntheses are considerably simpler than those of analogous imido complexes. While isolation of the final carbene complexes remains problematic, that does not hinder the examination of their reactivity nor their use directly after generation.

Experimental Section

General Considerations. Unless otherwise specified, all manipulations were performed in a nitrogen-filled Vac-Atmospheres drybox or by using standard Schlenk techniques under an atmosphere of argon. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves (Linde). ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a JEOL GX-400 spectrometer (399.1 MHz ^{1}H,140 MHz ^{13}C, 161.9 MHz ^{31}P), or a QE-300 Plus (300.10 MHz ^{1}H, 75.49 MHz ^{13}C) at 25 °C. All chemical shift values are given in ppm and are referenced with respect to residual protons in the solvent for proton spectra, or referenced with respect to phosphoric acid for phosphorus spectra. All coupling constants are reported in Hz. For the ^{1}H and ^{13}C NMR virtual triplet resonances of *trans* phosphine ligands, the coupling constant $N = |{}^{2}J_{HP} + {}^{4}J_{HP}|$ is given, where N is the separation of the outer lines of the triplet. Polymer molecular weights are referenced to polystyrene standards.

Materials:

Solvents: Toluene, benzene, pentane, hexanes, diethyl ether, benzene-d_6, methylene chloride and tetrahydrofuran were purified by methods developed in our research group.[54] Olefin-free pentane was made by stirring stock pentane over concentrated H_2SO_4. It was then washed with bicarbonate solution, dried over $MgSO_4$, CaH_2, vacuum transferred from a sodium-benzophenone ketyl solution and degassed with several freeze-pump-thaw cycles. THF-d_8 and CD_2Cl_2 were dried over sodium-benzophenone and CaH_2, respectively, and also degassed using the freeze-pump-thaw method.

$WCl_4(PMePh_2)_2$ (**1**),[44] $WCl_2(O)(PMePh_2)_3$ (**2**),[42] (also several modified

procedures explained below) 3,3-Diphenylcyclopropene (**5**),[55] $W(NPh)Cl_4$ (**6**),[56] $W(NPh)Cl_2(PMePh_2)_2(\eta^2$-diphenylcyclopropene) (**8**),[5] $WCl_4(PPh_3)_2$ (**9**),[43] and $Mo(O)Cl_2(PMePh_2)_3$ (**10a**) and $Mo(O)Cl_2(PMe_2Ph)_3$ (**10b**)[46] were prepared according to literature methods. $PMePh_2$ was purchased from Strem and degassed by several freeze-pump-thaw cycles. $(CF_3)_2(CH_3)COH$ was dissolved in dry Et_2O, deprotonated with 1 equivalent of n-BuLi, and purified by standard techniques. $W(O)Cl_2(PMePh_2)_2(\eta^2$-diphenylcyclopropene) (**3**), and $W(O)(PMePh_2)(OR_{F6})_2(=CH\text{-}CH=CPh_2)$ (**4**) [OR_{F6}=hexafluoro-*t*-butoxide] were prepared by modifying procedures developed in our group.[22]

All other reagents were used without further purification unless otherwise noted.

Procedures:

$W(O)Cl_2(PMePh_2)_3$ (**2**): Compound **2** was prepared by the published procedure as noted above, and by modifications of this procedure. Complete characterization can be found in the above reference.

(a) The median compound $WCl_4(PR_3)_2$ is not isolated: To a slurry of WCl_6 (2.02 g, 5.09 mmol) in 50mL of toluene in a 250mL Schlenk flask, $PMePh_2$ (5.5 mL, 5.92 g, 29.5 mmol) was added dropwise via syringe over a period of several minutes. The reaction is stirred, heated to reflux, and allowed to reflux for at least 6 hours. The reaction is cooled to room temperature, and 30mL of THF is added, along with $PMePh_2$ (2 mL, 11 mmol) and degassed water (0.46 mL, 25 mmol), in that order. The reaction is heated to 45°C and allowed to stir for 4 hours. The solution is concentrated to approximately 20mL, at which point 60mL of pentane are added to precipitate the product, and isolated as described below.

(b)A different base is used: To a solution of $WCl_4(PMePh_2)_2$ (**1**) (0.250 g,

0.34 mmol) in THF (15 mL) the following are added (in this order): $PMePh_2$ (0.14 g, 0.70 mmol), NEt_3 (0.105 g, 1.03 mmol), and H_2O (degassed, 0.031 g, 1.72 mmol). The reaction mixture is heated to 45°C for 4 hours, and then cooled to room temperature. The reaction is filtered, and washed with small portions of THF until the extractions are no longer purple. The combined washes are reduced in volume to less than 20mL, precipitated into pentane, and isolated as described below.

From both procedures, the light purple solid isolated is washed with ether (2x25 mL) and pentane (4x30 mL), and dried under vacuum. The powder is usually of sufficient purity at this point to continue, but crystalline material can be obtained from layering a concentrated solution of **2** in CH_2Cl_2 (about 1 g/ 5 mL) into the bottom of a Schlenk containing a large excess of pentane or other alkane. After a period of several days the supernant is removed and the dark purple crystalline product isolated. Yield of powder: 2.75g, 62%. Crystalline yields slightly lower, about 55%. Selected ^1H NMR data(C_6D_6): δ 2.22 (t, N=7.96, *trans* P*Me*Ph_2), 1.67 (d, J_{HP}= 7.92, single P*Me*Ph_2).

$W(O)Cl_2(PMePh_2)_2(\eta^2$-diphenylcyclopropene) (**3**):In the drybox, a 5mL benzene solution of 3,3-diphenylcyclopropene, (**5**), (0.486 g, 2.53 mmol) was added to a 45mL benzene slurry of $W(O)Cl_2(PMePh_2)_3$ (**2**) (2.00 g, 2.30 mmol) in a ~250mL teflon-needle valve Strauss flask. The reaction was stirred at 55°C for 12 hours. The reaction mixture was then taken back into the drybox, where it was filtered through a plug of glass wool into a stirring volume of pentane (~150 mL). The pale yellow solid was isolated on a medium-fritted glass filter and washed with pentane (3x30 mL), and dried under vacuum. Isolated 1.78g, 90%.

Selected ^1H NMR data (C_6D_6, for full NMR data plus elemental analysis see above reference):δ 4.35 (t, 2H, J_{HP}=6.0, HC=CH), 2.47 (t, 6H, N=9.6, P*Me*Ph_2);

$^{13}C(C_6D_6)$:δ 151.4 (C*Ph*Ph', C_{ipso}), 143.1 (CPh*Ph'*, C_{ipso}), 134.7-130.2 ($C_{aromatic}$), 76.8 (t, J_{CP}=6.5 Hz, HC=CH), 66.1 (s, CPh_2), 13.61 (t, N=35.5, $PMePh_2$); ^{31}P (C_6D_6): δ 13.3.

X-ray diffraction experiment for **3**: (see Appendix 2)

Crystals suitable for X-ray diffraction were grown at room temperature by the slow diffusion of a solution of **3** in CH_2Cl_2 (200mg, ~1 mL) layered into the bottom of ~15mL of pentane, over a period of approximately one week. Complete crystallographic data has been presented.[57] A crystal 0.4x0.2x0.2 mm was selected in a flow of argon, coated with epoxy, mounted on a fiber, and placed in an Enraf-Nonius CAD-4 spectrometer. The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out according to standard techniques. Room temperature data were collected via an omega scan technique with $Mo_{K\alpha}$ radiation. All 11266 data were corrected for absorption and for Lorentz and polarization effects to give 4481 independent reflections in a monoclinic system with a P2(1)/c space group. All crystallographic calculations were carried out using the SHELLX-93 system. Refinement of the model led to convergence with RF=3.7% and GOF=1.540 for 424 variables refined against those 4431 data. A final difference-Fourier map gave sigma(max)=1.39 eÅ^{-3}.

$W(O)(PMePh_2)(OC(CH_3)(CF_3)_2)_2$(=CH-CH=$CPh_2$) (**4**): In the drybox, a slurry is made with $W(O)Cl_2(PMePh_2)_2$(η_2-diphenylcyclopropene) (**3**) (0.5 g, 0.58 mmol) and $LiOC(CH_3)(CF_3)_2$ (0.240 g, 1.28 mmol) in 5mL of benzene in a ~75mL telfon-needle valve Strauss Flask. The reaction is stirred first at room temperature for 4 hours, then at 55°C for 12 hours and taken back into the drybox. The lithium salts are removed by filtering through a plug of celite. Isolation of this

complex continues to be a problem. However, by ^{1}H NMR, the reaction is complete, and solutions of the catalyst were used for study. See discussion section for details.

Selected ^{1}H NMR data (C_6D_6, for complete NMR data and elemental analysis see above reference) anti-rotamer:δ 12.07 (dd, J_{HH}=14.7, J_{HP}=5.4, H_α), 8.83 (dd, J_{HH}=14.7, J_{HP}=2.1, H_β), 1.66 (br s., 3H, P*Me*Ph_2), 1.79 and 1.83 (br s., 3H , -OC(C*H*$_3$)(CF_3)); syn rotamer: δ 11.48 (dd, J_{HH}=11.4, J_{HP}=3.3, H_α), 8.48 (dd, J_{HH}=11.4, J_{HP}=1.8, H_β), 1.69 (br s., 3H, P*Me*Ph_2), 1.90 and 1.83 (br s., 3H , -OC(C*H*$_3$)(CF_3)).

X-ray diffraction experiment for **4**: (See Appendix 3)

Crystals for X-ray diffraction were grown at -40°C (in the drybox freezer) by the slow diffusion of a solution of **4** in CH_2Cl_2 (100 mg, <1 mL, made from removing the solvent from a filtered reaction mixture and redissolving in CH_2Cl_2) layered into the bottom of ~18mL olefin free pentane. The first attempt gave a flaky brown solid, which was used in the second attempt to yield suitable crystals. The crystals were isolated, and stored in the drybox freezer. Crystals were chosen for investigation by preparing a slide in the drybox on which crystals were coated with Paratone oil, which was then kept in a sealed vial over solid dry ice until a crystal was chosen under a microscope. The mounted crystal, coated in oil, was then mounted and placed in the cold nitrogen stream at -150°C. More experimental details will be available after the refinement of the structure.

W(O)(THF)(OC(CH$_3$)(CF$_3$)$_2$)$_2$(=CH-CH=CPh$_2$) (4'):

(a)A mixture of W(O)Cl_2(P$MePh_2$)$_2$(η^2-diphenylcyclopropene) (**3**) (20 mg, 0.023 mmol) and LiOC(CH_3)(CF_3)$_2$ (9.5 mg, 0.048 mmol) is placed in a mixture

of C_6D_6/THF-d_8, or just THF-d_8, and stirred at room temperature for 2 hours and then 12 hours at 60°C.

(b)To a similar scale solution of W(O)($PMePh_2$)($OC(CH_3)(CF_3)_2$)$_2$(=CH-CH=CPh_2) (**4**) in C_6D_6, several drops of THF-d_8 are added. The resulting solutions contain **4'** and free phosphine.

Selected ^{1}H NMR data (C_6D_6/THF-d_8;10:1) anti-rotamer:δ 11.83 (d, J_{HH}=12.9, H_α), 9.28 (d, J_{HH}=12.9, H_β); syn rotamer: δ 10.25 (d, J_{HH}=10.8, H_α), 9.32 (d, J_{HH}=10.8, H_β).

W(NPh)Cl_2($PMePh_2$)$_3$ (**7**): A solution of W(NPh)Cl_4 (**6**) (1 g, 2.40 mmol) and $PMePh_2$ (1.44 g, 7.20 mmol) in 50mL of THF is placed above Mg powder (0.0585 mg, 2.41 mmol) which had been dried under vacccum, heating the flask with a Bunsen burner flame. The reaction is allowed to stir overnight (18 hrs), the THF is removed and the residue is extracted with benzene. The benzene solution is reduced in volume to ~10mL, and excess pentane is added. Isolate 1.90g (84%) of a brown solid.

Selected ^{1}H NMR data (C_6D_6, for full characterization see reference for preparation of **6**): δ 2.367 (t, 6H, N=7.92, P*Me*Ph_2), 1.89 (d, 3H, J_{HP}=7.64, P*Me*Ph_2).

Mo(O)Cl_2($PMePh_2$)$_2$(η^2-diphenylcyclopropene) (**11a**):In the drybox, a 1 mL benzene solution of 3,3-diphenylcyclopropene, (**5**), (0.135 g, 0.70 mmol) was added to a 10 mL benzene slurry of Mo(O)Cl_2($PMePh_2$)$_3$ (**10**) (0.500 g, 0.64 mmol) in a ~50mL teflon-needle valve Strauss flask. The reaction was stirred at 45°C for 6 hours. The reaction mixture was taken back into the drybox, where it was filtered through a plug of glass wool into a stirring volume of pentane (~40 mL). The pale yellow solid was isolated on a medium-fritted glass filter and washed

with 3x10 mL of pentane, dried under vacuum and stored in the drybox. Isolated 0.442g , 89%.

^{1}H NMR (C_6D_6):δ 7.75-6.7 (m, 30, H_{aryl}), 4.33 (t, 2H, J_{HP}=7.2, HC=CH), 2.51 (t, 6H, J=9.8, P*Me*Ph_2); ^{13}C(C_6D_6): δ 150.1 (C*Ph*Ph', C_{ipso}), 142.3 (CPh*Ph'*, C_{ipso}), 135.3-125.6 ($C_{aromatic}$), 80.1 (t, J_{CP}=10.1 Hz, HC=CH), 64.0 (s, CPh_2), 14.1 (t, J=46.9, $PMePh_2$); ^{31}P (C_6D_6): δ 22.6.

Mo(O)Cl_2(PMe_2Ph)$_2$(η^2-diphenylcyclopropene) (**11b**): Compound **11b** was prepared similarly to **11a**, starting with 1 g of Mo(O)Cl_2(PMe_2Ph)$_3$. Isolated yield 747 mg, 68%.

^{1}H NMR (C_6D_6) 7.5-6.7 (m, 15H, H_{aryl}), 4.41 (t, 2H, J_{HP}=7.3 Hz, HC=CH), 1.84 (t, 12H, J=4.88 Hz, P*Me*$_2$Ph); ^{31}P (C_6D_6): δ 6.59.

^{1}H NMR (CD_2Cl_2): 6.55-7.69 (m, 10H, H_{aryl}), 4.24 (t, 2H, J_{HP}=8.4 Hz, HC=CH), 2.15 and 2.05 (each: t, 6H, J=4.9 Hz, P*Me*$_2$Ph); ^{31}P (C_6D_6): δ 6.8.

Mo(O)($PMePh_2$)($OC(CH_3)(CF_3)_2$)$_2$(=CH-CH=CPh_2) (**12a**): In the drybox, a slurry is made with Mo(O)Cl_2($PMePh_2$)$_2$(η_2-diphenylcyclopropene) (**11a**) (0.050 g , 0.06 mmol) and $LiOC(CH_3)(CF_3)_2$ (0.025 g, 0.13 mmol) in 1 mL of benzene in a vial. The reaction is stirred at room temperature for 2 hours. Lithium salts are removed by filtering through a plug of celite.

^{1}H NMR (C_6D_6) anti-rotamer:δ 13.58 (dd, J_{HH}=14.6, J_{HP}=6.7, H_α), 8.88 (dd, J_{HH}=14.6, J_{HP}=1.5, H_β); syn rotamer: δ 13.22 (dd, J_{HH}=11.7, J_{HP}=5.5, H_α), 8.51 (dd, J_{HH}=11.7, J_{HP}=0.9, H_β).

Mo(O)(THF)($OC(CH_3)(CF_3)_2$)$_2$(=CH-CH=CPh_2) (**12'**):

(a)A mixture of Mo(O)Cl_2($PMePh_2$)$_2$(η^2-diphenylcyclopropene) (**3**) (0.050 g, 0.060 mmol) and $LiOC(CH_3)(CF_3)_2$ (0.025 g, 0.13 mmol) is placed in a mix-

ture of C_6D_6/THF-d_8, or just THF-d_8, and stirred at room temperature for 2 hours.

(b)To a similar scale solution of $Mo(O)(PMePh_2)(OC(CH_3)(CF_3)_2)_2(=CH-CH=CPh_2)$ (**4**) in C_6D_6, several drops of THF-d_8 are added. The resulting solutions contain **4'** and free phosphine.

Selected ^1H NMR data (C_6D_6/THF-d_8;10:1) anti-rotamer:δ 13.08 (d, J_{HH}=14.0, H_α), 9.29 (d, J_{HH}=14.0, H_β); syn rotamer: δ 13.47 (d, J_{HH}=11.5, H_α), 9.45 (d, J_{HH}=11.5, H_β).

$Mo(O)(PMe_2Ph)(OC(CH_3)(CF_3)_2)_2(=CH-CH=CPh_2)$ (12b): In a procedure identical to that for **12a** $Mo(O)Cl_2(PMePh_2)_2(\eta_2$-diphenylcyclopropene) (**11b**) is used. but done only on an NMR scale.

^1H NMR (C_6D_6) anti-rotamer:δ 13.58 (dd, J_{HH}=14.6, J_{HP}=6.7, H_α), 8.88 (dd, J_{HH}=14.6, J_{HP}=1.5, H_β); syn rotamer: δ 13.22 (dd, J_{HH}=11.7, J_{HP}=5.5, H_α), 8.51 (dd, J_{HH}=11.7, J_{HP}=0.9, H_β).

Typical ROMP experiment: A solution of 15 mg of catalyst in 0.5mL of benzene is added to a stirring solution of 100 of equivalents of monomer in 0.5mL of the same solvent under inert atmosphere. The reaction is allowed to stir for 15 minutes, at which point it is quickly transferred into a rapidly stirring excess (>25 mL) of methanol (in air). The precipitated polymer is decanted from the methanol, dissolved in methylene chloride and passed through a silica column to remove catalyst decomposition products, and again precipitated into methanol before being dried under vacuum before a 10mg sample is dissolved in 2mL of methylene chloride for analysis by Gel Permeation Chromatography (GPC).

Typical Temperature controlled ROMP experiment: A solution of 15 mg of catalyst in 0.5 mL of benzene is added to a stirring solution of 100 of equivalents of monomer in 0.5 mL of the same solvent under inert atmosphere. The reaction is heated for (a) norbornene:1 hour at 65°C, (b) cyclooctene:24 hours at 65°C, after which point it is quickly transferred into a rapidly stirring excess (>25 mL) of methanol (in air). The precipitated polymer is decanted from the methanol, dissolved in methylene chloride and passed through a silica column to remove catalyst decomposition products, and again precipitated into methanol before being dried under vacuum before a 10mg sample is dissolved in 2mL of methylene chloride for analysis by GPC.

Typical RCM experiment: To A solution of 15 mg of catalyst in 0.5 mL of benzene is added approximately 50 equivalents of the corresponding diene or diene-yne in 0.5 mL of the same solvent. The reaction was allowed to stir for several hours, the reaction mixture then exposed to air and passed through a short silica gel column. The remaining solvent is removed, and the organic residue analyzed by NMR and GC/MS.

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Appendix 1

How to Turn Your Graduate Research into an Undergraduate Laboratory:

Introduction to Metathesis: Synthesis and Reactivity of a Ruthenium Carbene

Abstract:

What follows is the transformation of a graduate research project into a laboratory experiment in an advanced undergraduate lab. Students make $Ru(H)(H_2)Cl(PCy_3)_2$ and transform it into the carbene $(PCy_3)_2Cl_2Ru(=CH-CH=CMe_2)$ with 3-chloro-3-methyl-1-butyne. This carbene is then used to: polymerize a substituted norbornene, ring close diethyl-diallyl malonate both by NMR and preparatively, and to make a poly-dicyclopentadiene mold. It exposes students to the techniques necessary for inert atmosphere chemistry (drybox and vacuum line techniques) without dealing with any totally unforgiving compounds.

Project: Introduction to Metathesis: Synthesis and Reactivity of a Ruthenium Carbene

Olefin metathesis has received increasing attention recently, with applications varying from the generation of polymers to the construction of macrocyclic peptide systems. Initially (and still industrially in some cases) performed with heterogeneous systems like $WCl_6/AlCl_3$, well characterized homogeneous systems have been developed, all containing a transition metal alkylidene (carbene). The generalized mechanism for metathesis is shown below (Figure 1). In this scheme, a metal carbene reacts with an olefin to form a

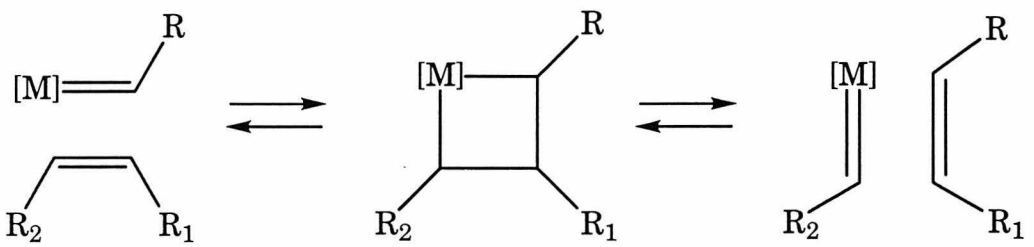

Figure 1-Generalized Metathesis Pathway

metallacyclobutane, which then either unproductively cleaves to form the starting materials, or productively cleaves to form a new metal carbene and a new olefin.

If, however, the olefin used is cyclic, then the resulting carbene and new olefin generated are tethered together by the backbone of the cyclic olefin. This process is suitably named Ring Opening Metathesis Polymerization (ROMP, Figure 2). The process ends when the reaction is terminated, usually by forming an inactive carbene species by cleaving the polymer from the metal center.

Another example of olefin metathesis is evident with reaction of an α–ω diene (where there is a diene at each end of a linear molecule) and a metal

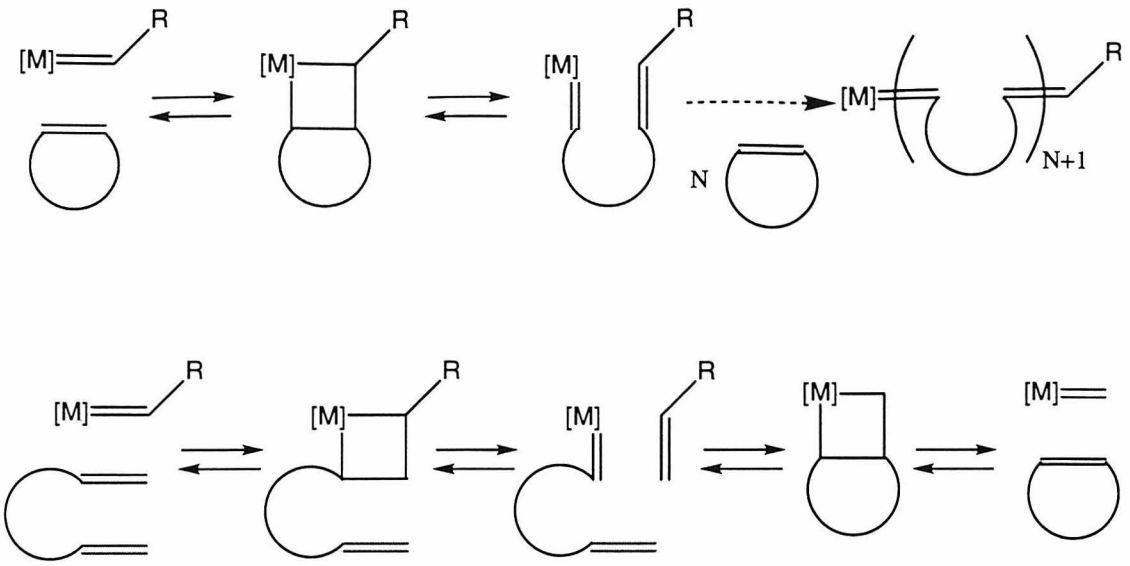

Figure 2-ROMP and RCM General Pathways

carbene. In this case, initial reaction with either olefin generates a metal carbene with the second olefin tethered to the metal. This second olefin reacts with the new carbene to form the second metallacycle. When this metallacyclobutane eliminates, it forms the metal-methylidene ($M=CH_2$) and a cyclic olefin (Figure 2). The methylidene serves as the catalyst for all subsuquent reactions, and the process is called Ring Closing Metathesis (RCM).

Some other types of metathesis reactions include: Acyclic Diene Metathesis Polymerization (ADMET), alkyne polymerization, and carbonyl olefination.

The choice of metal carbene moiety significantly affects the type of reactions which will occur. Carbenes of the early transition metals (W, Mo) are very reactive, but the reactivity has the trade off that they are also extremely sensitive to reaction conditions. Mo and W catalysts are sensitive to water, oxygen, protic solvents, and some functionalities (in some cases reacting with your functionality rather than your olefin; reactions are often cleanly killed with ketones, because the catalyst would rather react with a ketone than with an olefin). In addition to their sensitivities, these complexes are often very difficult to synthesize.

In comparison to the early metal systems, late metal systems show significant reactivity, while also having increased tolerances to many situations. The carbenes, developed by Grubbs, with the general formula $(PR_3)(Cl)_2Ru{=}CHR$ show stability to air, water (even to the extent of being able to conduct reactions in aqueous media), acids, and many functionalities. Generally, the preferred catalyst system involved tricyclohexylphosphine, because higher activity is seen with more electron donating phosphines, and very bulky phosphines. Electron donating ability goes roughly with the number of alkyl groups in the phosphine (more alkyl groups the more donating), and steric bulk generally follows standard steric arguments.

Initial preparations of these ruthenium catalysts are very simplistic reactions, especially compared to the preparation of the Mo and W systems. In these reactions a ruthenium(II) precursor, $Ru(Cl)_2(PPh_3)_3$ is reacted with either 3,3-diphenylcyclopropene or phenyldiazomethane, to generate the intermediate carbenes $(PPh_3)_2(Cl)_2Ru{=}CHR$ (R= $-CH{=}CPh_2$ or Ph, respectively) which then undergo a phosphine exchange to provide the tricyclohexylphosphine sys-

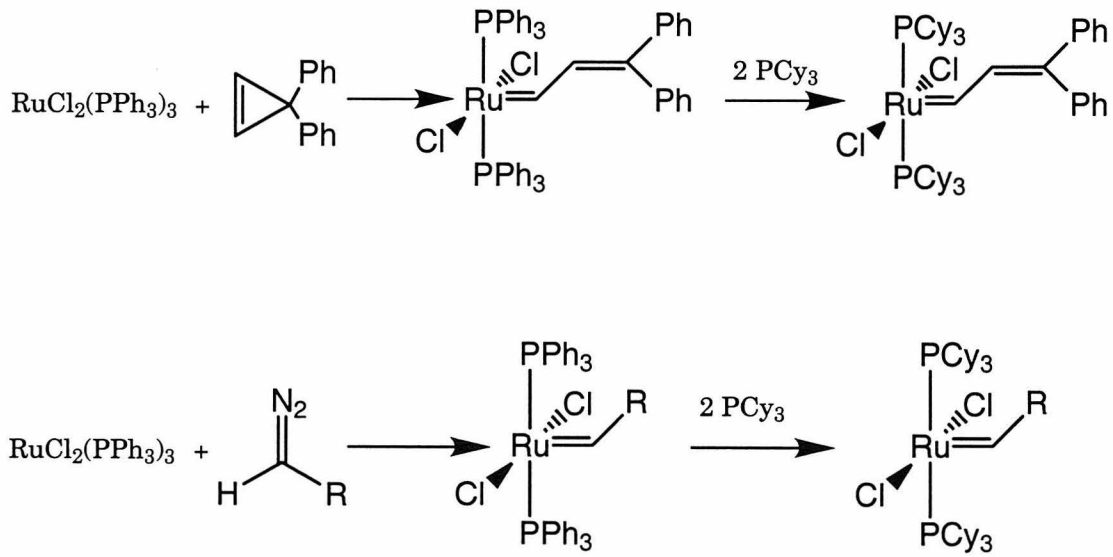

Figure 3-Original preparations of ruthenium carbenes

tems. The phosphine exchange is for two reasons, the first being the increase in activity gained with more electron donating phosphines, and the second being increased stability. Unfortunately there is significant difficulty realized in the preparation of both of these systems. For the former, the cyclopropene is not the easiest organic molecule to synthesize, and tends to decompose over time. For the latter, diazo compounds have an unfortunate tendency to explode–not something particularly desirable in a reagent. In addition to these difficulties, the reactions are not very efficient in reagents, and the yields are in the moderately high region (<70%).

More recently, the Grubbs group has focused on a more efficient method of catalyst generation which uses metal hydrides. These reactions have proven to be extremely high yield, require no complicated or dangerous organic reactions, require no excess phosphine, and are very easy to conduct.

In this experiment, you will make the metal hydride starting material, $Ru(H)(H_2)Cl(PCy_3)_2$, and use the hydride to make a ruthenium catalyst, $(PCy_3)(Cl)_2Ru{=}CH\text{-}CH{=}CMe_2$. Once the catalyst has been made, you will perform a ring opening metathesis polymerization and a ring closing metathesis.

Procedure:

This synthesis is with all commercially available reagents, and if you were to perform the reactions with no time constraint you would start with ruthenium(III) chloride. In the interest of time conservation, however, we will only discuss the first step and your TA will provide you with the resulting material, as well as some other starting materials for subsuquent steps.

All reagents for the first step should be carefully degassed. Dryness is nice, but not essential. Usually, the alcohol solvents are bought anhydrous,

degassed by bubbling argon through them for 30 minutes to one hour, and then stored in an air tight Strauss flask. 3,3-Dimethylpropargyl chloride should also be degassed, using the freeze-pump-thaw method to remove air. This reagent should also be completely colorless. If there is any yellowing to the liquid, pass it through a short plug of silica prior to degassing. This should remove any color, and the impurities which affect your reaction.

Part 1:Generation of the Carbene

Step 1: $[RuCl_2(COD)]_x$

This polymeric ruthenium(II) starting material is made by refluxing an ethanol suspension of $RuCl_3*H_2O$ with excess cyclooctadiene. In a round bottom flask 10g of ruthenium(III) chloride is placed, and 200mL of absolute ethanol is added. Excess (10 equivalents) of 1,5-cyclooctadiene is added, along with a reflux condenser and a stopcock connection to the vacuum line. Argon is purged through the system for ten minutes to remove air, then closed and exposed to a bubbler and then placed in an oil bath. The reaction is refluxed for one to three days, during which time a brown solid precipitates. The reaction is cooled, and the solid isolated on a medium frit and washed with ethanol. The brown solid is then placed in a schlenk tube, sealed, and placed under vacuum to dry, and then taken in the drybox where it is weighed and stored. Expected yield 95-97% of $[RuCl_2(COD)]_x$.

Obtain this brown powder in the drybox.

Step 2: $Ru(H)(H_2)Cl(PCy_3)_2$

In the interest of time and limited glassware, this reaction will be done in pairs.

CAUTION: This is a reaction done at >1atm pressure. Even though the bottles are designed for considerably more pressure than we will use it is **ABSOLUTELY NECESSARY** to use a **SHIELD** during the reaction.

A suitably sized, thick walled Fisher-Porter reaction vessel, equipped with a magnetic stir bar, and an apparatus which allows connection to a vacuum line, addition of solvent and other reagents, pressure regulation and measurement, and an overpressure vent (your TA has these assemblies put together already) is taken into the drybox. To this bottle, add 500mg of the $[RuCl_2(COD)]_x$ polymer from the box, and two equivalents of tricyclohexylphosphine. Put the assembly together (screw together the two parts) and make sure all the valves are closed before bringing out of the drybox.

Outside of the box, connect the bottle assembly to the vacuum line, and pump/backfill at least three cycles to remove air from the tubing. At this point also connect the Srauss flask with triethylamine and sec-butanol. Pump/backfill these hoses as well. You will use the top valve to add solvent and other reagents, just as if it were a septum.

Once all this is accomplished, add 1 equivalent of triethylamine, and approximately 20mL of sec-butanol, the former via a syringe and the latter by cannula transfer.

Make sure the next part is done in the hood, that way excess hydrogen is removed from the room. Seal the bottle again, and connect it to the hydrogen tank. Loosely connect the metal tubing to the bottle, and turn on a slow flow of hydrogen to purge the outside of the system. After purging the tubing for about

30 seconds, tighten the connection and open the valve to the bottle assembly, allowing hydrogen into the system. Open the purge valve and purge out the bottle for about 60 seconds. Close the top valve, and increase the pressure until the pressure gauge on the system reads about 24psi, and then close the source valve, and all the valves on the hydrogen tank. Remove the connection to the hydrogen tank.

Go back to your work area, and place the bottle in an 80°C oil bath, making sure to shield the vessel.

Watch the pressure, and if the internal pressure goes below 1atm (14psi) remove the flask from the oil bath (keep behind the shield) and allow to cool to room temperature. Reconnect to the hydrogen tank as before, and increase the internal pressure to 24psi. Repeat as necessary.

The reaction will take from 3-6 hours in the oil bath, and is done when there is an orange solid precipitated from solution, and there is no hydrogen consumption. At this point, remove from the oil bath and allow to cool (again, behind the shield). Connect to the vacuum line again.

At this point there are 3 options:

a)Isolate the orange solid (AIR SENSITIVE): Add a volume of methanol to the solution, ensuring complete precipitation. Cannula filter the solution, keeping the orange solid in the bottle. Wash three times with appropriate portions of methanol, until the washings are clear. Dry and isolate the solid. Take an NMR and observe the hyrdide shift at -17ppm.

b)Add a volume of methylene chloride, to partially solublize the orange solid, and continue to the next part.

c)Continue to the next part without doing anything.

Step 3:Preparation of the carbene

This section will be done individually or in pairs, depending on the method chosen at the end of part 2. The basic idea is to add 3,3-dimethylpropargyl chloride to the ruthenium hydride generated in part 2, which reacts to give carbene.

If you did part a)

Dissolve the orange solid in 50mL of degassed methylene chloride. Cool this solution to -30°C by slowly adding dry ice to acetone, monitoring with a thermometer. When the solution is cooled, inject one equivalent of the propargyl chloride, and watch the solution change color instantly. Allow to stir for 15 minutes, then concentrate the solution on the vacuum line until about 5mL of solvent remains. Proceed to the end of this section.

If you did part b)

Take the solution/suspension of the orange hydride from above, to which 50mL of methylene chloride has been added, and cool to 0°C. When the solution is cooled, add 3 equivalents of dimethylpropargyl chloride, and allow the reaction to stir for 30 minutes-60 minutes, until the solid is decidedly purple. Place the bottle under vacuum, until the volume is back to approximately 50mL (you are removing the methylene chloride), and proceed to the end of this section.

If you did part c)

Take the suspension of the orange solid, and cool to 0°C. When the solution is cool, add 3 equivalents of dimethylpropargyl chloride, and allow to stir

for 2 hours, or until the solid is completely purple. Proceed to the end of this section.

For all parts, a, b, and c:

Add a volume of methanol. If need be, scrape the sides of the flask by moving the stir bar from the outside with a magnet. Stir until all purple solid is precipitated. Cannula filter the solid, washing three times with methanol, or until the washings are clear. Dry and isolate the solid. Expected yield: 95%.

Take an NMR of the carbene in benzene or methylene chloride. Make sure the hydride is gone, and note the shifts of the alpha and beta protons. Get NMR data from someone else for the solvent you did not choose.

Discussion:

You have just made a hydride from hydrogen and a ruthenium(II) starting material, and then used that hydride to make carbene. Hopefully you are now wondering how these transformations occurred. These types of complexes, both the hydrides and carbenes are well known for ruthenium and osmium.

The first part, generation of the hyrdide, occurs by simple acid-base chemistry. Part of the proposed mechanism is shown below (Figure 4). In this mechanism, the cyclooctadiene coordinated in the beginning is completely hydrogenated to cyclooctene. Along the way, the ruthenium(IV) (dihydride-dichloride-bisphosphine) is generated as well, and in this reaction is in equilibrium with the hydrido-chloride, which is our desired product (equation B). The triethylamine serves to shift the equilibrium to the desired product by soaking up the acid generated.

Propose the remainder of the mechanism, and suggest experiments to

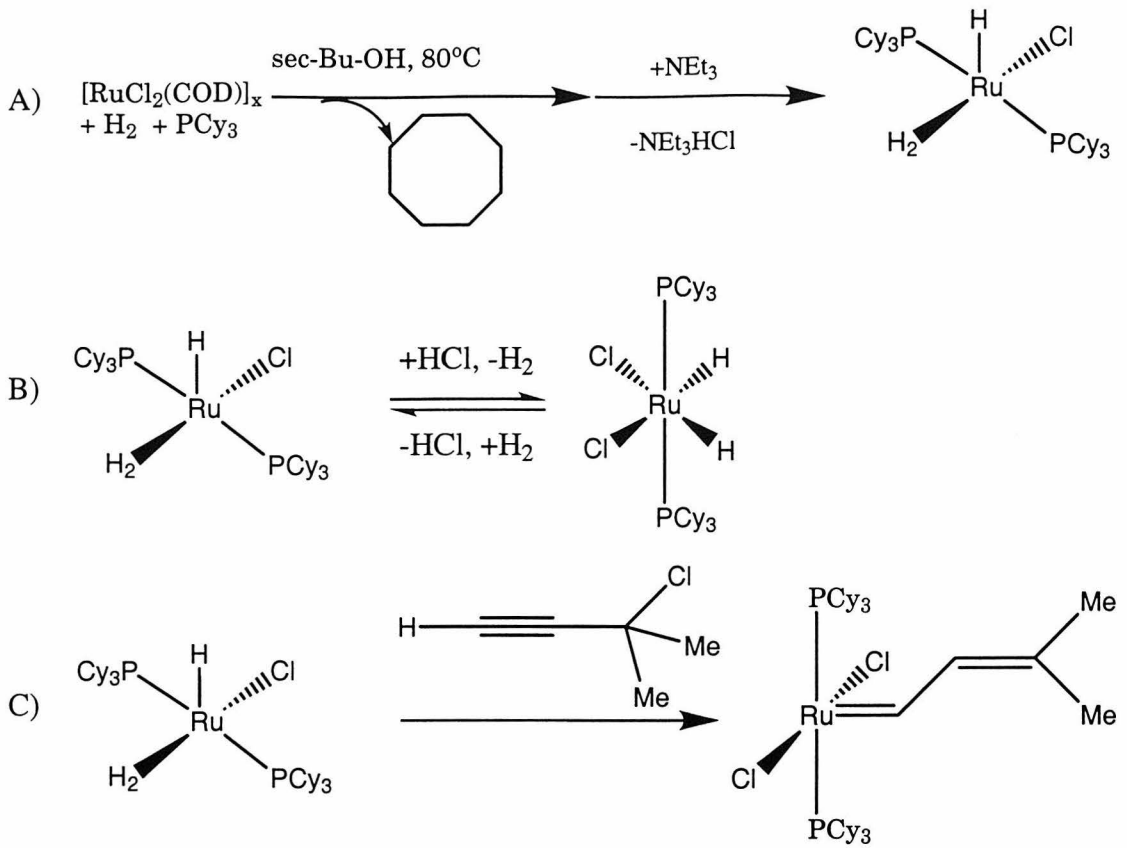

Figure 4-Project Transformations

support your proposal. Hints: The first hydride should come from the alcohol itself, dihydrogen must be split, and cyclooctadiene must be hydrogenated. Other possibly useful information: A secondary alcohol must be used, otherwise decarbonylation occurs to yield a hydrido-carbonyl complex rather than a hydrido-dihydrogen complex. In the absence of base, that is with only two equivalents of phosphine, the reaction does proceed, but only in 30-40% yield. The hydrido-hydride is a well known hydrogenation catalyst.

To generate the carbene, the first steps involve coordination of the alkyne and insertion into the alkyne triple bond by the metal hydride to give a metal vinyl complex. This is a well known process, and for a similar type of reaction this pendant vinyl compound can actually be isolated, and forced to rearrange to give a carbene (Figure 5). Given this insertion process, propose a mechanism

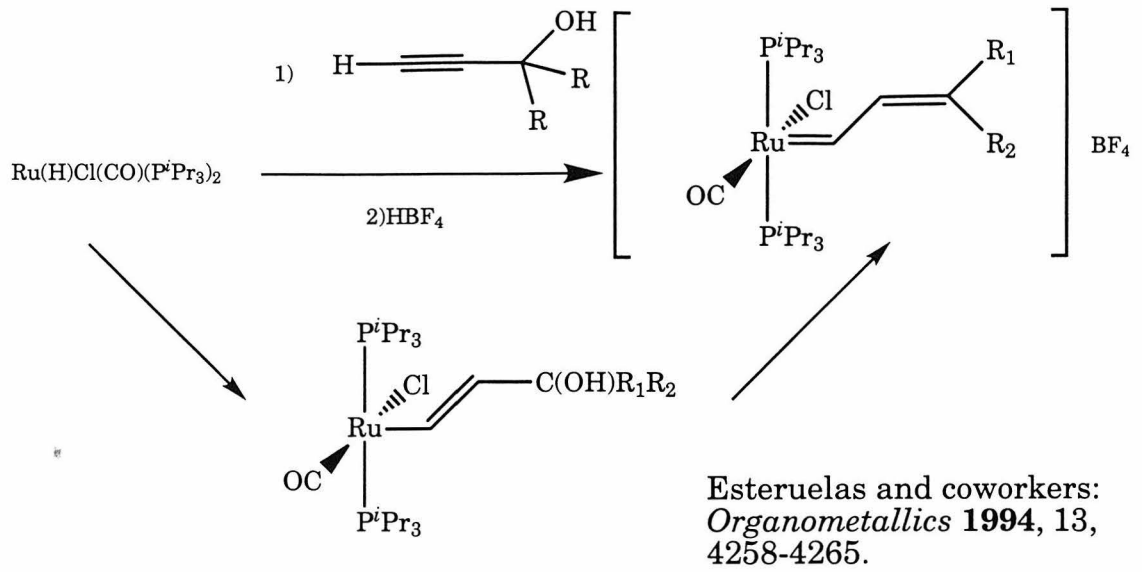

Figure 5-Insertion with CO complex

for the transformation of the pendant vinyl complex to the carbene, giving two possible pathways. Suggest experiments to support your proposal.

Part 2:Examiniation of Reactivity

As mentioned in the introduction, there are many different types of olefin metathesis which can be examined with a metal carbene complex. In this experiment, you will do three reactions. The first will be to make a polymer, and examine its properties. The second will to conduct a ring-closing metathesis, monitoring first by NMR, and then on a preparative scale. Finally, if time and amount of catalyst allows, you will make a solid mold of polydicyclopentadiene, by making a polymer, taking that viscous liquid polymer/oil and crosslinking to give a solid, amber colored mold which you can take home.

Step 1:Polynorbornene analog

Norbornene, bicyclo[2.2.1]-hept-5-ene, is a classical test for olefin metathesis activity. It's high strain energy provides an excellent driving force for the polymerization. Unfortunately, this is often too much of a driving force, and

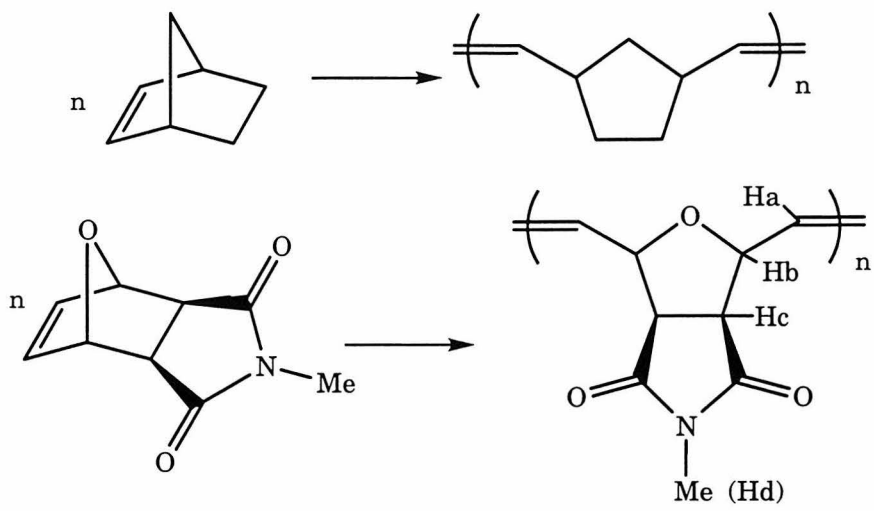

Figure 6-Norbornenes

the reagent itself is so easily polymerized it is not a very useful experiment from which other than qualitative data is obtained. In this experiment, you will use a norbornene analog: exo-N-methyl-7-oxabicyclo[2.2.1]-hept-5-ene-2,3-dicarboximide. Examples of these monomers and their resulting polymers are shown in Figure 6.

In concern for the amount of time, and the danger in preparing the monomer, you will be given the norbornene analog. It is made by a Diels-Alder condensation between furan and N-methylmaleamide in ether at 90°C (hence the danger).

Prepare in the box a schlenk flask with a measured amount of catalyst, about 10 mg. Take it outside, connect to your vacuum line, and cannula trans-

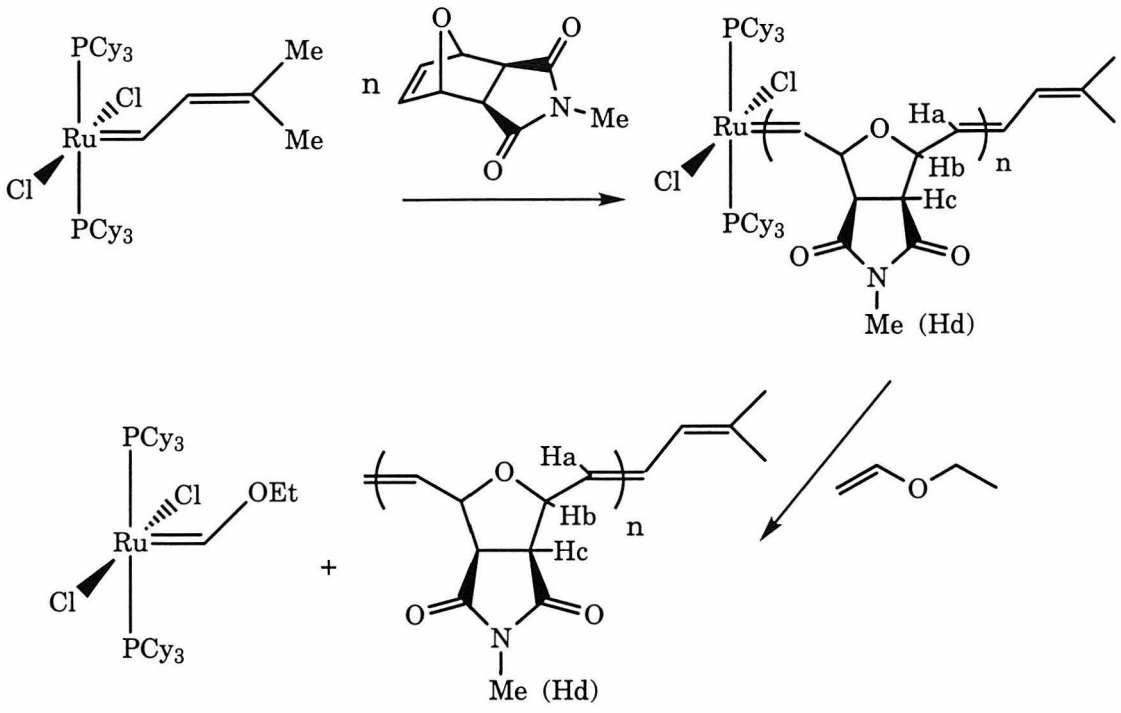

Figure 7- Polymerization Pathway

fer 20mL of methylene chloride into the flask. Under a gentle flow of argon, add in 100-200 equivalents of monomer. Stir at room temperature. The reaction should be done in an hour, at which point you need to terminate and precipitate the polymer. To your solution of polymer (if it is very viscous add more solvent) add 1-2mL of ethyl-vinyl ether. This forms a Fisher type carbene, which is inactive towards metathesis, and cleaves your polymer (Figure 7).

In a large erlenmeyer flask, place 250 mL of methanol. Stir this very rapidly, and slowly pipette your solution of polymer into the top, dropwise. Your polymer should be a white solid, which can be isolated on a buchner funnel. Collect the polymer, and dry under vacuum. Measure the yield, and take an NMR of the polymer in benzene. You should see six peaks. Two should be relatively sharp, representing the N-methyl hydrogens (H_d), and the "bridgehead" hydrogens (H_c). Since the resulting olefin can be cis or trans, the remain-

ing peaks come in two sets–one set for the trans and one for the cis (H_a and H_b). To help you in peak assignments, the majority of the polymer will be trans.

To determine the molecular weight, we use a gel permeation chromatographic method. This will be done if there is time in the Grubbs lab. GPC works on a size exclusive principle, with the lower molecular weight polymer being complexed on the column more effectively, and thus having a longer retention time. The GPC trace is then compared with a standarized spreadsheet, and a relative set of molecular weights is determined.

Step 2: RCM

One of the most facile RCM transformations is with the commercially available diethyl-diallyl malonate. To prepare this reagent, it should be degassed as above. Make sure to take and NMR of the pure reagent, so you know which peaks are starting material.

First, prepare an NMR reaction in methylene chloride to observe the rate of reaction. In the drybox, make an NMR tube with the following conditions: 0.2M diene, 0.01M catalyst and a ratio of 20 to 1 monomer:catalyst. Make sure to note the exact time of mixing of the two reagents– the best way to do this is to make a solution of known concentration diene, and add a known volume of this solution to your NMR tube in with the catalyst has already been measured. Do this only when you know you will be able to monitor almost immediately by NMR. Take NMR's of your reaction at as close to addition as possible, then 5, 10, 15, 20, 30, 45, and 60 minutes. Continue every 30 minutes until the reaction is complete.

Look for the following in your spectra: New carbene (the methylidene is

the propagating species), starting carbene, starting diene, ring-closed product. For determining how far the reaction has gone, compare the integration of the starting material and product in the alkyl region (look for the proton next to the olefin, not the olefinic proton itself). One of these two (starting material and product) is a doublet, the other a singlet, but their integration is reflective of the same number of protons.

Take your time versus percent complete data and make a graph of the reaction's progress. Attempt to fit the data to a line (it will not be linear), and

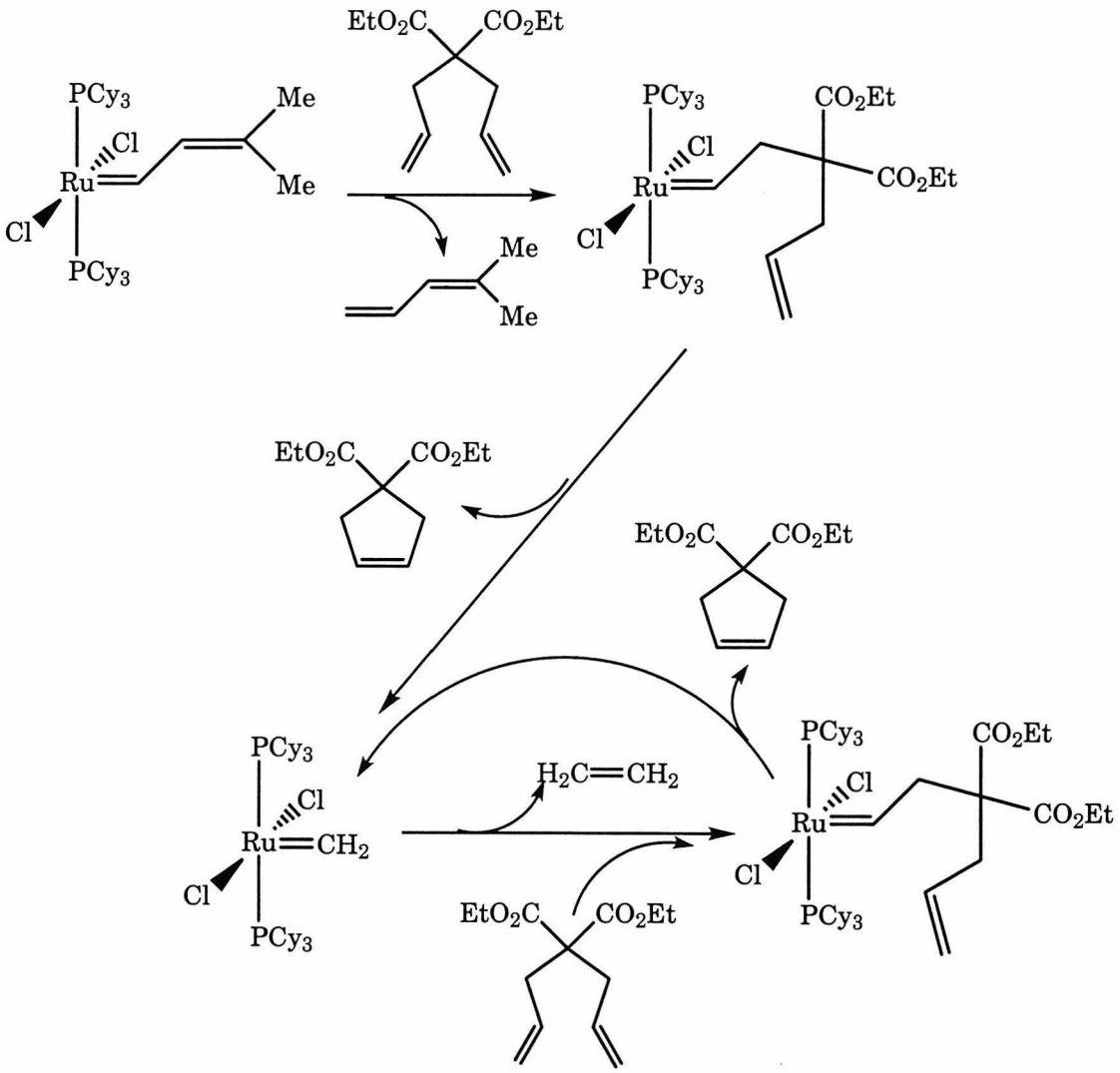

Figure 8-RCM Pathway

use this equation to derive how many turnovers you get in one hour.

Now that you have an idea for how long the reaction will take, do a preparative scale, starting with 0.5 gram of diene, and the same concentration/ ratio conditions as your NMR experiment. Do the reaction in a large schlenk flask on your line, in degassed methylene chloride. Add the diene via syringe, and periodically place your flask under dynamic vacuum for a few seconds to remove the gas generated by your reaction, and force the reaction to completion.

After the reaction is completed, you will need to isolate your product. This can be accomplished by distillation or column. With the amount of product generated, the most effective way is probably to run a column. If you think a distillation would be easier talk with your TA. To run the column, start by taking a TLC of your product in 10% ethylacetate in hexanes. Your product will be the spot with the highest R_f. Construct a 10cm silica gel column with the same solvent and isolate your spot. You can use 50-100 mL collections, testing each for your product.

When you have isolated your pure product, make sure to get a yield and an NMR.

Step 3:Make your own mold

If time allows, you will make a crosslinked polymer mold, which you can then take home. For this experiment, you will need a glass vessel, preferably one with a wide opening and with a volume of 200-300mL. This will be broken in the experiment, so don't choose anything expensive or irreplaceable. Small mineral water bottles work well, but you can use almost anything that is glass and breakable.

The polymer you will be making is dicyclopentadiene (DCPD), which is the Diels-Alder product of two cyclopentadiene molecules. If you draw out the structure you will see that there are two double bonds–one reminiscent of the norbornene you polymerized before. This will be the bond to initially polymerize, and while this is happening the reaction will exotherm. It is this exotherm, and the fact that you will pour it into a hot glass vessel, that will cause the crosslinking to give a very durable material.

First, measure the approximate volume of your vessel, leaving room at the top for expansion. This is the amount of DCPD you will use. Measure (roughly) this amount of DCPD into an erlenmeyer flask with a large stir bar at the bottom. The DCPD will already be degassed, but setup a flow of argon from your line into the opening, to prevent lots of air getting in the reaction (do this by gently placing a disposable pipette into one of the pieces of tubing connected to your line and gently clamping it at the insertion point.

Place your chosen glass vessel in an oven at 100°C for at least 30 minutes prior to setting up the rest of this reaction. Measure out enough catalyst to be in a ratio of 7000:1 monomer:catalyst, and dissolve this in a minimum amount of degassed methylene chloride. Add this quickly to the flask with DCPD. At this point remove your glass vessel from the oven, and place in a secure location in your hood. Have the shield ready, because the expansion of the DCPD once it is hot will most likely be enough to break the vessel you chose. This will not be a particularly violent break, but there is always the possiblity that a piece of glass will go further than expected. Most likely the glass will simply crack and will remain whole and on the outside of your mold.

When the reaction has become viscous (there is a fine line here between viscous and too viscous to pour) you will pour it into the hot mold. This can take anywhere from 60 seconds to several minutes. Have a magnet in hand to keep

the stir bar from being permanently held in your mold. Use the magnet to hold the stir bar at the bottom of the erlenmeyer and pour the reaction into the mold. Quickly put the shield in front of the vessel, and add some methylene chloride to the erlenmeyer with the stir bar to solublize the remainder of the polymer mixture. If you don't get it out now it will be very difficult later.

Wait for the reaction to solidify (will take less than 5 minutes), probably indicated by the expansion of the solid and breaking of your mold. In most cases while the mold is solid, it is not completely cured. To accomplish curing, carefully remove the glass from the outside of the mold. Use thick leather gloves, remembering how sharp broken glass can be. When this is accomplished, place the mold in a 100°C oven for an hour or two, or overnight.

Notes to teaching assistants:

What preceeds is a chapter of a lab manual for an advanced organic and inorganic laboratory course at Caltech. Below are a few specifics not presented in the manual, and why.

You will note that there are very few references in the lab manual. This was purposefully done because most of the answers to questions posed in the chapter are in the literature. Not giving the references directly means that if the students wish to read articles they must at least learn how to search for them in the library. A list of references which might be helpful to you, the TA's, will follow.

After doing this lab for a term, we discovered several important aspects of how undergraduates interpret instructions. In particular, they did not understand that "add a volume of methanol" means to double the current volume by adding methanol, nor that to run the 3-chloro-3-methyl-1-butyne through a short plug of silica does not mean to run a column. Pushing this material through a pipette filter of silica gel, however, is essential to the success of the reaction. Degassing this reagent is not necessary on the scale used.

Solvents used are all degassed by bubbling inert gas through them for at least 30 minutes. Degassed solvents are absolutely necessary in the preparation of the hydride. If this compound is exposed to air, it will turn black. As far as the generation of the carbene, suggest the pathway where the students do absolutely nothing to the hydride. This will give the best yields. Addition of solvent to solublize the hydride tends to give some decomposition.

The DCPD mold is a very tricky thing. I would suggest the TA's attempt this reaction several times so that they can get a feel for the colors and viscosi-

ties which occur in the reactions. In addition, because of the impurities in most purchased DCPD (Aldrich is only 95%), the reasonable time polymerization may require gentle heating with a heat gun.

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Appendix 2

X-Ray Diffraction Experiment for
$W(O)Cl_2(PMePh_2)_2(\eta^2$-diphenylcyclopropene)
Chapter 2 Compound **3**

Structure by
Michael W. Day

Beckman Institute
X-Ray Crystallography Laboratory
California Institute of Technology

Presented in: Day, M. W.; Wilhelm, T. E.; Grubbs, R. H. *Acta Crystallographica Section C, Crystal Structure Communications* **1996**, *52*, 2460-2462.

Table 1-Crystal data and structure refinement for **3**.

Empirical formula	$C_{41}H_{38}Cl_2OP_2W$	
Formula weight	863.40	
Crystallization Solvent		
Crystal Habit	Thick needles	
Crystal size	0.4 x 0.2 x 0.2 mm^3	
Crystal color	Colorless	
Data Collection		
Preliminary Photos		
Type of diffractometer	CAD-4	
Wavelength	0.71073 Å MoKa	
Data Collection Temperature	293(2) K	
Theta range for reflections used		
in lattice determination	9.5 to 10.3°	
Unit cell dimensions	a = 18.494(8) Å	a= 90°
	b = 9.857(3) Å	b= 100.83(3)°
	c = 20.886(8) Å	g = 90°
Volume	3740(2) $Å^3$	
Z	4	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Density (calculated)	1.534 Mg/m^3	
F(000)	1720	
Theta range for data collection	1.99 to 22.48°	
Completeness to theta = 22.48°	100.0 %	
Index ranges	-19<=h<=19, 0<=k<=10, -22<=l<=22	
Data collection scan type	Omega scans	

Table 1 (continued)

Reflections collected	11266
Independent reflections	4881 [R_{int}= 0.034; GOF_{merge}=]
Absorption coefficient	3.348 mm^{-1}
Absorption correction	Psi
Max. and min. transmission	1.00 and 0.82
Number of standards	3 reflections measured every 60min.
Variation of standards	Within counting statisics, zero%.

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Patterson method
Secondary solution method	Difference Forier map
Hydrogen placement	Calculated sites
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	4881 / 0 / 424
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.434
Final R indices [I>2s(I)]	R1 = 0.0362, wR2 = 0.0619
R indices (all data)	R1 = 0.0658, wR2 = 0.0708
Type of weighting scheme used	Sigma
Weighting scheme used	w=1/s^2^(Fo^2^)+(0.0000P)
Max shift/error	0.002
Average shift/error	0.000
Largest diff. peak and hole	1.379 and -0.733 e.$Å^{-3}$

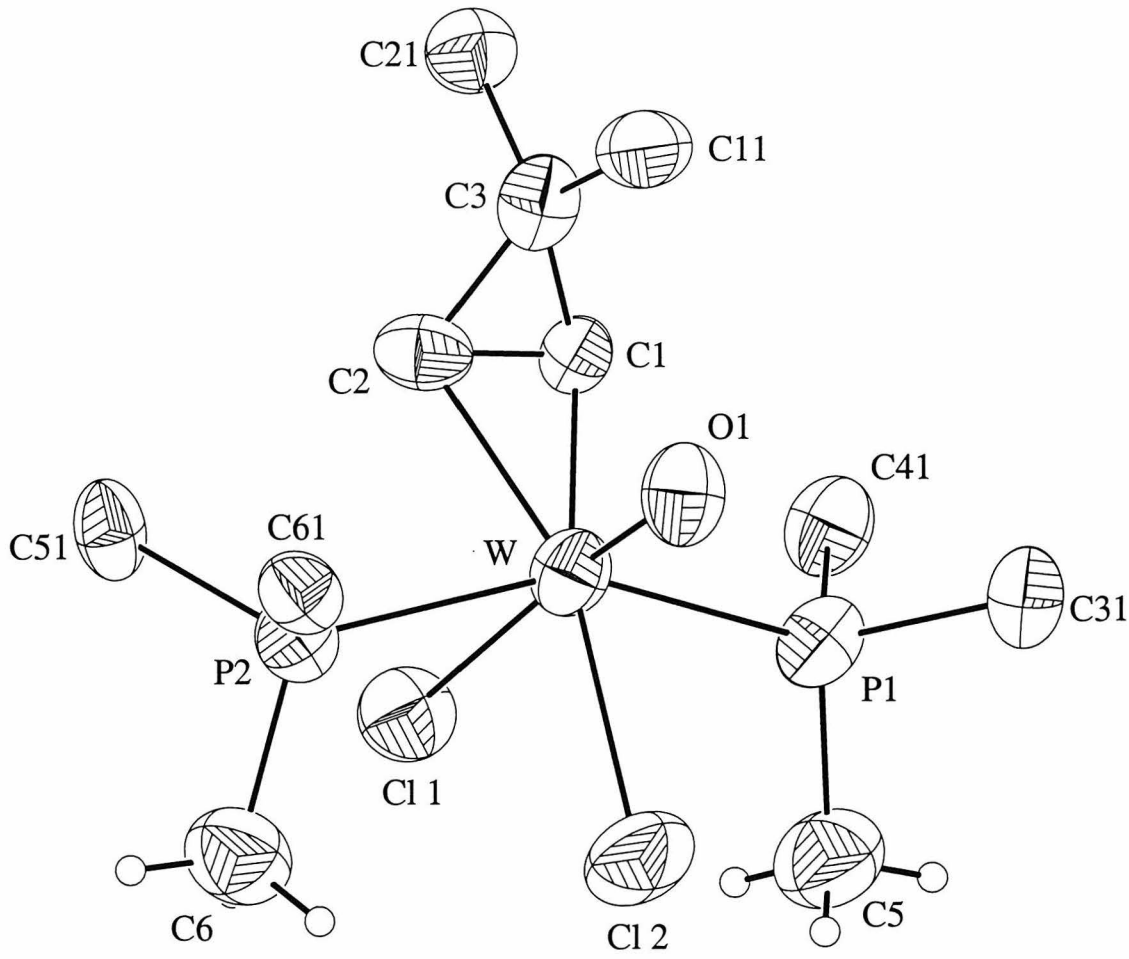

Figure 1- Labeled view of **3** with 50%probability ellipsoids; Hydrogen atoms and phenyl rings have been omitted for clarity

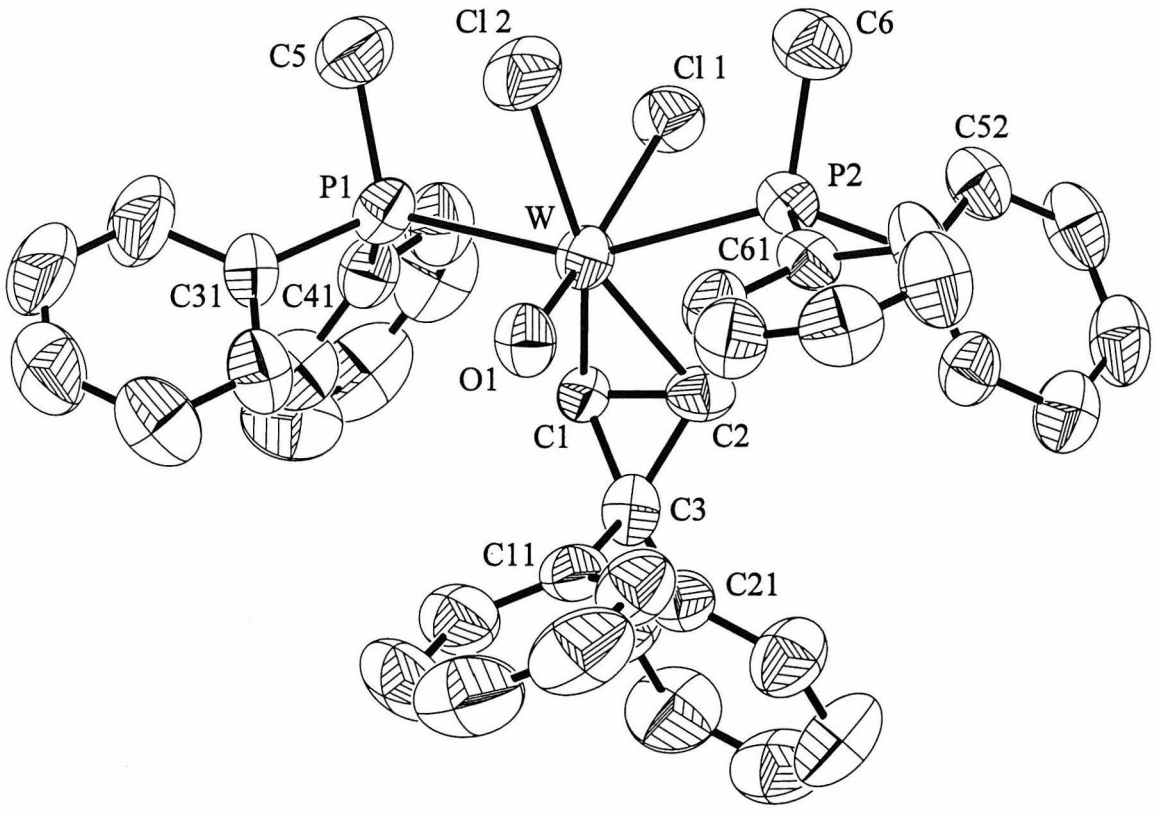

Figure 2- Labeled view of **3** with 50% probability ellipsoids, hydrogen atoms have been omitted for clarity.

Table 2-Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3**. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
W	3136(1)	4274(1)	6131(1)	48(1)
Cl(1)	3605(1)	2450(2)	5494(1)	61(1)
Cl(2)	4346(1)	5363(2)	6169(1)	76(1)
P(1)	2908(1)	5501(2)	5015(1)	54(1)
P(2)	3901(1)	2891(2)	7082(1)	49(1)
O(1)	2902(2)	5577(4)	6579(2)	54(1)
C(1)	2050(4)	3599(6)	5727(3)	48(2)
C(2)	2328(3)	2866(7)	6322(3)	50(2)
C(3)	1593(4)	3543(7)	6251(3)	49(2)
C(5)	3697(4)	5525(8)	4610(4)	78(2)
C(6)	4843(3)	2633(8)	7000(4)	73(2)
C(11)	1453(4)	4759(7)	6644(4)	55(2)
C(12)	1703(5)	4810(9)	7310(4)	78(3)
C(13)	1532(6)	5937(12)	7664(5)	109(4)
C(14)	1135(6)	6985(12)	7363(7)	114(4)
C(15)	896(5)	6976(10)	6693(6)	105(4)
C(16)	1053(4)	5829(9)	6343(4)	76(2)
C(21)	938(4)	2596(7)	6136(3)	51(2)
C(22)	803(5)	1762(8)	6621(4)	78(3)
C(23)	209(6)	878(10)	6527(5)	102(3)
C(24)	-263(5)	853(10)	5937(5)	95(3)
C(25)	-129(5)	1673(10)	5449(5)	97(3)
C(26)	470(4)	2553(9)	5539(4)	77(3)

Table 2 (continued)

C(31)	2629(4)	7268(7)	5063(4)	56(2)
C(32)	2743(6)	8191(9)	4608(5)	114(4)
C(33)	2507(6)	9511(10)	4633(6)	123(4)
C(34)	2143(5)	9922(9)	5103(6)	92(3)
C(35)	2006(5)	9015(10)	5558(4)	88(3)
C(36)	2258(5)	7676(8)	5535(4)	74(2)
C(41)	2184(4)	4802(8)	4391(3)	56(2)
C(42)	2290(5)	3544(9)	4110(4)	72(2)
C(43)	1727(6)	2935(10)	3663(4)	88(3)
C(44)	1065(6)	3613(13)	3512(4)	104(4)
C(45)	949(5)	4853(12)	3779(4)	98(3)
C(46)	1509(5)	5419(9)	4218(4)	74(2)
C(51)	3566(4)	1183(6)	7187(3)	49(2)
C(52)	3796(4)	89(7)	6853(4)	60(2)
C(53)	3513(5)	-1186(7)	6916(4)	69(2)
C(54)	2987(5)	-1394(8)	7296(4)	73(3)
C(55)	2757(5)	-304(8)	7628(4)	70(2)
C(56)	3044(4)	965(7)	7570(3)	58(2)
C(61)	3990(4)	3633(7)	7889(3)	47(2)
C(62)	3799(4)	4956(8)	7974(4)	60(2)
C(63)	3930(5)	5533(9)	8591(4)	77(2)
C(64)	4251(5)	4784(10)	9120(4)	76(3)
C(65)	4446(5)	3480(10)	9044(4)	84(3)
C(66)	4319(4)	2907(8)	8431(4)	71(2)

Table 3-Bond lengths [Å] and angles [°] for **3.**

W-O(1)	1.692(4)	C(11)-C(16)	1.371(10)
W-C(2)	2.131(7)	C(11)-C(12)	1.382(10)
W-C(1)	2.133(7)	C(12)-C(13)	1.403(11)
W-Cl(2)	2.471(2)	C(12)-H(12)	0.9300
W-Cl(1)	2.4872(19)	C(13)-C(14)	1.351(13)
W-P(1)	2.590(2)	C(13)-H(13)	0.9300
W-P(2)	2.598(2)	C(14)-C(15)	1.385(13)
P(1)-C(5)	1.818(7)	C(14)-H(14)	0.9300
P(1)-C(41)	1.819(7)	C(15)-C(16)	1.406(11)
P(1)-C(31)	1.825(7)	C(15)-H(15)	0.9300
P(2)-C(6)	1.800(7)	C(16)-H(16)	0.9300
P(2)-C(61)	1.818(7)	C(21)-C(22)	1.364(9)
P(2)-C(51)	1.821(7)	C(21)-C(26)	1.378(9)
C(1)-C(2)	1.447(8)	C(22)-C(23)	1.388(10)
C(1)-C(3)	1.505(9)	C(22)-H(22)	0.9300
C(1)-H(1)	0.9800	C(23)-C(24)	1.370(11)
C(2)-C(3)	1.497(9)	C(23)-H(23)	0.9300
C(2)-H(2)	0.9800	C(24)-C(25)	1.360(11)
C(3)-C(11)	1.502(9)	C(24)-H(24)	0.9300
C(3)-C(21)	1.513(9)	C(25)-C(26)	1.392(10)
C(5)-H(5A)	0.9600	C(25)-H(25)	0.9300
C(5)-H(5B)	0.9600	C(26)-H(26)	0.9300
C(5)-H(5C)	0.9600	C(31)-C(32)	1.360(10)
C(6)-H(6A)	0.9600	C(31)-C(36)	1.364(10)
C(6)-H(6B)	0.9600	C(32)-C(33)	1.377(12)
C(6)-H(6C)	0.9600	C(32)-H(32)	0.9300

Table 3 (continued)

C(33)-C(34)	1.353(12)	C(55)-C(56)	1.372(9)
C(33)-H(33)	0.9300	C(55)-H(55)	0.9300
C(34)-C(35)	1.363(11)	C(56)-H(56)	0.9300
C(34)-H(34)	0.9300	C(61)-C(62)	1.371(9)
C(35)-C(36)	1.404(10)	C(61)-C(66)	1.380(9)
C(35)-H(35)	0.9300	C(62)-C(63)	1.388(9)
C(36)-H(36)	0.9300	C(62)-H(62)	0.9300
C(41)-C(46)	1.375(10)	C(63)-C(64)	1.369(10)
C(41)-C(42)	1.401(10)	C(63)-H(63)	0.9300
C(42)-C(43)	1.397(10)	C(64)-C(65)	1.353(10)
C(42)-H(42)	0.9300	C(64)-H(64)	0.9300
C(43)-C(44)	1.378(12)	C(65)-C(66)	1.377(10)
C(43)-H(43)	0.9300	C(65)-H(65)	0.9300
C(44)-C(45)	1.377(12)	C(66)-H(66)	0.9300
C(44)-H(44)	0.9300	O(1)-W-C(2)	97.5(2)
C(45)-C(46)	1.368(10)	O(1)-W-C(1)	97.8(2)
C(45)-H(45)	0.9300	C(2)-W-C(1)	39.7(2)
C(46)-H(46)	0.9300	O(1)-W-Cl(2)	88.66(16)
C(51)-C(56)	1.382(9)	C(2)-W-Cl(2)	159.99(18)
C(51)-C(52)	1.393(9)	C(1)-W-Cl(2)	158.16(18)
C(52)-C(53)	1.377(10)	O(1)-W-Cl(1)	174.35(15)
C(52)-H(52)	0.9300	C(2)-W-Cl(1)	87.50(18)
C(53)-C(54)	1.382(10)	C(1)-W-Cl(1)	87.70(18)
C(53)-H(53)	0.9300	Cl(2)-W-Cl(1)	85.76(7)
C(54)-C(55)	1.388(10)	O(1)-W-P(1)	97.37(15)
C(54)-H(54)	0.9300	C(2)-W-P(1)	118.15(17)

Table 3 (continued)

C(1)-W-P(1)	78.91(18)	W-C(1)-H(1)	124.2
Cl(2)-W-P(1)	79.59(7)	C(1)-C(2)-C(3)	61.5(4)
Cl(1)-W-P(1)	82.54(7)	C(1)-C(2)-W	70.2(4)
O(1)-W-P(2)	97.74(15)	C(3)-C(2)-W	110.3(5)
C(2)-W-P(2)	79.35(18)	C(1)-C(2)-H(2)	124.1
C(1)-W-P(2)	118.42(18)	C(3)-C(2)-H(2)	124.1
Cl(2)-W-P(2)	80.96(7)	W-C(2)-H(2)	124.1
Cl(1)-W-P(2)	80.49(6)	C(2)-C(3)-C(11)	123.3(6)
P(1)-W-P(2)	154.99(6)	C(2)-C(3)-C(1)	57.6(4)
C(5)-P(1)-C(41)	102.6(4)	C(11)-C(3)-C(1)	123.1(6)
C(5)-P(1)-C(31)	105.9(4)	C(2)-C(3)-C(21)	115.2(6)
C(41)-P(1)-C(31)	102.9(3)	C(11)-C(3)-C(21)	111.4(6)
C(5)-P(1)-W	114.6(3)	C(1)-C(3)-C(21)	116.7(6)
C(41)-P(1)-W	116.2(2)	P(1)-C(5)-H(5A)	109.5
C(31)-P(1)-W	113.3(3)	P(1)-C(5)-H(5B)	109.5
C(6)-P(2)-C(61)	103.0(3)	H(5A)-C(5)-H(5B)	109.5
C(6)-P(2)-C(51)	103.8(4)	P(1)-C(5)-H(5C)	109.5
C(61)-P(2)-C(51)	103.5(3)	H(5A)-C(5)-H(5C)	109.5
C(6)-P(2)-W	113.5(3)	H(5B)-C(5)-H(5C)	109.5
C(61)-P(2)-W	116.1(2)	P(2)-C(6)-H(6A)	109.5
C(51)-P(2)-W	115.4(2)	P(2)-C(6)-H(6B)	109.5
C(2)-C(1)-C(3)	60.9(4)	H(6A)-C(6)-H(6B)	109.5
C(2)-C(1)-W	70.1(4)	P(2)-C(6)-H(6C)	109.5
C(3)-C(1)-W	109.8(4)	H(6A)-C(6)-H(6C)	109.5
C(2)-C(1)-H(1)	124.2	H(6B)-C(6)-H(6C)	109.5
C(3)-C(1)-H(1)	124.2	C(16)-C(11)-C(12)	118.9(8)

Table 3 (continued)

C(16)-C(11)-C(3)	119.8(7)	C(25)-C(24)-C(23)	119.3(9)
C(12)-C(11)-C(3)	121.3(7)	C(25)-C(24)-H(24)	120.4
C(11)-C(12)-C(13)	119.5(9)	C(23)-C(24)-H(24)	120.4
C(11)-C(12)-H(12)	120.2	C(24)-C(25)-C(26)	121.4(9)
C(13)-C(12)-H(12)	120.2	C(24)-C(25)-H(25)	119.3
C(14)-C(13)-C(12)	121.2(11)	C(26)-C(25)-H(25)	119.3
C(14)-C(13)-H(13)	119.4	C(21)-C(26)-C(25)	119.3(8)
C(12)-C(13)-H(13)	119.4	C(21)-C(26)-H(26)	120.3
C(13)-C(14)-C(15)	120.4(11)	C(25)-C(26)-H(26)	120.3
C(13)-C(14)-H(14)	119.8	C(32)-C(31)-C(36)	118.2(8)
C(15)-C(14)-H(14)	119.8	C(32)-C(31)-P(1)	121.1(7)
C(14)-C(15)-C(16)	118.2(10)	C(36)-C(31)-P(1)	120.5(6)
C(14)-C(15)-H(15)	120.9	C(31)-C(32)-C(33)	120.9(10)
C(16)-C(15)-H(15)	120.9	C(31)-C(32)-H(32)	119.5
C(11)-C(16)-C(15)	121.8(9)	C(33)-C(32)-H(32)	119.5
C(11)-C(16)-H(16)	119.1	C(34)-C(33)-C(32)	121.0(10)
C(15)-C(16)-H(16)	119.1	C(34)-C(33)-H(33)	119.5
C(22)-C(21)-C(26)	118.9(7)	C(32)-C(33)-H(33)	119.5
C(22)-C(21)-C(3)	120.4(7)	C(33)-C(34)-C(35)	119.5(9)
C(26)-C(21)-C(3)	120.7(7)	C(33)-C(34)-H(34)	120.2
C(21)-C(22)-C(23)	121.6(8)	C(35)-C(34)-H(34)	120.2
C(21)-C(22)-H(22)	119.2	C(34)-C(35)-C(36)	119.1(9)
C(23)-C(22)-H(22)	119.2	C(34)-C(35)-H(35)	120.4
C(24)-C(23)-C(22)	119.5(9)	C(36)-C(35)-H(35)	120.4
C(24)-C(23)-H(23)	120.3	C(31)-C(36)-C(35)	121.1(8)
C(22)-C(23)-H(23)	120.3	C(31)-C(36)-H(36)	119.4

Table 3 (continued)

C(35)-C(36)-H(36)	119.4	C(52)-C(53)-H(53)	119.6
C(46)-C(41)-C(42)	118.2(8)	C(54)-C(53)-H(53)	119.6
C(46)-C(41)-P(1)	122.0(6)	C(53)-C(54)-C(55)	119.1(8)
C(42)-C(41)-P(1)	119.6(7)	C(53)-C(54)-H(54)	120.5
C(43)-C(42)-C(41)	121.0(9)	C(55)-C(54)-H(54)	120.5
C(43)-C(42)-H(42)	119.5	C(56)-C(55)-C(54)	120.2(8)
C(41)-C(42)-H(42)	119.5	C(56)-C(55)-H(55)	119.9
C(44)-C(43)-C(42)	117.6(9)	C(54)-C(55)-H(55)	119.9
C(44)-C(43)-H(43)	121.2	C(55)-C(56)-C(51)	121.1(7)
C(42)-C(43)-H(43)	121.2	C(55)-C(56)-H(56)	119.5
C(45)-C(44)-C(43)	122.5(10)	C(51)-C(56)-H(56)	119.5
C(45)-C(44)-H(44)	118.7	C(62)-C(61)-C(66)	118.2(7)
C(43)-C(44)-H(44)	118.7	C(62)-C(61)-P(2)	121.5(6)
C(46)-C(45)-C(44)	118.5(10)	C(66)-C(61)-P(2)	120.1(6)
C(46)-C(45)-H(45)	120.7	C(61)-C(62)-C(63)	120.4(8)
C(44)-C(45)-H(45)	120.7	C(61)-C(62)-H(62)	119.8
C(45)-C(46)-C(41)	122.1(9)	C(63)-C(62)-H(62)	119.8
C(45)-C(46)-H(46)	118.9	C(64)-C(63)-C(62)	120.2(8)
C(41)-C(46)-H(46)	118.9	C(64)-C(63)-H(63)	119.9
C(56)-C(51)-C(52)	118.8(6)	C(62)-C(63)-H(63)	119.9
C(56)-C(51)-P(2)	120.3(5)	C(65)-C(64)-C(63)	120.1(8)
C(52)-C(51)-P(2)	120.8(6)	C(65)-C(64)-H(64)	119.9
C(53)-C(52)-C(51)	120.1(7)	C(63)-C(64)-H(64)	119.9
C(53)-C(52)-H(52)	120.0	C(64)-C(65)-C(66)	119.8(8)
C(51)-C(52)-H(52)	120.0	C(64)-C(65)-H(65)	120.1
C(52)-C(53)-C(54)	120.8(8)	C(66)-C(65)-H(65)	120.1

Table 3 (continued)C(65)-C(66)-C(61)

121.4(7)

C(65)-C(66)-H(66) 119.3

C(61)-C(66)-H(66) 119.3

Symmetry transformations used to generate equivalent atoms:

Table 4-Anisotropic displacement parameters ($Å^2 x\ 10^4$) for **3**. The anisotropic displacement factor exponent takes the form: $-2p^2$ [$h^2\ a^{*2} U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
W	521(2)	404(2)	497(2)	-21(2)	79(1)	-62(2)
Cl(1)	653(12)	576(12)	615(12)	-96(10)	188(10)	0(10)
Cl(2)	609(12)	733(15)	924(15)	16(12)	99(11)	-277(11)
P(1)	624(12)	489(13)	530(12)	25(10)	162(10)	-75(10)
P(2)	460(11)	434(11)	543(12)	-54(10)	27(9)	-12(9)
O(1)	700(30)	400(30)	520(30)	-80(20)	80(20)	0(30)
C(1)	580(50)	400(40)	470(40)	10(40)	140(40)	-10(40)
C(2)	480(40)	510(50)	500(40)	-40(40)	70(40)	-10(40)
C(3)	540(50)	470(40)	420(40)	10(40)	0(40)	-50(40)
C(5)	780(60)	840(60)	780(60)	70(50)	310(50)	-60(50)
C(6)	520(50)	790(60)	840(60)	-40(50)	50(40)	20(40)
C(11)	460(50)	560(50)	660(60)	-20(40)	190(40)	-50(40)
C(12)	940(70)	770(60)	700(60)	-130(50)	330(50)	-150(50)
C(13)	1360(100)	1140(90)	920(80)	-320(80)	640(70)	-220(80)
C(14)	1150(100)	840(90)	1590(120)	-420(90)	660(90)	-180(70)

Table 4 (continued)

C(15)	850(70)	660(70)	1650(110)	-180(80)	310(80)	150(60)
C(16)	620(50)	630(60)	1060(70)	-90(60)	210(50)	-50(50)
C(21)	490(50)	510(50)	540(50)	-40(40)	110(40)	-30(40)
C(22)	740(60)	790(60)	790(60)	70(50)	100(50)	-230(50)
C(23)	1200(80)	1020(80)	880(70)	40(70)	300(60)	-390(70)
C(24)	770(70)	880(70)	1270(90)	-210(80)	340(70)	-220(60)
C(25)	630(60)	1170(90)	1000(80)	-90(70)	-120(60)	-270(60)
C(26)	630(50)	910(70)	740(60)	70(50)	40(50)	-250(50)
C(31)	670(50)	410(40)	570(50)	70(40)	70(40)	10(40)
C(32)	1480(100)	540(60)	1570(100)	320(70)	760(80)	80(60)
C(33)	1420(100)	640(80)	1810(120)	350(80)	780(90)	-50(70)
C(34)	860(70)	460(60)	1350(100)	-60(60)	0(70)	-100(50)
C(35)	980(70)	860(70)	730(60)	-220(60)	0(50)	180(60)
C(36)	930(70)	580(60)	670(60)	0(50)	80(50)	120(50)
C(41)	730(60)	540(50)	410(40)	20(40)	110(40)	-50(40)
C(42)	970(70)	680(60)	510(50)	50(50)	130(50)	20(50)
C(43)	1230(90)	860(70)	530(60)	-140(50)	140(60)	-240(70)
C(44)	1140(90)	1450(110)	500(60)	-90(70)	70(60)	-450(80)
C(45)	820(70)	1310(90)	780(70)	-190(70)	60(60)	-40(70)
C(46)	720(60)	860(70)	590(50)	-80(50)	-20(50)	-140(50)
C(51)	540(50)	320(40)	530(50)	-60(40)	-100(40)	20(40)
C(52)	590(50)	480(50)	670(50)	-60(40)	0(40)	70(40)
C(53)	830(60)	390(50)	750(60)	-130(40)	-110(50)	60(40)
C(54)	820(70)	460(50)	820(60)	70(50)	-110(50)	-110(50)
C(55)	820(60)	590(60)	670(60)	50(50)	60(50)	-120(50)
C(56)	710(50)	380(50)	650(50)	-40(40)	140(40)	-90(40)

Table 4 (continued)

C(61)	390(40)	430(40)	550(50)	-90(40)	10(40)	-10(40)
C(62)	730(60)	590(50)	490(50)	0(40)	140(40)	-10(50)
C(63)	1080(70)	670(60)	630(50)	-70(50)	350(50)	150(50)
C(64)	840(60)	900(70)	520(60)	-150(50)	100(50)	-60(50)
C(65)	970(70)	850(70)	590(60)	10(50)	-170(50)	70(60)
C(66)	820(60)	550(50)	630(50)	30(50)	-180(50)	150(50)

Table 5-Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3**.

	x	y	z	U_{iso}
H(1)	1910	3173	5297	72
H(2)	2401	1881	6345	75
H(5A)	4117	5884	4902	117
H(5B)	3589	6085	4228	117
H(5C)	3802	4618	4486	117
H(6A)	4856	2238	6582	109
H(6B)	5080	2035	7338	109
H(6C)	5095	3489	7036	109
H(12)	1983	4103	7523	117
H(13)	1693	5964	8113	163
H(14)	1022	7718	7607	171
H(15)	639	7709	6481	157
H(16)	882	5795	5895	115
H(22)	1118	1785	7025	117
H(23)	131	307	6862	153

Table 5 (continued)

H(24)	-671	282	5871	143
H(25)	-445	1646	5046	145
H(26)	555	3105	5199	116
H(32)	2983	7927	4275	170
H(33)	2599	10130	4322	184
H(34)	1987	10817	5116	138
H(35)	1749	9280	5880	132
H(36)	2171	7056	5848	110
H(42)	2742	3107	4224	108
H(43)	1796	2103	3473	132
H(44)	682	3219	3218	156
H(45)	499	5296	3663	147
H(46)	1431	6248	4407	111
H(52)	4140	220	6587	90
H(53)	3679	-1915	6701	103
H(54)	2789	-2254	7329	110
H(55)	2407	-433	7889	105
H(56)	2885	1689	7793	87
H(62)	3580	5469	7616	90
H(63)	3799	6431	8645	115
H(64)	4335	5173	9534	114
H(65)	4666	2971	9403	127
H(66)	4457	2012	8382	106

Appendix 3

X-Ray Diffraction Experiment for
$W(O)(=CH\text{-}CH=CPh_2)(OC(CH_3)(CF_3)_2)_2(PMePh_2)$
Chapter 2 Compound **4**

Structure by

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Table 1-Crystal data and structure refinement for **4.**

Empirical formula	$C_{36}H_{31}F_{12}O_3PW$	
Formula weight	954.43	
Crystallization Solvent	toluene/pentane	
Crystal Habit	Blade	
Crystal size	0.33 x 0.23 x 0.12 mm^3	
Crystal color	Yellow	

Data Collection

Type of diffractometer	CAD-4	
Wavelength	0.71073 Å MoKa	
Data Collection Temperature	160 K	
Theta range for reflections used in lattice determination	11 to 12°	
Unit cell dimensions	a = 10.373(4) Å	a= 77.18(3)°
	b = 10.547(5) Å	b= 77.86(3)°
	c = 19.312(6) Å	g = 65.16(3)°
Volume	1853.1(13) $Å^3$	
Z	2	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Density (calculated)	1.710 Mg/m^3	
F(000)	936	
Theta range for data collection	1.5 to 23°	
Completeness to theta = 23°	99.7 %	
Index ranges	-11<=h<=11, -11<=k<=11, -21<=l<=18	
Data collection scan type	Ω–scan	

Table 1(continued)

Reflections collected	13272
Independent reflections	5146 [R_{int}= 0.032; GOF_{merge}= 1.37
Absorption coefficient	3.255 mm^{-1}
Absorption correction	Ψ–scan (North, Phillips & Matthews, 1968)
Max. and min. transmission	1.10 and 0.79
Number of standards	3 reflections measured every 75min.
Variation of standards	within counting statistics

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	direct methods
Secondary solution method	difference map
Hydrogen placement	geometrical calculation
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5146 / 0 / 478
Treatment of hydrogen atoms	no refinement of any parameters
Goodness-of-fit on F^2	1.855
Final R indices [I>2s(I)]	R1 = 0.0421, wR2 = 0.0790
R indices (all data)	R1 = 0.0539, wR2 = 0.0806
Type of weighting scheme used	calculated
Weighting scheme used	$w=1/\sigma^2(F_o^2)$
Max shift/error	0.017
Average shift/error	0.001
Largest diff. peak and hole	1.358 and -1.337 $e.Å^{-3}$

Table 1 (continued)

Special Refinement Details

Data were collected with 1.5 degree ω-scans.

Individual backgrounds were used; various background functions of two theta derived from weak reflections were tried but all were rejected.

A total of 13272 reflections were collected; the final 205 were thrown out due to crystal movement which led to weaker, poorly merging data.

The GOF_merge was 1.37 (4518 multiples); R_int was 0.032 for 3956 duplicates.

Weights w are calculated as $1/\sigma^2(F_o^2)$); variances ($\sigma^2(F_o^2)$) were derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data were obtained by propagation of error plus another additional term, $(0.014<I>)^2$.

The structure solved reasonably well except for disorder in one $C(CH_3)(CF_3)_2$ group. This disorder was not modelled successfully. The disorder apparently consists of rotation about both C-CF_3 bonds coupled with a rocking of the entire group about the W-O3 bond. A number of individual atoms were replaced by isotropic atoms at several different sites; this led to no real improvement in the model and only produced confusing pictures. A TLS analysis of the $C(CH_3)(CF_3)_2$ group (Acta Cryst B, October, 1998, probably Trueblood, Schomaker, and Maverick) in which the motion of the group is modelled by translation, libration and screw matrices also failed, with a negative eigenvalue for the L matrix. Finally, these atoms were refined as single anisotropic atoms although ellipsoids certainly do not represent the true disorder. Also somewhat puzzling was a peak of 1.2 electrons in the final difference map which was 1.16 A from H35c and 1.53 A from F34a. Both the largest positive and negative peaks in the final electron difference map were near the tungsten atom.

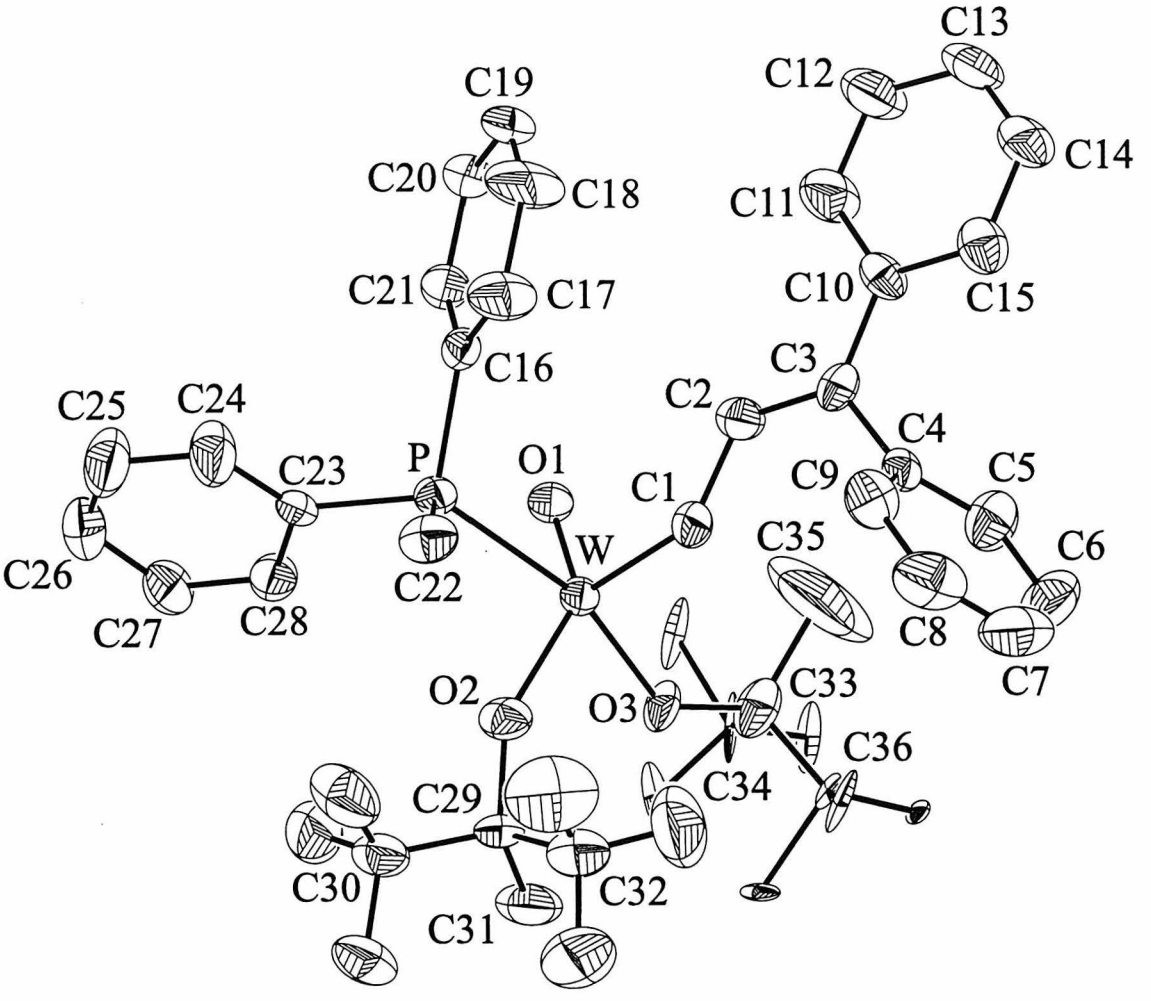

Figure 1- Labeled view of **4** with 50%probability ellipsoids; the U_{ij} for atoms C34, F34a, F34b, F34c, C36, F36a, F36b, F36c have been divided by 10 and the hydrogen atoms have been omitted, for clarity.

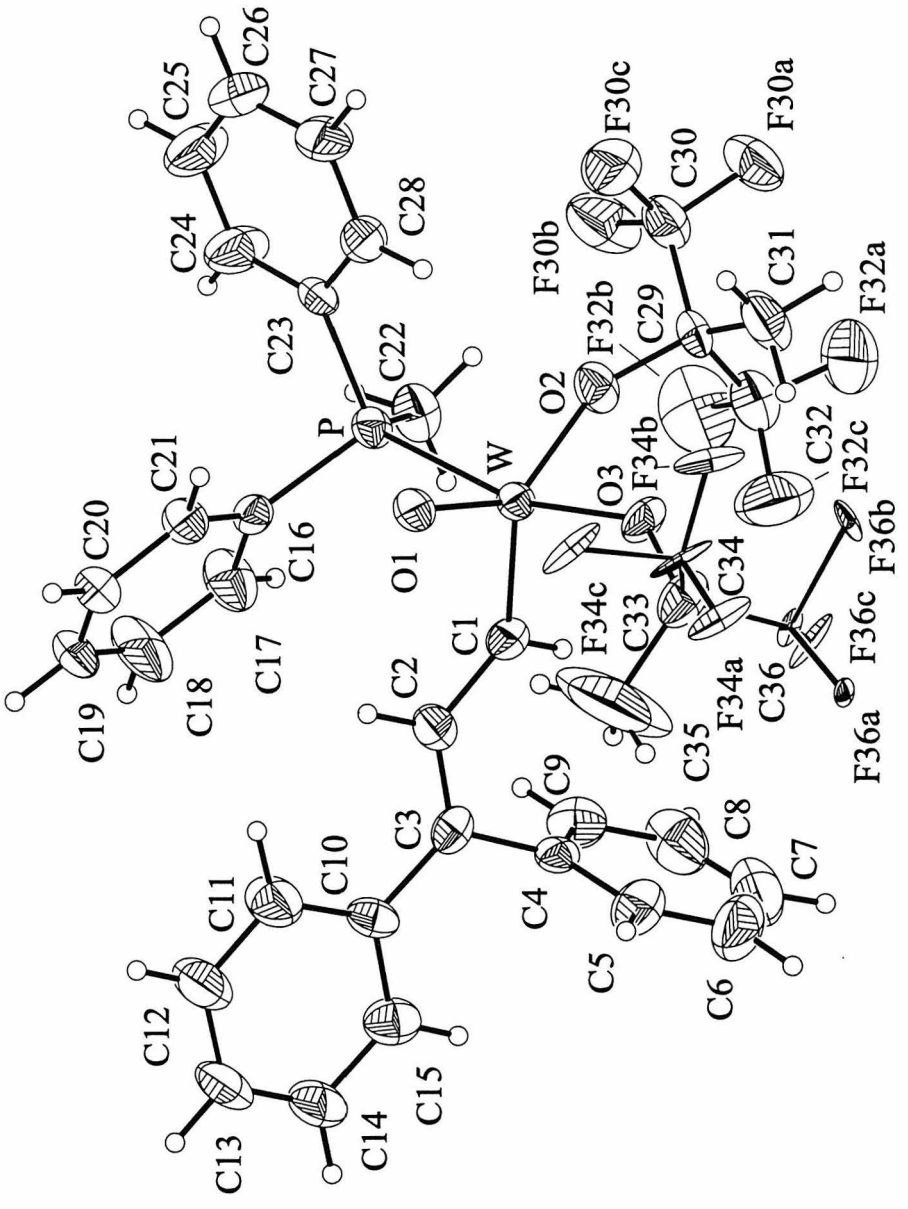

Figure 3- Labeled view of the molecule with 50% probability ellipsoids; the U_{ij} for atoms C34, F34a, F34b, F34c, C36, F36a, F36b, F36c have been divided by 10 for clarity; hydrogen atoms are shown at arbitrary size.

Table 2-Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4.** U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
W	8183(1)	5554(1)	7448(1)	24(1)
P	9801(2)	6871(2)	6876(1)	28(1)
O1	7860(5)	5720(5)	6610(2)	32(1)
C1	9866(8)	3824(7)	7532(4)	33(2)
C2	10723(8)	2892(8)	7034(4)	36(2)
C3	11661(8)	1532(8)	7201(4)	29(2)
C4	11808(7)	935(7)	7969(4)	29(2)
C5	11157(9)	50(9)	8330(5)	50(2)
C6	11250(11)	-475(10)	9052(6)	69(3)
C7	11994(11)	-78(12)	9422(5)	67(3)
C8	12617(11)	772(11)	9059(5)	64(3)
C9	12566(9)	1285(9)	8338(5)	46(2)
C10	12484(8)	627(8)	6650(4)	33(2)
C11	12357(10)	1100(9)	5923(4)	56(3)
C12	13113(11)	239(10)	5419(5)	69(3)
C13	14029(10)	-1123(9)	5614(5)	56(3)
C14	14207(9)	-1608(9)	6314(5)	50(2)
C15	13432(8)	-750(8)	6830(5)	43(2)
C16	11037(8)	6079(7)	6129(4)	29(2)
C17	12480(8)	5301(9)	6173(5)	51(2)
C18	13367(9)	4661(10)	5598(5)	66(3)

Table 2 (continued)

C19	12858(9)	4777(9)	4986(5)	46(2)
C20	11424(9)	5542(8)	4935(4)	38(2)
C21	10536(8)	6181(8)	5502(4)	37(2)
C22	10883(8)	6935(9)	7471(4)	42(2)
C23	8873(8)	8695(8)	6500(4)	32(2)
C24	9594(10)	9509(9)	6137(5)	65(3)
C25	8902(11)	10893(10)	5851(5)	73(3)
C26	7439(11)	11489(9)	5932(5)	59(3)
C27	6680(9)	10701(9)	6316(4)	46(2)
C28	7385(8)	9312(8)	6596(4)	37(2)
O2	7779(5)	6788(5)	8151(3)	37(1)
C29	7121(9)	7208(8)	8820(4)	36(2)
C30	6986(10)	8713(10)	8771(5)	43(2)
F30A	6387(5)	9228(5)	9383(2)	60(1)
F30B	8229(6)	8866(6)	8587(3)	74(2)
F30C	6171(6)	9566(5)	8277(3)	67(2)
C31	5639(9)	7189(10)	9035(4)	57(3)
C32	8106(12)	6191(11)	9370(5)	60(3)
F32A	7603(7)	6497(6)	10028(3)	86(2)
F32B	9406(7)	6228(7)	9219(3)	94(2)
F32C	8272(7)	4885(6)	9379(3)	96(2)
O3	6653(5)	4985(5)	8019(2)	34(1)
C33	6246(9)	3874(9)	8083(5)	43(2)
C34	4910(30)	4390(20)	7840(30)	300(20)
F34A	4289(12)	3544(11)	7878(9)	322(10)
F34B	4016(10)	5575(14)	8010(20)	363(16)

Table 2 (continued)

F34C	5150(20)	4830(20)	7097(9)	323(14)
C35	7240(15)	2744(14)	7622(8)	156(7)
C36	6150(40)	3230(30)	8800(9)	217(15)
F36A	5588(12)	2255(8)	8960(4)	172(4)
F36B	4920(30)	4429(18)	9132(10)	391(17)
F36C	7040(30)	2990(20)	9129(8)	335(15)

Table 3- Bond lengths [Å] and angles [°] for **4.**

W-O1	1.677(5)	C6-C7	1.386(13)
W-C1	1.927(7)	C6-H6	0.9500
W-O2	1.950(5)	C7-C8	1.315(13)
W-O3	1.965(5)	C7-H7	0.9500
W-P	2.544(2)	C8-C9	1.381(11)
P-C22	1.796(7)	C8-H8	0.9500
P-C23	1.809(8)	C9-H9	0.9500
P-C16	1.809(7)	C10-C15	1.384(10)
C1-C2	1.416(10)	C10-C11	1.397(10)
C1-H1	0.9500	C11-C12	1.363(11)
C2-C3	1.365(10)	C11-H11	0.9500
C2-H2	0.9500	C12-C13	1.368(11)
C3-C10	1.469(10)	C12-H12	0.9500
C3-C4	1.488(10)	C13-C14	1.358(11)
C4-C5	1.362(10)	C13-H13	0.9500
C4-C9	1.364(10)	C14-C15	1.381(11)
C5-C6	1.388(12)	C14-H14	0.9500
C5-H5	0.9500	C15-H15	0.9500

Table 3 (continued)

C16-C21	1.382(10)	C29-C31	1.513(11)
C16-C17	1.383(10)	C29-C30	1.517(11)
C17-C18	1.385(11)	C29-C32	1.535(12)
C17-H17	0.9500	C30-F30C	1.324(9)
C18-C19	1.354(11)	C30-F30B	1.331(9)
C18-H18	0.9500	C30-F30A	1.331(9)
C19-C20	1.376(11)	C31-H31A	0.9800
C19-H19	0.9500	C31-H31B	0.9800
C20-C21	1.373(10)	C31-H31C	0.9800
C20-H20	0.9500	C32-F32C	1.310(10)
C21-H21	0.9500	C32-F32A	1.323(9)
C22-H22A	0.9800	C32-F32B	1.333(11)
C22-H22B	0.9800	C33-O3	1.377(9)
C22-H22C	0.9800	C33-C34	1.397(19)
C23-C24	1.356(11)	C33-C36	1.406(19)
C23-C28	1.389(10)	C33-C35	1.526(13)
C24-C25	1.371(11)	C34-F34B	1.27(4)
C24-H24A	0.9300	C34-F34A	1.291(16)
C25-C26	1.366(12)	C34-F34C	1.41(5)
C25-H25	0.9500	C35-H35A	0.9800
C26-C27	1.376(11)	C35-H35B	0.9800
C26-H26	0.9500	C35-H35C	0.9800
C27-C28	1.374(10)	C36-F36C	1.14(3)
C27-H27	0.9500	C36-F36A	1.328(15)
C28-H28	0.9500	C36-F36B	1.52(3)
O2-C29	1.399(8)	O1-W-C1	103.0(3)

Table 3 (continued)

O1-W-O2	137.5(2)	C9-C4-C3	121.1(7)
C1-W-O2	115.7(3)	C4-C5-C6	121.5(9)
O1-W-O3	101.7(2)	C4-C5-H5	119.3
C1-W-O3	102.8(3)	C6-C5-H5	119.3
O2-W-O3	86.9(2)	C7-C6-C5	119.8(10)
O1-W-P	85.11(17)	C7-C6-H6	120.1
C1-W-P	88.9(2)	C5-C6-H6	120.1
O2-W-P	78.91(15)	C8-C7-C6	117.4(10)
O3-W-P	164.63(15)	C8-C7-H7	121.3
C22-P-C23	104.8(4)	C6-C7-H7	121.3
C22-P-C16	106.1(4)	C7-C8-C9	123.8(10)
C23-P-C16	104.3(3)	C7-C8-H8	118.1
C22-P-W	114.4(3)	C9-C8-H8	118.1
C23-P-W	114.7(3)	C4-C9-C8	119.7(9)
C16-P-W	111.6(2)	C4-C9-H9	120.2
C2-C1-W	131.7(6)	C8-C9-H9	120.2
C2-C1-H1	114.1	C15-C10-C11	116.5(7)
W-C1-H1	114.1	C15-C10-C3	121.2(7)
C3-C2-C1	125.6(7)	C11-C10-C3	122.3(7)
C3-C2-H2	117.2	C12-C11-C10	121.5(8)
C1-C2-H2	117.2	C12-C11-H11	119.2
C2-C3-C10	122.0(7)	C10-C11-H11	119.2
C2-C3-C4	118.8(7)	C11-C12-C13	120.6(9)
C10-C3-C4	119.2(6)	C11-C12-H12	119.7
C5-C4-C9	117.7(8)	C13-C12-H12	119.7
C5-C4-C3	121.1(7)	C14-C13-C12	119.5(8)

Table 3 (continued)

C14-C13-H13	120.3	P-C22-H22A	109.5
C12-C13-H13	120.3	P-C22-H22B	109.5
C13-C14-C15	120.3(8)	H22A-C22-H22B	109.5
C13-C14-H14	119.8	P-C22-H22C	109.5
C15-C14-H14	119.8	H22A-C22-H22C	109.5
C14-C15-C10	121.5(8)	H22B-C22-H22C	109.5
C14-C15-H15	119.2	C24-C23-C28	118.1(7)
C10-C15-H15	119.2	C24-C23-P	121.7(6)
C21-C16-C17	117.7(7)	C28-C23-P	120.2(6)
C21-C16-P	120.1(6)	C23-C24-C25	122.2(9)
C17-C16-P	122.1(6)	C23-C24-H24A	119.2
C16-C17-C18	119.8(8)	C25-C24-H24A	118.6
C16-C17-H17	120.1	C26-C25-C24	119.6(9)
C18-C17-H17	120.1	C26-C25-H25	120.2
C19-C18-C17	121.6(8)	C24-C25-H25	120.2
C19-C18-H18	119.2	C25-C26-C27	119.4(8)
C17-C18-H18	119.2	C25-C26-H26	120.3
C18-C19-C20	119.3(8)	C27-C26-H26	120.3
C18-C19-H19	120.4	C28-C27-C26	120.4(8)
C20-C19-H19	120.4	C28-C27-H27	119.8
C21-C20-C19	119.5(8)	C26-C27-H27	119.8
C21-C20-H20	120.3	C27-C28-C23	120.2(8)
C19-C20-H20	120.3	C27-C28-H28	119.9
C20-C21-C16	122.0(7)	C23-C28-H28	119.9
C20-C21-H21	119.0	C29-O2-W	150.0(5)
C16-C21-H21	119.0	O2-C29-C31	113.8(6)

Table 3 (continued)

O2-C29-C30	106.9(6)	O3-C33-C35	114.1(7)
C31-C29-C30	108.1(7)	C34-C33-C35	105(2)
O2-C29-C32	106.8(7)	C36-C33-C35	108.5(14)
C31-C29-C32	109.7(7)	F34B-C34-F34A	111(3)
C30-C29-C32	111.5(7)	F34B-C34-C33	116(3)
F30C-C30-F30B	105.7(7)	F34A-C34-C33	119.3(13)
F30C-C30-F30A	106.7(7)	F34B-C34-F34C	98.0(19)
F30B-C30-F30A	106.9(7)	F34A-C34-F34C	103(3)
F30C-C30-C29	110.7(7)	C33-C34-F34C	106(3)
F30B-C30-C29	113.8(7)	C33-C35-H35A	109.5
F30A-C30-C29	112.5(7)	C33-C35-H35B	109.5
C29-C31-H31A	109.5	H35A-C35-H35B	109.5
C29-C31-H31B	109.5	C33-C35-H35C	109.5
H31A-C31-H31B	109.5	H35A-C35-H35C	109.5
C29-C31-H31C	109.5	H35B-C35-H35C	109.5
H31A-C31-H31C	109.5	F36C-C36-F36A	113(2)
H31B-C31-H31C	109.5	F36C-C36-C33	119(2)
F32C-C32-F32A	107.9(8)	F36A-C36-C33	117.4(16)
F32C-C32-F32B	107.3(9)	F36C-C36-F36B	102.1(17)
F32A-C32-F32B	106.7(9)	F36A-C36-F36B	100(2)
F32C-C32-C29	110.8(8)	C33-C36-F36B	100(2)
F32A-C32-C29	112.4(8)	C33-O3-W	136.3(5)
F32B-C32-C29	111.6(8)		
O3-C33-C34	108.4(9)		
O3-C33-C36	110.6(9)		
C34-C33-C36	110(2)		

Table 4-Anisotropic displacement parameters ($Å^2 x\ 10^4$) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
W	211(2)	237(2)	263(2)	-41(1)	-13(1)	-78(1)
P	223(11)	292(12)	311(12)	-69(9)	27(9)	-108(10)
O1	230(30)	310(30)	360(30)	-60(20)	60(20)	-80(20)
C1	380(50)	270(40)	290(40)	0(40)	-70(40)	-100(40)
C2	340(50)	360(50)	320(50)	-90(40)	0(40)	-100(40)
C3	260(40)	330(50)	340(50)	10(40)	-40(40)	-200(40)
C4	190(40)	220(40)	390(50)	-50(40)	10(40)	-30(40)
C5	540(60)	460(60)	450(60)	60(50)	-140(50)	-180(50)
C6	540(70)	630(70)	680(80)	110(60)	130(60)	-210(60)
C7	530(70)	790(80)	400(60)	-80(60)	-20(50)	-10(60)
C8	590(70)	740(80)	440(70)	-150(60)	-210(50)	-30(60)
C9	390(50)	420(60)	540(60)	-60(50)	-150(50)	-100(50)
C10	210(40)	290(50)	460(50)	-130(40)	-40(40)	-40(40)
C11	570(60)	460(60)	420(60)	-70(50)	-130(50)	70(50)
C12	760(80)	520(70)	470(60)	-190(50)	-20(50)	90(60)
C13	560(60)	470(60)	530(60)	-280(50)	60(50)	-50(50)
C14	340(50)	400(60)	570(60)	-140(50)	-10(50)	30(40)
C15	350(50)	370(50)	540(60)	-70(50)	-90(40)	-100(40)
C16	270(50)	250(40)	320(50)	-10(40)	10(40)	-110(40)
C17	260(50)	680(70)	480(60)	-140(50)	-10(40)	-60(50)
C18	240(50)	820(80)	640(70)	-270(60)	70(50)	70(50)
C19	440(60)	410(60)	430(60)	-190(40)	160(50)	-120(50)

Table 4 (continued)

C20	390(50)	360(50)	350(50)	-100(40)	10(40)	-110(40)
C21	280(50)	350(50)	410(50)	-60(40)	30(40)	-90(40)
C22	380(50)	560(60)	390(50)	-120(40)	-10(40)	-260(50)
C23	350(50)	260(50)	310(50)	-130(40)	90(40)	-120(40)
C24	370(60)	330(60)	1020(80)	10(50)	160(50)	-90(50)
C25	520(70)	380(60)	1020(90)	120(60)	160(60)	-150(60)
C26	670(70)	290(50)	660(70)	10(50)	-30(60)	-120(50)
C27	320(50)	340(60)	570(60)	-50(50)	-40(40)	10(50)
C28	300(50)	350(50)	400(50)	-30(40)	-10(40)	-110(40)
O2	290(30)	450(30)	390(30)	-130(30)	60(30)	-200(30)
C29	450(50)	390(50)	210(50)	-110(40)	70(40)	-160(40)
C30	470(60)	510(60)	360(50)	-190(50)	40(50)	-210(50)
F30A	700(40)	600(30)	510(30)	-320(30)	40(30)	-190(30)
F30B	570(40)	700(40)	1100(50)	-490(30)	200(30)	-380(30)
F30C	920(40)	510(30)	500(30)	-50(30)	-110(30)	-220(30)
C31	560(60)	680(70)	530(60)	-320(50)	240(50)	-330(60)
C32	740(80)	620(80)	370(60)	-150(50)	50(50)	-230(60)
F32A	1170(50)	890(50)	360(30)	-50(30)	-100(30)	-290(40)
F32B	610(40)	1290(60)	820(40)	-120(40)	-280(40)	-190(40)
F32C	1370(60)	430(40)	850(40)	0(30)	-270(40)	-130(40)
O3	360(30)	280(30)	400(30)	50(20)	-20(30)	-220(30)
C33	370(50)	440(60)	510(60)	80(50)	-70(40)	-260(50)
C34	2500(300)	980(160)	6200(600)	2000(300)	-3200(400)	-1400(200)
F34A	2450(120)	1770(100)	6500(300)	1810(130)	-3060(150)	-1890(100)
F34B	590(60)	900(90)	9400(500)	-120(170)	-1550(140)	-250(60)
F34C	4800(300)	2560(170)	4200(200)	2500(170)	-4100(200)	-3100(200)

Table 4 (continued)

C35	1480(140)	1200(120)	2610(180)	-1300(130)	740(130)	-1070(120)
C36	5200(500)	2000(200)	930(140)	-220(150)	100(200)	-3100(300)
F36A	3160(130)	1290(70)	1100(60)	-440(50)	870(70)	-1670(80)
F36B	6300(300)	3150(180)	3450(190)	-2810(180)	4200(200)	-4100(200)
F36C	7400(400)	3400(200)	1770(130)	1930(140)	-2900(200)	-4600(300)

Table 5-Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **4**.

	x	y	z	U_{iso}
H1	10178	3545	7991	39
H2	10637	3245	6542	43
H5	10629	-213	8083	60
H6	10803	-1106	9291	83
H7	12053	-408	9918	81
H8	13132	1049	9308	76
H9	13057	1878	8101	55
H11	11729	2043	5775	68
H12	13002	587	4929	83
H13	14538	-1724	5262	67
H14	14867	-2542	6451	60
H15	13553	-1113	7319	52
H17	12862	5206	6596	62
H18	14356	4128	5633	79

Table 5 (continued)

'H19	13486	4335	4596	55
H20	11050	5627	4510	46
H21	9547	6709	5462	44
H22A	11425	5974	7696	50
H22B	10264	7504	7843	50
H22C	11550	7361	7200	50
H24A	10590	9121	6083	78
H25	9438	11434	5597	88
H26	6949	12440	5726	70
H27	5662	11119	6389	56
H28	6853	8772	6857	44
H31A	5702	6223	9070	68
H31B	5022	7814	8674	68
H31C	5233	7516	9500	68
H35A	8196	2317	7773	188
H35B	7300	3176	7118	188
H35C	6860	2013	7680	188