INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI

A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor MI 48106-1346 USA
313/761-4700 800/521-0600

SYNTHESIS OF TRIVALENT PHOSPHORUS COMPOUNDS FOR THE DIELS-ALDER REACTION

by

PING XU

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

1999

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy

Chair of Examining Committee

Prof. William H. Hersh William H. Hersh Date 1/21/99

Executive Officer

Prof. Gerald W. Koeppl Gerald Koeppl/WHH Date 1/27/99

Supervisory Committee

Prof. William H. Hersh Date

Prof. Arthur D. Baker Arthur D. Baker Date 1/21/99

Prof. Klaus G. Grohmann Klaus G. Grohmann Date 1/21/99

The City University of New York

Abstract

SYNTHESIS OF TRIVALENT PHOSPHORUS COMPOUNDS FOR THE DIELS-ALDER REACTION

by

Ping Xu

Adviser: Dr. William H. Hersh

Reaction of chelating phosphine $Bu^t_2PCH_2CH_2PPh_2$, *diphos*, *diphos-F*$_{20}$, or *diTosL* with trans-$BrW(CO)_4(NO)$ gave cis,cis,trans-$(chelate)(CO)_2(NO)WBr$ as the catalyst precursor, which further reacted with $AgSbF_6$ to form the reactive Lewis acidic tungsten cations as the SbF_6^- adduct.

Both catalytic and stoichiometric results showed that racemic catalyst **C7** was comparable to catalyst **C1** regarding the reactivity. This remarkable result excluded the possibility that simple steric bulk caused the extremely low reactivity of catalyst **C5** containing a C_2 symmetric ligand, and suggested a new direction for the design of ligands. Ferrocene derived chiral catalysts **Crs8-1** and

Crs8-2 confirmed the high catalytic reactivity of ligands having $Bu^t_2RP/PRPh_2$ moieties.

Reaction of N,N'-bis(tolysulfonyl)-1,2-diaminoethane with $PhPCl_2$ gave a 62% yield of *TosL*; while with Ph_2PCl, a 43% yield of *diTosL* was achieved. Reaction of (S)-N-tolylsulfonylvaline with $PhPCl_2$ gave a nearly quantitative yield of a novel 1,3,2-oxazaphospholidin-5-one (**14a** and **14b**) as a greater than 7:1 mixture of diastereomers.

The IR data are interpreted to suggest a relative order of ligand acceptor ability as $P(CF_3)_3 > TosL \approx P(OMe)_3 > PPh_3 \approx PP(NEt_2)_2$ and a relative order of a ligand donor ability as $PP(NEt_2)_2 \geq P(OMe)_3 > PPh_3 > TosL > P(CF_3)_3$. The IR data also suggests that **14a** is a strongly electron-deficient ligand, which is only less deficient than $P(CF_3)_3$, and the chelating ligand *diTosL* is about as electron-deficient as *diphos-F*$_{20}$.

Acknowledgment

First of all I would like to thank Professor William H. Hersh for providing me with five exciting and challenge years at Queens College of the City University of New York. The opportunity to learn from him and to hear his insights and critical analysis has been one not to be missed. I am particularly grateful for his patience. Without him it might take me much longer time to search inside the darkness.

Next I would like to thank my two other committee members, Professor Arthur D. Baker and Professor Klaus G. Grohmann who gave me many useful suggestions through out the years. I would also like to thank the Chemistry Department of Queens College for the financial support during the first four years, I could achieve nothing without it.

Many people have contributed to my Ph.D. research. Mr. Bing Wang is the one who first started the *TosL* project, while Mr. Jong Won Yom is the one who first tried to prepare *diTosL*. Especially, I would like to thank Mr. Wei Luo for the time we spent together

in research and helpful discussion. I also thank Mr. Cheslan K. Simpson for his work in the (S)-valine project.

Finally, but not the least, I thank my wife Yingzi for her love and constant encouragement.

To Gabrielle

Table of Contents

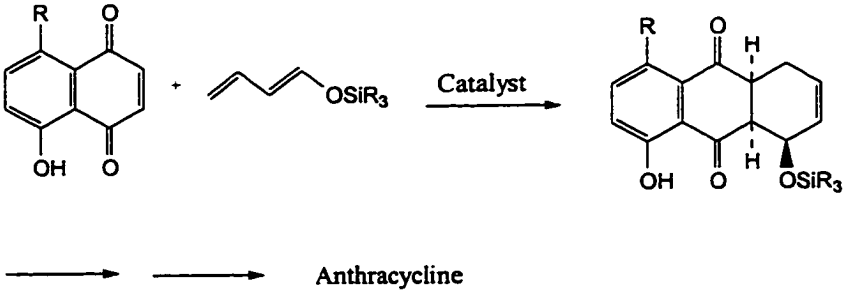
List of Tables

I. Introduction

The Diels-Alder reaction is a standard method for six-member ring formation.[1] Many natural products and pharmaceuticals can be prepared at early stage of the synthetic route by taking advantage of an asymmetric Diels-Alder reaction.

For example, naturally occurring anthracyclines and related analogue structures have been prepared via Diels-Alder approaches (Scheme I.1).[2,3]

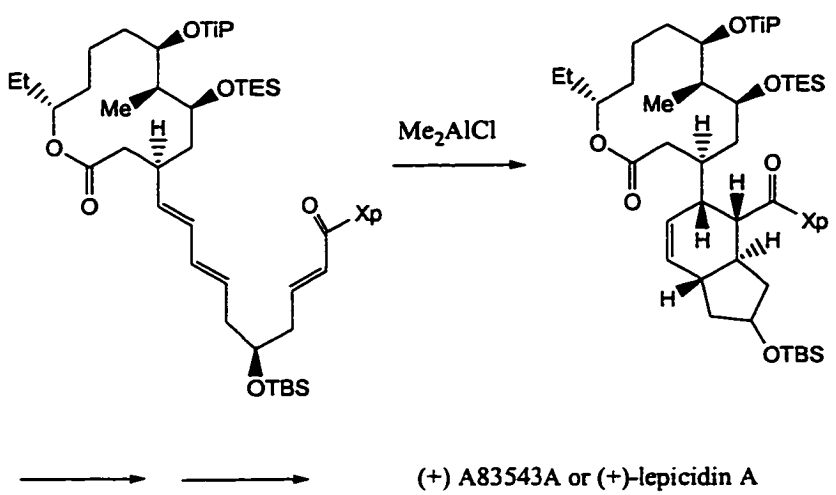
Scheme I.1



Tetracyclic macrolide A83543A (lepicidin),[4] which is an insecticide, particularly against lepidoptera larvae, was isolated in 1990 from the fermentation broth of the soil microbe Saccharo-

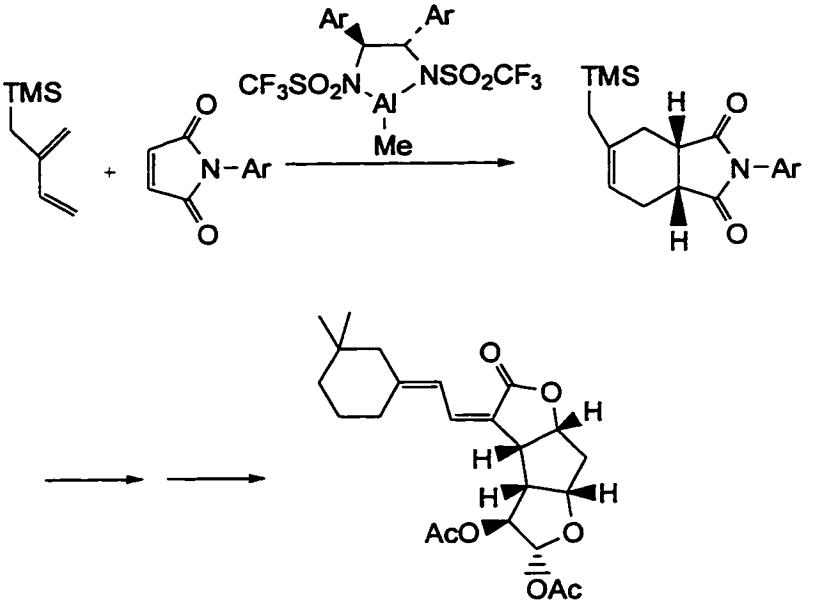
polyspora spinosa by Eli Lilly and Company researchers. The initial synthesis of this compound was also achieved via asymmetric Diels-Alder approach (Scheme I.2).

Scheme I.2



The first enantioselective total synthesis of the biosynthetically and structurally unusual marine nature products gracilin[5] B and C was also achieved via Diels-Alder approach, which relies on the initial Diels-Alder reaction using a readily available and recoverable chiral sulfonamide ligand (Scheme I.3).

Scheme I.3



97% e.e. gracilin B

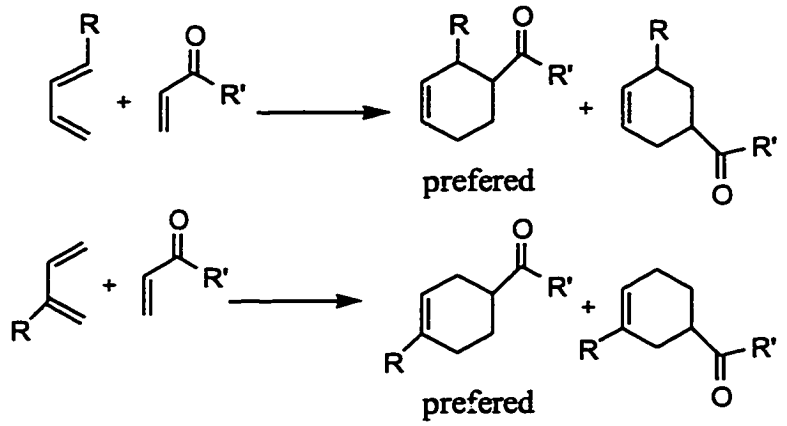
The concerted nature of Diels-Alder reaction was generally accepted and the stereospecificity of the reaction was firmly established before the importance of orbital symmetry was recognized. The transition state for a concerted reaction requires that the diene adopts the s-cis conformation. The diene and α,β-unsaturated aldehydes, or ketones (which is called the dienophile) approach each other in approximately parallel planes. It allows in principle the formation of four contiguous asymmetric centers (C-1 and C-4 of the diene and the two carbons of the dienophile).

Relative stereochemistry is usually well defined because of the formation of a cyclic transition state arising from the suprafacial-suprafacial interaction, with an endo approach whose product is often more sterically congested. The preference for the endo transition mainly results from the interaction between the dienophile substituent and the π electrons of the diene. Dipolar attractions and Van der Waals attractions may also be involved.

The regioselectivity arises when the diene is unsymmetrically substituted. Generally, there is a preference for the "ortho" or "para" orientation, respectively (scheme I.4).

This preference can also be understood in terms of frontier orbital theory.[6] Electron-rich dienes have high energy HOMOs and interact strongly with the LUMOs of electron-poor dienophiles. Because of this interaction, the reactants will be oriented in such a way that the carbons having the highest coefficients in the two frontier orbitals will begin the binding process.

Scheme I.4



The classic Diels-Alder reaction involving α,β-unsaturated aldehydes, or ketones, and 1,3-dienes is known to be promoted by Brønsted[7] and Lewis acids[8]. The most commonly used Lewis acids are the lighter halides of trivalent boron, aluminum, tetravalent titanium and tin, which all have a number of undesirable or inconvenient characteristics. Among these is , first, their extreme sensitivity to water, which is one of the reasons that they are generally employed at high catalytic loading. Second, the binding between traditional Lewis acid and the oxygen atom of dienophile or the Diels-Alder adduct is thermodynamically strong, and in some cases exchange may be kinetically slow.[9] Thus,

under catalytic conditions, due to the product binding (product inhibition), the turnover frequency decreases as the reaction goes on. This problem can be overcome by employing large loading of catalyst. Third, the catalysts, BF_3, $AlCl_3$, and $TiCl_4$ are powerful Lewis acids which are capable of polymerization of substrates.[9]

When the conventional Lewis acids are modified by incorporation of ligands, the complexity associated with the catalysis is increased. Not only are the original features of water sensitivity, product inhibition, and side reactions maintained but additional problems arise. First, since the parent halide is nearly always more active than the species incorporating the ligand, tiny amount of the starting halide could be responsible for a major part of the catalysis. This, of course, would lead to a reduction in the overall enantio-selection because of achiral pathway. Second, even if the ligated catalyst is isolated and purified, upon dissolution the traditional Lewis acids are known to form oligomers and to engage in ligand exchange depending on the nature of the ligand and the Lewis acid.[9] Thus even with

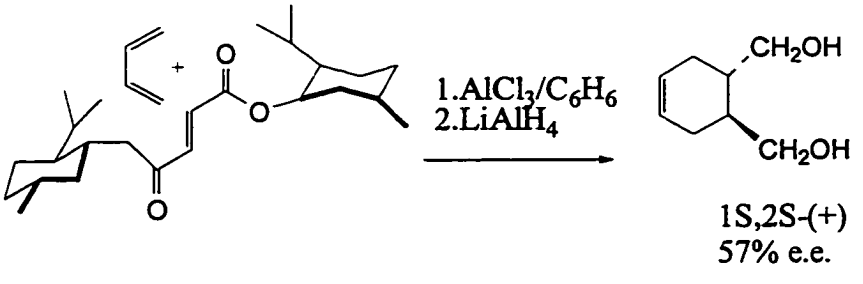
purification, the use of modified traditional Lewis acids presents a challenge in identifying the catalytic species.

For the reason stated above, ideally a chiral Lewis acid catalyst should have the following characteristics. First, the catalyst should accelerate the reaction by at least 100-fold over the thermal reaction at reasonable catalyst loading, therefore an achiral thermal pathway essentially could not contribute to the transformation. It, however, should not be so active as to induce polymerization of substrates. Second, in order to understand mechanism, a single well-defined species should exist under catalysis conditions. Third, the catalyst should have a fixed stable geometry so that the origins of the enantioselection can be defined. Fourth, the catalyst should bind the dienophile oxygen atom rapidly and reversibly. Finally the catalyst should not bind or only loosely bind the oxygen atom of Diels-Alder adduct, otherwise, such binding will inhibit catalysis.

A. **Chiral Auxiliaries**

The first asymmetric Diels-Alder reaction[10] can be traced to the work of Walborsky *et al* in 1961. The enantio-selection was achieved by introducing a removable chiral auxiliary menthol group on the dienophile (Scheme I.5). The presence of 0.74 equivalent of $AlCl_3$ gave rise to a 57% enantioselection of the 1S,2S-(+) product.

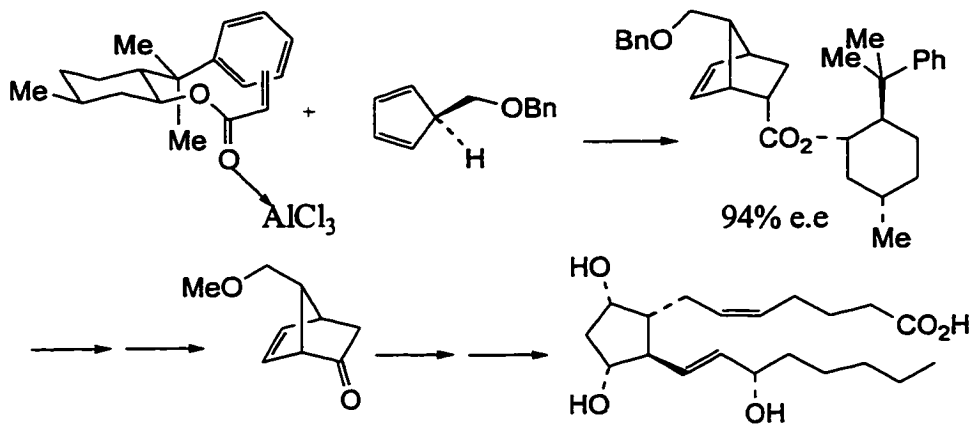
Scheme I.5



In 1975, Corey developed an asymmetric Diels-Alder approach[11] for the enantioselective synthesis of a bicycloheptenone, which has the correct chirality for the production of natural prostaglandins. In his method, a stereocontrolled $AlCl_3$ catalyzed Diels-Alder reaction between

benzyloxymethylcyclopentadiene and the acrylate ester of 8-phenylmenthol was used with the result that the required adduct was formed with high (32:1) enantioselectivity (scheme I.6).

Scheme I.6



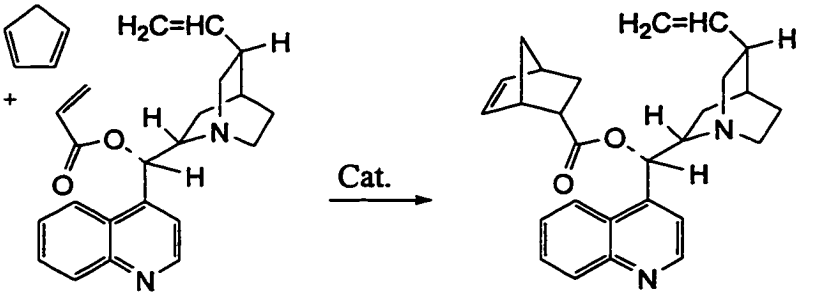
prostaglandin, $PGF_{2\alpha}$

Chiral auxiliaries of various kinds have been subsequently developed for catalytic Diels-Alder reaction, and some of them are now commercially available. Following examples are the applications of the most commonly used chiral auxiliaries.

In 1988 Suzuki[12] reported the highly si-facial selective (93% e.e.) addition of the dienophile (derived from cinchonidine) to cyclopentadiene in presence of $SnCl_4$. Surprisingly, the

replacement of $SnCl_4$ with $TiCl_4$ gave 33% e.e. and opposite facial selection (Scheme I.7).

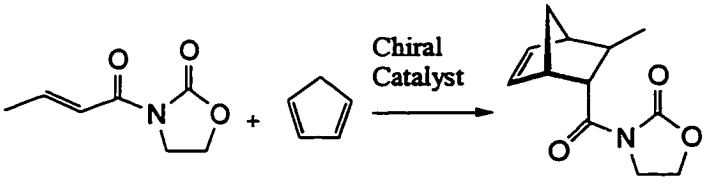
Scheme I.7



$SnCl_4$: S, 93% e.e.
$TiCl_4$: R, 33% e.e.

1,3-oxazolidin-2-one is one of the most useful chiral auxiliaries (Scheme I.8). Narasaka has been using it as an auxiliary combined

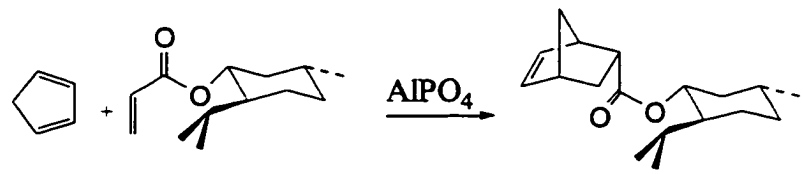
Scheme I.8



with chiral titanium catalyst[13] since 1980's, while recently, Kobayashi used it as an auxiliary combined with chiral scandium catalyst.[14]

Menthol is another useful chiral auxiliary. In 1993 Cativiela[15] reported a catalytic asymmetric Diels-Alder reaction between cyclopentadiene and menthyl acrylate in the presence of heterogeneous catalyst $AlPO_4$ (Scheme I.9). Moderate diastereo-selectivity was achieved.

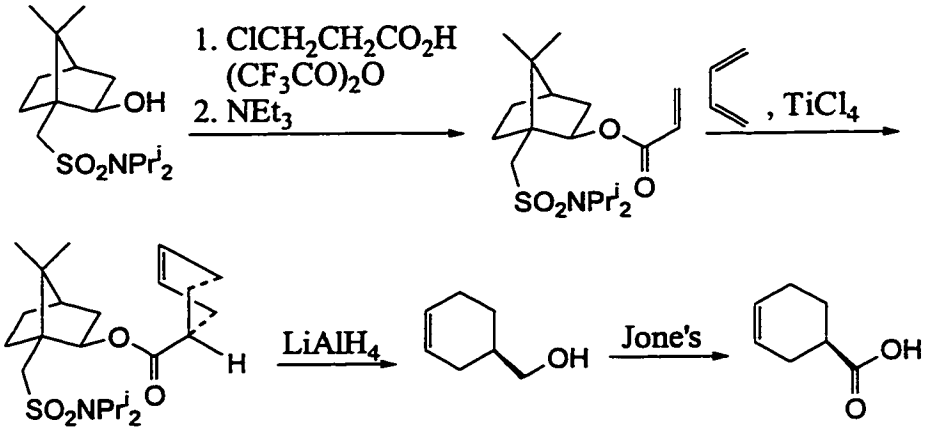
Scheme I.9



46% e.e.

Camphor-10-sulfonic acid is also a useful chiral auxiliary. Oppolzer[16] achieved enantioselection of Diels-Alder reaction not only between the acrylate and cyclopentadiene, but also between the acrylate and less reactive 1,3-butadiene by using camphor-10-sulfonic acid as the auxiliary (Scheme I.10).

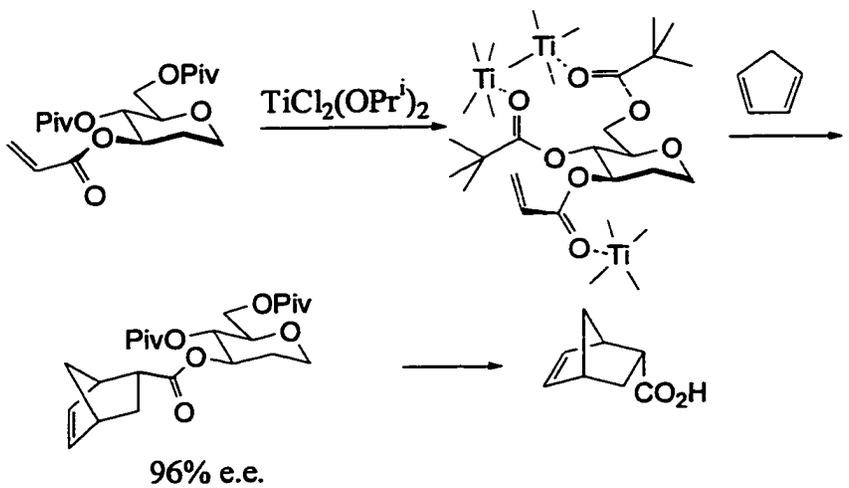
Scheme I.10



95.6% d.e.

In 1991 Kunz[17] reported stereoselective Diels-Alder synthesis by using carbohydrate auxiliaries. Both the highly reactive dienes (such as cyclopentadiene) and less reactive dienes (such as 1,3-butadiene and isoprene) were transformed to Diels-Alder adducts. Two facial selectivity was achieved by two carbohydrate templates. It was suggested that the effective diastereoselection at the carbohydrate-linked dienophile was caused by steric effects rather than by chelate control (scheme I.11, scheme I.12).

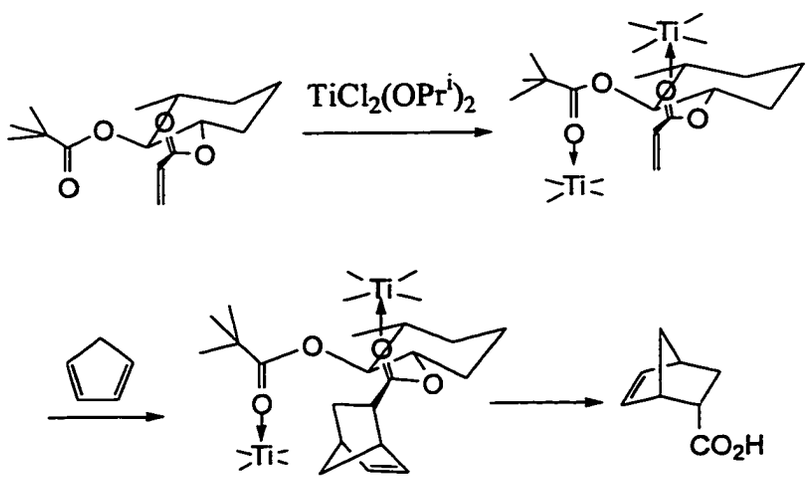
Scheme I.11



96% e.e.

Piv: $(CH_3)_3CCO$

Scheme I.12



B. Chiral Lewis Acid Catalysts

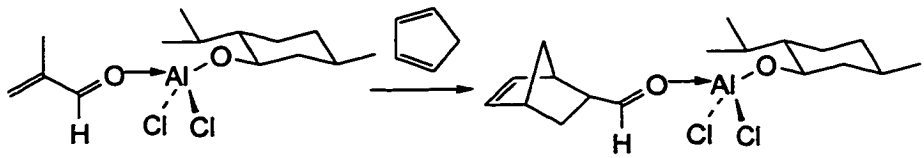
Even though chiral auxiliaries bring excellent enantio-selectivity for the asymmetric Diels-Alder reactions, many auxiliaries are now commercially available (such as cinchonidine, cinchonine, quinine, menthol)[12] and some of them are recyclable, separation steps are still required. Each time only one equivalent of chiral product is obtained for each equivalent of chiral auxiliary. Therefore the development of chiral Lewis acid for the asymmetric Diels-Alder reaction is both synthetically and economically necessary. The potential advantages of chiral catalysts are multiple: a small amount of chiral ligand is required, and the final product is obtained directly.

The asymmetric catalytic Diels-Alder reaction is a relatively new area, which began in the late 1970's, and now is under rapid development.

The first positive asymmetric catalytic Diels-Alder reaction can be traced to Koga's work in 1979,[18] the cycloaddition of 2-

methacrolein with cyclopentadiene catalyzed by $AlCl_2(OMen)$ (Scheme I.13). In 1987 Koga confirmed the cycloadduct result (57% e.e.), and proposed an interpretation based on the observed configuration.[19]

Scheme I.13



Mixing a chiral diol with $EtAlCl_2$ at -78°C in CH_2Cl_2 forms a chelated aluminum alcoholate complex which is similar to Koga's catalyst. An intensive investigation of such chiral alkoxy-aluminum complexes as Diels-Alder catalysts gave disappointing results.[20,21] Few brought out asymmetric inductions over 50% e.e. for the catalytic Diels-Alder reactions. Wulff's catalyst (Figure I.1) was the rare one which gave a 97% e.e. for cycloaddition of cyclopentadiene with 2-methacrolein.[22]

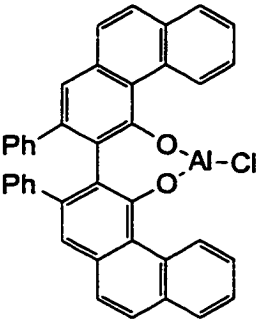


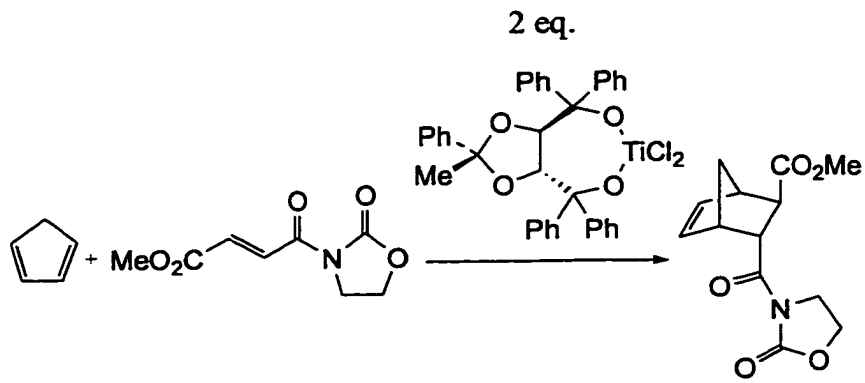
Figure I.1

Chiral alkoxytitanium complexes prepared from chiral diol have also been used as chiral catalysts for Diels-Alder reactions. Stoichiometric amounts of alkoxytitanium complexes were first utilized. Enantiomeric excess in the range of 90-95% has been achieved in the condensation of cyclopentadiene and some specific acrylamide, crotonamide or methyl acrylate.[23-25]

Narasaka[26] found that a class of crotonamide reacted with cyclopentadiene to give cycloadduct in the presence of certain titanium complex. The crotonamide derivative has been chosen because it could form a chelate complex with chiral titanium complex, resulting an increased stereoselectivity during the Diels-

Alder reaction. Indeed the major product (endo diastereomer) was obtained with 94% e.e. (Scheme I.14).

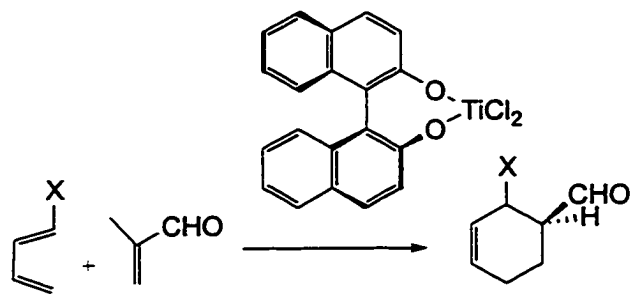
Scheme I.14



94% e.e.

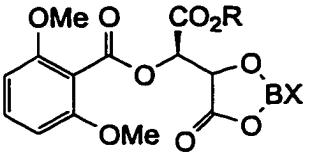
Catalytic use of titanium complexes is a later development. Mikami found that 1,1'-binaphthoxydichloro titanium catalyzed the formation of cycloaduct (~80% e.e.) between 2-methacrolein and substituted 1,3-butadiene (Scheme I.15).[27]

Scheme I.15



X= OMe, 71% e.e.
X=OAc, 80% e.e.
X=$OCONMe_2$, 86% e.e.

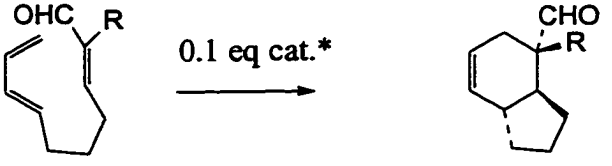
Chiral boron compounds have also been explored as promoters for the Diels-Alder reaction. Yamamoto *et al* found that a controlled amount of diboran on a carboxylic acid led to a boron compound which behaved as a Lewis acid. The boron complex formed *in situ* from monoacyl tartaric acid and diboran is an excellent asymmetric Diels-Alder catalyst. For the cycloaddition of 2-methacrolein with isoprene, a 93% e.e. was achieved, while with 2,3-dimethyl butadiene, a 97% e.e. was achieved (Figure I.2).[28]



R=H or Alkyl
X=H or Acyloxy

Figure I.2

Scheme I.16

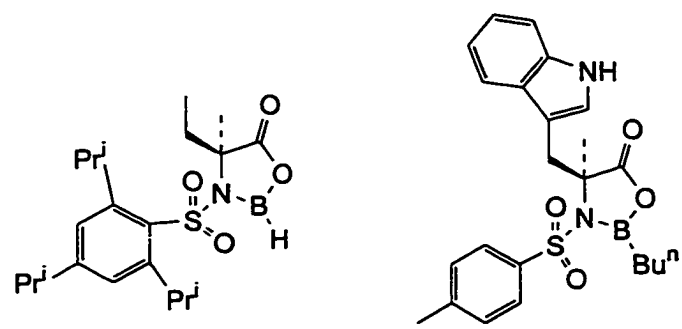


R=H, 46% e.e
R=Me, 92% e.e

cat.*: Yamamoto's catalyst in Figure I.2

Yamamoto's catalyst (Figure I.2) was also applied to asymmetric intramolecular Diels-Alder reaction and a α-substituent of dienophile was found to be essential for high enantioselection (Scheme I.16).[29] 92% e.e. was obtained for the α-methyl aldehyde while the same aldehyde devoid of a methyl group in the α-position afforded an adduct with only moderate enantioselection (46% e.e).

It was found that N-sulfonyl derivatives of α-amino acids reacted with diboran, giving 1,3,2-oxazaboronlidin-5-one derivative (Figure I.3). These complexes catalyze various



Yamamoto Corey

Figure I.3

asymmetric cycloaddition including less reactive acyclic dienes such as isoprene and substituted 1,3-butadiene. For example, 92% e.e. was achieved for cycloaddition between 2-bromoacrolein and isoprene catalyzed by Corey's amino acid derived catalyst shown in Figure I.3.[30] 65% e.e. was achieved for cycloaddition between 2-methacrolein and isoprene catalyzed by Yamamoto's amino acid derived catalyst shown in Figure I.3.[31]

Just as seen for Yamamoto's catalyst in Scheme I.16, a α-substituent on the dienophile was essential for high enantio-selection by Corey's amino acid derived catalyst. For example, catalyzed cycloaddition of cyclopentadiene and 2-bromo acrolein forms the Diels-Alder adduct with high enantioselection (R:S > 200:1, s-cis transition state for the major product.), while the similar reaction with acrolein exhibit low enantioselectivity (R:S = 30:70, s-trans transition state for the major product) and opposite face selectivity.

Even though many asymmetric Lewis acids have been reported as excellent Diels-Alder catalysts, only one catalyst is effective for the cycloaddition of isoprene and acrolein. In 1996, Yamamoto reported a Brønsted acid-assisted chiral Lewis acid (BLA, Figure I.4) which is an excellent Diels-Alder catalyst not only for the cyclic diene but also for less reactive acyclic diene such as 2,3-dimethylbutadiene and isoprene. The catalytic cycloaddition of isoprene with acrolein gave rise to a 95% yield and 99% e.e.[32] However the synthesis of this BLA catalyst is difficult which makes it unlikely to find extensive application in industry.

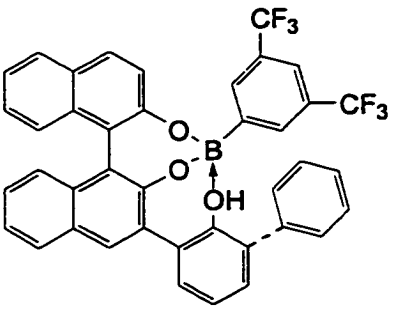
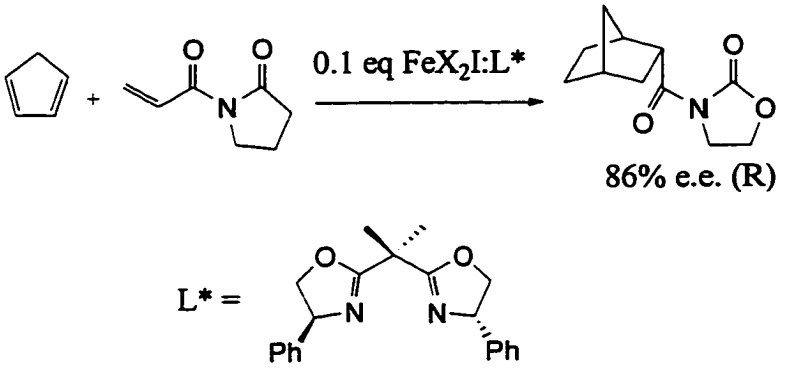


Figure I.4

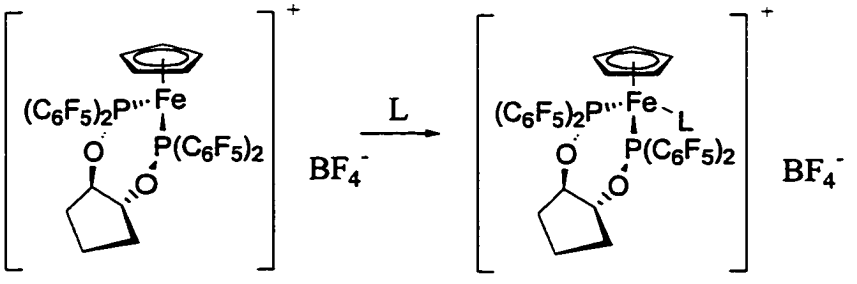
Besides titanium catalysts, applications of other transition metal catalysts in the asymmetric Diels-Alder reaction have also been reported. One example is chiral iron(III) Lewis acid L*FEX_2I. It was prepared *in situ* by treatment of anhydrous FeX_2 (X = halogen) and ligand L* followed by oxidation of the iron (II) complex with iodine. The resulting iron (III) complex catalyzes the Diels-Alder reaction between cyclopentadiene and bidentate dienophile, the product is isolated with 86% e.e. and 99/1 endo/exo diastereoselectivity (Scheme I.17).[33]

Scheme I.17



Some other iron complexes have also been reported to catalyze Diels-Alder reaction. A C_2-chiral phosphorus ligand incorporated [CpFeL*]BF_4 Lewis acid (Scheme I.18) was reported as an

Scheme I.18

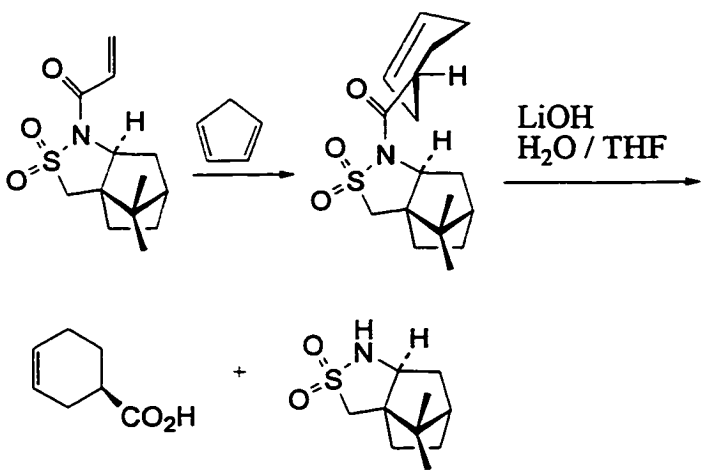


L: CH_3CN
dienophile

excellent asymmetric Diels-Alder catalyst by Kundig in 1994. Catalytic cycloaddition of isoprene and 2-bromo acrolein forms the Diels-Alder adduct with 96% e.e.[34]

However, the current cost of chiral Diels-Alder catalysts is still too high, which counterbalances their advantages. For this reason, large quantities of R-(+)-cyclohex-3-ene-carboxylic acid for the production of immunosuppresant FK-506[35] are made via chiral auxiliary rather than via chiral Diels-Alder catalyst (Scheme I.19).

Scheme I.19

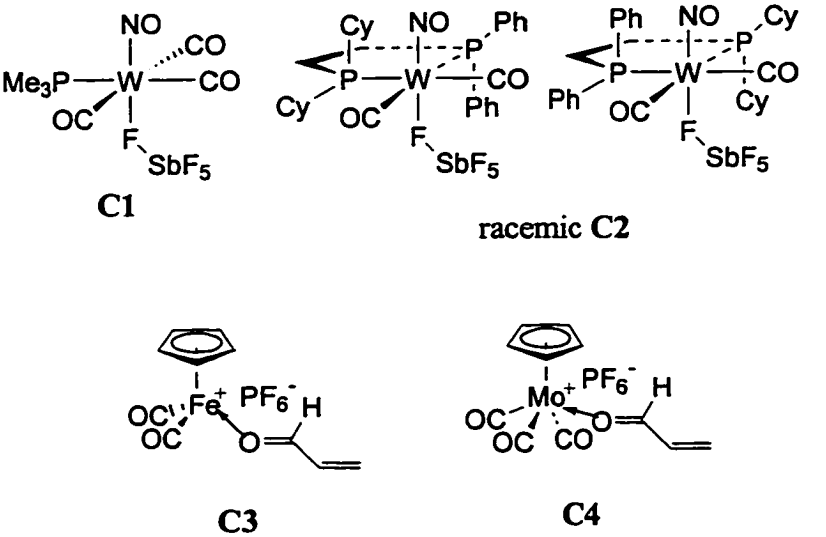


II. Catalyst Design

While much excellent work has been carried out in the asymmetric Diels-Alder reaction as described in the introduction, the development of easily prepared Lewis acid catalysts which would give suitable regioselectivity, stereoselectivity and enantioselectivity for a wide range of Diels-Alder reactions is still needed. In our approach, we have chosen to examine transition metals rather than aluminum or boron. Transition metals exhibit rigid octahedral structures, and one can image chelating of a ligand at equatorial sites with the dienophile positioned at an axial site, giving a rigid structure with relatively narrower 90° angles between the attached groups rather than the more flexible tetrahedral structures associated with aluminum or boron with their wider 109.5° angles. We hope such rigid structures will give rise to a better enantioselection.

In 1989 Hersh *et al* reported[36] that catalysis of Diels-Alder reactions between the dienes cyclopentadiene, butadiene, isoprene, and piperylene and the dienophile enones acrolein, methyl vinyl

ketone, and methyl acrylate was induced by 0.1-2.5 mol% of four transition metal catalysts, namely mer-(cis-Me_3P)(trans-NO)$(CO)_3W(\mu\text{-}F)SbF_5$ (**C1**), cis,cis,trans-$(Cy_2PCH_2CH_2PPh_2)(CO)_2(NO)W(\mu\text{-}F)SbF_5$ (**C2**), $Cp(CO)_2(\eta^1\text{-acrolein})FePF_6$ (**C3**), and $Cp(CO)_3(\eta^1\text{-acrolein})MoPF_6$ (**C4**). Compared with the thermal reactions, enhancement of cycloaddition rates, regioselectivity and stereoselectivity was observed.[36]



C1 racemic **C2**

C3 **C4**

Figure II.1

In the case of cyclopentadiene, high yields were obtained in the reactions with acrolein or methyl vinyl ketone even in the presence of only 0.1 mol% of **C1** or **C3**. Moreover, the cycloaddition of

acrolein with cyclopentadiene in the presence of 1 mol% of **C1** at room temperature for 1 h gave an 89% yield of product in an 84:16 endo/exo ratio; while the same reaction by **C3** gave an 83% of yield in a 92:18 endo/exo ratio. In comparison, the same reaction without catalyst present only gave a 16-35% of yield in an 80:20 endo/exo ratio.

For the reaction of cyclopentadiene with methyl acrylate, the presence of 1 mol% **C1** at room temperature for 1 h gave an 85% yield in a 92:8 endo/exo ratio, while under the same reaction conditions, application of **C3** for 24 h gave a 17% yield in an 86:14 endo/exo ratio, and **C4** gave a 24% yield in an 82:18 endo/exo ratio. By comparison, without any catalyst present, the yield was 2% in an 87:13 endo/exo ratio at room temperature for 1 h, and for 24 h the yield was 57% in an 84:16 endo/exo ratio.

As the data above indicate, only **C1** is clearly catalytically active and enhances the endo/exo ratio; **C3** and **C4** have little effect since the 24 h yields for both catalysts are even lower than that of the thermal reaction, which may be accounted by competitive polymerization of the diene.[37]

However, for the reactions involving acyclic dienes, the rate enhancement is significant. For instance, 17 h room temperature reaction of butadiene with acrolein in the presence of 0.1 mol% of **C1** allowed isolation of the corresponding Diels-Alder adduct with a 77% yield, while essentially no uncatalyzed reaction occurred at room temperature, and the typical thermal reaction occurred at ~130°C.[38] It should be noted that oligomeric products were found when carried out exclusively at room temperature in the presence of catalysts, but addition of dienes to a solution of the enone and catalyst held at 0°C eliminated this problem.

For convenience and consistence, the catalytic reactivity and regioselectivity of above four Lewis acid catalysts **C1**, **C2**, **C3**, and **C4** were compared by the catalytic reaction of isoprene with acrolein, 2-methacrolein or methyl vinyl ketone. Here, uncatalyzed room temperature reaction of isoprene with either acrolein or methyl vinyl ketone for 24 h gave less than 5% yield in a ~ 70:30 ratio of 1,4- to 1,3-substituted cyclohexene isomers, and for the uncatalyzed reaction with methyl acrylate, no product was found.

However, 1 h room temperature reaction of isoprene with acrolein catalyzed by 1 mol% of **C1** gave a 84% yield in a 93:7 ratio of 1,4- versus 1,3-substituted acrolein adducts, and 98% yield was achieved for 24 h. For 24 h room temperature reaction of isoprene with methyl vinyl ketone catalyzed by 1 mol% of **C1**, a 68% yield in a 95:5 ratio of 1,4- versus 1,3-substituted adducts was achieved, while for the reaction with methyl acrylate, a 12% yield in a 96:4 ratio of 1,4- versus 1,3- adducts was obtained, accompanied by a 62% yield of polyisoprene.

Catalyzed by 1 mol% of **C2** at room temperature, 24 h reaction of isoprene with acrolein gave a 88% yield in a 87:13 ratio of 1,4- versus 1,3-substituted acrolein adducts.

In the presence of 1 mol% of **C3**, 24 h room temperature reaction of isoprene with acrolein gave a 43% yield in a 92:8 ratio of 1,4- versus 1,3-substituted acrolein adducts, while 24 h reaction of isoprene with methyl vinyl ketone gave a 27% yield in a 91:9 ratio of 1,4- versus 1,3-substituted methyl vinyl ketone adducts in the presence of 1mol% of $Cp(CO)_2(\eta^1\text{-THF})FeSbF_6$ (same cation but different anion as **C3**).

In the presence of 1 mol% of **C4**, 24 h room temperature reaction of isoprene with acrolein gave a 47% yield in an 88:12 ratio of 1,4- versus 1,3-substituted acrolein adducts.

Clearly, **C1** is the most reactive one among above four catalysts. **C3** and **C4** are comparable in reactivity, chelate tungsten catalyst **C2** has a little bit higher reactivity.

A central problem in any study of catalysts is that of whether the true catalytic species is derived from the catalyst precursor being added to the reaction mixture or is simply an adventitious impurity introduced by an impure reagent or a minor decomposition pathway.

Experiments with $NOSbF_6$ suggested that it was not involved in the activity of **C1**; while a series of experiments with the hindered acid trap 2,6-di-tert-butylpyridine showed that this rendered $Cp(CO)_2Fe^+$ a much less active catalyst, suggesting that around 70% its reactivity was due to adventitious acidic impurities. For **C4**, even though experiments with $Ph_3C^+PF_6^-$ (which was used to generate **C4**) showed similar regio- and stereoselectivity, a ~ 10% of impurity of $Ph_3C^+PF_6^-$ in **C4** would have been required to give

the observed yields, but the purity of **C4** was much better than 90%.[36]

Furthermore the stoichiometric and kinetic results[36] provide good evidence that the organometallic cations derived from catalysts **C1**, **C2**, **C3**, and **C4** are true Diels-Alder catalysts. The stoichiometric cycloaddition rates and observed catalytic yields are in complete agreement for catalysts **C1** and **C2**, while for catalysts **C3** and **C4**, the true catalysis by $Cp(CO)_2Fe$ or $Cp(CO)_3Mo$ is much slower than the observed catalytic yields. Thus, for these latter two systems, adventitious catalytic impurities were present.

One would expect a strong acid to give a rapid rate of Diels-Alder cycloaddition but a slow rate of catalyst turnover (or catalyst regeneration). That is, in a truly catalytic reaction, as opposed to a stoichiometric reaction with one equivalent of acid, these factors may oppose each other, so the overall rate as a function of acidity would appear unpredictable. But for these four catalysts, the cycloaddition rates followed the order: **C1** $>>$ **C2** $>$ **C4** $\approx$ **C3**, which is directly correlated with the Lewis acidity of the cations (order **C1** $>>$ C2$>$ C3 $>$ **C4**), where the Lewis acidity was based on

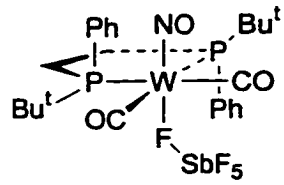
NMR chemical shift differences between free and Lewis acid complexed-crotonaldehyde.[39]

Since **C3** and **C4** are not especially reactive and are contaminated by catalytic impurities, we decided to pursue as initial targets Diels-Alder catalysts based only on analogues of catalysts **C1** and **C2**.

In order to render the tungsten complex chiral for inducing asymmetric Diels-Alder reactions, the PMe_3 ligand could be replaced by a monodentate chiral phosphine, or along with one of the cis CO ligands by a chelating phosphine like **C2**. Since it is difficult to carry out the resolution of racemic **C2** (chiral cellulose column might be a choice as Togni has always done in the resolution of phosphine ligands),[40] a C_2 symmetric chiral ligand of the form $ArRPCH_2CH_2PArR$ becomes another choice. The latter approach readily allows one to design a chiral pocket that might give rise to the desired enantioselectivity.

The asymmetric induction of the Diels-Alder reaction was achieved in the presence of the chiral tungsten catalyst,

($Bu^tPhPCH_2CH_2PPhBu^t$)$W(CO)_2(NO)Br$ (**C5**, Figure II.2).[41] Stoichiometric cycloaddition of isoprene and



C5

Figure II.2

metal-acrolein adduct (**5a**) gave a ~60:40 diastereoselection (1,4-substituted) of the coordinated Diels-Alder adducts, while larger scale reaction in presence of 2 mol% of **C5**, at room temperature for 24 h, gave a 10% yield in a 24% e.e. Cycloaddition of isoprene and 2-methacrolein in the presence of 0.9 mol% of **C5**, at room temperature for 24 h, gave an 8% yield in a 35% e.e.

While the low yield is due to the low catalyst turnover, these are the first two asymmetric inductions of Diels-Alder reactions catalyzed by this series of tungsten catalysts, hence providing evidence that these series of tungsten catalysts rather than adventitious acid impurities are true Diels-Alder catalysts.

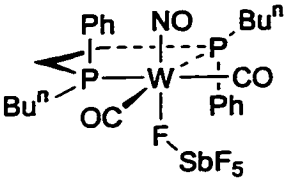
From a comparison of the catalytic reactivity of tungsten Lewis acid **C1** and **C2** (Figure II.1), successive incorporation of electron rich phosphine ligands leads to a diminution of Lewis acidity. Even though the catalytic reactivity of **C2** is low, but it is still acceptable.

What is worrisome is the extremely low reactivity of the C_2 symmetric chiral tert-butyl phosphine catalyst **C5** (Figure II.2). Several factors could cause the problem.

First, the tert-butyl group might be too bulky. If this were true, it would be a fatal problem since the computer modeling suggests the use of even bulkier groups for high enantioselection.

Second, it might be caused by a simple electronic effect. The moderate reactivity of a C_2 symmetric chiral n-butyl phosphine catalyst **C6** (Figure II.3) excluded this possibility. For example, cycloaddition of isoprene with acrolein in presence of 1.7 mol% **C6** at room temperature for 23 h gave a 49% yield, while in the same condition, a 73% yield was achieved for methacrolein.[41]

Figure II.3



C6

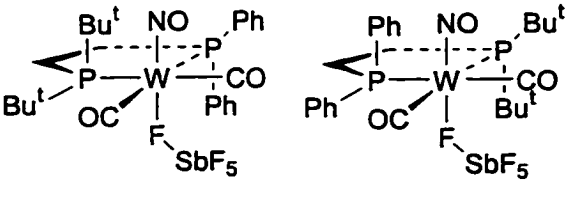
The last reason might be the ring conformation and distortion of the octahedral angles of tungsten, for instance as seen in Figure III.7, the C-P-W-P dihedral angle and the N-W-O (acrolein oxygen) angle. Generally speaking, the smaller the dihedral angle, the higher torsional energy of the 5-member ring; the more far away from 180° of the N-W-O angle, the higher angle strain about tungsten. The ring distortion appears to be related to the distortion about tungsten, and the combined effect seems to influence the reactivity of the catalytic W-enone center.

III. Electron-Rich Phosphine Ligands

The extremely low reactivity of the C_2 symmetric chiral tert-butyl phosphine catalyst **C5** might be caused by first, the bulky tert-butyl group, second, simple electronic effects such as $Alkyl_3P/AlkylPh_2P$ moieties versus $Alkyl_2PhP/Alkyl_2PhP$, and third, the conformation of the 5-member chelate ring and angles about tungsten.

With all these questions unanswered, we decided to synthesize catalyst **C7** (which is a tert-butyl analogue of **C2**) to investigate its catalytic reactivity for the Diels-Alder reaction (Figure III.1).

Figure III.1

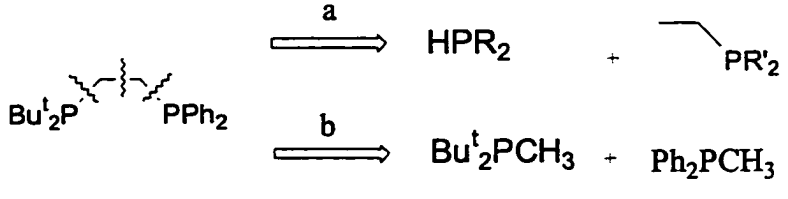


racemic **C7**

A. Synthesis of $Bu^t_2PCH_2CH_2PPh_2$ (7)

In considering the retro-synthetic analysis of $Bu^t_2PCH_2CH_2PPh_2$ (7), there are three major bond breaking positions that are acceptable and lead to two different synthetic strategies (scheme III.1). Route *a* involves disconnecting a carbon-phosphorus bond, while route *b* involves breaking a carbon-carbon bond.

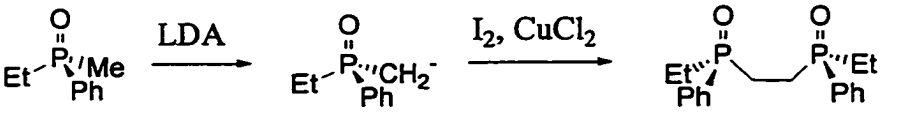
Scheme III.1



For route *b*, the synthetic step involves the formation of a carbon-carbon bond at the two P-Me groups. In 1968 Mislow and co-workers developed a method involving oxidation of a carbon anion for the formation of such a carbon-carbon bond.[42] The deprotonation of a P-Me group in phosphine oxide occurs with the

preservation of configurational integrity of the neighboring phosphorus stereogenic center. The oxidative coupling of the P-CH_2^- anion yields directly the symmetrical bisphosphine.[43]

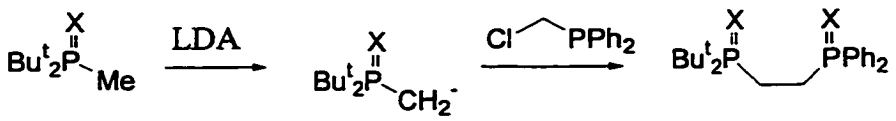
Scheme III.2



The C_2 symmetric bisphosphine ligands **5** and **6** for the catalysts **C5** and **C6** (Figure II.2 and Figure II.3) were prepared via similar routes.[44-46] However, the oxidative coupling procedure is not suitable for ligand **7**, because the two phosphine anion intermediates are different.

An alternative synthetic route which might work is, that first it forms a carbon anion as Mislow did, then reacts with PCH_2-EWG, knocking off a leaving group such as chloride or tosylate, and forming the carbon-carbon bond via an S_N2 reaction.

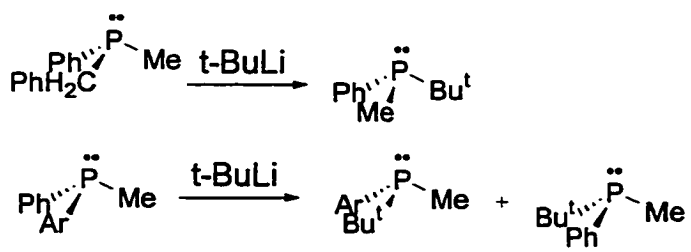
Scheme III.3



X: O, S, or lone pair electron

One disadvantage of this alternative is that some possible competitive reactions do exist, such as nucleophilic attack at the phosphorus atom to displace a phenyl group, instead of nucleophilic attack at carbon. Kyba demonstrated reactions involving the displacement of benzyl and phenyl groups with t-BuLi or n-BuLi under similar conditions (Scheme III.4).[47,48]

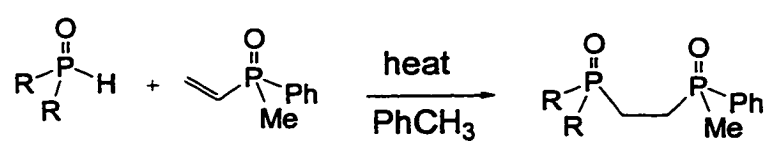
Scheme III.4



Ar: p-t-Bu benzene

For route a, the synthetic step involves the formation of a carbon-phosphorus bond which could be achieved by several known reactions. One of them is the Michael type addition of phosphorus nucleophiles to vinyl phosphine or vinyl phosphine oxide. With such phosphorus nucleophiles, use of thermal conditions and non-polar solvents proved advantageous as after heating of equal-molar mixtures of phosphine and vinyl phosphine in refluxing toluene, the poorly soluble bisphosphine typically crystallized out from the reaction mixture upon cooling and could be isolated pure by filtration. In 1988 Pietrusiewicz *et al* reported several examples of preparation of bisphosphine via such type of addition (Scheme III.5).[49]

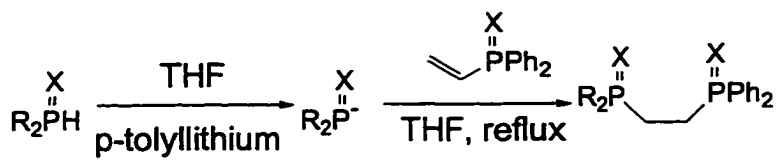
Scheme III.5



R: CH_2Ph, n-Hex, Cy, Ph, t-Bu

The base catalyzed Michael type addition of phosphorus nucleophiles to vinyl phosphine has also been used. For example, in 1971 King reported[50,51] the synthesis of *diphosoxide* (Scheme III.6). Similarly the bisphosphine ligand **2** for the tungsten catalyst **C2** was also prepared using this method by Hersh in 1989.[36]

Scheme III.6



diphosoxide: R = Ph, X=O
ligand **2** : R = Cy, X=lone pair

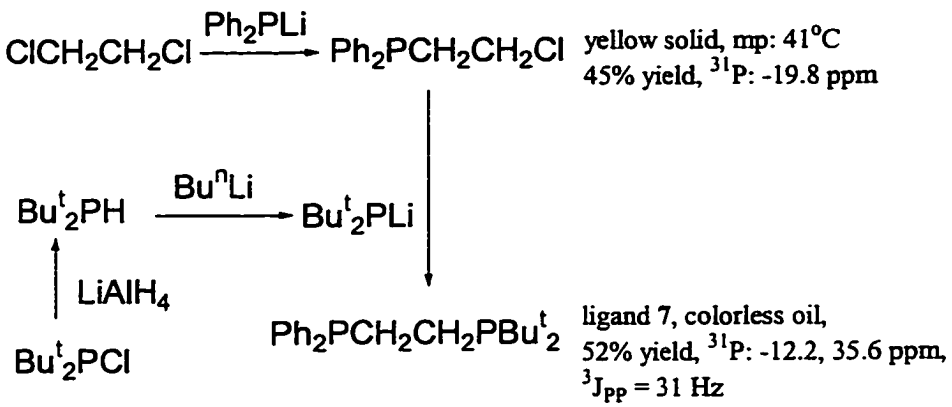
Results and discussions. Since both t-Bu_2PH and $Ph_2PCH_2{=}CH_2$ are commercially available, the preparation of ligand **7** via the base catalysis method analogous to the preparation of *diphos* (Scheme III.6) seemed straightforward.

But in a fact the preparation of ligand **7** via the base catalysis method was unsuccessful. The method of Dubiois' using AIBN to

promote a radical reaction,[52] also failed to give the desired product in the reaction of $Ph_2PCH_2{=}CH_2$ with t-Bu_2PH.

Eventually the ligand **7** was prepared from commercially available t-Bu_2PCl and known $Ph_2PCH_2CH_2Cl$ as shown in Scheme III.7, [53,54] where $Ph_2PCH_2CH_2Cl$ was made analogously to Uriarte's method.[53]

Scheme III.7



Addition of n-BuLi to a solution of Ph_2PH in THF at room temperature gave a THF solution of Ph_2PLi. Dropwise addition of the Ph_2PLi solution to $ClCH_2CH_2Cl$ at 0°C gave after work-up the desired product $Ph_2PCH_2CH_2Cl$ in a 43% yield as a white powder containing 0.5% of *diphos* and 3% of an unknown phosphorus impurity. Further purification was achieved by the crystallization

in ether to give a 36% yield of product as white crystals containing less than 1% of *diphos* and the unknown phosphorus impurity.

Reduction of t-Bu_2PCl with $LiAlH_4$ gave rise to the desired t-Bu_2PH, and reaction with n-BuLi gave the required anion t-Bu_2PLi. This was then added dropwise at room temperature to a solution of $Ph_2PCH_2CH_2Cl$ in THF to give after work-up an 89% yield of crude $Bu^t_2PCH_2CH_2PPh_2$ as a pale yellow oil. Purification was accomplished by flash chromatography to give the analytically pure product as a colorless oil in 89% yield. The characterization of ligand **7** was achieved by NMR, mass spectroscopy, and elemental analysis.

The ^1H NMR spectrum of ligand **7** exhibited similar peaks to those of the starting materials $Ph_2PCH_2CH_2Cl$ and t-Bu_2PCl, while the integration of the whole spectrum is consistent with the desired structure. More convincingly, the two doublet peaks having the same 33 Hz coupling constant in the ^{31}P NMR spectrum indicated the bisphosphine structure. The assignment of the -12.24 ppm doublet to the Ph_2P moiety is based on the position of the ^{31}P peak of *diphos* at -12.30 ppm, and the ^{31}P peak of $Ph_2PCH_2CH_2Cl$ at -

19.48 ppm; the assignment of the 35.56 ppm doublet to the t-Bu_2P moiety is consistent with the appearance of the ^{31}P peak of t-Bu_2PH at 20.32 ppm. The ^{13}C NMR spectrum is also consistent with the proposed structure.

The 70 eV mass spectrum is also consistent with the proposed structure of ligand **7**. The peak (*m/z* 57) represented by the ion $(CH_3)_3C^+$ is the base peak (100 % of relative intensity). The intensity of another fragment peak (*m/z* 301) caused by the simple cleavage of Me_3C-P bond was also very strong. Similar cleavage of Ph-P bond at the other end of the molecule caused a pair of fragment peaks (*m/z* 77, 281). The peak (*m/z* 77) was relatively larger than the other because of the stability of the fragment.

The peaks (*m/z* 41, 317) represent one pair of rearrangement fragment peaks of $C_3H_5^+$ and $Bu^t(Ph_2PCH_2CH_2)MeHP^+$. The peaks (*m/z* 185, 245) are the ions Ph_2P^+ and t-Bu_2P^+ caused by simple cleavage of the methylene carbon - phosphorus bond.

The molecular ion peak (*m/z* 358) is weak, only 0.7% of the base peak. The intensity of M+1 peak is 0.3% of the base peak or about 40% of the molecular ion peak, while the calculated M+1

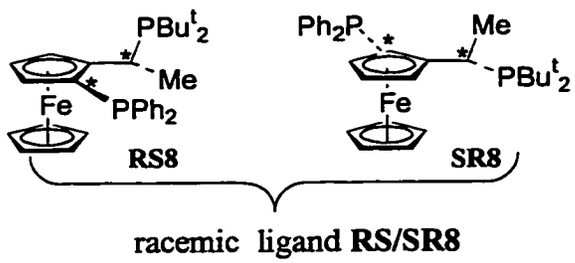
intensity is 25% of the molecular ion. The measured value is higher than calculated value for the (M+1):M peak height ratio which could be caused by no calibration of the peak intensity of the mass spectrum or just experiment error.

B. Synthesis of Ferrocene Ligand (RS8)

The extremely low reactivity of catalyst **C5** (Figure II.2) brought great concern about the potential possibility of development of this kind of C_2 symmetric Lewis acid as a Diels-Alder catalyst. Achiral t-butyl phosphine ligand **7** was prepared to test whether the low reactivity of **C5** was due just to steric bulk. Since the resolution of racemic tungsten Lewis acid catalyst **C7** is difficult, the synthesis of a chiral analogue of ligand **7**, if it were possible, would be desirable.

In 1994 Togni *et al* reported[55,56] a chiral diphosphine, R-1-[S-2-(diphenylphosphino)ferrocenyl]ethyl di-tert-butylphosphine (**RS8**, Figure III.1), which meets our requirements for a chiral

Figure III.2



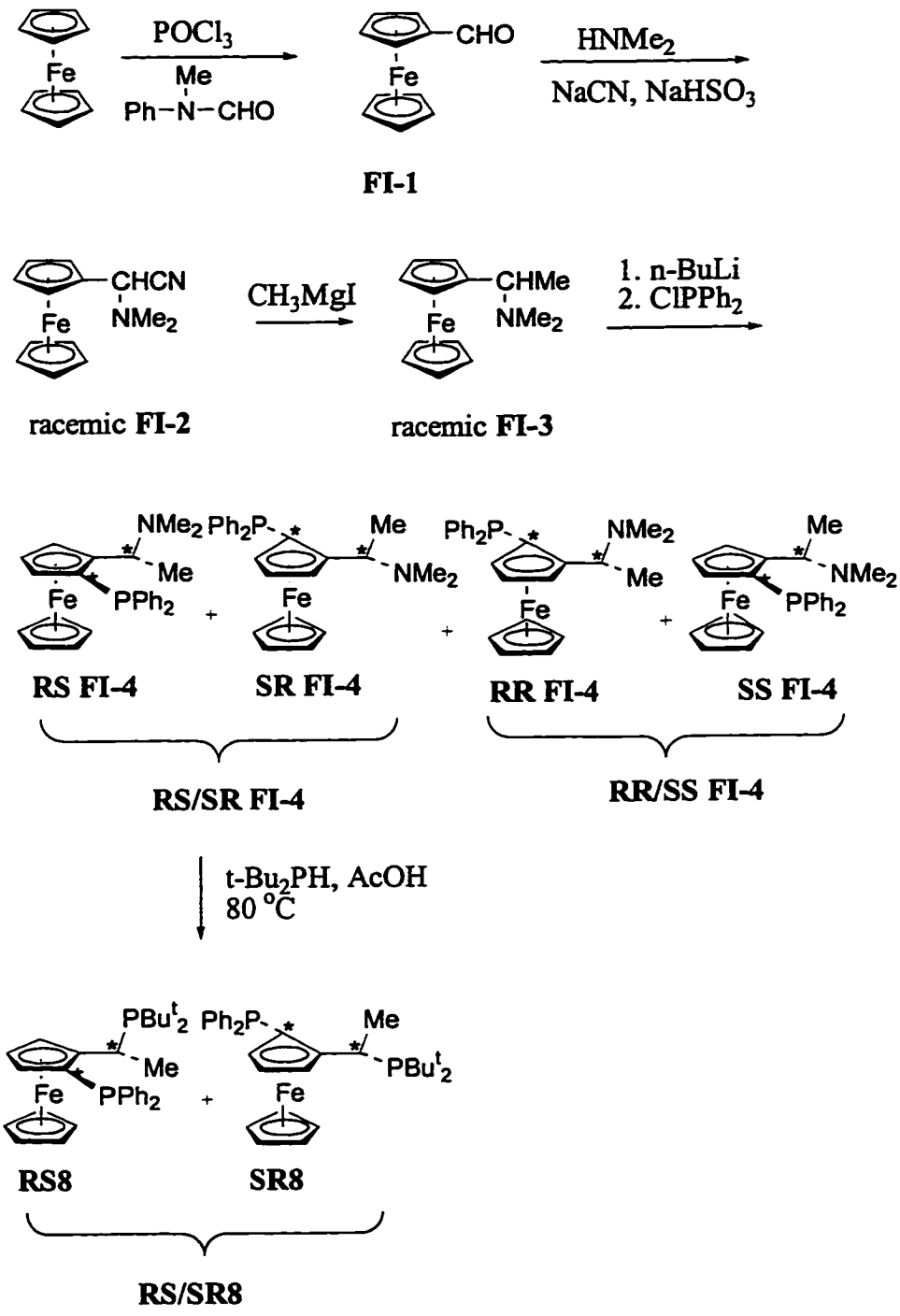
racemic ligand **RS/SR8**

analogue of ligand **7** except that **RS8** has a three carbon bridge between the phosphines instead of a two carbon bridge in ligand **7**.

Since the ferrocene derived ligand **RS8** was not commercially available[56] and was costly to prepare, racemic **RS/SR8** (Figure III.2) was synthesized first in order to test this ligand.

The procedure is shown in Scheme III.8.[57] Formyl ferrocene (**FI-1**) was prepared from the reaction of ferrocene and a large excess N-methyl formanilide in the presence of excess phosphorus oxychloride according to Rosenblum's procedure.[57] In order to achieve a high yield, a longer reaction time (4 h instead of 2 h) was required. The dark purple crystals of **FI-1** showed a sharp transition temperature at 45°C and melted at 124°C which agreed with Graham's data.[58] A singlet aldehyde peak at 9.96 ppm in the ^{1}H NMR spectrum and a very strong conjugated aldehyde band at

Scheme III.8



1680.7 cm^{-1} in the infrared spectrum confirmed the structure of the product.

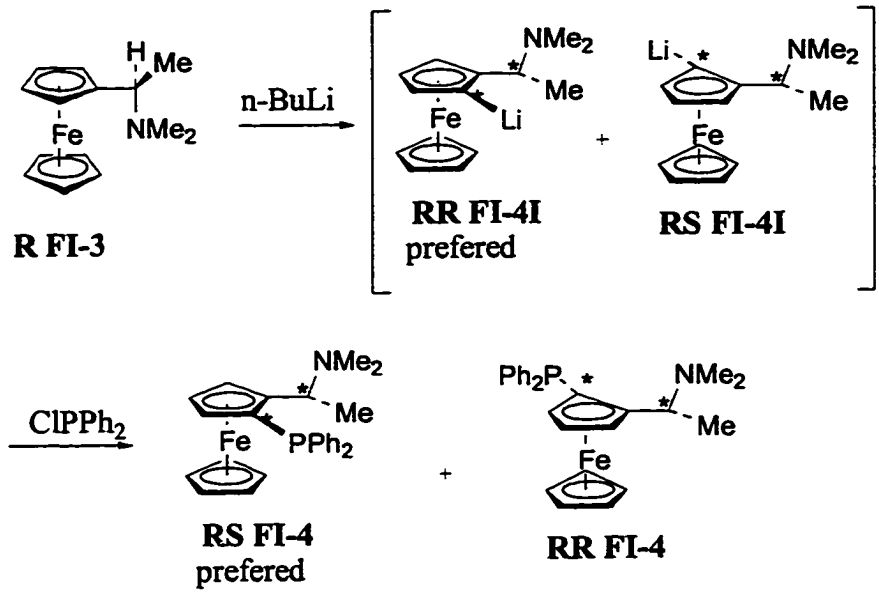
The amino nitrile (racemic **FI-2**) was prepared from the reaction of formyl ferrocene (**FI-1**) with dimethyl amine and sodium cyanide in the presence of sodium bisulfite according to Hauser's procedure.[59] The amber oil was crystallized from petroleum ether to give light brown crystals (mp:84°C). The disappearance of aldehyde peak in the ^1H NMR spectrum, along with the presence of Cp ring hydrogen peaks, a sharp singlet methine peak at 4.63 ppm, and a singlet methyl peak at 2.28 ppm were consistent with the designated structure.

The Grignard reaction of the amino nitrile (racemic **FI-2**) with CH_3MgI gave racemic **FI-3** as clear amber oil,[59] further purified by vacuum distillation at 0.1 Torr, 110°C, in 88% yield. In comparison to the spectrum of the amino nitrile (racemic **FI-2**), the 200 MHz ^1H NMR spectrum of racemic **FI-3** was much simpler. For instance, all the Cp ring hydrogen peaks collapsed into a singlet at 4.11 ppm, which had a shoulder peak at 4.12 ppm. The CHN peak moved up-field consisted with replacement of the

electron-withdrawing CN group with the electron-donating Me group and became a quartet because of the coupling with the neighboring Me group. The Me peak was a doublet with the same coupling constant, 6.9 Hz. The NMe_2 peak was still a singlet but also moved up-field, because of the replacement of the CN group with Me group.

In 1970, Ugi *et al* reported[60] the highly diastereo-selective (96:4) lithiation of optically resolved N,N-dimethyl-1-ferrocenylethylamine (**R FI-3**) (Scheme III.9). 10 years later, Kumanda *et al* reported[61] the synthesis of the optical resolved ferrocene phosphine (**RS FI-4**) from the optical resolved ferrocenyl tertiary amine (**R FI-3**) via Ugi's lithiation method; after removal of the diastereomeric impurity **RR FI-4** via chromatography, Kumanda reported a 50% yield of optically resolved **RS FI-3** (Scheme III.9).[61] The racemic mixture **RS/SR FI-4** (scheme III.8) was therefore prepared via Kumada's method (Scheme III.9). The racemic **FI-3** was lithiated by n-BuLi, followed by the addition of $ClPPh_2$ to give corresponding four isomers of the ferrocenyl phenyl phosphine **FI-4**. Alumina

Scheme III.9



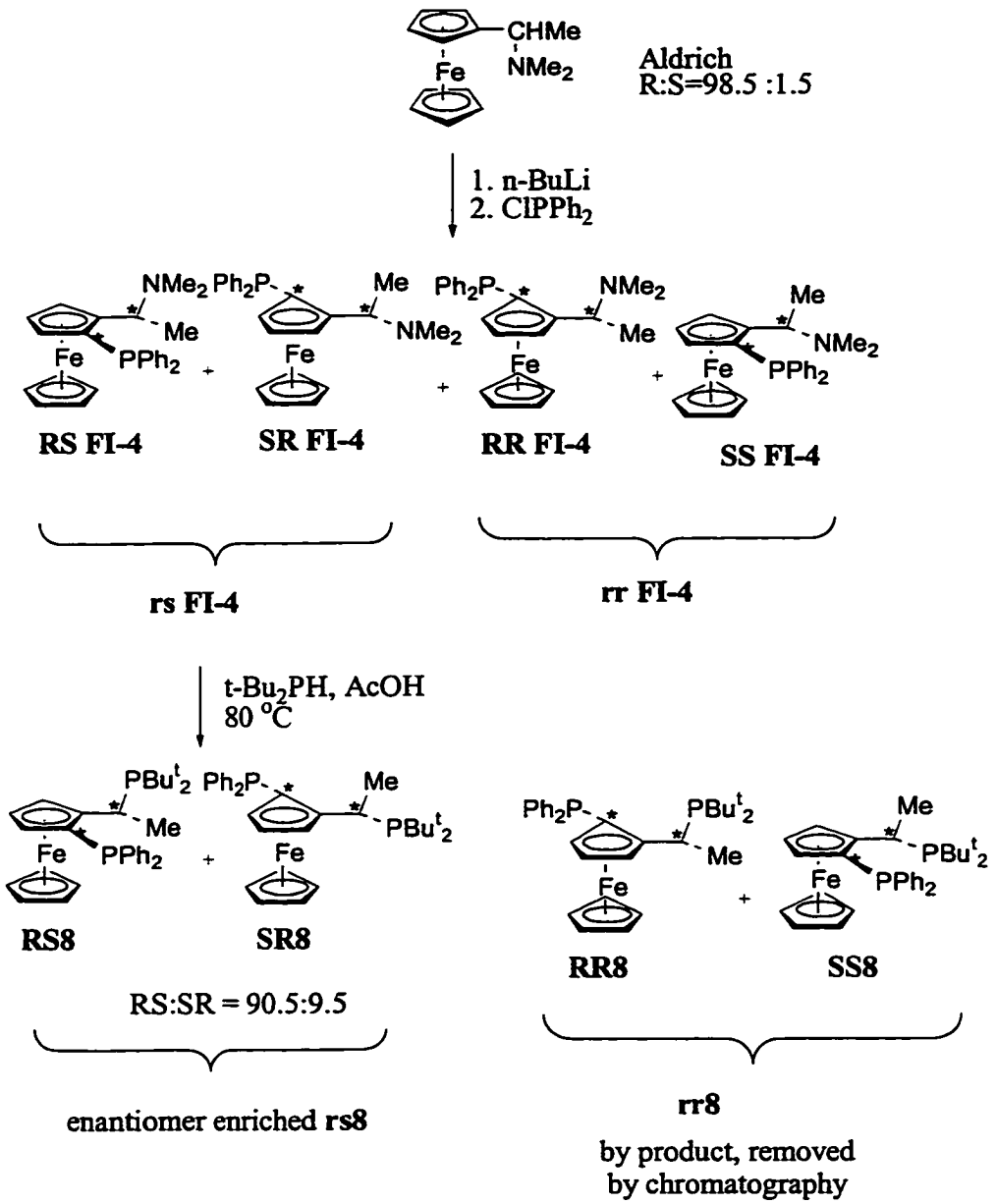
chromatography eluting with Benzene/Hexanes solution removed the RR- and SS- diastereomers, giving the racemic mixture **RS/SR FI-4** in 47% yield as a yellow powder as expected. ^{1}H NMR spectral data of our racemic **RS/SR FI-4** is consistent with literature data.[61] In particular, a singlet at -22.37 ppm in the ^{31}P NMR spectrum confirmed the introduction of the PPh_2 group.

The final racemic mixture **RS/SR8** was prepared via Togni's procedure as shown in Scheme III.8.[55] After crystallization in boiling ethanol, a 63% yield of product as orange yellow crystals

was obtained. The structure of the product was confirmed by ^{1}H NMR, ^{31}P NMR, ^{13}C NMR spectra, and elemental analysis. Even though the ^{1}H NMR and ^{31}P NMR spectral data agreed with Togni's data in $CDCl_3$, we found that **RS/SR8** was unstable in $CDCl_3$. Decomposition peaks were detected within 1 h by both ^{1}H NMR and ^{31}P NMR.

The tungsten complex of **RS/SR8** was found to give a highly active Diels-Alder catalyst, so the preparation of enantiomerically pure ferrocene phosphine ligand **RS8** became necessary. Enantiomerically enriched **rs8** was prepared from commercially available **R FI-3** (Aldrich, 97% e.e.) via the same route (Scheme III.10) as described before. The structure of the product was verified via ^{1}H NMR, ^{31}P NMR, ^{13}C NMR spectroscopy, and elemental analysis. The value of the specific rotation of **rs8** $[\alpha]^{29}_{D}$ = -337° (c 0.6, $CHCl_3$) was lower than Togni's value for **RS8**, $[\alpha]^{22}_{D}$ = -417° (c 0.6, $CHCl_3$). Based on Togni's specific rotation data, the enantiomeric purity of our product is 81% rather than 97% e.e. as was expected based on the enantiomeric purity of the Aldrich starting material.

Scheme III.10



There are several possible explanations for the lower optical rotation. First, trace of highly optically active impurities can always affect such values. As noted above, we detected

decomposition in $CDCl_3$, but this seems not to be a problem since we observed no change in optical rotation over several hours in $CHCl_3$. Second, the enantiomeric purity of the commercially available **R FI-3** might not be the claimed 97% e.e. The rotation value of 13.0° (Aldrich) is slightly lower than Kumada's rotation of 14.1°, so the starting material may be only 92% optically pure instead of the 97% claimed. We did not check the optical rotation of the compound we purchased before it was used. Third, epimerization may have occurred during the reactions but it would seem possible to affect the final e.e. only if a true epimerization of the $CHMeNMe_2$ center occurred during the lithiation reaction. All other steps give rise to the diastereomer that are removed via chromatography.

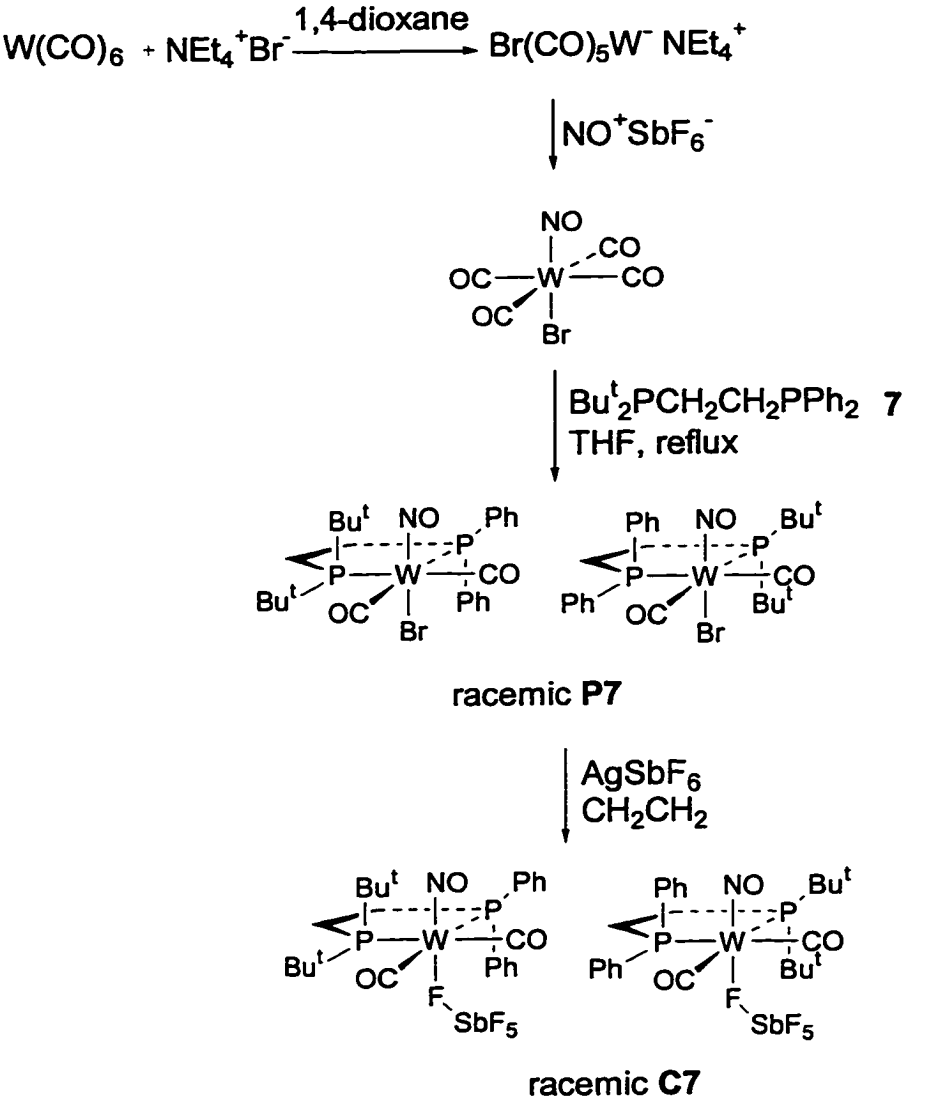
C. Tungsten Complexes

Racemic catalyst **C7** was conveniently prepared from **7** shown in Scheme III.11.[36] The known trans-$(NO)W(CO)_4Br$ was prepared from $W(CO)_6$ according to Barraclough's procedure[62] as shown and was reproducibly found to be contaminated by 26% by weight of $W(CO)_6$ (on the basis of elemental analysis).[36]

Under a nitrogen atmosphere, refluxing of a THF solution of trans-$(NO)W(CO)_4Br$ and **7** gave the desired racemic tungsten bromide complex **P7**. At this point, the excess $W(CO)_6$ is readily removed by sublimation to give a 92% yield of crude racemic **P7** as a yellow powder. Further purification was achieved via crystallization in 1:1 CH_2Cl_2/Hexanes to give a 76% yield of spectroscopically pure racemic **P7** as pale yellow crystals.

P7 exhibits two carbonyl bands at 2024 and 1952 cm^{-1} and a nitrosyl band at 1619 cm^{-1}, which are similar to those of known chelate nitrosyl bromide analogues[36,63] and so it is presumed to be isostructural. The NMR spectra of racemic **P7** also confirmed the desired structure. In the ^{31}P NMR spectrum and compared to

Scheme III.11



ligand **7**, two doublets moved down-field because of the coordination with tungsten, and each doublet exhibits ^{183}W satellites (due to the 14% of tungsten present as ^{183}W having I = ½). Compared to ligand **7**, two multiplets of bridge hydrogens in

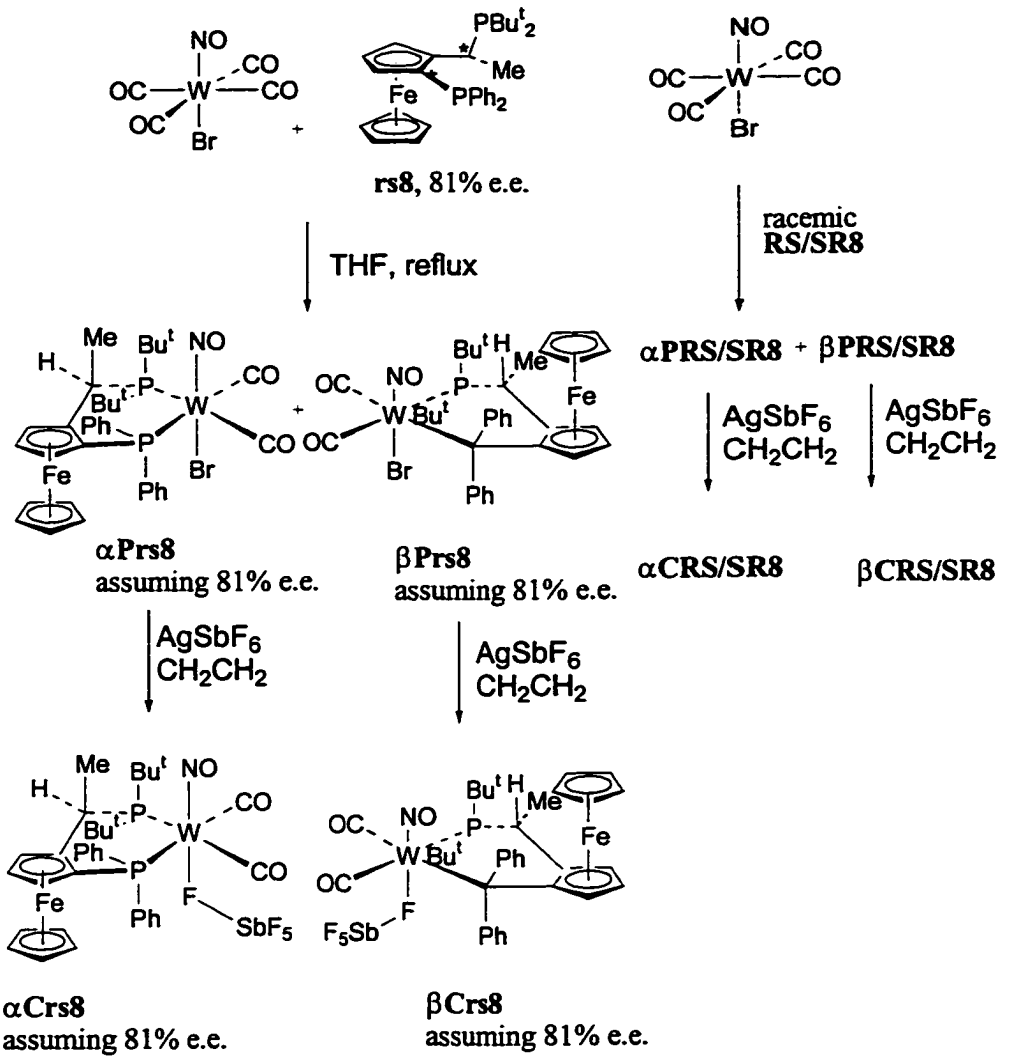
the ^{1}H NMR spectrum expand to four multiplets at 3.3 ppm, two near 2.5, and 1.6 ppm due to the CH hydrogens that are cis to each of the NO and Br ligands. The ^{13}C NMR spectrum exhibits two CO peaks as two doublets of doublets corresponding to two different CO ligands, each CO coupled with two different phosphorus atoms. The mass spectrum of racemic **P7** exhibits an envelop of M^{+} - 2CO peaks representing the overlap of ^{182}W, ^{183}W, ^{184}W, ^{186}W with ^{79}Br, ^{81}Br, ^{16}O, ^{17}O, ^{18}O, ^{12}C, ^{13}C, ^{14}C, ^{1}H, and ^{2}H. As shown in the experimental, the intensities of isotope peaks of M^{+}- 2CO (M^{+}- 2CO, M^{+}- 2CO +1, M^{+}- 2CO +2, M^{+}- 2CO +3, M^{+}- 2CO +4, M^{+}- 2CO +5, M^{+}- 2CO +6) are in excellent agreement with the calculated data (via hand calculation). Finally, the elemental analysis data also agreed with calculated data. The results from ^{1}H NMR, ^{31}P NMR, infrared, mass spectroscopy and elemental analysis all confirmed the identity of the above compound as the desired tungsten bromide complex **P7**.

Racemic catalyst **C7** was prepared via our routine method by combining racemic **P7** with one equivalent of $AgSbF_6$ to give the desired racemic catalyst **C7** and AgCl. After removal of AgCl by

filtering through a pad of Celite, the CD_2Cl_2 solution of **C7** was checked by NMR and immediately used as the catalyst in order to minimize any adventitious impurities due to decomposition. The similar splitting pattern and slight chemical shift differences between the NMR spectra of **C7** and **P7** provides evidence that the structures are similar.

Similarly ferrocene derived tungsten carbonyl complexes were conveniently prepared from **rs8** shown in Scheme III.12. Under a nitrogen atmosphere, a THF solution of trans-$(NO)W(CO)_4Br$ and enantiomerically enriched ferrocene phosphine ligand **rs8** was allowed to stand at room temperature for 2 days to give two enantiomerically enriched diastereomers of chiral tungsten bromide complexes, one with the ferrocene syn to the nitrosyl ligand β**Prs8** and the other with the ferrocene anti to the nitrosyl ligand α**Prs8**. The reaction was monitored by following the disappearance of bands at 2050 and 1975 cm^{-1} bands in the IR spectrum due to the starting material. After removal of solvent on a vacuum line, $W(CO)_6$ was then sublimed off by warming up at 45°C under dynamic vacuum to give a mixture of α**Prs8** and

Scheme III.12



βPrs8 as a yellow powder. Separation of the two diastereomers was achieved via silica gel chromatography eluting with 1:1 benzene/hexanes to give a 52% yield of two bands in roughly a 1:1

ratio. Without X-ray data and just by NMR, it is impossible to determine which fraction is "syn" and which one is "anti". So we simply call them **Prs8-1** (first band from column) and **Prs8-2** (second band from column). In the ^{31}P NMR spectra of **Prs8-1** and compared to ligand **7**, two doublets moved down-field because of the coordination with tungsten, and each doublet exhibits ^{183}W satellites. The ^{31}P NMR spectrum of **Prs8-2** is similar. Both the ^{13}C NMR spectra of **Prs8-1** and **Prs8-2** exhibit the two CO bands as two pairs doublets of doublets as expected for the geometry shown, as explained above. Finally the elemental analysis data of **PRS/SR8-1** and **PRS/SR-2** (prepared from racemic **RS/SR8**) also agreed with calculated data. The results from ^{1}H NMR, ^{31}P NMR, infrared, mass spectroscopy and elemental analysis all confirmed the identity of the above two compound as the desired two diastereomers **Prs8-1** and **Prs8-2**.

Enantiomerically enriched catalysts **Crs8-1** and **Crs8-2** were prepared via our routine method: **Prs8-1** or **Prs8-2** was combined with a little bit less than one equivalent of $AgSbF_6$ in CD_2Cl_2 to

give the desired enantiomerically enriched catalysts **Crs8-1** or **Crs8-2** as described before.

It is important to note, however, that the presence of even a slight excess of $AgSbF_6$ in the reaction pot caused competitive oxidation of the ferrocene moiety, indicated by broad and messy NMR signals. Using an excess of **Prs8-1** or **Prs8-2** over $AgSbF_6$ eliminates this side reaction and made it possible to acquire sharp NMR spectra.

D. Catalytic and Stoichiometric Reactions

Catalytic reactions. All catalytic Diels-Alder reactions were carried out in a similar way. Inside the drybox, pre-cooled (-35°C) acrolein and one equivalent of isoprene were added into pre-cooled CH_2Cl_2, and then a CD_2Cl_2 solution of the catalyst (checked by NMR) was added. After stirring at room temperature for several hours, the solution was brought out of the dry-box and filtered through a pad of silica gel in CH_2Cl_2 on a frit to remove catalyst, the product was washed down with CH_2Cl_2, followed by solvent removal on a rotary evaporator to give the Diels-Alder adducts. The 1,4:1,3 regio isomer ratios were determined by ^{13}C NMR, since the ^{13}C NMR spectrum of the Diels-Alder adducts gave two well-resolved sets of peaks (Figure III.3) corresponding to these structural isomers. The average of the corresponding sets of peak-heights was used to calculate the ratio of 1,4- versus 1,3-substituted structures. The enantiomer ratio of the major structural isomer (1,4-) was determined by addition of the chiral shift reagent europium tris[3-(heptafluoropropyl-hydroxylmethylene)-(-)

camphorate] ($Eu(hfc)_3$) to the Diels-Alder adduct, giving rise to just barely-separated peaks for the aldehyde proton. Typically 30~60 mg (0.025~0.05 mmol) of $Eu(hfc)_3$ were added to a solution of 5~10 mg (0.04-0.08 mmol) of acrolein/isoprene adduct in 0.5 mL of CD_2Cl_2. These concentration gave rise to a downfield shift in the aldehyde peaks from 9.5 ppm (in the absence of $Eu(hfc)_3$) to 17~24 ppm, with a chemical shift difference of 0.09~0.13 ppm at 400 MHz for the two enantiomers. The range of chemical shift difference depends both on the concentration of $Eu(hfc)_3$ and the dryness of the sample. For instance and as shown in Figure III.4, the aldehyde peak of the methacrolein/isoprene adduct has been shifted from 9.5 ppm to 21.8 ppm giving 0.13 ppm chemical shift difference, by adding 60 mg of $Eu(hfc)_3$ in 11 mg of the aldehyde in 0.5 mL CD_2Cl_2. On the other hand, as shown in Figure III.5, the aldehyde peak of the methacrolein/isoprene adduct has only been shifted from 9.5 ppm to 17.3 ppm with a 0.09 ppm chemical shift difference, even though 60 mg of $Eu(hfc)_3$ were added to 6 mg of the aldehyde in 0.5 mL CD_2Cl_2. Moisture is the suspected cause of the difference results because the failure to dry the

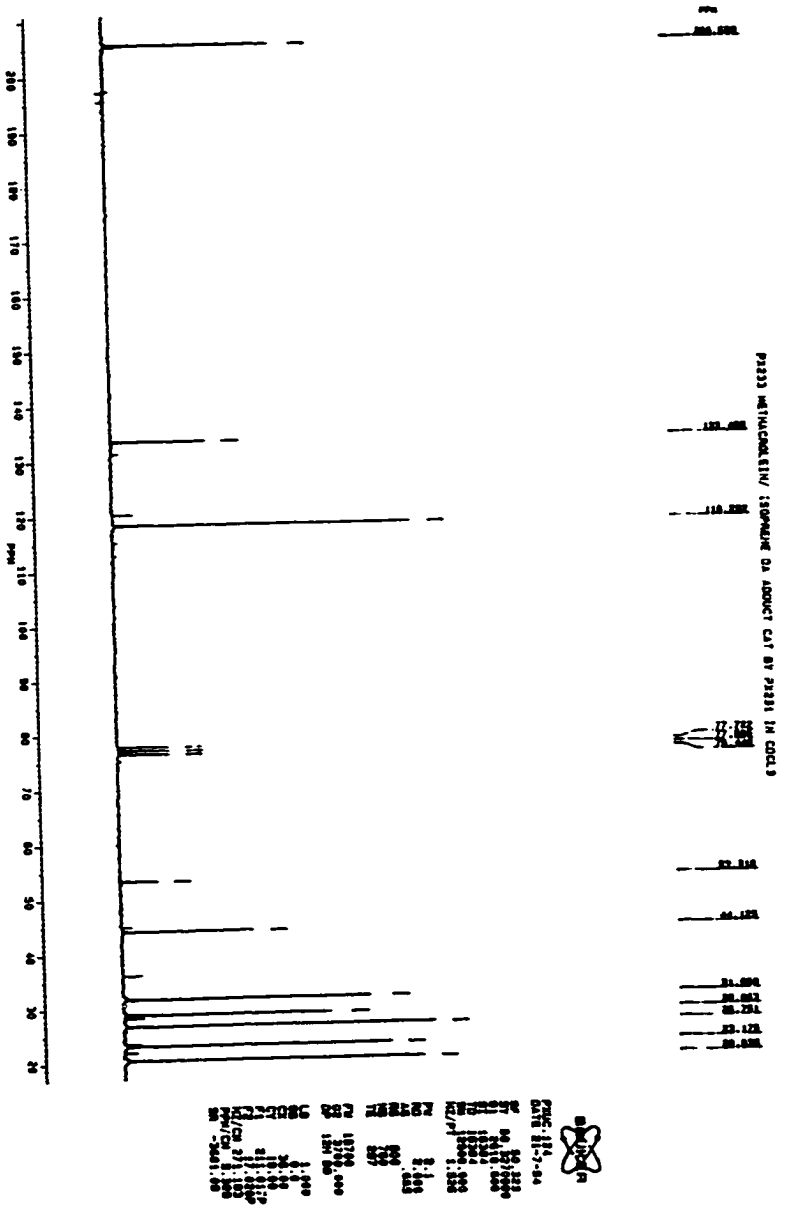


Figure III.3 ^{13}C NMR ($CDCl_3$) spectrum of isoprene/2-methacrolein adducts (catalyzed by Crs8-1)

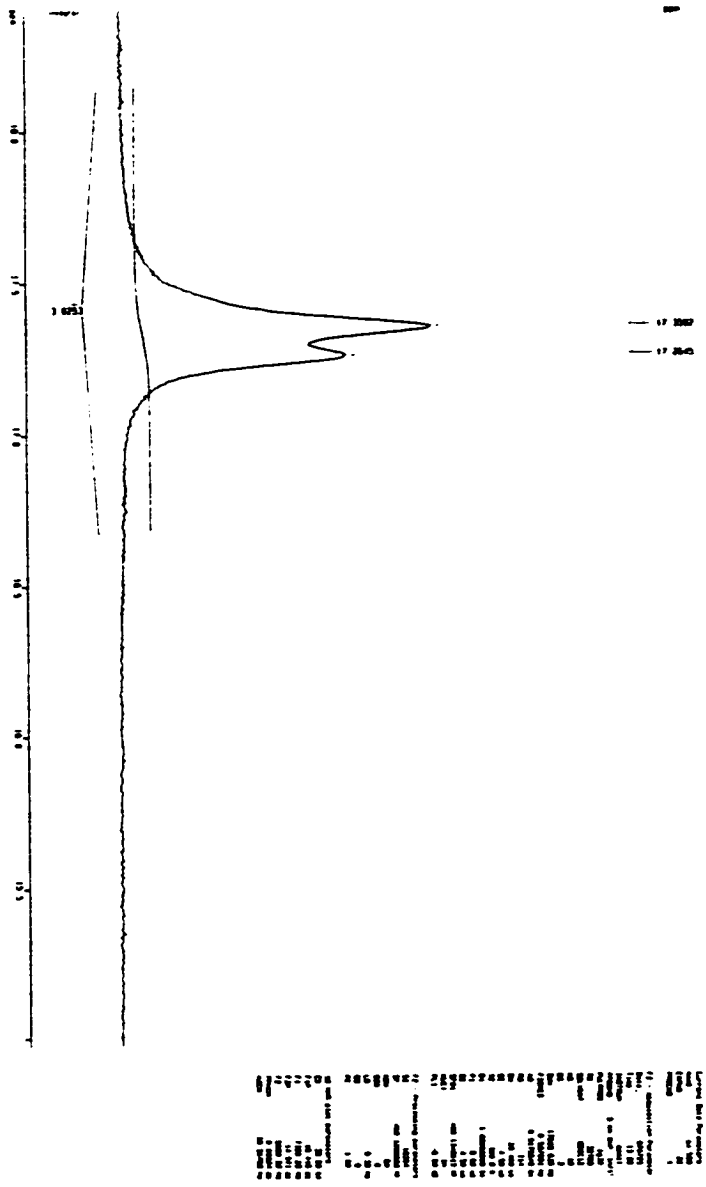


Figure III.4 Expanded ^{1}H NMR spectrum of aldehyde peaks of isoprene/2-methacrolein adducts (catalyzed by Crs8-2) in the presence of Eu(hfc)$_3$

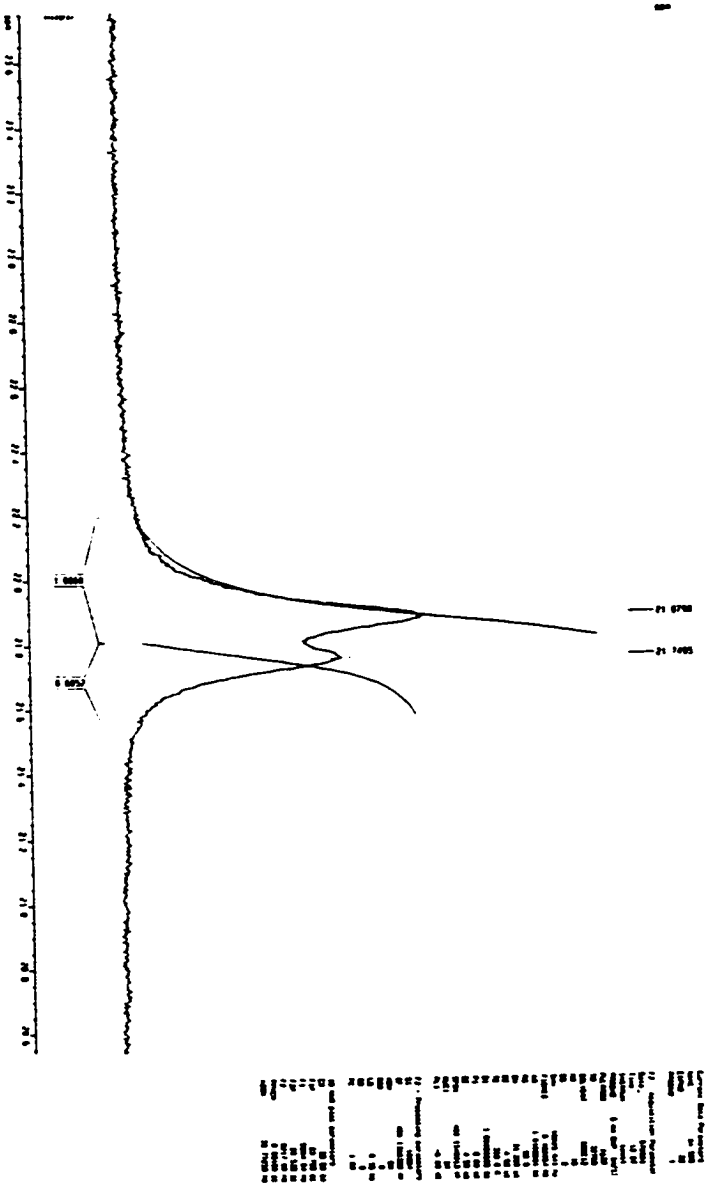


Figure III.5 Expanded ^{1}H NMR spectrum of aldehyde peaks of isoprene/2-methacrolein adducts (catalyzed by **Crs8-1**) in the presence of Eu(hfc)$_3$

glassware gave rise to no downfield shifting of the chemical shift of the aldehyde peaks.

The results of cycloaddition of acrolein or methacrolein with isoprene in the presence of this series of tungsten catalysts **C1** to **C10, C14** are collected in Table III.1. Without catalyst, room temperature reaction[36] of isoprene and acrolein or 2-methacrolein yields at most 4-5% of the Diels-Alder adduct in 24 h, giving a ~70:30 ratio of 1,4 versus 1,3-substituted cyclohexene isomers. Previously, the most active catalyst was the monodentate catalyst **C1**, giving an 84% yield for the 1 h room temperature reaction of isoprene with acrolein.[36] Surprisingly, racemic catalyst **C7** is one of most reactive catalysts in this tungsten catalyst series, since the one hour room temperature cycloaddition of isoprene and acrolein in the presence of 1 mol% **C7** gave an 81% yield of the Diels-Alder adduct, similar to that of **C1**.

The unexpected high catalytic activity of racemic **C7** excludes the steric bulk hypothesis as the cause of the low reactivity of **C5**, and suggested that the design of bulky catalysts for better enantio-selection is still possible.

Table III.1 Diels-Alder Reactions of Isoprene with Acrolein or 2-Methacrolein[a]

diene (eq)	enone (eq)	catalyst (eq)	time (h)	1,4:1,3	yield (%)	% e.e.
IP (101)	A (100)	none[b]	24	69:31	5	-
IP (106)	A (102)	**C1** (1)[b]	1	93:7	84	-
IP (101)	A (103)	**C2** (1)[b]	24	87:13	88	-
IP (106)	A (102)	**C3** (1)[b]	24	92:8	43	-
IP (100)	A (99)	**C4** (1)[b]	24	89:11	68	-
IP (51)	A (95)	**C5** (2)[c]	24		10	24
IP (71)	A (168)	**C6** (2)[c]	23		49	0
IP (106)	A (102)	**C7** (1)	1	92:8	81	-
IP (256)	A (222)	**CRS/SR8** (1)	2.5	95:5	75	-
IP (256)	A (222)	**CRS/SR8** (1)	1.5	95:5	65	-
IP (186)	A (174)	**CRS/RS8** (1)	2	96:4	80	-
IP (115)	A (100)	**Crs8-1** (0.3)	5	96:4	82	0
IP (105)	A (100)	**Crs8-1** (0.7)	3	95:5	77	0
IP (115)	A (100)	**Crs8-2** (0.3)	3	93:7	76	18[d]
IP (105)	A (100)	**Crs8-2** (0.9)	3	94:6	68	0
IP (103)	MA (100)	none[e]	24	72:28	0	-
IP (109)	MA (100)	**C1** (1)[b]	24	95:5	68	-
IP (101)	MA (97)	**C4** (1)[b]	24	92:8	68	-
IP (130)	MA (119)	**C5** (1)[c]	24		8	35
IP (62)	MA (131)	**C6** (2)[c]	23		73	0
IP (115)	MA (100)	**Crs8-1** (0.3)	5	92:8	71	26
IP (105)	MA (100)	**Crs8-1** (0.7)	3	95:5	82	16
IP (115)	MA (100)	**Crs8-2** (0.3)	3	92:8	64	7[d]
IP (105)	MA (100)	**Crs8-2** (0.9)	3	94:6	81	16

[a] All reaction were carried on in CH_2Cl_2 at room temperature. [b] Hersh's results reported in *J. Am. Chem. Soc.* **1989**, *111*, 6070. [c] **C5** was done by Rofeim, O., while **C6** was done by Marcune, B. [d] Enantioselection is not reliable because of the poor phase of the whole spectrum. [e] Bosnich's result, more than 105 h is needed to 90% completion of reaction, *J. Am. Chem. Soc.* **1992**, *114*, 6392.

The catalytic results by the ferrocene catalysts **Crs8-1** and **Crs8-2** also confirmed that steric bulk was not the cause of the low reactivity of **C5**. Room temperature reaction of isoprene and acrolein in the presence of 0.3 mol% of **Crs8-1** gave a 65% yield of the Diels-Alder adduct in 3 h, but no enantioselection was

achieved. In the case of 2-methacrolein, under the same reaction conditions, an 82% yield and a 16% e.e. were achieved. The diastereomeric catalyst **Crs8-2** showed similar reactivity. In the presence of 0.3 mol% of **Crs8-2**, room temperature reaction for 3 h gave a 65% yield and a 0% e.e. for the reaction of isoprene with acrolein, and an 82% yield and a 16% e.e. for the reaction of isoprene with 2-methacrolein. It is surprising that these two diastereomers have the same face selection (either R or S, Figure III.3 and Figure III.4). It means that the ferrocene moiety is not an innocent bystander, but rather must effect a conformational change resulting in diene attack preferentially on the same face of the metal-acrolein adduct, despite the opposite configuration at tungsten.

Without further looking into the conformation of the catalyst, the high catalytic reactivities of racemic **C7** and **Crs8-1**, **Crs8-2** might suggest that the Lewis acidity remains sufficiently high when the phosphine residues consist of (alkyl)Ar_2P/$(alkyl)_3P$ moieties as in the $Bu^t_2PCH_2CH_2PPh_2$ ligand of **C7**, where the two combined aryl groups mitigate the donor effects of the alkyl

groups. However, when the phosphine residues have two $(alkyl)_2ArP$ moieties as in **C5**, the now isolated phenyl groups cannot mitigate the donor alkyl effects, and the chelating phosphine is too strong a donor for catalytic activity to be exhibited.

Stoichiometric Reactions. For racemic **C7**, two stoichiometric reactions of isoprene with acrolein and one stoichiometric reaction of isoprene with 2-methacrolein were conducted. The reactions were completed by the time of first measurements (~5 min), which are comparable to the stoichiometric result of **C1**.

Under a nitrogen atmosphere, addition of 1.88 equivalent acrolein to a solution of freshly prepared racemic **C7** (0.04 mmol) in 0.5 mL of CD_2Cl_2 gave rise to a 0.6:1 ratio of free acrolein to coordinated acrolein (measured by ^1H NMR), and addition of 1.88 equivalent isoprene to the solution then gave a mixture of corresponding Diels-Alder adducts. The immediate (~5 min) measurement showed no free acrolein left, and the ratio of free Diels-Alder adducts to coordinated Diels-Alder adducts was 0.7:1.

The reaction was apparently complete since the ratio did not change upon subsequent measurement.

Another stoichiometric reaction also showed that the reaction was complete within 4 min. Under a nitrogen atmosphere, addition of 2 equivalent acrolein to a solution of racemic **C7** (0.07 mmol) in 0.5 mL of CD_2Cl_2 gave rise to a 3:1 ratio of free to coordinated acrolein, and addition of 1 equivalent isoprene to the solution gave a mixture of free acrolein : coordinated acrolein : free Diels-Alder adducts : coordinated Diels-Alder adducts of 7:7:9:1. This ratio (obtained at ~4 min reaction time) did not change with time.

Stoichiometric reaction of isoprene with 2-methacrolein also confirmed the high reactivity of **C7**. Under a nitrogen atmosphere, addition of 1.88 equivalent 2-methacrolein to a solution of freshly prepared racemic **C7** (0.04 mmol) in 0.5 mL of CD_2Cl_2 gave rise to a 0.7:1 ratio of free methacrolein to coordinated methacrolein, and addition of 1.88 equivalent of isoprene gave a mixture of corresponding Diels-Alder adducts. The immediate (~5 min) measurement showed no free 2-methacrolein left, and the ratio of

free Diels-Alder adducts to coordinated Diels-Alder adducts was 1:1. Further reaction brought no change in the ratio.

The essence of the stoichiometric reaction is to check the aldehyde peaks of the initially formed coordinated Diels-Alder adducts. The ratio of the corresponding two peak-heights represents the ratio of the two diastereomeric tungsten adducts due to attack of isoprene on both prochiral faces of coordinated acrolein; these peaks are resolved at 400 MHz. If the catalyst were enantiomerically pure, this ratio would be comparable to the e.e. When the catalyst is racemic, this ratio is only of value if exchange of the Diels-Alder adducts is slow. For racemic **C2**, this appears to be the case, and a 10% d.e. was observed. However, the reactivity of racemic **C7** is unexpectedly high, and within 5 min, free acrolein and free Diels-Alder adduct displaces the initially formed coordinated Diels-Alder adducts. Now the NMR spectra only represent the thermal equilibrium products rather than the initially formed ones, and information about the kinetic product stereochemistry is not available for the reactive system.

In order to test the possibility of free Diels-Alder adducts exchanging with coordinated Diels-Alder adducts, the following two experiments were conducted. Under a nitrogen atmosphere, addition of 1.2 equivalent *acr/iso adduct* (acrolein/isoprene adduct shown in Figure III.6) to a solution of freshly prepared racemic **C7** (0.04 mmol) in 0.5 mL of CD_2Cl_2 gave rise to a 1.0:3.2 ratio (aldehyde hydrogen peaks in ^1H NMR spectrum) of free to coordinated equivalent *acr/iso adduct*. Addition of 1.2 equivalent of *mvk/iso adduct* (methylvinyl ketone/isoprene adduct shown in Figure III.6) gave a mixture of the corresponding Diels-Alder

Figure III.6

acr/iso adduct *mvk/iso adduct*

adducts. The immediate (5 min) measurement showed that ketone exchange with coordinated aldehyde did happen since the ratio of free and coordinated *acr/iso adduct* has been changed to 1.7:1.0.

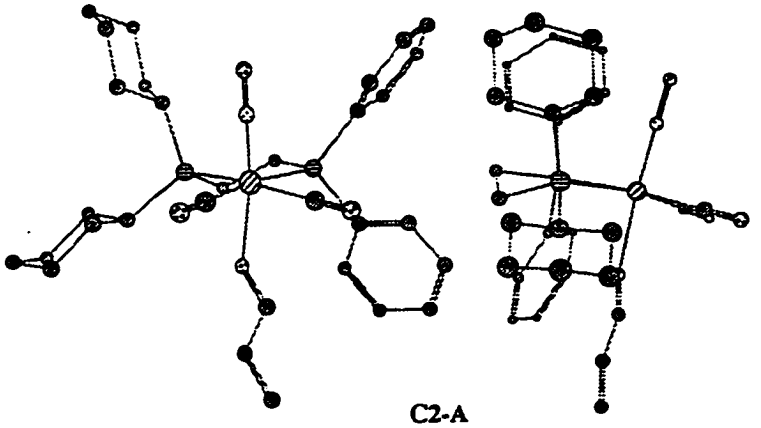
There was no change upon standing. Since the upfield portion of the spectra are very complicated, it is difficult to measure the free to coordinated *mvk/iso adduct* ratio by integration of the CH_3 peaks.

Another experiment was carried out in which the order of addition was switched: first addition of 1.2 equivalent *mvk/iso adduct* to 0.4 mmol **C7** in 0.5 mL CD_2Cl_2 was carried out followed by addition of 1.2 equivalent *acr/iso adduct*. The immediate (~5 min) measurement showed the free to coordinated *acr/iso adduct* ratio was 4.6:1.0. These two exchange reactions confirmed that the free Diels-Alder adducts exchanged with the coordinated Diels-Alder adducts very quickly for racemic **C7**. An alternative reaction which might bring us the desired information (d.e. of coordinated adducts) is using a little bit less than 1 equivalent of acrolein or 2-methacrolein. If the dissociation rate of the coordinated adducts is not too high, since there will be no free acrolein left, now the immediate measurement might represent the initially formed coordinated adducts.

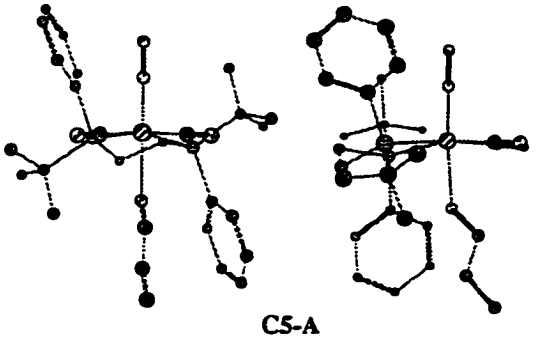
Molecular Modeling. The MM2 force field provided with the program *Chem 3D Plus* was augmented to allow our tungsten nitrosyl compounds to be minimized. The advantage of this program is that it allows the organic "shrubbery" to arrange itself around the octahedral transition metal by turning on 1,3-non-bonded van-der Waals interaction. Optimal bond lengths and angles were entered, based on our own and other X-ray structures.[37,64,65] The biggest problem with such modeling is the complete absence of any information about torsional strain about tungsten-phosphorus bonds, and such force constants are simply set to zero.

The minimized structures of catalyst-acrolein adducts **C2-A**, **C5-A** and **C7-A** (Figure III.7) showed some conformational differences which might be the cause of the differences of their catalytic activity. For **C2-A**, **C5-A**, and **C7-A**, the N-W-O bond angle are 177°, 176° and 163°. In the case of **C7-A**, it is obvious that as the catalyst tries to minimize the crowded transition state, the N-W-O bond angle deviates significantly from 180°, that is , the acrolein is pushed away from the phosphine ligands. Once the

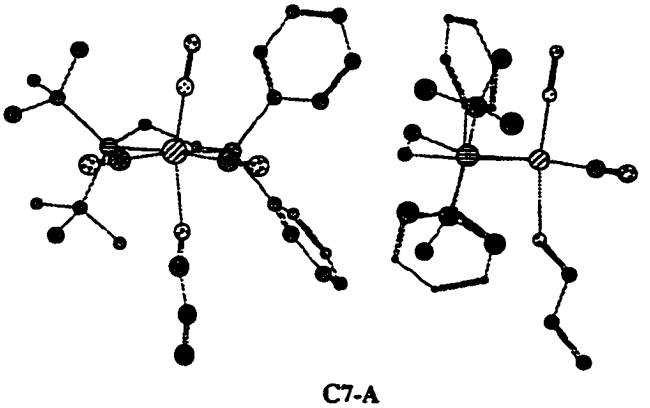
Diels-Alder adduct forms, the structure of the coordinated Diels-Alder adduct is even more crowded, and the N-W-O bond angle bends even further away from 180°. We propose that this makes the compound relatively more unstable, and hence labile, so the turnover of the catalyst becomes faster, the catalyst becomes more reactive.



C2-A



C5-A



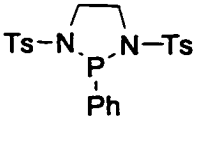
C7-A

Figure III.7 W-acrolein adducts for C2, C5, and C7

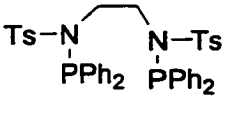
IV. Achiral Electron-Deficient Ligands: *TosL* and *diTosL*

Since the lower catalytic reactivities of catalyst **C2** and **C5** are partially due to the lower Lewis acidity caused by the chelating phosphine ligand, electron-deficient ligands might be better suited for this type of catalyst.

Synthesis of transition metal ligands that mimic the strong π-acidity of carbon monoxide, but are larger and so can play a steric role in reactivity at the metal, has focused on fluorinated phosphines.[66-69] Another strongly electron-withdrawing group that might affect phosphorus σ-donation and π-acidity is the sulfonyl group. Rather than attempt to directly attach the sulfonyl group to phosphorus, the N-sulfonated phosphoramides such as *TosL* and *diTosL* were chosen as the target ligands. Reaction with



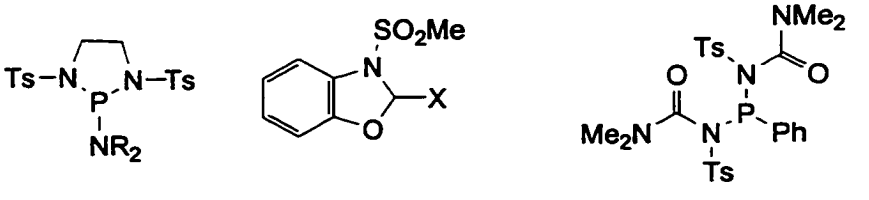
TosL



diTosL

Figure IV.1 Ts = p-tolySO$_2$

phosphorus chlorides in a manner analogous to secondary amines seems straight forward,[70-72] but since sulfonamides are relatively acidic compounds, the possibility existed that the nitrogen would not be nucleophilic enough to displace chloride from phosphorus. A small number of fully heteroatom-substituted phosphorus compounds have been prepared in this manner (Figure IV.2).[73-77] None of them have been used as ligands in the transition metal compounds.



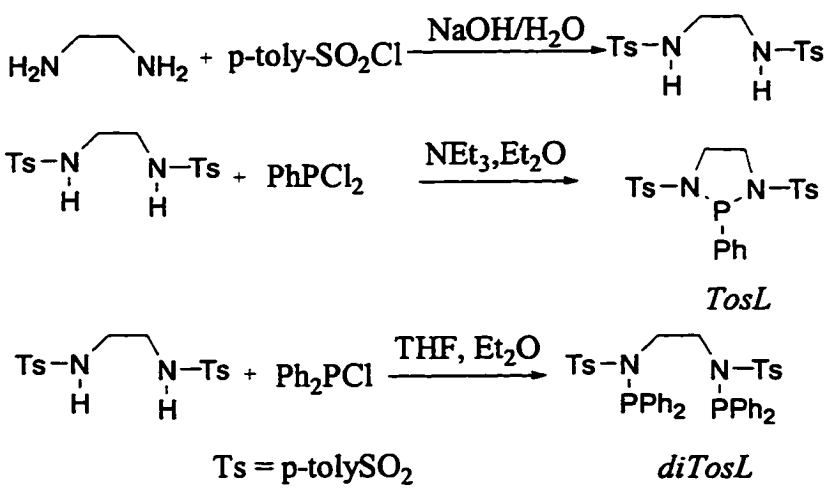
Ts = p-tolySO$_2$, X=NR$_2$, OR

Figure IV.2 Hetereoatom-substituted phosphorus compounds

A. Synthesis of *TosL* and *diTosL*

According to Berkowitz's procedure,[78] 1,2-diaminoethane reacted with p-toluenesulfonyl chloride in aqueous NaOH solution to give N,N'-di-p-toluenesulfonyl-1,2-diaminoethane in 50% yield (Scheme IV.1). Further reaction of N,N'-di-p-toluenesulfonyl-1,2-

Scheme IV.1



diaminoethane with one equivalent $PhPCl_2$ in the presence of NEt_3 in diethyl ether at room temperature gave after work-up a 62% yield of the desired product 2-phenyl-1,3-di-p-toluenesulfonyl-

1,3,2-diazaphospholidine (*TosL*) as white powder. Reaction of N,N'-di-p-toluenesulfonyl-1,2-diaminoethane with two equivalent Ph_2PCl in the presence of NEt_3 in refluxing THF gave after work-up a 43% yield of the product N,N'-bis(diphenylphosphino)-N,N'-di-p-toluenesulfonyl-1,2-ethanediamine (*diTosL*) as a white powder.

The ^1H NMR spectra of *TosL* and *diTosL* are consistent with the cyclic and acyclic structures shown. In the case of *TosL* the signals for the CH_2CH_2 ring hydrogens are split into two multiplets, one due to the two hydrogen atoms cis to the phenyl on the pyramidal phosphorus, the other due to the two hydrogen atoms trans to the phenyl. In the case of *diTosL*, these two pairs of methylene hydrogens give rise to a singlet, as expected. Otherwise the spectral characterization of *TosL* and *diTosL* is straight forward.

Like N, N'-di-p-tolunesulfonyl-1,2-diaminoethane, *TosL* and *diTosL* are apparently polar materials as judged by their insolubility in ether, but other solubility properties are peculiar.

TosL is benzene insoluble and slightly soluble in acetone, while *diTosL* is insoluble in acetone and ethanol, but soluble in benzene.

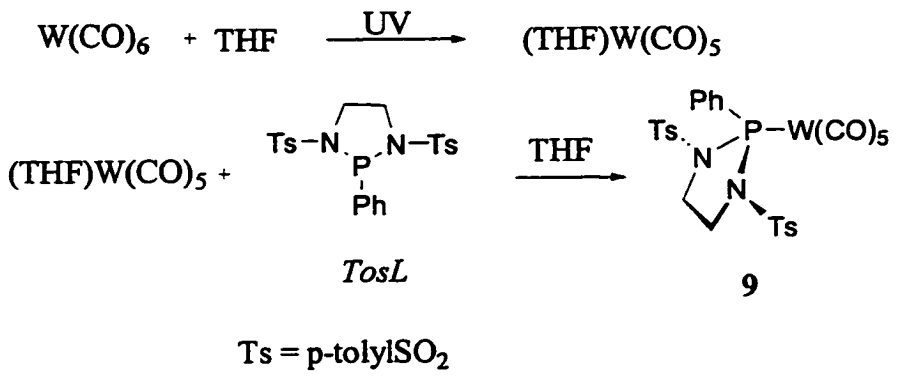
B. Synthesis of Tungsten Carbonyl Complexes.

Tungsten pentacarbonyl complex. According to Strohmeier's procedure[79] (SchemeIV.2), irradiating a THF solution of $W(CO)_6$ with a 450 W Hanovia medium pressure mercury lamp gave the solvent coordinated tungsten carbonyl complex $(THF)W(CO)_5$. Further reaction of the $(THF)W(CO)_5$ solution with *TosL* at room temperature for 2 to 3 h gave the desired tungsten complex $(TosL)W(CO)_5$ (**9**). After removal of solvent, purification was achieved via sublimation of unreacted $W(CO)_6$ under vacuum at 45°C, followed by silica gel chromatography eluting with CH_2Cl_2. A 77% yield of white powder was obtained as the final spectroscopically pure **9**, although repeated crystallization from 1:3 CH_2Cl_2/Hexanes was needed to give analytically pure material.

Coordination of *TosL* to tungsten via the phosphorus atom is clear on the basis of the observed chemical shifts and the tungsten-phosphorus satellites (due to the 14% natural abundance of ^{183}W) in the ^{31}P NMR (*TosL*: 91.3 ppm; **9**: 121.3 ppm, $^1J_{PW} = 329$ Hz) and phosphorus-carbon coupling in the ^{13}CNMR spectra ($J_{PC} = 37$

Hz and 8 Hz for the trans and cis carbonyl ligands, respectively). In addition, a non sulfonyl analog[80], $(Et_2N)_2PhPW(CO)_5$ was prepared by Hersh via the same route and found to exhibit NMR and IR spectra that were sufficiently comparable to conclude that the compounds are both P-ligated $LW(CO)_5$ adducts.

Scheme IV.2

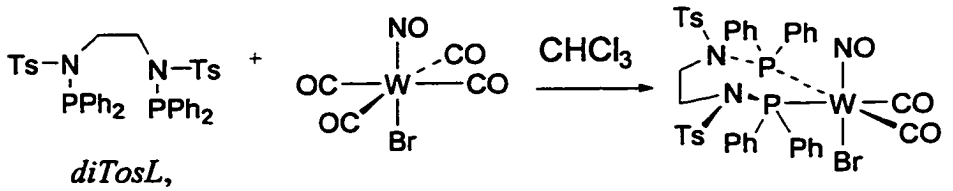


Ts = p-tolylSO$_2$

Chelate tungsten nitrosyl complexes. In order to prepare the chelated tungsten complex **10** from *diTosL*, a reaction was carried out with trans-$(NO)W(CO)_4Br$, since the resultant adduct **10** would be the precursor for the desired Lewis acid Diels-Alder catalyst.[36] Using our standard method (30 min refluxing in THF) or letting

the reactants stand in $CHCl_3$ for a day gave a high yield of the desired **10** (Scheme IV.3).

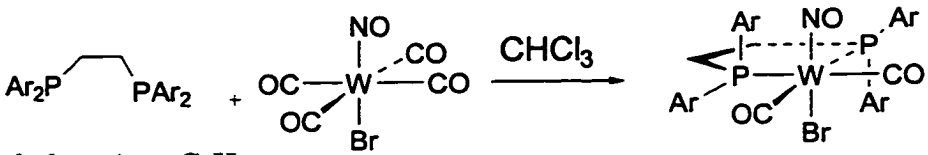
Scheme IV.3



diTosL,

10, diTosLW(CO)$_2$(NO)Br

Ts = p-tolylSO$_2$



diphos: Ar = C_6H_5
diphos-F$_{20}$: Ar = C_6F_5

complex **11**: Ar = C_6H_5
complex **12**: Ar = C_6F_5

In order to compare the electronic properties of the *diTosL* tungsten complex **10**, the known complex **11**,[63] as well as complex **12** were prepared from the commercial available phosphines *diphos* and *diphos-F$_{20}$*, respectively, using the routine method of reaction with trans-(NO)W(CO)$_4$Br. Unfortunately complex **12** was too insoluble to acquire a ^{13}C NMR spectrum,

although the IR, ^{1}H, and ^{31}P NMR spectral features are comparable to the spectra of complex **10** and complex **11**.

The IR and NMR spectra of complex **10** are similar to those of known nitrosyl bromide analogues[36,63], and so it is presumed to be isostructural. Each of complex **10**, **11** and **12** exhibit two carbonyl bands and a nitrosyl band in the infrared spectra, although complex **10** reproducibly exhibits a small splitting of this band (~4 cm^{-1}) suggestive of two conformational isomers either due to the 7-member chelate ring or more likely due to rotation about the N-S bonds of the tosyl moieties. In addition, complex **12** exhibits bands at 1522 and 1483cm^{-1} that are even stronger than the carbonyl and nitrosyl bands, but these are assigned to C_6F_5 ring modes since they are virtually unchanged from bands observed in the IR spectrum of the free ligand. The molecular symmetry of complex **10** is confirmed by the fact that complex **10** and complex **11** each exhibits a singlet in the ^{31}P NMR spectrum while complex **12** exhibits a single fluorine-coupled multiplet, each with the expected ^{183}W satellites; furthermore, each of complex **10**, **11**, and **12** exhibits two multiplets in the ^{1}H NMR spectrum for the two

pairs of chelate backbone hydrogens that are syn to the NO and Br ligands, respectively. In addition, complex **10** exhibits a single tosyl methyl singlet, so if there is any conformational isomerism involving the relative orientations of the tolyl moieties, it is fast on the ^{1}H NMR time-scale. Similarly, the ^{13}C NMR spectra of complex **10** and complex **11** confirm the proposed symmetry, with a single signal for the chelate backbone carbon, two signals for each of the phenyl carbons (two phenyl rings syn to NO, the other two to Br), and for complex **10**, a single set of tolyl carbons, again indicating the absence of conformational differences on the NMR time-scale.

During the course of this work it was found that if the ligand *diTosL* was contaminated with any $Et_3NH^+Cl^-$ remaining from its synthesis, the reaction with trans-$(NO)W(CO)_4Br$ gave complex **10** contaminated by compound **10a** which is spectroscopically similar to **10**. Using *diphos* to do a testing experiment, reaction of *diphos* with trans-$(NO)W(CO)_4Br$ in the presence of a large excess of $Et_3NH^+Cl^-$ also gave a compound **11a** which is spectroscopically similar to **11.** Finally **10a** was prepared by the reaction of *diTosL*

with trans-$(NO)W(CO)_4Br$ in the presence of a large excess of $Et_3NH^+Cl^-$ in $CHCl_3$. Elemental analysis showed that **10a** is (*diTosL*)$W(CO)_2(NO)Cl$, and **11a** is undoubtedly the known[63] chloride adduct (*diphos*)$W(CO)_2(NO)Cl$.

C. Interpretation of NMR Spectra

Electronic properties of ligands have been evaluated by correlations with their NMR chemical shifts and coupling constants.[81-86] For phosphorus tungsten pentacarbonyl complexes, there appears to be a positive correlation between $^{1}J_{PW}$ and the electron-withdrawing ability of the ligand.[54,83,87,88] In order to determine whether or not the NMR data for the *N*-sulfonylphosphoramide ligands fits this correlation, ^{13}C and ^{31}P NMR spectra were collected for PPh_3, $PPh(NEt_2)_2$, $P(OMe)_3$, and their $W(CO)_5$ adducts for comparison to *TosL* and its tungsten adduct complex **9**, along with data for the chelating phosphines (Tables I, II).

The order of $^{1}J_{PW}$ increases as $PMe_3 < PPh_3 < PPh(NEt_2)_2 < P(CF_3)_3 <$ *TosL* $< P(OMe)_3$, and for the chelating ligands as *diphos* < *diphos-F*$_{20}$ < *diTosL*, supporting the notion that the phosphoramides are highly electron-withdrawing, although the precise ordering on this basis is suspect. The change in

Table IV.1 ^{31}P NMR Data[a]

compound	free ligand (ppm)	complex (ppm)	$\Delta\delta_P$ (ppm)[b]	$^1J_{PW}$ (Hz)	J_{PP} (Hz)[c]	
$PMe_3W(CO)_5$	-62.0	-49.8	22.2	230		
$PPh_3W(CO)_5$	-4.8	21.4	26.3	244		
$PPh(NEt_2)_2W(CO)_5$	97.7	105.4	7.7	290		
$P(CF_3)_3W(CO)_5$	-2.5	55.4	57.9	300		
(*TosL*)$W(CO)_5$	91.3	122.1	30.8	330		
$P(OMe)_3W(CO)_5$	141.6	141.0	-0.6	387		
(*diphos*)$W(CO)_2(NO)Br$	-12.0	33.7	44.8	249		3
(*diphos-F_{20}*)$W(CO)_2(NO)Br$	-43.6	7.8	51.3	262		
(*diTosL*)$W(CO)_2(NO)Br$	60.4	77.1	16.7	271		5

[a] $CDCl_3$ solution except as noted. [b] δ(complex)-δ(free ligand). [c] Derived from the ^{13}C NMR spectra: for *diphos*, $^3J_{PP} \approx 35$ Hz, for free *diTosL*, $^5J_{PP} = 0$ Hz. [d] C_6D_6 solution.

phosphorus chemical shift upon coordination, $\Delta\delta_P$, varies from -0.6 ppm for $P(OMe)_3$ to +57.9 ppm for $P(CF_3)_3$, and does not appear to be of any utility. For instance, $P(OMe)_3$ and $P(CF_3)_3$ are both electron-withdrawing ligands and both exhibit large tungsten-phosphorus coupling constants of 300 and 386 Hz, respectively, yet their $\Delta\delta_P$ values fall at the two extremes. Of the remaining ligands, all except $PPh(NEt_2)_2$ (for which $\Delta\delta_P = +7.7$ ppm) fall in the relatively narrow range of 24 ± 7 ppm after one takes account of the well-documented "ring contribution" ΔR for chelating phosphines.[89] That is, five member chelate rings typically are de-shielded by ~30 ppm compared to the related non-chelate adducts;

for instance ΔR for (*diphos*)$W(CO)_4$ is + 27.3 ppm.[90] The limited data available for larger rings suggests that ΔR = 0 for the seven-member ring of complex **10**. After this adjustment, then, all three of the chelating adducts would have $\Delta\delta_p$ values near +20 ppm. In the ^{13}C NMR, $^2J_{PC}$ for the trans carbonyl ligand (22, 26, 37, and 38 Hz, respectively for PPh_3, $PPh(NEt_2)_2$, *TosL*, and $P(OMe)_3$) follows the same pattern as $^1J_{PW}$ (the cis-CO's follow the same trend but lie in a range from 7.3 Hz to 10.9 Hz). A unique feature of this set of phosphines is the presence of the phenyl group on phosphorus, so in addition to the comparisons of $^1J_{PW}$ obtained from the ^{31}P NMR, comparisons of phenyl coupling constant and chemical shift data obtained from the ^{13}C NMR can be made. Another unique feature is that in all cases for the non-chelating set, the ^{13}C NMR spectra were measured at both 50 and 100MHz, so assignments involving doublets due to coupling to phosphorus are unambiguous. While the chemical shifts do not change much from compound to compound, coupling constants of the phosphorus-phenyl carbons do vary although at this point the differences are

Table IV.2 ^{13}C NMR Data[a]

Compound	trans-CO ($^2J_{PC}$, $^1J_{CW}$)	cis-CO ($^2J_{PC}$, $^1J_{CW}$[b])	ΔJ_{ipso}[c]	PPh C_{ipso} ($^1J_{PC}$)	PPh C_2 ($^2J_{PC}$)	PPh C_3 ($^3J_{PC}$)	PPh C_4 ($^4J_{PC}$)
PPh_3				137.1 (11)	133.7 (19)	128.5 (7)	128.7 (s)
$PPh_3W(CO)_5$	199.1 (22)	197.3 (7, 126)	31	135.2 (42)	133.0 (12)	128.6 (10)	130.3 (s)
$PPh(NEt_2)_2$				142.0 (3)	131.0 (16)	128.1 (3)	127.2 (1)
$PPh(NEt_2)_2W(CO)_5$	200.3 (26)	197.3 (8, 126)	67	141.8 (70)	130.1 (11)	128.6 (9)	129.4 (s)
TosL				138.4 (32)	129.4 (21)	128.8 (6)	130.5 (s)
(TosL)$W(CO)_5$	198.2 (37)	196.0 (8, 127)	-12	136.5 (20)	132.8 (18)	128.4 (11)	132.8 (s)
$P(OMe)_3W(CO)_5$[d]	197.8 (38, 139)	195.2 (11, 126)					
diphos				138.1 (13)[e]	132.7 (19)[f]	128.4 (6)[e]	128.6 (s)
(diphos)$W(CO)_2(NO)Br$	208.8 (49, 152)	208.8 (7)	29	132.4 (41), 131.7 (45)	132.8 (12),[e] 132.3 (11)	129.0 (11),[e] 128.5 (10)	130.8 (s), 130.3 (s)
diTosL				134.7 (18)	132.6 (22)	128.5 (6)	127.5 (3)
(diTosL) $W(CO)_2(NO)Br$	204.6 (55)	204.6 (0)	26	131.4 (44), 130.8 (43)	133.8 (11), 132.7 (13)	128.4 (10), 127.7 (10)[e]	131 (s), 131.1 (s)

[a] Solvent: $CDCl_3$. All chemical shifts in ppm, all coupling constants in Hz, and all peaks are doublets except noted. [b] In the cases where the trans-CO peak was too weak to permit observation of the tungsten satellites, $^1J_{PW}$ is not listed. [c] [$^1J_{PC}$ (complexed ligand) - $^1J_{PC}$ (free ligand)] for ipso carbon. [d] For free $P(OMe)_3$, 48.8 ppm, $^2J_{PC}$ = 11 Hz. [e] triplets, different of out line. [f] Quintet, difference of lines 2 and 4.

better described as a curiosity than an illuminating point of comparison. Thus, PPh_3 exhibits an increase in the one-bond P-C_{ipso} coupling constant (ΔJ_{ipso}) of 31 Hz upon coordination (from 10.7 Hz to 41.6 Hz), while *TosL* exhibits a decrease of 12 Hz (from 32.1 Hz to 20.1 Hz). While $PPh(NEt_2)_2$ exhibits an increase like PPh_3, the actual values are quite different, namely a 67 Hz increase from 3.4 Hz to 70.2 Hz. The chelating ligands exhibit ΔJ_{ipso} values (26 Hz and 29 Hz for complex **10** and complex **11**) that are similar to that of PPh_3, so *TosL* is anomalous in the sign and $PPh(NEt_2)_2$ in the magnitude of ΔJ_{ipso}.

An obvious question is whether or not $PPh(NEt_2)_2$ is an appropriate model compound for *TosL*. We chose not to examine the more-appropriate cyclic analog, 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine (i.e. the analog of *TosL* in which the tosyl moieties are replaced by methyls), because of a warning about acute nausea and vomiting caused by several related cyclic compounds.[72] In fact, J_{PC} for $PPh(NEt_2)_2$ has been reported to vary with temperature, rising from 0 Hz in 20 to 45°C range to 2 Hz at 85°C (we have no explanation for the discrepancy between

these values and our room-temperature value of 3.4 Hz; the chemical shifts are comparable). In contrast, in 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine, $^{1}J_{PC} = 42$ Hz and is temperature independent.[91] The temperature effect was proposed to be due to rotation about the P-N bonds, while the large disparity in coupling constants despite the near-identity of attached atoms was presumed to be due to hybridization changes at phosphorus as well as fixing the P-N lone pair dihedral angles. This would suggest that for $PPh(NEt_2)_2$ the steric and electronic consequences of coordination to tungsten are simply larger than for the other compounds, while the cyclic *TosL* perhaps undergoes a somewhat different hybridization change upon coordination than do the other (acyclic) compounds.

Further close inspection of the data reveals curious points - for instance $^{2}J_{PC}$ is larger than $^{1}J_{PC}$ for free PPh_3, $PPh(NEt_2)_2$, *diphos*, and *diTosL*, but smaller for *TosL* and all of the tungsten complexes. One-bond phosphorus-carbon coupling constants in particular are well-known to be quite variable,[92] so this switching in absolute magnitude of one and two-bond coupling constants is

not unusual. This comparison depends on the validity of the assignments of the ortho- and meta- phenyl carbons, but phosphorus coupling to ortho- and meta- phenyl carbons is known[92] to follow the order $^{2}J_{PC} > {}^{3}J_{PC}$. Further confidence in the ortho/meta assignment arises from the internal consistency of chemical shift data: all of the ortho carbons are downfield of the meta carbons. Nonetheless, the limited data set does not permit further generalizations.

D. Evaluation of Electronic Properties By IR Stretching

The qualitative theory that the metal to carbon monoxide bonding in the metal carbonyls involves a combination of C→M coordinate σ bonding with M→C π bonding is universally accepted. It can be formulated in both the valence bond[93] and molecular orbital theories[94] in a qualitative manner. Cotton-Kraihanzel CO force constants calculated from infrared data are frequently used to interpret this theory in a semi-quantitative way.[95] Two approximations are made for this theory. First no account is taken of the interaction of CO stretching with other deformation of molecules, since the CO stretching frequencies are 3 ~ 30 times higher than any of the skeletal fundamentals of the molecules. Second the observed frequencies of the fundamentals are used without making any anharmonicity correction since not enough experimental data are available for making such correction.

As long ago as 1937 Tompson and Linnett[96] observed that relative magnitudes and the signs of stretch-stretch interaction constants could be obtained from valence theory. In a metal

carbonyl having six octahedrally disposed ligands, the valence shell orbitals fall into the following three groups (Table IV.3).

Table IV.3 Relationship among Symmetry, Orbital and Bonding Type

Group #	Symmetry type	Orbitals	Bonding type
I	A_{1g}	S	σ
	E_g	$d(z^2)$, $d(x^2-y^2)$	σ
II	T_{2g}	d(xz), d(yz), d(xy)	π
III	T_{1u}	p(x), p(y), p(z)	σ or π

If it is assumed that p orbitals are used entirely in σ bonding, the $A_{1g} + E_g + T_{1u}$ representations may be used for a full set of six octahedral hybrid orbitals, leaving only the T_{2g} orbitals remain for π bonding. For symmetry reasons, this set of orbitals cannot mix with other valence shell orbitals, so that π bonding can be separated from σ bonding.

On the basis of this symmetry method, Cotton and Kraihanzel derived the following secular equations of kinetic energy matrices and potential energy matrices, resulting in the "approximate" secular equation.

Table IV.4. Secular Equation and Realated Information on CO Stretching Modes

Mol. Type	Mol. Sym.	Modes of ν	Activities	"Exact" equation	"approximate" equation
$M(CO)_6$	O_h	A_{1g}	Raman	$\lambda=\mu(k+k_t+4k_c)$	$\lambda=\mu(k+6k_i)$
		E_g	Raman	$\lambda=\mu(k+k_t-2k_c)$	$\lambda=\mu k$
		T_{1u}	T_{1u}	$\lambda=\mu(k-k_t)$	$\lambda=\mu(k-2k_i)$
$ML(CO)_5$	C_4	$A_1^{(1)}$ $A_1^{(2)}$	IR and Raman	$\begin{vmatrix} \mu k_1-\lambda & 2\mu k_c \\ 2\mu k_c & \mu(k_2+k_t+2k_c')-\lambda \end{vmatrix} = 0$	$\begin{vmatrix} \mu k_1-\lambda & 2\mu k_i \\ 2\mu k_i & \mu(k_2+4k_i)-\lambda \end{vmatrix} = 0$
		B_1	Raman	$\lambda=\mu(k_2+k_t-2k_c')$	$\lambda=\mu k_2$
		E	IR and Raman	$\lambda=\mu(k_2-k_t)$	$\lambda=\mu(k_2-2k_i)$

[a] Force constants in dynes/cm; m represents the reciprocal of the reduced mass of the CO group, $\mu=(1/16 + 1/12)$, $\lambda=0.005889\nu^2$, where ν is the frequency in cm^{-1}.

Several assumptions are incorporated into the Cotton-Kraihanzel model. First, all CO - CO stretching interactions should give rise to positive interaction force constants (k_i). As a CO bond is stretched the π bonding becomes weaker and the π* bonding orbital drops in energy. This causes increased M-CO π interaction from dπ electrons drifting to this M-CO group, decreasing the available electrons for the others.

Second, it is assumed that $k_t \approx 2k_c$, where k_c and k_t are the interaction constants between pairs of cis and trans CO groups respectively. This follows simply from the fact that a pair of cis

CO groups directly share only one dπ orbital whereas a pair of trans CO groups directly share two dπ orbitals.

Third, the CO stretching force constants should decrease steadily as CO groups are successively replaced by other ligands which make less demand for metal dπ electrons.

Fourth, CO groups cis to substituents of the type considered above should have higher stretching force constants than those trans to such substituents due to having only one (as opposed to two) dπ interaction with the cis ligand.

Fifth, stretching-stretching interaction constants should probably increase with increasing replacement of CO by ligands of lower π bonding ability. This might be expected because the total number of dπ electrons per CO increases and this should magnify the effect responsible for the interaction constants.

The "approximate" secular equations were derived from the "exact" equation by substitutions of $k_i=k_c=k_c'=k_t/2$, where k_c and k_c' represent interaction of cis pairs of CO groups and k_t represents interaction of a trans pair of CO groups. These substitutions are

dictated by the second assumption and the fact that it will be impossible to detect any meaningful difference between k_c and k_c'.

Since the Cotton-Kraihanzel approximate force constant method was devised in 1962, it has been applied to a large number of metal carbonyl derivatives, and in 1967 Graham tried to separate σ- and π-bonding effects in this system.

When force constants for two compounds $LM(CO)_5$ and $L'M(CO)_5$ are compared, the differences ($\Delta k_1=k_1'-k_1$ and $\Delta k_2=k_2'-k_2$; here k_1 is for CO trans to L, and k_2 is for CO cis to L) will be due to the combined effect of the difference in the σ-inductive properties of the ligands ($\Delta\sigma=\sigma'-\sigma$) and the difference in their π-acceptor properties ($\Delta\pi=\pi'-\pi$). Then Graham made two assumptions. First, the inductive property of a given ligand is assumed to operate equally on all five CO groups. Thus, for the σ-inductive portion only of the over-all change in force constants, one can write $\Delta k_1=\Delta\sigma$ and $\Delta k_2=\Delta\sigma$. Second, the change in the π-acceptor property ($\Delta\pi$) in going from L to L' will affect Δk_1 more than Δk_2 by a factor of 2. Thus, for the π-inductive portion of the

overall change in force constants, $\Delta k_1=2\Delta\pi$ and $\Delta k_2=\Delta\pi$. This assumption is made based on the idea that the trans CO shares two d orbitals with L, but each cis CO only shares one d orbital with L. If L has no π-orbital that interacts with the metal d-orbitals, then the CO ligands alone interact the d-π electrons; as is the case for the amine ligands. For the overall changes in force constants that result from changing ligands, now we have $\Delta k_1=\Delta\sigma+2\Delta\pi$, $\Delta k_2=\Delta\sigma+\Delta\pi$. By choosing one compound as reference (typically an amine for which $\Delta\pi=0$) and determining all of the Δ values relative to it, a scale of relative σ and π parameters can be set up.

In 1967 Brown and Dobson[97] investigated twelve $LW(CO)_5$ complexes containing amine, pyridine and phosphine ligands. The variation of Cotton-Kraihanzel force constants, k_1 (axial CO) and k_2 (equatorial CO) as a function of pk_a of the amine was plotted, which showed differences in k_1 and k_2 from the corresponding values for a specially selected member for the series, (cyclohexylamine)$W(CO)_5$; this ligand was expected to be a strong σ-donor and have no π-interaction. The data indicate that while

the value of k_2 decreases regularly with increasing amine pk_a, k_1 remains essentially constant. A close examination of the results of Angelici and Malone[98] also reveals no trend in k_1 as a function of pk_a. This was interpreted as a limiting ability of ligands to affect CO stretching frequencies via σ-donation. Further, it is generally observed in substitution products of group VIB metal carbonyls that k_1 changes more than k_2 as the bonding properties of π-accepting ligands are varied. The fact that k_1 is invariant to pk_a is a strong evidence that there is a negligible change in M-CO π-bonding in this series of complexes. This would seemingly indicate that the separation of σ- and π-bonding, expected on the basis of symmetry only for the octahedral complexes $M(CO)_6$, also holds for this series of $LW(CO)_5$ complexes.

The results also dictate revision of Graham's equations for separation of σ and π bonding effects in these systems.[99] Following Graham, but assuming a direct ligand to ligand donation effect, depending on ligand basicity but exerted only at the radial CO ligands, Dobson set up the equations, $\Delta k_1=2\Delta\pi$, $\Delta k_2=\Delta d+\Delta\pi$,

using the CO stretching force constants for (cyclohexylamine)$W(CO)_5$ as the reference standards for k_1 and k_2.

As a new type of ligand, whether *TosL* and *diTosL* are electron-deficient ligands as we desired is unknown. The donor properties of the nitrogen atom and phosphorus atom might mitigate the acceptor properties of the oxygen atoms of the sulfonyl group. Infrared data, calculated Cotton-Kraihanzel CO force constants, and derived Dobson parameters are collected in Table IV.5 for $LW(CO)_5$ adducts,[100,101] where the ligands are $PPh(NEt_2)_2$, PPh_3, $P(OMe)_3$, *TosL*, and $P(CF_3)_3$.

Consideration of the CO stretching frequencies themselves or the trans and cis CO stretching force constants k_1 and k_2 clearly shows that while *TosL* is not as good a π-acceptor nor as poor a σ-donor as $P(CF_3)_3$, it is somewhat comparable to $P(OMe)_3$ despite the presence of the phenyl group in place of a third heteroatom.

Consideration of Dobson's Δd and $\Delta\pi$ suggests that *TosL* is comparable in a π-acceptor ability to $P(OMe)_3$ but is a much weaker σ-donor.

The effect of the sulfonyl groups is enormous, since $PPh(NEt_2)_2$ is a much stronger σ-donor and weaker π-acceptor than *TosL*. The data suggests a relative ordering of ligand acceptor ability of $P(CF_3)_3 > TosL \approx P(OMe)_3 > PPh_3 \approx PPh(NEt_2)_2$, and the relative ordering of ligand donor ability of $PPh(NEt_2)_2 \geq P(OMe)_3 > PPh_3 > TosL > P(CF_3)_3$. On the basis of the infrared data, the N-sulfonylphosphor-amide ligand is second only to fluorinated phosphines in electron-deficiency.

A smaller set of data was collected for comparison of *diTosL*, *diphos*, *diphos-F20* as well as the N-donor ligand acetonitrile

Table IV.5 CO Stretching Frequencies, Force Constants and Derived σ and π Bonding Parameters for $LW(CO)_5$ Complexes[a]

	ν (CO) cm^{-1}			F(CO) md/Å				
L	A_1^2(w)	A_1^1(m)	E(s)	k_1	k_2	k_i	Δd	Δπ
$PPh(NEt_2)_2$	2069.6	1941.7	1935.9	15.46	15.78	0.32	-0.1346	0.1789
PPh_3	2071.2	1942.0	1942.0	15.45	15.87	0.31	-0.0131	0.1583
$P(OMe)_3$	2078.9	1962.2	1947.8	15.79	15.96	0.32	-0.0934	0.3324
TosL[b]	2081.1	1960.0	1958.4	15.72	16.10	0.30	0.0787	0.2967
$P(CF_3)_3$[c]	2101	2006	1998	16.38	16.53	0.27	0.1848	0.6268

[a] Solvent is hexane except noted. [b] ν(CO) in CH_2Cl_2: 2079.9 (w , A_1^2), 1992.6 (w, shoulder, B_1), 1951.6 cm^{-1} (s, overlapping with A_1^1 and E), giving k_1=15.59, k_2=16.03, and k_i=0.31mdyn/Å. The IR in hexane was taken by FT-IR with nitrogen purging of the sample chamber, acquiring 250 scans at1cm^{-1} resolution. The saturated solution (baseline at 99.90% transmittance (%T).with a noise level of ±0.03%T) gave for the A_1^2 band an intensity of 99.7%T and for the overlapping A_1^1 and E bands an intensity of 98.4%T. [c] Cyclohexane solution.

Table IV.6 CO and NO Stretching Frequencies, and Force Constants for cis,cis,trans - $L_2(CO)_2(NO)WBr$ Complexes[a]

	ν (CO) cm^{-1}		ν (NO) cm^{-1}	F(CO/NO) md/Å		
L_2[b]	A^2(m)	B(m)	A^1(m)	k_{NO}	k_{CO}	k_i
$(CH_3CN)_2$[c]	2015	1930	1630	11.82	15.66	0.62
diphos	2025.8	1954.4	1630.0	11.78	15.96	0.53
diTosL	2035.0	1966.6	1652.4[d]	12.11	16.14	0.51
diphos-F20	2055.3	1994.4	1649.2	12.03	16.54	0.46

[a] Solvent is benzene except noted. [b] *diphos* and *diphos-F20* = $Ar_2PCH_2CH_2PAr_2$ (Ar = Ph and C_6F_5 respectively). [c] solvent is CH_2Cl_2. [d] Average of reproducibly observed splitting of peak (1654.1, 1650.8 cm^{-1}).

using the compound cis,cis,trans-$(CH_3CN)_2(CO)_2(NO)WBr$. As before Cotton-Kraihanzel force constants were calculated by Hersh, but no attempt was made to compare σ and π effects for this limited data set.

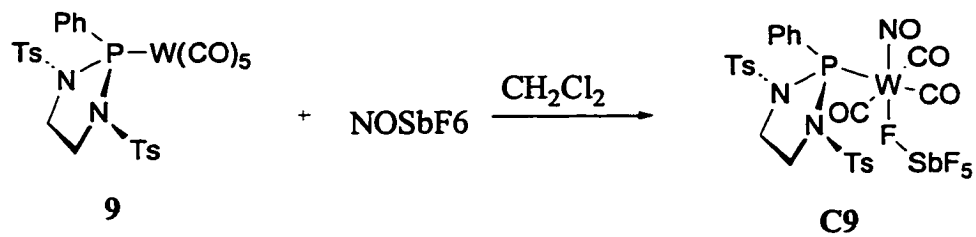
The data show that the electron-withdrawing *diTosL* and fluorinated ligands are qualitatively quite different from the stronger donor *diphos* and acetonitrile ligands; *diTosL* actually exhibits the highest ν(NO) and k(NO) of the group. What makes this particularly interesting is that the substitution of two perfluorophenyl groups for the phenyl rings of *diphos* has a comparable effect to substitution of one sulfonamide for the CH_2

linker of *diphos*. Once again, the infrared data suggest that the sulfonyl moiety is a quite effective electron-withdrawing group.

E. Catalytic Diels-Alder Reactions.

Diels-Alder catalysts were prepared using *TosL* and *diTosL* following our usual procedures. Under a nitrogen atmosphere, room temperature reaction of complex **9** with $NOSbF_6$ in CH_2Cl_2 gave what we believe to be the desired solution of catalyst **C9**. After filtering through a pad of Celite, the CH_2Cl_2 solution was used as the catalyst (Figure IV.4).[102]

Scheme IV.4



9 **C9**

The characterization of **C9** is difficult since peaks in the NMR spectrum are broad. We propose that the oxygen lone pair of the sulfonyl group displaces SbF_6^- to form a five member ring, and that

the equilibrium reaction is relatively fast on the NMR scale time scale, giving the broad peaks.

Using the above CH_2Cl_2 solution as the catalyst, **C9** was highly active in the Diels-Alder reaction. Room temperature cycloaddition of isoprene with acrolein in the presence of 1 mol% of **C9** gave an 81% yield of the corresponding Diels-Adduct in 1 h.[102]

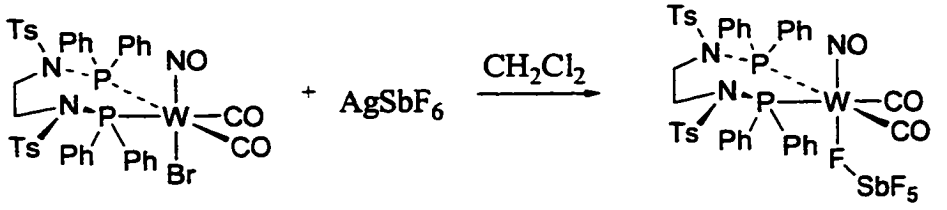
Table IV.7 Diels-Alder Reactions of Isoprene with Acrolein[a]

diene (eq)	enone (eq)	catalyst (eq)	time (h)	1,4:1,3	yield (%)
IP (101)	A (100)	none[b]	24	69:31	5
IP (106)	A (102)	C1 (1)[b]	1	93:7	84
IP (101)	A (103)	C2 (1)[b]	24	87:13	88
IP (51)	A (95)	C5 (2)[c]	24		10
IP (71)	A (168)	C6 (2)[c]	23		49
IP (106)	A (102)	C7 (1)	1	92:8	81
IP (100)	A (100)	C9 (1)	1	94:6	81
IP (115)	A (100)	C10 (1)	24	94:6	50

[a] All reaction were carried on in CH_2Cl_2 at room temperature. [b] Hersh's results reported in *J. Am. Chem. Soc.* **1989**, *111*, 6070. [c] **C5** was done by Rofeim, O., while **C6** was done by Marcune, B.

Catalyst **C10** was prepared from complex **10** in a manner similar to that for the preparation of **C7** (Scheme IV.5). Under a nitrogen atmosphere, complex **10** reacted with one equivalent of $AgSbF_6$ to give the desired catalyst **C10** and AgCl. After removal

Scheme IV.5



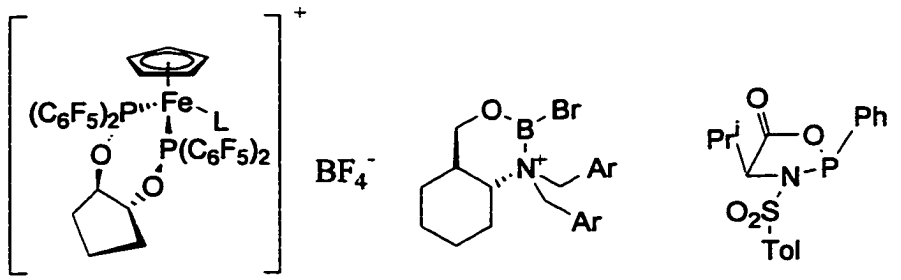
10 **C10**

of AgCl by filtering through a pad of Celite, the CH_2Cl_2 solution was used directly as the catalyst.

Room temperature cycloaddition of isoprene with acrolein in the presence of 1 mol% of **C10** gave rise to a 50% yield in a 94:6 ratio of 1,4: 1,3 substituted adducts in 24 h. The low catalytic activity of **C10** is unexpected, but was not further explored.

V. *TosvaL*, an (S)-Valine Derived N-Sulfonylphosphoramide

The presumed advantage of transition metal catalysts is that more design parameters can be incorporated into the Lewis acid, with the resultant hope that asymmetric induction can be carried out for a wider range of reactants. Electron-rich phosphines are poor choices in the design of Lewis acid catalysts since they would lead to low Lewis acidity and hence of low catalytic reactivity. Besides fluorinated phosphines such as shown in Figure V.1,[34] Corey has suggested alternative chiral sources, including a chiral cationic amino alcohol (Figure V.1)[103] and N-sulfonyl amino acids (Figure I.3)[30] which have great utility in Lewis acid design. We recently discovered a new class of trivalent phosphorus compounds (*TosL* and *diTosL*). The related (to *TosL*) phosphorus compounds such as the 1,3,2-oxazaphospholidine **13** prepared by Brown[104] and separately by Juge and Genet (Scheme V.1)[46] suggested an obvious route to the preparation of *TosvaL* (Figure V.1), a chiral analog of *TosL*.

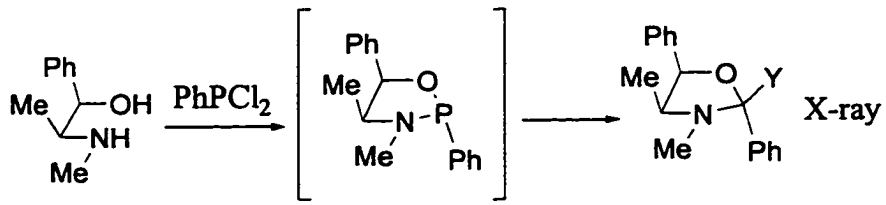


L=acrolein Ar=3,5-$Me_2C_6H_3$

Kundig's Cat. Corey's Cat. *TosvaL* or **14a**

Figure V.1

Scheme V.1

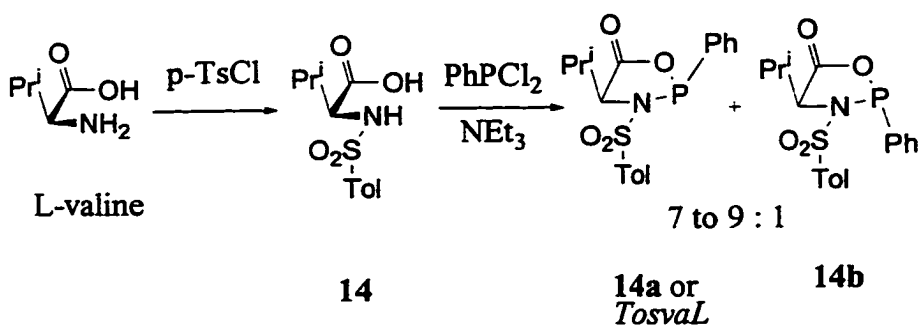


ephedrine **13** **13a**: Y=O
13b: Y=BH_3

A. Synthesis of *TosvaL* and *diTosvaL*

The monodentate 1,3,2-oxazaphospholidinone ligand *TosvaL* was prepared via a similar procedure to that used for the synthesis of *TosL*.

Scheme V.2



L-valine **14** **14a** or *TosvaL* **14b**

While (S)-N-tolylsulfonylvaline has been previously reported, details are sparse (mp: 147°C, $[\alpha]^{25}_D$=25°) and the yield was at most ~50%.[105,106] Modifications of the literature procedures, including the addition of p-toluenesulfonyl chloride to an aqueous solution of L-valine and sodium carbonate in three portions over 25 h followed by stirring for five more days at room temperature, allowed a 78% yield to be achieved.

Two equivalent of NEt_3 was first added to an ether solution of (S)-N-tolysulfonylvaline, giving a white suspension of what is presumably the Et_3NH^+ salt of the sulfonamido carboxylate. An ether solution of $PPhCl_2$ was then added to the stirred suspension, resulting in a visible change to a merely cloudy white suspension, presumable due to the less voluminous two equivalents of $Et_3NH^+Cl^-$. Reaction was continued for one more hour, then filtered through a frit funnel to remove the ammonium salts, followed by removal of solvent to give a greater than a 90% yield of pale yellow powder as the crude product. Analysis of the reaction mixture by ^{31}P NMR spectroscopy indicated the presence of two new phosphorus-containing compounds at 133.04 ppm and 136.70 ppm, subsequently identified as the desired 1,3,2-oxazaphospholidinone diastereomers (**14a** and **14b**), along with excess $PPhCl_2$ at 161.37 ppm. The ratio was 7 to 9 versus 1. The product ratios determined by ^{31}P NMR spectroscopy were confirmed by analysis of the more complex ^1H NMR spectra.

Approximately twenty experiments were conducted in which the reaction time (up to three days), temperature, and reactant

concentrations were varied (Table V.1), but no correlation with diastereoselectivity emerged when using Et_2O, THF or CH_2Cl_2 as the reaction solvent. For instance, while a 2.7:1 ratio was observed in refluxing ether, lowering the reaction temperature to -35°C gave a 6.3:1 ratio, lower than most room temperature runs. Use of methylene chloride, a solvent in which all reactants and products were soluble, was even less reproducible. Room temperature reactions gave ratios from 3.3 to 10.6 versus 1, a -78°C reaction gave a 6.1:1 ratio, and a reaction conducted at reflux gave a 4.3:1 ratio. Most of the room temperature reactions in methylene chloride gave ratios greater than 6:1. The lack of reproducibility in methylene chloride is puzzling since all reactions were carried out with strict exclusion of air and water. Eventually reactions in toluene[80] gave the fixed diastereomer ratio 9:1, perhaps because of lower concentrations of the weak acid $Et_3NH^+Cl^-$ in toluene.

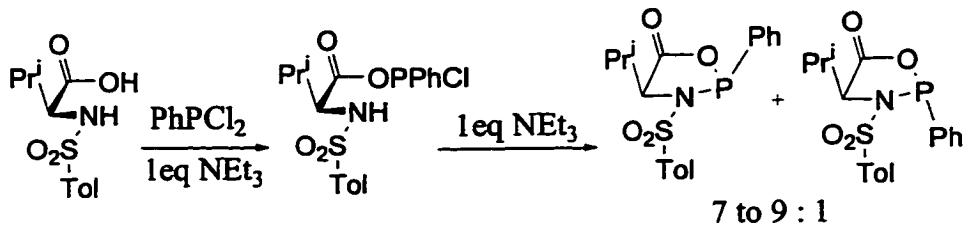
TableV.1 Preparation of *TosvaL* in various reaction conditions

#	ratio of reactant*	Solvent	Conc. of 14 (M)	T (°C)	t (hr)	14a:14b by ^{31}P	14a:14b by ^{1}H
1	1.0:1.4:3.5	Et_2O	0.153	-42	0.50	5.1	5.4
2	1.0:1.4:3.5	Et_2O	0.061	-35	0.30	6.3	6.6
3	1.0:1.4:3.5	Et_2O	0.077	25	22	7.2	7.6
4	1.0:1.4:3.5	Et_2O	0.094	25	1.5	7.3	7.6
5	1.0:1.4:3.5	Et_2O	0.094	25	18	7.9	8.2
6	1.0:1.4:3.5	Et_2O	0.118	25	72	6.2	6.2
7	1.0:1.3:3.5	Et_2O	0.122	25	48	9.8	
8	1.0:1.4:3.5	Et_2O	0.153	25	0.5	6.4	5.7
9	1.0:1.4:3.5	Et_2O	0.191	25	1.0	9.2	10.0
10	1.0:1.4:3.5	Et_2O	0.191	25	1.0	9.2	9.1
11	1.0:1.4:3.5	Et_2O	0.153	reflux	0.33	2.7	3.4
12	1.0: 1.1:2.1	THF	0.153	25	2.0	6.2	5.1
13	1.0:1.4:3.5	CH_2Cl_2	0.153	-78	0.33	6.1	7.2
14	1.0:1.4:3.5	CD_2Cl_2	0.102	25	0.17	5.6	5.3
15	1.0:1.1:2.1	CH_2Cl_2	0.153	25	0.5	3.9	4.1
16	1.0:1.1:2.1	CH_2Cl_2	0.612	25	0.5	3.3	3.4
17	1.0:1.4:3.5	CH_2Cl_2	0.153	25	0.5	10.6	10.9
18	1.0:1.1:2.1	CH_2Cl_2	0.153	25	1.0	6.9	7.0
19	1.0:1.1:2.1	CH_2Cl_2	0.153	25	4.0	10.9	11..3
20	1.0:1.1:2.1	CD_2Cl_2	0.102	25	24	3.8	3.2
21	1.0:1.1:2.1	CH_2Cl_2	0.102	25	24	6.4	6.6
22	1.0:1.4:3.5	CH_2Cl_2	0.153	reflux	30	4.3	5.0

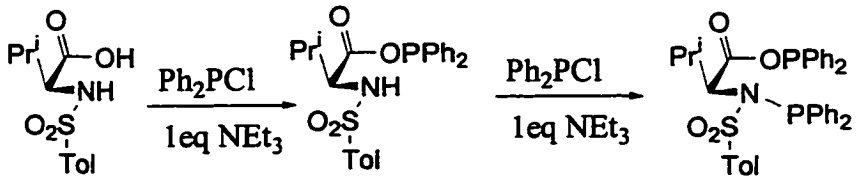
* ratio of reactant=14:$PhPCl_2$:NEt_3.

While it is presumed that the sulfonamide nitrogen lone-pair has low nucleophilicity, we were still surprised that addition of one equivalent of NEt_3 leads to formation of an O-P bond earlier than a N-P bond; a 3.6:1 ratio of two diastereomers (major isomer at 156 ppm, minor isomer at 150 ppm in the ^{31}P NMR) was observed. Identification of the bands as being due to P-O bond is based on the chemical shift of 60 ppm of *diTosL* and two singlets at 104 ppm and 49 ppm of ligand **17**. Continuing addition of second equivalent of NEt_3 gives a 4:1 ratio of **14a**:**14b** (major isomer at 133 ppm, minor isomer at 136 ppm) as shown in Scheme V.3. This was verified again by the reaction of (S)-N-tolysulfonylvaline with Ph_2PCl. The reaction of (S)-N-tolysulfonylvaline with Ph_2PCl in the presence of one equivalent of base forms the P-O bond first, giving a ^{31}P peak at 107 ppm, while reaction in the presence of two equivalents base gives ligand **17** (two singlets at 104 ppm and 49 ppm). The assignment of the 49 ppm peak to $NPPh_2$ moiety is based on the appearence of the *diTosL* peak at 60 ppm.

Scheme V.3



14 **15** **14a** or TosvaL **14b**

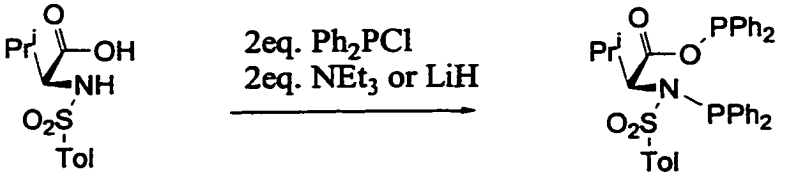


14 **16** **17**

A single crystallization of the mixture of diastereomers **14a** and **14b** from diethyl ether at -35°C reproducibly gave a 50% yield of the major isomer (2R,4S)-4-isopropyl-5-oxo-2-phenyl-3-p-tolysulfonyl-1,3,2-oxazaphospholindine (*TosvaL* or **14a**) free of any detectable minor isomer **14b**. Subsequent crystallizations gave the major isomer contaminated by small amounts of the minor isomer, but absent the need for large amounts for the pure diastereomer, no attempt to optimize the yield has been made.

Similarly, the chelate ligand *diTosvaL* (**17**) was prepared in a manner like that for *TosvaL* as shown in SchemeV.4. Two

Scheme V.4



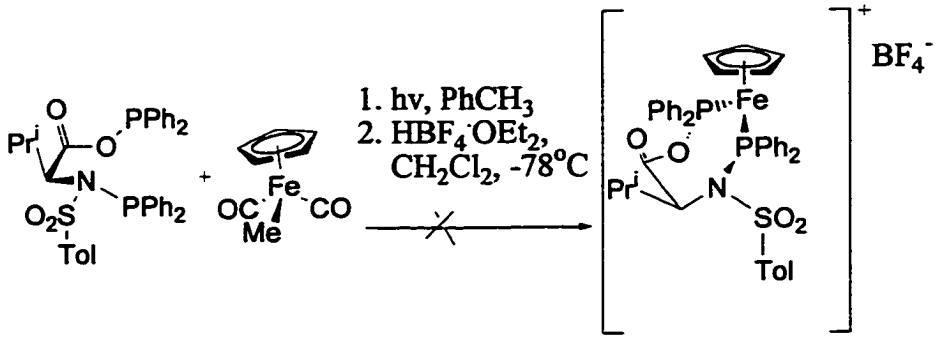
14 **17**

equivalents NEt_3 or LiH were first added into an ether solution of (S)-N-tolysulfonylvaline, and then two equivalents of Ph_2PCl were added dropwise into the reaction pot at room temperature. Reaction was continued for two more hours, then filtered through a pad of Celite to remove salts, followed by solvent removal to give ~50% yield of **17** as a white powder. The preparation conditions are extremely exacting. If NEt_3 is used as the base, the substrate concentration is critical for the completion of the reaction. It is difficult to remove LiCl since **17** immediately decomposes in air, water and silica gel. In most organic solvents **17** is only stable for

several hours. Even though $CDCl_3$ has been used as a solvent for NMR spectra, **17** reacts with $CDCl_3$ in several hours to form unknown compounds. Compound **17** is also thermally unstable in the solid state, which makes it difficult to isolate and to remove excess $PhPCl_2$ in the reaction work up.

Finally, we tried to prepare tungsten adduct according to our routine method and iron adduct via Kundig's procedure.[34] Reaction of **17** with trans-$(NO)W(CO)_4Br$ in CD_2Cl_2 or $CDCl_3$ at room temperature lead to immediately decompose to unknown stuff at ~20 ppm in the ^{31}P NMR spectrum, then continuing decomposition gave rise to no phosphorus bands. According to Kundig's procedure,[34] photo reaction of **17** with iron complex **18** (Scheme V.5) in THF at room temperature 1 hr failed to gave the desired compound, only gave unknown stuff presumed from decompositions.

Scheme V.5



17 18 19

B. Characterization and Structure Determination

The air, water and thermal stability of the major diastereomer **14a** is surprisingly high. It exhibited no decomposition upon exposure to air overnight when in the solid state, as judged by ^{1}H and ^{31}P NMR spectroscopy, but roughly half decomposed in $CDCl_3$ solution upon overnight exposure to air; no analysis has been carried out on the decomposition product. Addition of water (1 to 15 equivalent) to a $CDCl_3$ solution in the air gave only traces of decomposition with one hour. Heating in benzene with strict exclusion of air and water overnight at 78°C gave no change.

Spectroscopic data for **14a** are consistent with the proposed structure. The starting material (S)-N-p-tolylsulfonylvaline (**14**) exhibits carboxylic acid and amide hydrogen resources at 9.00 ppm and 5.18 ppm, respectively; the latter in particular does not exchange in $CDCl_3$ and is a doublet due to coupling to the neighboring chain methine hydrogen. Both of these signals are absent in major diastereomer **14a**. The chain methine hydrogen in

(S)-N-p-tolylsulfonylvaline is a doublet of doublets at 3.78ppm due to the amide hydrogen ($^3J_{HH}$=9.9 Hz) and the isopropyl methine hydrogen ($^3J_{HH}$=4.7 Hz). In the major diastereomer **14a** this hydrogen - now the ring hydrogen - at 3.53ppm is still a doublet of doublets due to coupling to phosphorus ($^3J_{PH}$=3.7 Hz) and the coupling to the isopropyl methine hydrogen ($^3J_{HH}$=7.1 Hz).

Two types of experiment were carried out in order to confirmed this assignment of coupling. The 2D COSY NMR showed the only hydrogen to which the ring hydrogen is coupled is the methine hydrogen. Perhaps more convincingly, selective heteronuclear decoupling of the ortho phenyl hydrogens resulted in collapse of the broad phosphorus signal to a doublet with $^3J_{PH}$=3.1 Hz in the ^{31}P NMR spectrum, (Figure V.2, a and b) and selective homonuclear decoupling of the isopropyl methine hydrogen resulted in collapse of the ring hydrogen doublet of doublets to a doublet with $^3J_{PH}$=3.5 Hz in the ^{1}H NMR spectrum (Figure V.2, c and d). Both N-p-tolylsulfonylvaline and the major diastereomer 1,3,2-oxazaphospholidinone **14a** exhibit two doublets and a multiplet for the two diastereotopic methyls and

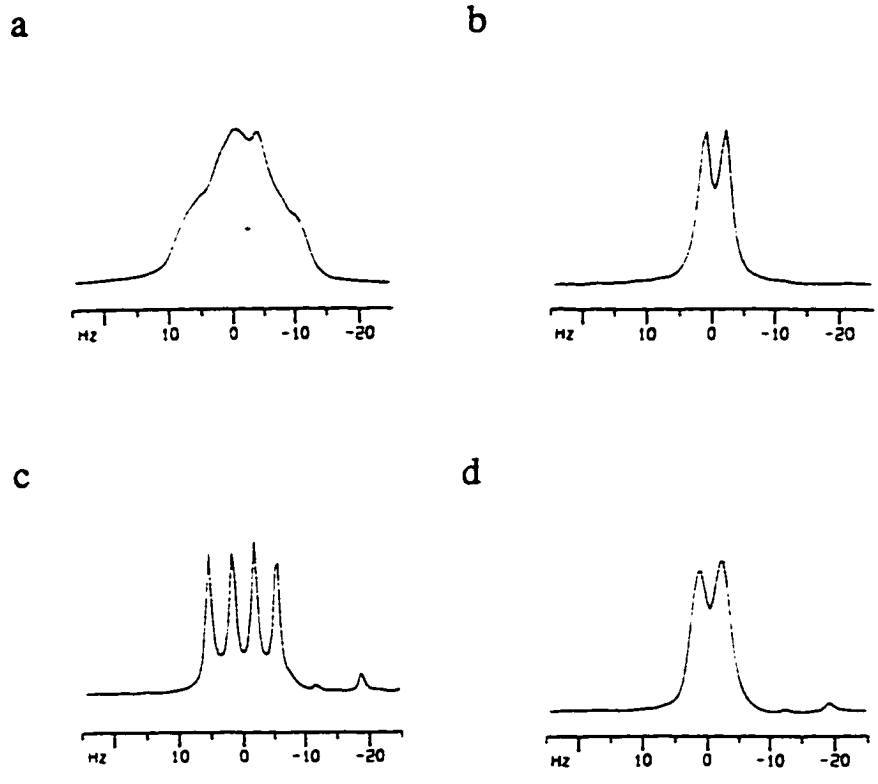


Figure V.2 Selective proton decoupling in the 162 MHz ^{31}P and 400MHz ^{1}H NMR spectra of major diastereomer **14a** ($CDCl_3$); all spectra are plotted on the same horizontal scale.

a undecoupled ^{31}P NMR spectrum, peak at 133.0ppm.

b. ^{31}P NMR spectrum of peak at 133.0ppm with selective heteronuclear ^{1}Hdecoupling of the ortho phenyl hydrogen atoms at 7.61ppm, giving a doublet with $^{3}J_{PH}$=3.1Hz.

c. ^{1}H NMR spectrum of the ring methine hydrogen at δ3.53 ($^{3}J_{HH}$=7.1Hz, $^{3}J_{PH}$=3.7 Hz).

d. ^{1}H NMR spectrum of the δ3.53 signal with homonuclear ^{1}H decoupling of the isopropyl methine at δ1.71, giving a doublet with $^{3}J_{PH}$=3.5 Hz.

methine hydrogen of the isopropyl group as expected; for the major diastereomer 1,3,2-oxazaphos-pholidinone **14a** the methine hydrogen is an octet since the methyl and ring hydrogen coupling constants are nearly the same, while in N-p-tolylsulfonylvaline, it is a multiplet since the methyl and chain hydrogen coupling constants differ by 2 Hz. In the ^{13}C NMR spectrum, the carbonyl peak is shifted from 176.5 ppm in N-p-tolylsulfonylvaline to 171.3 ppm in the major diastereomer 1,3,2-oxazaphos-pholidinone **14a**, but more importantly it is a doublet in the major diastereomer **14a** due to coupling to phosphorus ($^2J_{PC}$=12.4 Hz); all other peaks except those due to the PPh carbons are singlets.

In order to identify the minor diastereomer 1,3,2-oxazaphospholidinone **14b**, fractional crystallization was attempted, since the compounds are too polar to move on TLC. No crystallization solvent could be found that would selectively precipitate minor diastereomer **14b** and numerous crystallizations from ether were carried out to remove the major diastereomer **14a**. Since this crystallization also resulted in increasing amounts of precipitation of the minor diastereomer **14b** as its concentration in

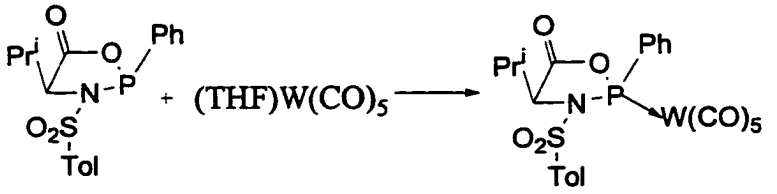
the residue increased, the best purification we could achieve was a 1:1 ratio of the major diastereomer **14a** versus the minor diastereomer **14b**. This was sufficient to identify all peaks due to the minor diastereomer **14b**. The largest shifts were found for the two methine hydrogen atoms, both in chemical shift (from 3.53 and 1.71 ppm in the major diastereomer **14a** to 4.06 and 2.50 ppm in the minor diastereomer **14b** and in coupling constants (from $^3J_{PH}$=3.7 Hz and $^3J_{HH}$=7.1 Hz for the ring methine in the major diastereomer **14a** to $^3J_{PH}$=1.4 Hz and $^3J_{HH}$=3.0 Hz for that in the minor diastereomer **14b**. The assignment of the 3.0 Hz coupling constant in the minor diastereomer **14b** to $^3J_{HH}$ rather than to $^3J_{HH}$ follows from simulation of the observed isopropyl methine multiplet and homonuclear decoupling of the 4.06 ppm signal. Elemental analysis of the mixture was consistent with **14b** being an isomer of the **14a**, and the optical rotation of the mixture showed that the minor diastereomer **14a** as expected has a non-zero rotation. There is no reason to suppose that this compound is anything other than the stereoisomer of **14a**, in which the isopropyl and phenyl groups are trans rather cis to each other (*vide infra*).

X-ray crystals[107] of the major diastereomer 1,3,2-oxaza-phospholidinone **14a** were obtained on the first recrystallization from diethyl ether. The absolute configuration[108] was assumed to be that from the naturally-occurring amino acid (S) carbon atom. The structure is unique - to the best of our knowledge it is the only 1,3,2-oxazaphospholidinone and the only acetoxylphosphine and just the second trivalent 1,3,2-oxazaphospholidine structure,[109] but the key results are stereochemical: the isopropyl and phenyl groups are cis to each other, and the tolyl moiety is in the s-trans conformation relative to the carbon and phosphorus ring atoms and hence is distant from the 1,3-substituents on the heterocycle.

C. Synthesis of Tungsten Carbonyl Adducts

Tungsten pentacarbonyl adduct. In order to assess the electronic properties of the major diastereomer **14a** as we have done before, it reacted with $(THF)W(CO)_5$ to give the tungsten complex **P14** in 63% yield.

Scheme V.6



14a **P14**

Coordination of the major isomer **14a** to tungsten via phosphorus was evident from the change in the ^{31}P NMR chemical shift from 133.04 ppm in **14a** to 146.87 ppm in complex **P14**, as well as from the presence of the characteristic tungsten-phosphorus satellites due to the 14% nature abundance of ^{183}W, giving $^{1}J_{PW}$=346 Hz. The ^{1}H NMR is again similar to those of **14a** and

14b, and once again the methine hydrogen shifts and coupling constants seem most sensitive to the environment. The ring methine is further shifted from that seen in the minor diastereomer **14b** downfield to 4.21 ppm, while the isopropyl methine at 2.05 ppm falls between those of the diastereomers **14a** and **14b**. The coupling constants for the ring methine are comparable to those of the minor isomer **14b**, with $^{3}J_{PH} \approx {}^{3}J_{HH}$=3.4 Hz. In the ^{13}C NMR spectrum, the carboxylate carbonyl is further shifted upfield to 165.27 ppm and exhibits a smaller phosphorus-carbon coupling constant ($^{2}J_{PC}$=6.0 Hz), and the tungsten carbonyl ligands exhibit the characteristeric trans ($^{2}J_{PC}$=38.4 Hz) and cis ($^{2}J_{PC}$ =8.5 Hz) phosphorus-carbon coupling constants of phosphine tungsten pentacarbonyl complexes.[101]

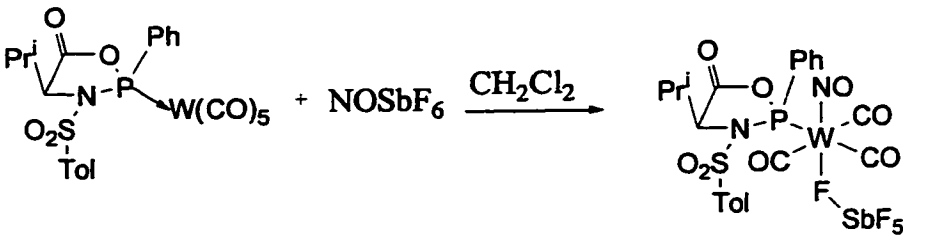
A by-product of the design of this new type of ligand is the surprising discovery that it is apparently more electron-deficient than the prototype sulfonylphosphoramide *TosL* on the basis of the high CO vibrational frequencies of the $W(CO)_5$ adducts. As can be in Table V.2, all three CO bands for (*TosvaL*)$W(CO)_5$ are higher in frequency than those of the adducts of both $P(OMe)_3$ and *TosL*.

Table V.2 CO Stretching Frequencies and ^{31}P NMR Data for $LW(CO)_5$ Complexes

	V(CO) cm^{-1}			^{31}P NMR
L	A_1^2 (w)	A_1^1 (m)	E (s)	$^1J_{PW}$ (Hz)
$PPh(NEt_2)_2$	2069.6	1941.7	1935.9	289.5
PPh_3	2071.2	1942.0	1942.0	244.1
$P(OMe)_3$	2078.9	1962.2	1947.8	386.5
TosL	2081.1	1960.0	1958.4	329.5
TosvaL	2084.3	1970.6	1960.9	346.5
$P(CF_3)_3$	2101	2006	1998	300

Catalytic Diels-Alder reaction. Catalyst **C14** was prepared from the complex **P14** according to our routine method (Scheme V.4). Under a nitrogen atmosphere, room temperature reaction of complex **P14** with $NOSbF_6$ in CH_2Cl_2 gave the desired solution of catalyst **C14**. After filtering through a pad of Celite and solvent removal from the filtration, the green solid was purified by washing with hexanes to gave the catalyst **C14** as a green powder.

Scheme V.7



P14 **C14**

Like **C9**, chiral catalyst **C14** is highly catalytically active in the Diels-Alder reaction. Room temperature cycloaddition of isoprene with acrolein in the presence of 1 mol% of chiral catalyst **C14** gave a 72% yield in a 92:8 ratio of 1,4:1.3 substituted adducts. Even though **C14** is a chiral catalyst, no enantioselection was observed, presumably due to the free rotation about W-P bond of the catalyst.

VI. Conclusion

It is a surprise that racemic **C7** is such an active catalyst for the Diels-Alder reaction and that its catalytic reactivity is comparable to **C1**. In the presence of 1 mol% of either **C1** or racemic **C7**, 1 h room temperature reaction of isoprene with acrolein gave a yield between 81% to 84% with a 92:8 ratio of 1,4:1,3 substituted adducts. In the absence of catalysts, 24 h room temperature reaction[36] of isoprene with acrolein produced only 4-5% of the Diels-Alder adducts, giving a ~70:30 ratio of 1,4 to 1,3-substituted cyclohexene isomers. The results of the stoichiometric reaction also verified that these two catalysts are comparable regarding the catalytic reactivities.

These results exclude the steric bulk hypothesis as the cause of the low reactivity of chiral catalyst **C5**, and suggested that the design of bulky catalysts for better enantioselectivity is still possible.

The unexpected high catalytic reactivity of racemic catalyst **C7**, **Crs8-1** and **Crs8-2** might also suggest that the Lewis acidity

remains sufficiently high when the phosphine residues consist of an (alkyl)Ar_2P and an $(alkyl)_3P$ moiety as in racemic catalyst **C7**, where the two combined aryl groups mitigate the donor effects of the alkyl groups. However, when the phosphine residues consist of two $(alkyl)_2ArP$ moieties as in catalyst **C5**, the now isolated phenyl groups cannot mitigate the donor alkyl effects, and the chelating phosphine is too strong a donor for catalytic activity to be exhibited.

Another possible cause of the low catalytically activity of **C5** is the conformation of the catalyst suggested by the MM2 results. In the case of acrolein adduct **C7-A**, the N-W-O band angle bends a lot away from 180°. The coordinated Diels-Alder adduct is even more crowded, and N-W-O band angle has to bend more away from 180°, making the adduct less stable, increasing the turnover, and hence the reactivity.

The same face selection (either R or S) by chiral catalyst **Crs8-1** and **Crs8** suggests that the ferrocene moiety is not an innocent bystander, but rather must effect a conformational change that

causes the dienes to prefer attack on only one face of the Metal-acrolein adducts.

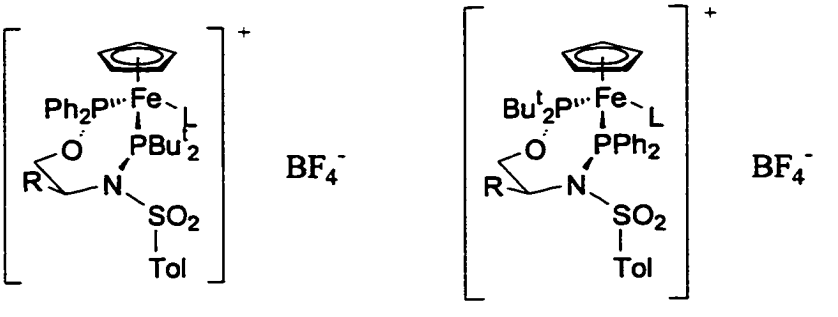
The ease of synthesis of *TosL* and *diTosL* opens up a variety of research opportunities. Infrared data, calculated Cotton-Kraihanzel CO force constants, and derived Dobson's parameters suggested that the sulfonamide moiety is strongly electron-withdrawing in character, on a par with perfluorinated alkyl groups.

The 1,3,2-oxazaphospholidine *TosvaL* is a chiral analogue of *TosL*, which is prepared from an inexpensive and readily-available amino acid. A single crystallization gives one diastereomer in overall 50% yield of an enantiomerically pure trivalent phosphorus compound. This work extends the number of sulfonamide-substituted heterocycles that exhibit interesting and high stereoselectivity, so exploration of the steric space of this substituent appears to be in order.

The difficulty we encountered in the preparation of ligand **17** and the failure to coordinate **17** to our tungsten complex suggested that ligand **17** is too sensitive to survive in solution. Since one sulfonyl group is already electron-withdrawing enough for us to

make the phosphorus amide ligand, maybe we do not need a carboxyl group. In the future, the amino alcohol rather than the amino acid may be a better chiral source. Besides making the tungsten complex, chelating analogues of iron catalyst **C3** are another possibility based on the success of Kundig's catalyst (Scheme I.18). Combining the best features of the electron withdrawing sulfonamide group with iron catalyst, **C7** (having Bu^t_2RP/RPh_2P moiety), and using an amino alcohol as the starting material, ligand **20** and **21** (Figure VI.1) may be the next candidate we should investigate.

SchemeVI.1



20 **21**

VII. Experimental

General . All manipulations of air-sensitive compounds were carried out either in a Vacuum Atmospheres inert atmosphere dry-box under recirculating nitrogen, or by using standard Schlenk techniques. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on an IBM/Bruker WP-200SY and a Bruker DPX-400 spectrometer; chemical shifts are reported relative to TMS or hydrogen in CD_2Cl_2 (δ5.32) or $CDCl_3$ (δ7.24), to $CDCl_3$ at 77.0 ppm for ^{13}C NMR, and to external 85% H_3PO_4 at 0 ppm (positive values downfield) for ^{31}P NMR. Infrared spectra were obtained on a Mattson Galaxy 4020 FT-IR spectrometer with 0.1 mm NaCl solution cells. Elemental analyses were performed by Desert Analytics, Tucson, AZ, and Quantitative Technologies, Inc., Whitehouse, NJ. Mass spectra (EI, 70 eV) were obtained on an HP5988A spectrometer.

All solvents were treated under nitrogen. Benzene, diethyl ether, and tetrahydrofuran were distilled from sodium benzophenone ketyl. Hexane was purified by washing successively with 5% nitric acid in sulfuric acid, water, sodium bicarbonate solution, and water, and then dried over calcium chloride and distilled from n-butyllithium in hexane.

Methylene chloride was distilled from phosphorus pentoxide; $CDCl_3$ and CD_2Cl_2 were vacuum-transferred from phosphorus pentoxide.

Silica gel (200-400 mesh) was dried for several hours under vacuum while heating with a heat gun and was transferred under vacuum into the dry-box. $PhPCl_2$, Ph_2PCl (Aldrich), $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (Strem), $W(CO)_6$ (Pressure Chemical) and $NO^+SbF_6^-$ (Ozark Mahoning) were used as received, PCl_3 (Aldrich) was purified by vacuum transfer from CaH_2, t-Bu_2PH was prepared according to published procedures[110] from PCl_3 or t-Bu_2PCl (Aldrich), then purified by vacuum transfer, and *trans*-$BrW(CO)_4NO$ (contaminated by ~26% by weight of $W(CO)_6$ on the basis of elemental analysis) was prepared according to a published procedure.[36,111] Ligand **rs8** was prepared according to published procedures starting from (+)-R-N,N-dimethyl-1-ferrocenylethylamine (Aldrich, 97% pure), 80.8% e.e. on the basis of the literature value $[\alpha]^{25}_D$ -417° (c 0.6, $CHCl_3$).[55]

$Ph_2PCH_2CH_2Cl$. To 1.384 g (7.43 mmol) Ph_2PH in 50 mL of THF, 4.64 mL (7.43 mmol) of n-BuLi (1.6 M in hexane) was slowly added under a nitrogen atmosphere at room temperature to give a Ph_2PLi/THF solution. Dropwise addition of above Ph_2PLi/THF solution to 7.326 g (74.33 mmol) of $ClCH_2CH_2Cl$ at 0°C, followed by solvent removal on a

vacuum line gave the crude product. Inside the glove box the crude product was dissolved in 20 mL of hexane, filtered through a pad of Celite and the solvent was removed by a vacuum pump to give 0.787 g (43% yield) of product as a white powder containing 0.5% *diphos* and 3% unknown phosphorus impurity. Further crystallization of above powder in ether gave 0.671 g (36% yield) of product as white crystals containing less than 1% *diphos* and unknown phosphorus impurity. ^{1}H NMR ($CDCl_3$): δ7.3 (m, 10H), 3.6 (m, 2H), 2.6(m, 2H). ^{31}P NMR ($CDCl_3$):-19.5 ($Ph_2PCH_2CH_2Cl$) (lit.19.9 ppm), -14.4 (unknown impurity), -12.1 ppm (*diphos*).

$Bu^t_2PCH_2CH_2Ph_2$. Inside the dry-box, 1.4 mL of n-BuLi solution (1.6 M in hexane, 2.2 mmol) was added slowly at room temperature to a solution of 328 mg of t-Bu_2PH (2.25 mmol) in 5 mL of THF to give a clear green solution of t-Bu_2PLi. This solution was then added dropwise at room temperature to a solution of $Ph_2PCH_2CH_2Cl$ (557 mg, 2.24 mmol) in 5 mL of THF. After stirring for an additional 30 min to ensure complete reaction, the solvent was removed, the residue was re-dissolved in 10 mL of hexane, filtered through a pad of Celite and stripped again to give 0.713 g (89% crude yield) of crude **$Bu^t_2PCH_2CH_2Ph_2$** as pale yellow oil. Purification of 0.230 g of the

crude material by flash chromatography on a 18x1 cm silica gel column eluting with 4:1 hexane/benzene gave 0.180 g (78% purification yield) of colorless oil as the spectroscopically pure product. ^{1}H NMR (C_6D_6):δ 7.47 (m, 4H), 7.06 (m, 6H), 2.37 (m, 4H, CH_2), 1.52 (m, 4H, CH_2), 0.99 (d, $^{3}J_{PH}$=10.6 Hz, 18H, t-Bu). ^{1}H NMR (CD_2Cl_2): δ7.44 (m, 4H), 7.32 (m, 6H), 2.24 (m, 4H, CH_2), 1.41 (m, 4H, CH_2), 1.04 (d, $^{3}J_{PH}$=10.9 Hz, 18H, t-Bu). ^{31}P NMR (C_6D_6): 35.56 (d, $^{3}J_{PP}$=31 Hz, t-Bu_2P), -12.24 ppm (d, $^{3}J_{PP}$=31 Hz, Ph_2P). ^{31}P NMR (CD_2Cl_2): 35.81 (d, $^{3}J_{PP}$=34 Hz, t-Bu_2P), -12.58 ppm (d, $^{3}J_{PP}$=33 Hz, Ph_2P). ^{13}C NMR (C_6D_6): 139.59 (d, $^{1}J_{PC}$=16 Hz, C_{ipso} of Ph), 133.35 (d, $^{2}J_{PC}$=19 Hz, C_2 of Ph), 128.64 (d, $^{3}J_{PC}$=5 Hz, C_3 of Ph), 128.69 (s, C_4 of Ph), 31.59 (d, $^{1}J_{PC}$=25 Hz, $(CH_3)_3CP$), 29.75 (d, $^{2}J_{PC}$=14 Hz, $(CH_3)_3CP$), 29.72 (dd, $^{1}J_{PC}$=28 Hz, $^{2}J_{PC}$=14 Hz, CH_2), 17.73 ppm (dd, $^{1}J_{PC}$=25 Hz, $^{2}J_{PC}$=16 Hz, CH_2). ^{13}C NMR (CD_2Cl_2): 139.23 (d, $^{1}J_{PC}$=14.4 Hz, C_{ipso} of Ph), 133.12 (d, $^{2}J_{PC}$=18.2 Hz, C_2 of Ph), 128.71 (d, $^{3}J_{PC}$=6.8 Hz, C_3 of Ph), 128.85 (s, $(CH_3)_3CP$), 31.72 (d, $^{1}J_{PC}$=22.0 Hz, $(CH_3)_3CP$), 29.70 (d, $^{2}J_{PC}$=13.5, CH_3 of t-Bu_2P), 29.19 (dd, $^{1}J_{PC}$=28.4 Hz, $^{2}J_{PC}$=13.2 Hz, CH_2), 17.34 ppm (dd, $^{1}J_{PC}$=23.3 Hz, $^{2}J_{PC}$=16.3 Hz, CH_2). MS (70 eV): *m/e* 359 (0.30%, M^+ + 1), 358 (0.74%, M^+), 317 (45.10%, M^+ - C_3H_5), 301 (50.81%, M^+- t-Bu), 185 (15.11%, Ph_2P^+), 77 (37.71%, $C_6H_5^+$), 57 (100%, $C_4H_9^+$).

Anal. Calcd for $C_{22}H_{32}P_2$: C, 73.72; H, 8.00. Found: C, 72.72; H, 8.58.

Formylferrocene (FI-1) According to the literature procedure,[57,58] 20.32 g (0.12 mol) of ferrocene was added in a N_2 atmosphere in portions into a solution of 39 mL (0.32 mol) of N-methylformanilide in 19 mL (0.20 mol) of $POCl_3$ over 30 min, and then the purple viscous solution was stirred for 1 h at room followed by 4 h at 60°C. A solution of 100 g NaOAc in 800 mL of water was added into the reaction pot at 0°C, and then the reaction mixture was extracted twice with 1 L of ether and the ethereal solution was washed successively with 1 N HCl, water, saturated $NaHCO_3$ solution, water, and brine. Solvent removal gave 21 g (82% yield) of product as dark purple powder, mp:124 - 5°C. ^1H NMR ($CDCl_3$): δ9.96 (s, CHO), δ4.80 (s, 2H), δ4.61 (s, 2H), δ4.28 (s, 5H).

Aminonitrile (racemic FI-2) According to the literature procedure,[59] 5.35 g (25 mmol) of crude formylferrocene in 16 mL of MeOH was added to a stirred solution of 2.6 g (25 mmol) of $NaHSO_3$ in 25 mL of water, and after stirring for 5 min, a solution of Me_2NH (1.5 g, 35 mmol) in 5 mL of 50% MeOH was added. The reaction mixture was cooled to 0°C, and a solution of 1.22 g (25 mmol) of NaCN in 5 mL of

water was added dropwise with stirring. The color changed from red to orange. Ether (13 mL) was added and reaction mixture was stirred at room temperature for 4 h, and then extracted with ether three times. Following solvent removal 4.50 g (67% crude yield) of product as dark brown solid was obtained. Crystallization from hexane gave 3.54 g (52% yield) of light brown crystals, mp: 84-85°C. ^{1}H NMR ($CDCl_3$): δ4.63 (s, 1H of CH), 4.42 (s, 2H of Cp), 4.25 (s with triplet split on top, $^3J_{HH}$=1.7 Hz, 2H of Cp), 4.24 (s, 5H of Cp), 2.28 (s, 6H of NMe_2).

N,N-dimethyl-1-ferrocenyl-ethylamine(racemic FI-3). A solution of 5.36 g (20 mmol) of **FI-2** in 35 mL Et_2O was added dropwise to a stirred solution of CH_3MgI (20 mL, 40 mmol) according to the literature procedure.[59] After stirring for 1 h and standing overnight, the reaction mixture was cooled and quenched with 200 mL of saturated aqueous NH_4Cl solution, and extracted with Et_2O. Solvent removal gave 4.74 g (92% crude yield) of crude product as an amber oil. Purification was achieved via distillation at 110°C, 0.1 Torr, giving 4.50g (88% yield) of spectroscopically pure racemic **FI-3** as an amber oil. ^{1}H NMR ($CDCl_3$): δ4.11 (s & shoulder peak at 4.12 ppm, 9 H of Cp), 3.59 (dd, quartet, $^3J_{HH}$=6.86 Hz, NCH), 2.07 (s, 6H of NMe_2), 1.44 (d, $^3J_{HH}$=6.89 Hz, 3H of CH_3).

N,N-Dimethyl-1-[2-(diphenylphosphino)ferrocenyl]ethylamine (rs/sr FI-4). According to the literature procedure,[61] 5 mL of n-BuLi (1.6 M in hexane, 8 mmol) was added to a solution of 1.43 g (5.57 mmol) of racemic **FI-3** in 7 mL of Et_2O at room temperature over a period of 20 min. The reaction mixture was stirred at room temperature for 1.5 h and then 2.0 mL (30 mmol) of $ClPPh_2$ in 3 mL Et_2O was added while heating under gentle reflux over 45 min. After 4 h additional reflux, aqueous $NaHCO_3$ was slowly added with cooling in an ice-bath. The resulting organic layer and benzene extracts were combined and washed with water. Solvent removal gave 3.78 g of crude product as a reddish oil. Purification was accomplished by flash chromatography on an 18x2 cm Alumina (activated neutral) column eluting with a 1:3 ratio of benzene/hexane solution to give 1.15 g (47% yield) of yellow powder in the expected yield. ^1H NMR ($CDCl_3$): δ7.57 (m, 2H of Ph), 7.30 (m, 3H of Ph), 7.17 (m, 5H of Ph), 4.35 (s, 1H of Cp), 4.22(s & d split on top, $^3J_{HH}$=2.15 Hz, 1 H of Cp), 4.11 (m, 1H of Cp), 3.92 (s, 5H of Cp), 3.84 (s, 1H of NCH), 1.74 (s, 6H of NMe_2), 1.23 (d, $^3J_{HH}$=6.72 Hz, 3H of CH_3). ^{31}P NMR ($CDCl_3$): -22.37 ppm.

R-N,N-Dimethyl-1-[(S)-2-(diphenylphosphino)ferrocenyl]ethyl amine (rs FI-4). According to literature procedure,[61] 1.8 mL of n-

BuLi (1.6 M in hexane, 8 mmol) was added to a solution of 0.500 g (1.94 mmol) of (+)-R-N,N-dimethyl-1-ferrocenylethylamine (Aldrich, 97% pure) in 7 mL of Et_2O at room temperature over a period of 5 min. The reaction mixture was stirred at room temperature for 1 h and then 0.858 g (3.89 mmol) of $ClPPh_2$ in 3 mL Et_2O was added with heating under gentle reflux over 10 min. After 3 h additional reflux, aqueous $NaHCO_3$ was slowly added with cooling in an ice-bath. The resulting organic layer and benzene extracts were combined and washed with water. Solvent removal gave 1.00 g of crude product as a reddish oil. Purification was accomplished by flash chromatography on an 18x1 cm silica gel column eluting with a 1:3 ratio of Et_2O/hexane solution to give 0.40 g (47 % yield) of product as a yellow powder in the expected yield. ^1H NMR ($CDCl_3$): δ7.57 (m, 2H of Ph), 7.30 (m, 3H of Ph), 7.17 (m, 5H of Ph), 4.35 (s, 1H of Cp), 4.22 (s & d split on top, $^3J_{HH}$=2.15 Hz, 1 H of Cp), 4.11 (m, 1H of Cp), 3.92 (s, 5H of Cp), 3.84 (s, 1H of NCH), 1.74 (s, 6H of NMe_2), 1.23 (d, $^3J_{HH}$=6.72 Hz, 3H of CH_3). ^{31}P NMR ($CDCl_3$): -22.37 ppm.

1-[2-(Diphenylphosphino)ferrocenyl]ethyldi-t-butylphosphine (ligand rs/sr8). According to the literature procedure,[55] 1.05 g (2.37 mmol) of **rs/sr FI-4** was suspended in 20 mL degassed AcOH under N_2

atmosphere. After addition of 0.35 g (2.39 mmol) neat t-Bu_2PH (Aldrich), the mixture was stirred at 80°C for 3.5 h. The solvent was then evaporated under vacuum at 70°C and the residue was dissolved in 25 mL boiling EtOH. Cooling to room temperature gave 0.81 g (63% yield) of spectroscopically pure product as orange yellow crystals. ^1H NMR ($CDCl_3$): δ7.61 (m, 2H of Ph), 7.33 (m, 3H of Ph), 7.17 (m, 5H of Ph), 4.36 (s, 1H of Cp), 4.22 (s with d split on top, $^3J_{HH}$=0.99 Hz, 1 H of Cp), 3.99 (m, 1H of Cp), 3.82 (s, 5H of Cp), 3.44 (m, 1H of PCH), 1.82 (dd, J_1=7.3 Hz, J_2=3.0 Hz, 3H of CH_3), 0.86-1.23 (m, t-Bu_2P). ^1H NMR (C_6D_6): δ7.75 (m, 2H of Ph), δ7.47 (unsym. tri, J=3 Hz, 3H of Ph), 7.08 (m, 5H of Ph), 4.22 (m, 1H of Cp), 4.10(m, 1 H of Cp), 3.8-4.0 (m, 1H of Cp), 3.82 (s, 5H of Cp), 3.0-3.8 (m, 1H of PCH), 1.80 (dd, J_1=7.3 Hz, J_2=2.9 Hz, 3H of CH_3), δ1.28 (d, $^3J_{PH}$=10.3 Hz, 9H of t-Bu), δ1.08 (d, $^3J_{PH}$=10.4 Hz). ^{31}P NMR ($CDCl_3$): 50.74 (d, $^4J_{PP}$=52 Hz), -25.54 ppm (d). ^{31}P NMR(C_6D_6): 50.34 (d, $^4J_{PP}$=53 Hz), -25.65 ppm (d, $^4J_{PP}$=53 Hz).

R-1-[(S)-2-(Diphenylphosphino)ferrocenyl]ethyldi-tert-butyl phosphine (ligand rs8). According to the literature procedure,[55] 0.400 g (0.906 mmol) of **rs FI-4** was suspended in 10 mL degassed AcOH under N_2 atmosphere. After addition of 0.133 g (0.906 mmol) neat t-Bu_2PH (Aldrich), the mixture was stirred at 80°C for 3.5 h. The solvent

was then evaporated under vacuum at 70°C and residue was dissolved in 25 mL boiling EtOH. Upon cooling to room temperature gave 0.400 g (81% yield of spectroscopically pure product as orange yellow crystals. $[\alpha]^{27}_D$= -337° (c 0.6, $CHCl_3$), 81% e.e. on the basis of the literature value $[\alpha]^{25}_D$= -417° (c 0.6, $CHCl_3$).[55] ^1H NMR ($CDCl_3$): δ7.61 (m, 2H of Ph), 7.33 (m, 3H of Ph), 7.17 (m, 5H of Ph), 4.36 (s, 1H of Cp), 4.22(s with d split on top, $^3J_{HH}$=0.99 Hz, 1 H of Cp), 3.99 (m, 1H of Cp), 3.82 (s, 5H of Cp), 3.44 (m, 1H of PCH), 1.82 (dd, J_1=7.3 Hz, J_2=3.0 Hz, 3H of CH_3), 0.86-1.23 (m, t-Bu_2P). ^1H NMR (C_6D_6): δ7.75 (m, 2H of Ph), δ7.47 (unsym. tri, J=3 Hz, 3H of Ph), 7.08 (m, 5H of Ph), 4.22 (m, 1H of Cp), 4.10(m, 1 H of Cp), 3.8-4.0 (m, 1H of Cp), 3.82 (s, 5H of Cp), 3.0-3.8 (m, 1H of PCH), 1.80 (dd, J_1=7.3 Hz, J_2=2.9 Hz, 3H of CH_3), δ1.28 (d, $^3J_{PH}$=10.3 Hz, 9H of t-Bu), δ1.08 (d, $^3J_{PH}$=10.4 Hz). ^{31}P NMR ($CDCl_3$): 50.74 (d, $^4J_{PP}$=52 Hz), -25.54 ppm (d). ^{31}P NMR (C_6D_6): 50.34 (d, $^4J_{PP}$=53 Hz), -25.65 ppm (d, $^4J_{PP}$=53 Hz).

$BrW(CO)_5^-NEt_4^+$. Under a nitrogen atmosphere, 300 mL of freshly distilled 1,4-dioxane (dried over Na) was transferred into a round-bottom flask containing 14.52 g (70 mmol) $NEt_4^+Br^-$ and 25.01 g (1.01 eq) $W(CO)_6$. The green solution was heated to reflux for 2 h, and then cooled to 0°C to give a yellow solid. Hexane was added into the

reaction pot to break up the solid, and filtration through a frit funnel gave 36.00 g (97% yield) of crude $BrW(CO)_5^-NEt_4^+$ as a yellow powder. IR (THF): 2060 (w, cis CO), 1911 (s, trans CO), 1855 cm^{-1} (m, W-Br).

trans-(NO)W(CO)$_4$Br. Inside the dry-box, 8.00 g (14.98 mmol) crude $BrW(CO)_5^-NEt_4^+$ and 4.00 g (1.0 eq) $NO^+SbF_6^-$ were mixed in CH_2Cl_2 and the suspension stirred at room temperature for 30 min. The mixture was then filtered through a pad of Celite, and then a pad of silica gel, to give after solvent removal 4.60 g (75% yield) of trans-(NO)W(CO)$_4$Br which was contaminated by ~26% by weight of $W(CO)_6$.[36] IR (CH_2Cl_2): 2050 (s), 1975 (s), 1701 cm^{-1} (m & br).

($Bu^t_2PCH_2CH_2Ph_2$)(NO)(CO)$_2$WBr . A solution of 713 mg of trans-$BrW(CO)_4NO$ (assuming 74% purity,[36] ~1.3 mmol of the pure compound) and 390mg (1.09 mmol) of $Bu^t_2PCH_2CH_2PPh_2$ in 15 mL of THF was heated at reflux for 30 min. under a nitrogen atmosphere. The solvent was removed on a vacuum line and unreacted $W(CO)_6$ was then sublimed off by warming at 45°C under dynamic vacuum, to give 712 mg of crude product as a yellow solid. Recrystallization from 40 mL of 1:1 CH_2Cl_2/hexane at -35°C gave 586 mg of pure product as a yellow solid (76% yield). IR (C_6H_6): 2024 (s), 1952 (s), 1619 (m, br) cm^{-1}. ^1H NMR (CD_2Cl_2): δ7.65-7.68 (m, 2H), 7.57-7.60 (m, 2H), 7.45-7.47 (m,

3H), 7.39-7.41 (m, 3H), 3.20-3.40 (m, 1H of CH_2), 2.40-2.70 (m, 2H of CH_2), 1.60-1.69 (m, 1H of CH_2), 1.47 (d, $^3J_{PH}$=13.3 Hz, 9H, t-Bu), 1.15 (d, $^3J_{PH}$=13.3 Hz, 9H, Bu^t). ^{31}P NMR (CD_2Cl_2): 68.82 (d, $^3J_{PP}$=7.1 Hz, $^1J_{PW}$=229.5 Hz, t-Bu_2P), 33.96 ppm (d, $^3J_{PP}$=7.1 Hz, $^1J_{PW}$=252.9 Hz, Ph_2P). ^{13}C NMR (CD_2Cl_2): 211.38 (dd, $^2J_{PC(trans)}$=49.4 Hz, $^2J_{PC(cis)}$=6.1 Hz, CO); 208.27 (dd, $^2J_{PC(trans)}$=46.2 Hz, $^2J_{PC(cis)}$=6.6 Hz, CO); 133.55 (dd, $^1J_{PC}$=43.1 Hz, $^3J_{PC}$=3.6 Hz, C_{ipso} of Ph), 132.77 (d, $^2J_{PC}$=14.9 Hz, C_2 of Ph), 132.67 (d, $^2J_{PC}$=13.3 Hz, C_2 of Ph'), 131.62 ppm (d, $^1J_{PC}$=38.4 Hz, C_{ipso} of Ph'), 131.11 (s, C_4 of Ph), 130.54 (d, $^4J_{PC}$=2.11 Hz, C_4 of Ph), 129.42 (d, $^3J_{PC}$=9.8 Hz, C_3 of Ph), 128.69 (d, $^3J_{PC}$=9.76 Hz, C_3 of Ph'), 39.43 (d, $^1J_{PC}$=15.3 Hz, $(CH_3)_3CP$), 38.69 (d, $^1J_{PC}$=11.5Hz, $(CH_3)_3CP$), 31.32 (d, $^2J_{PC}$=3.6 Hz, $(CH_3)_3CP$), 29.98 (d, $^2J_{PC}$=4.2 Hz, $(CH_3)_3CP$), 29.08 (dd, $^1J_{PC}$=30.0 Hz, $^2J_{PC}$=9.6 Hz, CH_2), 18.18ppm (dd, $^1J_{PC}$=17.9 Hz, $^2J_{PC}$=10.8 Hz, CH_2). MS (70 eV): *m/e* 655 (2.17%, M^+ + 6 - 2CO), 654 (1.03%, M^+ + 5 - 2CO), 653 (4.569%, M^+ + 4 - 2CO), 652 (2.11%, M^+ + 3 - 2CO), 651 (4.07%, M^+ + 2 -2CO), 650 (1.56%, M^+ + 1 - 2CO), 649 (1.90%, M^+ - 2CO), 185 (12.47%, Ph_2P^+), 81 (2.59%, ^{81}Br), 79 (2.32%, ^{79}Br), 40 (100%, C_3H_4). Calcd relative integration from peak (M^+ + 6 - 2CO) to peak (M^+ - 2CO): 112.4, 56.9, 241.3, 108.5, 232.2, 79.4, 100. Found: 113.9, 54.2, 240.2, 111.1, 213.9, 81.9,

100. Anal. Calcd for $C_{24}H_{32}NO_3P_2BrW$: C, 40.70; H, 4.55; N, 1.98. Found: C, 39.90; H, 4.31; N, 1.92.

Racemic ferrocene tungsten bromide (complex PRS/SR8-1, PRS/SR8-2). A solution of 0.928 g trans-$BrW(CO)_4NO$ (assuming 74% purity,[36] ~1.7 mmol of the pure compound) and 0.765 g (1.41 mmol) racemic ferrocene ligand **rs/sr8** in 15 mL of THF was treated as described above to give 1.338 g of crude product after sublimation of unreacted $W(CO)_6$. Recrystallization from 50 mL of 1:1 CH_2Cl_2/hexane at -35°C gave 1.014 g of the racemic mixture of two diastereomers as a yellow solid (81% yield). IR (CH_2Cl_2): 2018 (s), 1941 (s), 1630 (m, br) cm^{-1}. The two diastereomers were separated by eluting with 1:1 hexane/benzene on a 16x1 cm silica column, giving two well-resolved yellow bands.

For complex **PRS/SR8-1** (first band eluted from column), ^1H NMR (CD_2Cl_2): δ8.27 (m, 2H), 7.46 (m, 5H), 7.33 (m, 3H), 4.94 (unsym quintet, $^3J_{HH}$≈6.8 Hz, $^2J_{PH}$≈5.4 Hz, C*H*CH_3), 4.70 (m, 1H, (η^5-C_5H_3)Fe) : 4.65(m, 2H, (η^5-C_5H_3)Fe), 3.73 (s, 5H, η^5-CpFe), 2.02 (dd, $^3J_{HH}$=8.9 Hz, $^3J_{PH}$=7.4 Hz, CH_3), 1.68 (s&br, 9H, Bu^t), 1.01 (d, $^3J_{PH}$=12.5 Hz, 9H, Bu^t). ^{31}P NMR (CD_2Cl_2): 58.71 (d, $^4J_{PP}$=19 Hz, $^1J_{PW}$=243 Hz, Bu^t_2P), -1.81 ppm (d, $^1J_{PW}$=247 Hz, PPh_2). ^{13}C NMR (CD_2Cl_2): 212. 43 (dd,

$^2J_{PC}$=4.9 Hz, $^2J_{PC}$=49.3 Hz, CO), 210.01 (dd, $^2J_{PC}$=7.4 Hz, $^2J_{PC}$=43.2 Hz, CO), 138.45 (d, $^1J_{PC}$=48.5 Hz, C_{ipso} of Ph), 135.78 (d, $^1J_{PC}$=44.3 Hz, C_{ipso} of Ph'), 135.55 (d, $^2J_{PC}$=9.9 Hz, C_2 of Ph), 133.42 (d, $^2J_{PC}$=11.0 Hz C_2 of Ph'), 130.52 (s, C_4 of Ph), 129.11 (d, $^4J_{PC}$=2.5 Hz, C_4 of Ph'), 128.10 (d, $^3J_{PC}$=9.8 Hz, C_3 of Ph), 127.81 (d, $^3J_{PC}$=9.1 Hz C_3 of Ph'), 74.85 (s, (η^5-C_5H_3)Fe), 72.57 (d, $^2J_{PC}$=9.1 Hz, (η^5-C_5H_3)Fe), 71.56 (d, $^1J_{PC}$=37.0 Hz, (η^5-C_5H_3)Fe), 71.46 (s, (η^5-C_5H_3)Fe & (η^5-C_5H_5)Fe), 70.74 (d, $^2J_{PC}$=4.8 Hz, (η^5-C_5H_3)Fe), 40.25 (d, $^1J_{PC}$=9.9 Hz, $(CH_3)_3CP$), 40.25 (d, $^1J_{PC}$=4. Hz, $(CH_3)_3CP$), 40.03 (d, $^1J_{PC}$=9.5 Hz, CHP), 32.66 (d, $^2J_{PC}$=4.7 Hz, $(CH_3)_3CP$), 32.47 (d, $^2J_{PC}$=2.8 Hz, $(CH_3)_3CP$), 18.38 ppm (d, $^2J_{PC}$=5.7 Hz, CH_3). Anal. Calcd for $C_{34}H_{40}NO_3P_2FeWBr$: C, 45.77; H, 4.52; N, 1.57. Found: C, 47.75; H, 5.17; N, 1.72.

For complex **PRS/SR8-2** (second band eluted from column), ^{1}H NMR (CD_2Cl_2): δ7.88 (m, 2H), 7.52 (m, 5H), 7.34 (s, 3H), 4.66 (s, 1H, (η^5-C_5H_3)Fe), 4.57 (m, 1H, (η^5-C_5H_3)Fe), 4.43 (m, 1H, (η^5-C_5H_3)Fe), 4.00 (dq, $^3J_{HH}$=7.1 Hz, $^2J_{PH}$=3.7 Hz, 1H, CHMe), 3.75 (s, 5H, η^5-CpFe), 2.07 (t, $^3J_{HH}\approx{}^3J_{PH}\approx$7.6 Hz, CH_3), 1.52 (s&br, 9H, Bu^t), 1.15 (d, $^3J_{PH}$=12.6 Hz, 9H, Bu^t). ^{31}P NMR (CD_2Cl_2): 58.74 (d, $^4J_{PP}$=18 Hz, $^1J_{PW}$=240 Hz, Bu^t_2P), 9.18ppm (d, $^4J_{PP}$=18 Hz, $^1J_{PW}$=252 Hz, Bu^t_2P). Anal. Calcd for

$C_{34}H_{40}NO_3P_2FeWBr$: C, 45.77; H, 4.52; N, 1.57. Found: C, 46.69; H, 4.83; N, 1.64.

Enantiomer enriched ferrocene tungsten bromide (complex Prs8-1, Prs8-2). A solution of 243 mg of trans-$BrW(CO)_4NO$ (assuming 74% purity,[36] ~0.443 mmol of the pure) and 170 mg (0.313 mmol) of ligand **rs8** in 10 mL of THF was allowed to stand at room temperature for 2 days under a nitrogen atmosphere. The solvent was removed on a vacuum line and unreacted $W(CO)_6$ was then sublimed off by warming at 45°C under dynamic vacuum, gave 315 mg of crude product as a yellow solid. Chromatography of 286 mg of crude product on an 18x1cm silica gel column eluting with 1:1 benzene/hexane gave 49 mg of complex **Prs8-1** and 70 mg of complex **Prs8-2**.

For complex **Prs8-1**, ^{1}H NMR (CD_2Cl_2): δ8.27 (m, 2H), 7.46 (m, 5H), 7.33 (m, 3H), 4.96 (unsym quintet, $^3J_{HH}$=7.1 Hz, $^2J_{PH}$=5.0 Hz, 1H, C*H*CH_3), 4.70 (m, 1H, (η^5-C_5H_3)Fe) : 4.65(m, 2H, (η^5-C_5H_3)Fe), 3.73 (s, 5H, η^5-CpFe), 2.02 (dd, J_1=8.9 Hz, J_2=7.4 Hz, CH_3), 1.70 (s&br, 9H, Bu^t), 1.02 (d, $^3J_{PH}$=12.5 Hz, 9H, Bu^t). ^{31}P NMR (CD_2Cl_2): 58.71 (d, $^4J_{PP}$=19 Hz, $^1J_{PW}$=243 Hz, Bu^t_2P), -1.80 ppm (d, $^1J_{PW}$=247 Hz, PPh_2). ^{13}C NMR (CD_2Cl_2): 212. 45 (dd, $^2J_{PC}$=6.2 Hz, $^2J_{PC}$=48.8 Hz, CO), 210.02 (dd, $^2J_{PC}$=8.5 Hz, $^2J_{PC}$=44.7 Hz, CO), 138.45 (d, $^1J_{PC}$=46.7 Hz,

C_{ipso} of Ph), 135.78 (d, $^1J_{PC}$=44.7 Hz, C_{ipso} of Ph'), 135.56 (d, $^2J_{PC}$=10.5 Hz, C_2 of Ph), 133.42 (d, $^2J_{PC}$=10.7 Hz C_2 of Ph'), 130.53 (d, $^4J_{PC}$=2.0Hz, C_4 of Ph), 129.11 (d, $^4J_{PC}$=2.5 Hz, C_4 of Ph'), 128.10 (d, $^3J_{PC}$=9.7 Hz, C_3 of Ph), 127.81 (d, $^3J_{PC}$=9.1 Hz C_3 of Ph'), 74.86 (s, (η^5-C_5H_3)Fe), 72.58 (d, $^2J_{PC}$=9.3 Hz, (η^5-C_5H_3)Fe), 71.47 (s, (η^5-C_5H_3)Fe & (η^5-C_5H_5)Fe), 70.75 (d, $^2J_{PC}$=4.8 Hz, (η^5-C_5H_3)Fe), 70.56 (d, $^1J_{PC}$=35.7 Hz, (η^5-C_5H_3)Fe), 40.26 ppm (d, $^1J_{PC}$=9.7 Hz, $(CH_3)_3CP$), 40.25 (d, $^1J_{PC}$=3.9 Hz, $(CH_3)_3CP$), 40.04 (d, $^1J_{PC}$=9.7 Hz, CHP), 32.67 ppm (d, $^2J_{PC}$=4.8 Hz, $(CH_3)_3CP$), 32.48 (d, $^2J_{PC}$=2.9Hz, $(CH_3)_3CP$), 18.39 (d, $^2J_{PC}$=5.8 Hz, CH_3).

For complex **Prs8-2,** $[\alpha]^{25}_D$= -90.4° (c 0.38,CH_2Cl_2). ^{1}H NMR (CD_2Cl_2): δ7.88 (m, 2H), 7.50 (m, 5H), 7.34 (s, 3H), 4.67 (s, 1H, (η^5-C_5H_3)Fe), 4.58 (m, 1H, (η^5-C_5H_3)Fe), 4.43 (m, 1H, (η^5-C_5H_3)Fe), 4.01 (dq, $^3J_{HH}$=7.1 Hz, $^2J_{PH}$=3.7 Hz, 1H, CHMe), 3.76 (s, 5H, η^5-CpFe), 2.07 (tri, J=7.6 Hz, CH_3), 1.61 (s&br, 9H, Bu^t), 1.16 (d, $^3J_{PH}$=12.6 Hz, 9H, Bu^t). ^{31}P NMR (CD_2Cl_2): 58.75 (d, $^4J_{PP}$=18 Hz, $^1J_{PW}$=242 Hz, Bu^t_2P), 9.19 ppm (d, $^4J_{PP}$=18 Hz, $^1J_{PW}$=250 Hz, Bu^t_2P). ^{13}C NMR (CD_2Cl_2): 211.15 (dd, $^2J_{PC}$=7.3 Hz, $^2J_{PC}$=51.8 Hz, CO), 210.34 (dd, $^2J_{PC}$=7.3 Hz, $^2J_{PC}$=46.8 Hz, CO), 139.22 (d, $^1J_{PC}$=49.0 Hz, C_{ipso} of Ph), 134.89 (d,

$^2J_{PC}$=10.2 Hz, C_2 of Ph), 134.78 (d, $^2J_{PC}$=12.0 Hz, C_2 of Ph'), 133.30 (d, $^1J_{PC}$=45.7Hz, C_{ipso} of Ph'), 130.55 (s, C_4 of Ph), 129.70 (s, C_4 of Ph'), 128.57 (d, $^3J_{PC}$=9.9Hz,C_3 of Ph), 128.48 (d, $^3J_{PC}$=9.7 Hz,C_3 of Ph'), 74.88 (s, (η^5-C_5H_3)Fe), 73.95 (d, $^1J_{PC}$=37.4 Hz, (η^5-C_5H_3)Fe), 72.39 (d, $^2J_{PC}$=8.7 Hz, (η^5-C_5H_3)Fe), 71.07 (s, (η^5-C_5H_3)Fe) & (η^5-Cp)Fe), 70.28 (d, $^2J_{PC}$=6.0 Hz, (η^5-C_5H_3)Fe), 40.52 (d, $^1J_{PC}$=6.0 Hz, CHMe), 40.08 (d, $^1J_{PC}$=4.9Hz, $(CH_3)_3CP$), 40.07 (d, $^1J_{PC}$=9.8 Hz, $(CH_3)_3CP$), 35.21 (d, $^2J_{PC}$=5.5 Hz, $(CH_3)_3CP$), 32.55 (d, $^2J_{PC}$=2.5 Hz, $(CH_3)_3CP$), 18.84 (d, $^2J_{PC}$=5.8 Hz, CH_3).

($Bu^t_2PCH_2CH_2Ph_2$)(NO)$(CO)_2W(\mu$-F)SbF_5 (racemic C7). Under a nitrogen atmosphere, a solution of racemic complex **P7** (52 mg, 0.074 mmol) and $AgSbF_6$ (25 mg, 1 eq) in CD_2Cl_2 (0.5 mL) was stirred for 2 h, and then filtered through a pad of oven-dried Celite to remove AgBr and any unreacted silver salt. ^{1}H NMR (CD_2Cl_2): δ7.50 (m, 10H of Ph), 2.0-3.4 (m, 4H of CH_2), 1.36 (d, $^3J_{PH}$=13.8 Hz, 9H of Bu^t), 1.16 (d, $^3J_{PH}$=13.8 Hz, 9H of Bu^t). ^{31}P NMR(CD_2Cl_2): 82.14 (d, $^3J_{PP}$=7 Hz, $^1J_{PW}$=248 Hz, Bu^t_2P), 47.08 (d, $^3J_{PP}$=7 Hz, $^1J_{PW}$=270 Hz, Ph_2P).

Enantiomer enriched ferrocene catalysts (Crs8-1, Crs8-2). Under a nitrogen atmosphere, a solution of racemic complex **Prs8-1 (or Prs8-2)** (~50 mg) and $AgSbF_6$ (0.95 eq) in CH_2Cl_2 (1 mL) was stirred

for 2 h, and then filtered through a pad of oven-dried Celite to remove any silver salt, giving a solution of catalyst. ^{31}P NMR spectra show multiple sets doublets. In each spectrum there is one set of doublets, possibly due to W-F-SbF_5 adduct, since line broadening due to SbF_6^- is well known.[65] Other sets of doublets are relatively sharp and it is impossible to determine what (if any) ligand is present in place of the bromine atom of **Prs8-1 or Prs8-2**. One possibility is adventitious water which is particular problem when experiments such as this particular set are carried out at low concentration. There is no direct evidence that any of the observed peaks are due to achiral Lewis acids, but we cannot rule out the possiblity that the low e.e.'s are due to a mixture of catalytic species.

Catalytic Diels-Alder reactions. All reactions were carried out in a similar way. Inside the drybox, pre-cooled (-35°C) acrolein (200 mg) and isoprene (1.05 eq) were added into 5 mL of pre-cooled CH_2Cl_2, and then a CD_2Cl_2 solution of the catalyst (checked by NMR) was added. After stirring at room temperature for several hours, the solution was brought out of the dry-box and filtered through 10 mL of silica in 10 mL CH_2Cl_2 on a frit to remove the catalyst, and the product was washed down with a further 15-25ml of CH_2Cl_2. Solvent removal on a rotary

evaporator gave the Diels-Alder adduct. The ^{13}C NMR spectrum of the Diels-Alder adducts gave 2 sets of peaks corresponding to the 1,4-substituted and the 1,3-substituted structural isomers. The average of the corresponding 2 sets of peak heights was used to calculated the ratio of 1,4- versus 1,3- ratio. The enantiomer ratio of the major structural isomer (1,4-) was determined by the integration of the aldehyde hydrogens of the Diels-Alder adducts, in the presence of chiral chemical shift reagent $Eu(hfc)_3$. The preparation of the NMR sample with $Eu(hfc)_3$ is as follows: inside the dry-box, dissolve ~6 mg of *acr/iso adduct* (Figure III.6) in 0.5 mL CD_2Cl_2, then dry the solution with activated molecular sieve (160°C oven dry over night) for ~10 min, weigh ~30 mg of $Eu(hfc)_3$ in a vial, dissolve the europium reagent in the solution, then transfer the clear solution to the NMR tube. Typically 30~60 mg of $Eu(hfc)_3$ added into a solution of 5~10 mg of *acr/iso adduct* in 0.5 ml of CD_2Cl_2, shifts the aldehyde peaks from 9.5 ppm to 17~24 ppm, with a chemical shift difference for the enantiomers of 0.09~0.13 ppm at 400 MHz. The range of chemical shift difference is dependent both on the amount of $Eu(hfc)_3$ and the dryness of the sample.

Stoichiometric Diels-Alder reactions. All reactions were carried out in a similar way: inside the drybox, pre-cooled acrolein (1.8 eq) was added into a pre-cooled solution of the catalyst (0.04 mmol, prepared via above method) in 0.5 mL CD_2Cl_2 via a micro-syringe, followed by addition of isoprene (1.8 eq). All steps of the reaction were monitored by ^1H NMR and ^{31}P NMR, and the reaction rate was determined by the integration of aldehyde hydrogen peaks of the free and coordinated aldehydes.

2-phenyl-1,3-di-*p*-toluenesulfonyl-1,3,2-diazaphospholidine (*TosL*). Under a nitrogen atmosphere, a solution of 1.17 mL $PhPCl_2$ (8.62 mmol) in 40 mL anhydrous ether was added dropwise over a 50 min period to an ice-cooled suspension of 3.18 g $CH_3C_6H_4SO_2N(H)CH_2CH_2N(H)SO_2C_6H_4CH_3$ (8.63 mmol) and 3.0 mL Et_3N (distilled under N_2 from CaH_2; 21.5 mmol) in 220 mL of anhydrous ether. The mixture was then stirred at room temperature for an additional 30 min. and then the solvent was removed on a rotary evaporator. The resultant white powder was purified by dissolving in 50 mL CH_2Cl_2 and the solution was then filtered through a pad (~100 mL) of silica gel packed in CH_2Cl_2 on a 150 mL sintered glass frit. The product was eluted with 300 mL more CH_2Cl_2, and the solvent removed

on a rotary evaporator to give 2.54 g (62% yield) of *TosL* as a spectroscopically pure white powder. Material submitted for elemental analysis was crystallized from 3:1 CH_2Cl_2/hexane at -40°C in the glove box. ^1H NMR ($CDCl_3$): δ7.69 (m, 2H, Ph), 7.63 (d, J=8.2 Hz, 4H, Ts), 7.45 (m, 3H, Ph), 7.18 (d, J=8.2Hz, 4H, Ts), 3.50 (m, 2H, HCCH), 3.20 (m, 2H, HCCH), 2.44 (s, 6H, CH_3). . ^{31}P NMR ($CDCl_3$): 91.28 ppm. ^{13}C NMR ($CDCl_3$): 143.87 (br, s, C_{ipso} of Ts), 138.40 (d, $^1J_{PC}$=32.1 Hz, C_{ipso} of Ph), 135.80 (s, C_{ipso} of Ts), 130.54 (s, C_4 of Ph), 129.74 (s, CH of Ts), 129.42 (d, $^2J_{PC}$=20.5 Hz, C_2 of Ph), 128.78 (d, $^3J_{PC}$=5.6 Hz, C_3 of Ph), 127.25 (s, CH of Ts), 47.98 (d, $^2J_{PC}$=5.7 Hz, CH_2), 21.65 ppm (s, CH_3). MS (70 eV): *m/e* 410 (13%, $M^+ - SO_2$), 409 (17%, $M^+ - HSO_2$), 397 (2%, $P(N(Ts)CH_2CH_2NTs)^+$), 255 (72%, $M^+ - Ts - SO_2$), 155 (14%, Ts^+), 91 (100%, C_7H_7); the 20 eV MS of *TosL* was virtually the same as that at 70 eV. Anal. Calcd for $C_{22}H_{23}N_2O_4S_2P$: C, 55.69; H, 4.89; N, 5.90. Found: C, 55.44; H, 4.83; N, 5.94.

N,N'-bis(diphenylphosphino)-N,N'-di-*p*-toluenesulfonyl-1,2-ethanediamine (*diTosL*). Under a nitrogen atmosphere, 3.59 g (16.3 mmol) of Ph_2PCl was added dropwise to a solution of 3.00 g (8.14 mmol) of $CH_3C_6H_4SO_2N(H)CH_2CH_2N(H)SO_2C_6H_4CH_3$ and 2.06 g (20.35 mmol) of Et_3N in 50 mL of THF, and the mixture was heated at

reflux for 21.5 h. After solvent removal on a rotary evaporator, the resultant pale yellow solid was taken up in 100 mL benzene and filtered to remove $Et_3NH^+Cl^-$. Solvent removal on a rotary evaporator again gave a pale yellow powder (5.90 g) which was dissolved (in the air) in 20 mL of hot CH_2Cl_2 and then treated with 20 mL of hot anhydrous ether. Cooling to room temperature gave white crystals, and crystallization was completed at -10°C overnight; filtration and rinsing with hexane gave 2.57 g (43% yield) of *diTosL* as air-stable white crystals. ^{1}H NMR ($CDCl_3$): δ7.46 (d, J=8.2 Hz, 4H, Ts), 7.36 (m, 4H, Ph), 7.29-7.20 (m, 20H, Ph), 7.18 (d, J=8.2 Hz, 4H, Ts), 3.30 (br s, 4H, CH_2), 2.41 (s, 6H, CH_3). ^{31}P NMR($CDCl_3$): 60.37 ppm. ^{13}C NMR($CDCl_3$): 143.43 (s, C_{ipso} of Ts), 137.17 (s, C_{ipso} of Ts), 134.66 (d, $^1J_{PC}$=17.5 Hz, C_{ipso} of Ph), 132.56 (d, $^2J_{PC}$=21.9 Hz, C_2 of Ph), 129.57 (s, CH of Ts), 129.40 (s, CH of Ts), 128.48 (d, $^3J_{PC}$=6.0 Hz, C_3 of Ph), 127.48 (d, $^4J_{PC}$=2.6 Hz,C_4 of Ph), 49.20 (s, CH_2), 21.55 ppm (s, CH_3). MS (70 eV): *m/e* 581 (1.5%, M^+ - Ts), 396 (2%, M^+ - Ts, - PPh_2), 183 (100%, $TsNCH_2^+$). Anal. Calcd for $C_{40}H_{38}N_2O_4S_2P_2$: C, 65.20; H, 5.20; N, 3.80. Found: C, 64.84; H, 5.05; N, 3.75.

(TosL)W(CO)5. Tungsten hexacarbonyl (1.10 g, 3.13 mmol) and 80 mL THF were placed in a 250 mL septum-capped flask with a

magnetic stirring bar, placed in a water-cooled water bath, and irradiated under a nitrogen atmosphere with a 450W Hanovia medium pressure mercury lamp for 3h. The resultant yellow solution was transferred via syringe into a solution of *TosL* (1.09 g, 2.30 mmol, 0.73 eq. based on $W(CO)_6$) in 10 mL THF. No color change was observed, and the reaction mixture was stirred at room temperature under a nitrogen atmosphere and monitored periodically by IR. After 2.5h little further change was observed, and the THF was removed on a vacuum line at room temperature. The resultant off-white powder was then warmed at ~45°C on the vacuum line to facilitate sublimation of unreacted $W(CO)_6$, and 1.65 g (90% yield based on *TosL*) of crude product was obtained. Attempts to crystallize this material from CH_2Cl_2, toluene, or mixtures of CH_2Cl_2/hexane and CH_2Cl_2/1,1,2-trichlorotrifluoroethane all failed. Final purification was achieved by filtration of a CH_2Cl_2 solution of the material through silica gel, eluting first with CH_2Cl_2 and then 1:1 CH_2Cl_2/THF, to give **(TosL)W(CO)$_5$** (~85% recovery after solvent removal and washing with hexane, 77% overall yield) as a spectroscopically pure white powder. A small sample of analytically pure material was obtained with difficulty by recrystallization from 3:1 hexane: CH_2Cl_2. IR (CH_2Cl_2): 2080 (m),

1952 cm^{-1} (s). ^1H NMR ($CDCl_3$): δ 7.56, 7.43, 7.32 (m, 5H, Ph), 7.12, 7.06 (AB quartet, J=8.5 Hz, 8H, Ts), 3.90 (m, (approx. quintet, J=5 Hz), 2H, HCCH), 3.51 (m, (approx. quintet, J=5 Hz), 2H, HCCH), 2.35 (s, 6H). ^{31}P NMR($CDCl_3$): 122.06 ppm ($^1J_{PW}$=329.5 Hz). ^{13}C NMR($CDCl_3$): 198.24 (d, $^2J_{PC}$=37.2 Hz, trans-CO), 196.00 (d, $^2J_{PC}$=8.0 Hz, $^1J_{PW}$=127.0 Hz, cis-CO), 144.39 (s, C_{ipso} of Ts), 136.51 (d, $^1J_{PC}$=20.1 Hz, C_{ipso} of Ph), 135.37 (s, C_{ipso} of Ts), 132.81.42 (d, $^2J_{PC}$=17.9 Hz, C_2 of Ph), 132.79 (s, C_4 of Ph), 129.45 (s, CH of Ts), 128.42 (d, $^3J_{PC}$=10.7 Hz, C_3 of Ph), 127.49 (s, CH of Ts), 46.45 (s, CH_2), 21.55 ppm (s, CH_3). MS (70 eV): *m/e* 410 (3%, M^+ - SO_2), 409 (5%, $M^{+\cdot}$ - HSO_2), 255 (30%, M^+ - Ts, -SO_2), 155 (11%, Ts^+), 91 (100%, C_7H_7). Anal. Calcd for $C_{27}H_{23}N_2O_9S_2PW$: C, 40.62; H, 2.90; N, 3.51. Found: C, 40.76; H, 2.75; N, 3.44.

cis,cis,trans-(diTosL)W(CO)$_2$(NO)Br (10). In the dry-box a solution of 226 mg (0.412 mmol) of *trans*-$BrW(CO)_4NO$ and 206 mg (0.280 mmol) of *diTosL* in 4 mL of $CHCl_3$ was allowed to stand in a screw-capped 1 dram vial at room-temperature for 24 h. The solvent then was removed on a vacuum line to gave 320 mg of crude product as a yellow solid. Purification was accomplished by flash chromatography on an 18x1 cm silica gel column eluting with 9:1 CH_2Cl_2/hexane to give

261 mg (86% yield) of analytically pure product as a yellow powder. IR (CH_2Cl_2): 2036 (s), 1968 (s), 1650 (br, m), 1598 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ7.91 (m, 4H, Ph), 7.69 (m, 4 H, Ph), 7.47 (m, 12H of Ph), 7.07 (d, J=8.2 Hz, 4H, Ts), 6.82 (d, J=8.2 Hz, 4H, Ts), 4.45 (m, 2H, HCCH), 4.03 (m, 2H, HCCH), 2.38 (s, 6H, CH_3). . ^{31}P NMR ($CDCl_3$): 77.11 ppm ($^1J_{PW}$=270.8 Hz). ^{13}C NMR ($CDCl_3$): 204.62 (d, $^2J_{PC}$=55.2 Hz, CO), 144.32 (s, C_{ipso} of Ts), 136.41 (s, C_{ipso} of Ts), 133.82 (d, $^2J_{PC}$=11.1 Hz, C_2 of Ph), 132.74 (d, $^2J_{PC}$=12.6 Hz, C_2 of Ph'), 131.4 (d, $^1J_{PC}$=44 Hz, C_{ipso} of Ph), 130.76 (d, $^1J_{PC}$=43.3 Hz, C_{ipso} of Ph'), 131.18 (s,C_4 of Ph), 131.08 (s,C_4 of Ph'), 129.58 (s, CH of Ts), 128.40 (d, $^3J_{PC}$=9.7 Hz, C_3 of Ph), 127.67 (d, $^3J_{PC}$=9.7 Hz, C_3 of Ph'), 51.66 (s, CH_2), 21.56 ppm (s, CH_3). Anal. Calcd for $C_{42}H_{38}N_3O_7P_2S_2WBr$: C, 46.43; H, 3.52; N, 3.87. Found: C, 46.50; H, 3.85; N, 3.94.

$Et_3NH^+Br^-$. Concentrated HBr (16 mL, 143 mmol, 48% aqueous solution) was added dropwise into a solution of Et_3N (10 mL, 71.7 mmol) of in 20 mL of benzene and allowed to stir for 30 min at room temperature. Solvent removal on a rotary evaporator gave white powder as a crude product. Crystallization from 20 mL of ethanol gave white crystals which was further dried on a vacuum line to give 13.0 g of pure

product as white crystals. ^{1}H NMR (CD_2Cl_2): δ3.12 (d of quart, $^3J_{HH}$= 5.0 Hz, $^3J_{HH}$= 7.4 Hz), δ1.38 (tri, $^3J_{HH}$= 7.4 Hz)

$Et_3NH^+Cl^-$. Concentrated HCl (12ml,143 mmol, 37% aqueous solution) of was added dropwise into a solution of Et_3N (10 mL, 71.7 mmol) of in 20 mL of benzene and allowed to stir for 30 min at room-temperature. Solvent removal on a rotary evaporator to give white powder as a crude product. Crystallization from 100 mL of ethanol gave white crystals which was further dried on a vacuum line to give 5.67 g of pure product as white crystals, mp: 261°C. ^{1}H NMR (CD_2Cl_2): δ3.08 (d of quart, $^3J_{HH}$= 5.0 Hz, $^3J_{HH}$= 7.3 Hz), δ1.36 (tri, $^3J_{HH}$= 7.3 Hz)

cis, cis, trans-(diTosL)W(CO)$_2$(NO)Cl (10a). In the glove box a solution of 217 mg (assuming 74% purity,[36] ~0.407 mmol of the pure) *trans*-$BrW(CO)_4$ NO, 75 mg (0.543 mmol) Et_3NHCl, and 200 mg (0.271 mmol) *diTosL* in 4 mL of $CHCl_3$ was allowed to stand in a screw-capped 1 dram vial at room-temperature for 24 h. Solvent removal on a vacuum line gave 350 mg of crude product as a yellow solid. Purification was accomplished by flash chromatography on an 15x1 cm silica gel column eluting with CH_2Cl_2 to give 235 mg (83% yield) of analytically pure product as a yellow powder. IR (CH_2Cl_2): 2035 (s), 1967 (s), 1649 (br, m), 1596 cm^{-1} (w). IR (C_6H_6): 2034 (s),

1964 (s), 1649 (br, m), 1596 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ7.93 (m, 4H, Ph), 7.71 (m, 4 H, Ph), 7.45 (m, 12H of Ph), 7.06 (d, J= 8.2 Hz, 4H, Ts), 6.81 (d, J=8.2 Hz, 4H, Ts), 4.42 (m, 2H, HCCH), 4.04 (m, 2H, HCCH), 2.38 (s, 6H, CH_3). ^{31}P NMR ($CDCl_3$): 80.90ppm ($^1J_{PW}$=261.3 Hz). Anal. Calcd for $C_{42}H_{38}N_3O_7P_2S_2WCl$: C, 48.41; H, 3.68; N, 4.03; Cl, 3.40. Found: C, 48.01; H, 3.64; N, 4.03; Cl, 3.41.

(diphos)W(CO)$_2$(NO)Br (11). Under a nitrogen atmosphere a solution of 0.570 g (1.02 mmol) of *trans*-$BrW(CO)_4NO$ and 0.400 g (1.00 mmol) of *diphos* in 15 mL of THF was stirred at reflux temperature for 1 h. The reaction mixture was filtered through a pad of celite and the solvent was removed on a vacuum line to gave 720 mg (96% yield) of crude product as a yellow solid. Purification was accomplished by flash chromatography on an 18x1 cm silica gel column eluting with CH_2Cl_2 to give 406 mg (54% yield) of yellow powder identified by comparison to literature data[63] as the *diphos* tungsten adduct **11**. ^{31}P NMR ($CDCl_3$): 32.74 ppm ($^1J_{PW}$=249.1 Hz). ^{13}C NMR($CDCl_3$): 208.81 (d, $^2J_{PC}$=48.5 Hz, $^1J_{PW}$=152.4 Hz,CO), 132.79 (d, $^2J_{PC}$=12.4 Hz, C_2 of Ph), 132.39 (d, $^1J_{PC}$=40.8 Hz, C_{ipso} of Ph), 132.30 (d, $^2J_{PC}$=10.5 Hz, C_2 of Ph'), 131.73 (d, $^1J_{PC}$=44.6 Hz, C_{ipso} of Ph'),

130.82 (s,C_4 of Ph), 130.34 (s,C_4 of Ph'), 129.03 (d, $^3J_{PC}$=10.5 Hz, C_3 of Ph), 128.46 (d, $^3J_{PC}$=10.3 Hz, C_3 of Ph'), 10.7 (s, CH_2).

cis,cis,trans-(1,2-bis(dipentafluorophenylphosphino)ethane) $(CO)_2W(NO)Br$ (12). Inside the glove box a solution of 227 mg (0.414 mmol) of *trans*-$BrW(CO)_4NO$ and 210 mg (0.277 mmol, diphos-F_{20}) of 1,2-bis(dipentafluorophenylphosphino)ethane in 12 mL of $CHCl_3$ was stirred at room temperature for 23 h. The reaction mixture was filtered through a pad of Celite and the solvent was removed on a vacuum line to gave 390 mg of crude product as a yellow solid. Purification was accomplished by flash chromatography on an 18x1 cm silica gel column eluting with CH_2Cl_2 to give 304 mg of yellow powder, followed by washing with hexane (in which **P12** is slightly soluble) to give 186 mg (61% yield) of analytically pure product as a yellow powder. IR (CH_2Cl_2): 2054 (s), 1992 (s), 1650 (br, s), 1522 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ3.33 (m, 2H, HCCH), 3.02 (m, 2H, HCCH). ^{31}P NMR ($CDCl_3$): 7.75 ppm ($^1J_{PW}$=262.2 Hz). Anal. Calcd for $C_{28}H_4NO_3P_2WBrF_{20}$: C, 30.35; H, 0.36; N, 1.26. Found: C, 30.57; H, 0.52; N, 1.24

***(TosL)*$(CO)_3W(NO)(\mu\text{-}F)SbF_5$ (C9).** Under a nitrogen atmosphere, $NOSbF_6$ (21 mg, 2.3 eq) was slowly added to a solution of complex **P9**

(25 mg, 0.036 mmol) in 0.5 mL CH_2Cl_2, and stirred for an additional 20 min until no more gas was given off, and then filtered through a pad of oven-dried Celite to gave the catalyst solution.

***(diTosL)*(NO)(CO)$_2$W(μ-F)SbF$_5$ (C10).** Under a nitrogen atmosphere, a solution of **10** (40 mg, 0.036 mmol) and $AgSbF_6$ (13 mg, 1 eq) in CD_2Cl_2 (0.5 mL) was stirred for 2 h, and then filtered through a pad of oven-dried Celite to remove AgBr and any unreacted silver salt. Like that of **C9**, the NMR spectrum of **C10** are too complicated to describe.

N-p -Toluenesulfonyl-(*S*)-valine (14). While this compound has previously been reported, details are sparse and the yield was at most ~50%.[105,106] A total of 11.54 g (60.54 mmol, 1.2 eq) of p-toluenesulfonyl chloride was added in three portions (at 0, 18, and 25 h reaction time) to a magnetically-stirred solution of 5.91 g (50.45 mmol, 1 eq) of (S)-valine and 15.01 g (121.08 mmol, 2.4 eq) of sodium carbonate in 100 mL of H_2O. Stirring at room temperature was continued for five more days to give a colorless solution. Acidification with 6 M HCl resulted in precipitation of the product as a white solid, which was filtered, washed with a small amount of water, and then taken up in ether and dried over anhydrous magnesium sulfate. Solvent

removal on a rotary evaporator gave 10.72 g (78% yield) of product as a spectroscopically pure white powder. ^{1}H NMR ($CDCl_3$): δ9.01 (b, 1H of COOH); d 7.72 (d, J=8.3 Hz, 2H of Ts), 7.27 (d, J=9.0 Hz, 2H of Ts), 5.18 (d, J=9.9 Hz, 1H of NH), 3.78 (dd, J=9.9 Hz, J=4.7 Hz, 1H of CHN), 2.41 (s, 3H of CH_3 of Ts), 2.09 (m, 1H of i-Pr.), 0.95 (d, J=6.8 Hz, 3H of i-Pr.), 0.86 (d, J=6.8 Hz, 3H of i-Pr.)

(2S,4S) and (2R, 4S)-4-isopropyl-5-oxo-2-phenyl-3-p-toly-1,3,2 oxazaphospholidine (14a, 14b). Under a nitrogen atmosphere, 4.15 mL (29.8 mmol, 3.5 eq) of triethylamine was added dropwise to a solution of 2.31 g (8.51 mmol, 1 eq) of N-p -toluenesulfonyl-(*S*)-valine (**14**) in 80 mL of ether to give a white suspension. A solution of 2.13 g (11.9 mmol, 1.4 eq) of $PPhCl_2$ in 3 mL of ether was then added dropwise to form a cloudy white solution, which was stirred at room-temperature for 1 h. The suspended Et_3NHCl was removed by filtration and washed with 3x5mL of diethyl ether. The solvent was removed the from the combined ethereal solution on a vacuum line, giving a pale yellow solid in a clear yellow oil. This residue was heated under vacuum at 50°C for 1.5 h to remove the unreacted starting material $PhPCl_2$, resulting in formation of a pale yellow powder (2.91 g, 91% yield) consisting of a spectroscopically pure mixture of the two

diastereomeric products in 9.2:1 ratio. Fractional crystallization then proceeded as follows. Inside the glove box, the 2.91 g of the mixture was dissolved in 45 mL of ether and the solution was allowed to stand at -35°C for several days to give 1.62 g (50% yield) of small pale yellow crystals. The filtrate was stripped to dryness and the residue (1.30 g) was recrystallized from 20 mL of diethyl ether at -35°C to give 0.33 g (10% yield) of a second crop of small white crystals. Recrystallization of 0.89 g of residue from 10 mL diethyl ether gave 0.18 g (6% yield) of crystals as a third crop. The first crop contained no detectable **14b**, the second crop contained 1% of **14b** and the third crop contained 9% of **14b**. The final residue (0.70 g) consisted of 1.04:1 ratio of **14a:14b**. For the non-crystalline 57:43 mixture of **14a:14b**, $[\alpha]^{27}_{D}$= +88.65° (c 2.14, C_6H_6) Anal. Calcd for $C_{18}H_{20}NO_4SP$: C, 57.29; H, 5.34; N, 3.71. Found C, 57.18; H, 5.33; N, 3.70. **Major isomer (14a)**:mp: 129-131°C. $[\alpha]^{27}_{D}$= +84.83° (c 2.43, C_6H_6). Anal. Calcd for $C_{18}H_{20}NO_4SP$: C, 57.29; H, 5.34; N, 3.71. Found C, 57.15; H, 5.24; N, 3.64. IR ($CHCl_3$): 3023, 1791 (CO), 1360,1164 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$): δ7.84 (d, J=8.3 Hz, 2H of Ts), 7.60 (m, 2H of Ph), 7.46 (m, 3H of Ph); 7.38 (d, J=8.1 Hz, 2H of Ts), 3.53 (dd, $^3J_{HH}$=7.1 Hz, $^3J_{PH}$=3.7 Hz, 1H of CHN.), 2.46 (s, 3H of CH_3 of Ts); 1.71 (oct, J=6.9 Hz, 1H of CH of i-

Pr.), 0.94 (d, J=6.9 Hz, 3H of CH_3 of i-pr.), 0.74 (d, J=6.8 Hz, 3H of CH_3 of i-pr.). ^{31}P NMR ($CDCl_3$): 133.04 ppm. ^{13}C NMR ($CDCl_3$) : 171.30 (d, $^2J_{PC}$=12.4 Hz, CO); 145.20 (s, C_{ipso} of Ts); 139.64 (d, $^1J_{PC}$ =38.6 Hz, C_{ipso} of Ph); 134.69 (s, C_{ipso} of Ts); 131.26 (s, C_2 of Ts); 130.33 (s, C_3 of Ts); 128.92 (d, $^4J_{PC}$=4.4 Hz, C_4 of Ph); 128.305 (d, $^2J_{PC}$=18.8 Hz, C_2 of Ph); 127.67 (d, $^2J_{PC}$=4.8 Hz, C_3 of Ph); 61.63 (s, CHN); 31.48 (s, CH of i-Pr); 21.67 (s, CH_3); 19.66 (s, CH_3); 18.17 (s, CH_3). **Minor isomer(14b)**: $[\alpha]^{27}_D$= +93.8° (calculated from $[\alpha]^{27}_D$= +88.65° (c 2.14, C_6H_6) for a 57.4:42.6 mixture of **14a:14b**. ^1H NMR ($CDCl_3$): δ7.60 (m, 3H of Ph), 7.46 (m, 2H of Ph & 2H of Ts), 7.21 (d, J=8.2 Hz, 2H of Ts), 4.06 (dd, $^3J_{HH}$=3.0 Hz, $^3J_{PH}$=1.4 Hz, 1H of CHN.), 2.50 (oct, J=3.1 Hz, 1H of CH of i-Pr.), 2.41 (s, 3H of CH_3 of Ts),), 1.16 (d, J=7.1 Hz, 3H of CH_3 of i-pr.), 0.64 (d, J=6.7 Hz, 3H of CH_3 of i-pr.). ^{31}P NMR ($CDCl_3$): 136.70 ppm. ^{13}C ($CDCl_3$) : 171.01 (d, $^2J_{PC}$=13.0 Hz, CO); 144.48 (s, C_{ipso} of Ts); 139.43 (d, $^1J_{PC}$=50.4 Hz, C_{ipso} of Ph); 136.78 (s, C_{ipso} of Ts); 132.56 (s, C_2 of Ts); 130.66 (s, C_2 of Ph); 130.41 (s, C_4 of Ph); 129.71 (s, C_3 of Ts); 127.13 (s, C_3 of Ph); 60.89 (s, CHN); 29.20 (s, CH of i-Pr); 21.59 (s, CH_3); 18.04 (s, CH_3); 14.86 (s, CH_3).

Preparation of ligand 17. Under a nitrogen atmosphere, 0.25 mL (1.79 mmol, 2.1 eq) of triethylamine was added dropwise to a solution of 0.231 g (0.85 mmol) of N-p -toluenesulfonyl-(*S*)-valine (**14**) in 4 mL of ether to give a white suspension. 0.31 mL (1.7 mmol, 2 eq) of $PPhCl_2$ was then added dropwise via syringe to form a cloudy white solution, which was stirred at room-temperature for 1.5 h. The suspended Et_3NHCl was removed by filtration and washed with 1 mL of diethyl ether. The solvent was removed the from the combined ethereal solution on a vacuum line, giving a pale yellow solid in a clear yellow oil. Further washing the solid with 3x4 mL hexane gave 490 mg (90% yield) of **17** as an off-white powder. ^{31}P NMR ($CDCl_3$): 104.49 (s), 49.35 ppm (s).

{(2S,4S)-4-isopropyl-5-oxo-2-phenyl-3-p-toly-1,3,2-oxaza-phospholidine}$W(CO)_5$ (P14). Tungsten hexacarbonyl (0.573 g, 1.628 mmol) and 40 mL of THF were placed in a 250 mL septum-capped flask with a magnetic stirring bar, placed in a water-cooled water bath, and irradiated under a nitrogen atmosphere with a 450W Hanovia medium pressure mercury lamp for 2.5 h. The resultant yellow solution was transferred via syringe into a solution of major isomer of **(14a)** (0.430 g, 1.139 mmol, 0.70 eq based on $W(CO)_6$ in 10 mL THF. No

color change was observed, and the reaction mixture was stirred at room temperature under a nitrogen atmosphere overnight. After solvent removal on a vacuum line at room temperature, the resultant pale yellow powder was then warmed at ~45°C on the vacuum line to facilitate sublimation of unreacted $W(CO)_6$. Further purification was achieved via following procedure: under nitrogen atmosphere, above crude compound was dissolved in CH_2Cl_2, and filtered through 20 ml of silica gel in 20 mL of CH_2Cl_2 on a frit, and product was washed through a further 100 mL of CH_2Cl_2. After solvent removal from the filtration, the crude powder was further washed with hexane to get 0.500 g (62.6% yield)of off-white powder as a final spectroscopic pure product. IR (THF): 2082.4(m), 2046.2 (vw), 1999.2 (shoulder & w), 1955.3 (vs), 1805.8 (w) cm^{-1}; IR (Hexane): 2084.3 (w), 1999.9 (vw), 1970.6 (vs), 1960.9 (shoulder & m), 1810.6 (w) cm^{-1}. $[\alpha]^{25}_D = +10.78°$ (c 0.371, C_6H_6). ^1H NMR ($CDCl_3$): δ7.86 (m, 2H of Ph), 7.61 (m, 3H of Ph), 7.30 (d, J=8.4Hz, 2H of Ts), 7.19 (d, J=8.2 Hz, 2H of Ts), 4.21 (tri, J=3.4 Hz, 1H of CHN.), 2.39 (s, 3H of CH_3 of Ts),), 2.05 (m, 1H of methine of i-Pr.), 1.11 (d, J=7.12 Hz, 3H of CH_3 of i-pr.), 0.32 (d, J=6.8 Hz, 3H of CH_3 of i-pr.). ^{31}P NMR ($CDCl_3$): 146.87 ppm, ($^1J_{PW}$=346.5 Hz). ^{13}C NMR ($CDCl_3$) : 197.340 (d, $^2J_{PC}$=38.4 Hz, trans-CO); 194.64

(d, $^1J_{PW}$=127.0 Hz, $^2J_{PC}$=8.5 Hz, cis-CO); 165.27 (d, $^2J_{PC}$=6.04 Hz, COP); 145.20 (s, C_{ipso} of Ts); 140.549 (d, $^1J_{PC}$=31.39Hz, C_{ipso} of Ph); 136.29 (s, C_4 of Ph); 132.93 (s, C_{ipso} of Ts); 129.91 (s, C_2 of Ts); 129.34 (d, $^3J_{PC}$=16.30 Hz, C_3 of Ph); 128.87 (d, $^3J_{PC}$=10.87 Hz, C_3 of Ph); 127.37 (s, C_{ipso} of Ts); 63.95 (s, CHN); 29.07 (s, CH of i-Pr); 21.61 (s, CH_3); 18.64 (s, CH_3); 15.60 (s, CH_3). Anal. Calcd for $C_{23}H_{20}NO_9PSW$: C, 39.39; H, 2.87; N, 2.00. Found: C, 39.07; H, 2.66; N, 1.99.

***(TosvaL)*(CO)$_3$W(NO)(μ-F)SbF$_5$ (C14).** Under a nitrogen atmosphere, $NOSbF_6$ (168 mg, 2.3 eq) was slowly added to a solution of complex **P14** (150 mg, 0.27 mmol) in 4 mL CH_2Cl_2, and stirred for an additional 20 min until no more gas was given off. Filteration through a pad of oven-dried Celite followed by solvent removal gave 186 mg (91% yield) of the desired **C14** as a green powder. ^{31}P NMR (CD_2Cl_2): 154 ppm $^1J_{PW}$=348 Hz, $^1J_{PW}$=486 Hz. Two adventitious impurity bands (less than 7% for each band) at ~154 ppm and several other adventitious bands near 0 ppm existed in the catalyst powder.

Bibliography

(1) *Organic Reactions , IV, Chapter 1 & 2; V , Chapter 3.*

(2) Trost, B. M.; O'Krongly, D.; Belletire, J. L. *J. Am. Chem. Soc.* **1980,** *102*, 7595.

(3) Mikami, K.; Terada, M.; Motoyama, Y.; Nakai, T. *Tet. Asym.* **1991,** *2(7)*, 643.

(4) Evans, D. A.; Black, W. C. *J. Am. Chem. Soc.* **1993,** *115*, 4497.

(5) Corey, E. J.; Letavic, M. A. *J. Am. Chem. Soc.* **1995,** *117*, 9616.

(6) Eisensten, O.; Lefour, J. M.; Anh, N. T.; Hudson, R. F. *Tetrahedron* **1977,** *33*, 523.

(7) Wasermann, A. *J. Chem. Soc.* **1942,** 618.

(8) Masamune, S.; Reed, L. A.; Davis, J. T.; Choy, W. *J. Org. Chem.* **1983,** *48*, 4441.

(9) Odenkirk, W.; Rheingold, A. L.; Bosnich, B. *J. Am. Chem. Soc.* **1992,** *114*, 6392.

(10) Walborsky, H. M.; Barash, L.; Davis, T. C. *J. Org. Chem.* **1961,** *26*, 4478.

(11) Corey, E. J.; Ensley, H. E. *J. Am. Chem. Soc.* **1975,** *97*, 6908.

(12) Suzuki, H.; Mochizuki, K.; Hattori, T.; Takahashi, N. *Bull. Chem. Soc. Jpn.* **1988,** *61*, 1999.

(13) Narasaka, K.; Tanaka, H.; Kanai, F. *Bull. Chem. Soc. Jpn.* **1991,** *64*, 387.

(14) Kobayashi, S.; Araki, M.; Hachiya, I. *J. Org. Chem.* **1994,** *59*, 3758.

(15) Cativiela, C.; Fraile, J. M.; Garcia, J. I.; Mayoral, J. A.; Campelo, J. M.; Luna, D.; Marinas, J. M. *Tet. Asym.* **1993**, *4*, 2507.

(16) Oppolzer, W.; Chapuis, C.; Kelly, M. J. *Helv. Chim. Acta* **1983**, *66*, 2358.

(17) Stahle, W.; Kunz, H. *Synlett* **1991**, 261.

(18) Hashimoto, S.; Komshima, N.; Koga, K. *J. Chem. Soc., Chem. Commun.* **1979**, 437.

(19) Takemura, H.; Komeshima, M.; Takahashi, I.; Hashimoto, S.; Ikota, N.; Tomioka, K., K. *Tet. Lett.* **1987**, *28*, 5687.

(20) Kagan, H. B.; Riant, O. *Chem. Rev.* **1992**, *92*, 1007.

(21) Rebiere, F.; Riant, O.; Kangan, H. B. *Tet. Asymm.* **1990**, 199.

(22) Bao, J. M.; Wulff, W. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 3814.

(23) Chapuis, C.; Jurczak, J. *Helv. Chim. Acta* **1987**, *70*, 437.

(24) Narasaka, K.; Inoue, M.; Okada, N. *Chem. Lett.* **1986**, 1109.

(25) Seebach, D.; Beck, A. K.; Imwinkelried, R.; Roggo, S.; Wonnacott, A. *Helv. Chem. Acta* **1987**, *70*, 954.

(26) Narasaka, K.; Iwasawa, N.; Inoue, M.; Yamada, T.; Nakashima, M.; Sugimori, J. *J. Am. Chem. Soc.* **1989**, *111*, 5340.

(27) Mikami, K.; Terada, M.; Motoyama, Y.; Nakai, T. *Tet. Asym.* **1991**, *2*, 643.

(28) Furuta, K.; Shimizu, S.; Miwa, Y.; Yamamoto, H. *J. Org. Chem.* **1989**, *54*, 1481.

(29) Furuta, K.; Kanematsu, A.; Yamamoto, H.; Takaoka, S. *Tet. Lett.* **1989**, *30*, 7231.

(30) Corey, E. J.; Loh, T. P. *J. Am. Chem. Soc.* **1991**, *113*, 8966.

(31) Takasu, M.; Yamamoto, H. *SYNLETT* **1990**, 194.

(32) Ishihara, K.; Kurihara, H.; Yamamoto, H. *J. Am. Chem. Soc.* **1996**, *118*, 3049.

(33) Corey, E. J.; Imai, N.; Zhang, H. Y. *J. Am. Chem. Soc.* **1991**, *113*, 728.

(34) Kundig, E. P.; Bourdin, B.; Bernardinelli, G. *Angew. Chem. Int. Ed. Engl.* **1994**, *33(18)*, 1856.

(35) Thom, C.; Kocienski, P.; Jarowicki, K. *Synthesis* **1993**, 475.

(36) Bonnesen, P. V.; Puckett, C. L.; Honeychuck, R. V.; Hersh, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 6070.

(37) Honeychuck, R. V.; Bonnesen, P. V.; Farahi, J.; Hersh, W. H. *J. Org. Chem.* **1987**, *52*, 5293.

(38) Bailey, W. J.; Baylouny, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 2126.

(39) Childs, R. F.; Mulholland, D. L.; Nixon, A. *Can. J. Chem.* **1982**, *60*, 801.

(40) "Personal Communication" with Dr. Guozhi Wang from SK Corp., New Jersey Research Center.

(41) Hersh, W. H. , Unpublished result.

(42) Korpiun, O.; Lewis, R. A.; Chickos, J.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4842.

(43) Maryanoff, C. A.; Marytanoff, B. E.; Tang, R.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 5839.

(44) Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244.

(45) Corey, E. J.; Chen, Z. L.; Tanoury, G. J. *J. Am. Chem. Soc.* **1993**, *115*, 11000.

(46) Juge, S.; Stephan, M.; Laffitte, J. A.; Genet, J. P. *Tet. Lett* **1990**, *31*, 6357.

(47) Kyba, E. P. *J. Am. Chem. Soc.* **1975**, *97*, 2554.

(48) Kyba, E. P. *J. Am. Chem. Soc.* **1976**, *98*, 4805.

(49) Pietrusiewicz, K. M.; Zablocka, M. *Tet. lett.* **1988**, *29*, 1991.

(50) King, R. B.; Kapoor, P. N. *J. Am. Chem. Soc.* **1971**, *93*, 4158.

(51) King, R. B. *Acc. Chem. Res.* **1972**, *5*, 177.

(52) DuBois, D. L.; Myers, W. H.; Meek, D. W. *J. Chem. Soc., Dalton* **1975**, 1011-15.

(53) Uriarte, e. a. *Inorg. Chem.* **1980**, *19*, 80.

(54) Grim, S. O.; Barth, R. C. *J. Organomet. Chem.* **1975**, *94*, 327.

(55) Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. *J. Am. Chem. Soc.* **1994**, *116*, 4062.

(56) This chiral ferrocene ligand now is commercially available.

(57) Rosenblum, M.; Banerjee, A. K.; Danieli, N.; Fish, R. W.; Schlatter, V. *J. Am. Chem. Soc.* **1963**, *85*, 316.

(58) Graham, P. J.; Lindsey, R. V.; Parshall, M. L.; Peterson, M. L.; Whaitman, G. M. *J. Am. Chem. Soc.* **1957**, *79*, 3416.

(59) Hauser, C. R.; Lindsay, J. K. *J. Org. Chem.* **1957**, *22*, 906.

(60) Marquarding, D.; Klusacek, H.; Gokel, G.; Hoffamann, P.; Ugi, I. *J. Am. Chem. Soc.* **1970**, *92*, 5389.

(61) Hayashi, T.; Takaya, M.; Fukushima, M.; Kagotani, M.; Nagashima, N.; Hamada, Y.; Matsumoto, A.; Kawakami, S.; Konishi, M.; Yamamoto, K.; Kumada, M. *Bull. Chem. Soc. Jpn* **1980**, *93*, 1138.

(62) Barraclough, C. G.; Bowden, J. A.; Colton, R.; Commons, C. J. *Aust. J. Chem.* **1973**, *26*, 241.

(63) Connelly, N. G. *J. Chem. Soc., Dalton Trans.* **1973**, 2183.

(64) Loncharich, R. J.; Crowe, W. E.; Schreiber, S. L. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 256.

(65) Honeychuck, R. V.; Hersh, W. H. *Inorg. Chem.* **1989**, *28*, 2869.

(66) King, R. B. *Acc. Chem. Res.* **1980**, *13*, 243.

(67) Ernst, M. F.; Roddick, D. M. *Inorg. Chem.* **1989**, *28*, 1624.

(68) Brookhart, M.; Chandler, W. A.; Pfister, A. C.; Santini, C. C.; White, P. S. *Organometallics* **1992**, *11*, 1263.

(69) Kundig, E. P.; Dupre, C.; Bourdin, B.; Cunningham, A.; Pons, D. *Helv. Chim. Acta.* **1994**, *77*, 421.

(70) Stuebe, C.; Lankelma, H. P. *J. Am. Chem. Soc.* **1956**, *78*, 976.

(71) Ewart, G.; Payne, D. S.; Dorte, A. L.; Lane, A. P. *J. Chem. Soc.* **1962**, 3984.

(72) Ramirez, F.; Patwardhan, A. V.; Kugler, H. J.; Smith, C. P. *J. Am. Chem. Soc.* **1967**, *89*, 6276.

(73) Chen, R.; Liu, Z.; Li, C. *Gaodeng Xuexiao Huaxue Xuebao* **1989**, *10*, 655.

(74) *Chem. Abstr.* **1990**, *112*, 217071q.

(75) Jacob, P.; Richter, W.; Ugi, I. *Liebigs Ann. Chem.* **1991**, 519.

(76) Hunsch, S.; Richter, W.; Ugi, I.; Chattopadhyaya, J. *Liebigs Ann. Chem.* **1994**, 269.

(77) Puri, N.; Hunsch, S.; Sund, C.; Ugi, I.; Chattopadhyaya, J. *Tetrahedron* **1995**, *51*, 2991.

(78) Berkowitz, W. F. *J. Chem. Ed.* **1970**, *47*, 536.

(79) Strohmeier, W.; Muller, F. J. *Chem. Ber.* **1969**, *102*, 3608.

(80) Made by fellow colleagues in Hersh's group.

(81) Grobe, J.; Le. Van, D. Z. *Anorg. Allg. Chem.* **1984**, *518*, 36.

(82) Grim, S. O.; Wheatland, D. A.; McFarlane, W. *J. Am. Chem. Soc.* **1967**, *89*, 5573.

(83) Keiter, R. L.; Verkade, J. G. *Inorg. Chem.* **1969**, *8*, 2115.

(84) Mathieu, R.; Lenzi, M.; Poilblanc, R. *Inorg. Chem.* **1970**, *9*, 2030.

(85) Guns, M. F.; Claeys, E. G.; Van der Kelen, G. P. *J. Mol. Struct.* **1979**, *54*, 101.

(86) Honeychuck, R. V.; Hersh, W. H. *Inorg. Chem.* **1987**, *26*, 1826.

(87) Verkade, J. *Coord. Chem. Rev.* **1972/73**, *9*, 1.

(88) Schumann, H.; Hroth, H. J. Z. *Naturforsch* **1977**, *32B*, 768.

(89) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(90) Andrews, M. A.; Voss, E. J.; Gould, G. L.; Klooster, W. T.; KOetzle, T. F. *J. Am. Chem. Soc.* **1994**, *116*, 5741-6 (Supporting information. S-1).

(91) Gray, G. A.; Nelson, J. H. *Org. Magn. Reson.* **1980**, *14*, 8.

(92) Gorenstein, D. G. *NMR Spectrosc.* **1983**, *16*, 1-98.

(93) Pauling, L. *The Nature of the Chemical Bond*; 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(94) Orgel, L. E. *An Introduction to Transition-Metal Chemistry*; John Wiley and Sons, Inc.: New York, NY, 1960.

(95) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432.

(96) Thompson, H. W.; Linnett, J. W. *J. Chem. Soc.* **1937**, 1384.

(97) Brown, R. A.; Dobson, G. R. *Inorg. Chim. Acta* **1972**, *6*, 65.

(98) Angelici, R. I.; Malone, M. D. *Inorg. Chem.* **1967**, *6*, 1731.

(99) Graham, W. A. G. *Inorg. Chem.* **1968**, *7*, 315.

(100) Calculation was done by W. H. Hersh.

(101) Hersh, W. H.; Xu, P.; Wang, B.; Yom, J. W.; Simpson, C. K. *Inorg. Chem.* **1996**, *35*, 5453.

(102) This work was done B. Wang.

(103) Hayashi, Y.; Rohde, J. J.; Corey, E. J. *J. Am. Chem. Soc.* **1996**, *118*, 5502.

(104) Brown, J. M.; Carey, J. V.; Russell, M. J. H. *Tet. Lett.* **1990**, *31*, 6357.

(105) Karrer, P.; van der Sluys Veer, F. C. *Helv. Chim. Acta* **1932**, *15*, 746.

(106) McChesney, E. W.; Swann, W. K. *J. Am. Chem. Soc.* **1937**, *59*, 1116.

(107) X-ray crystal was prepared by Cheslan K. Simpson.

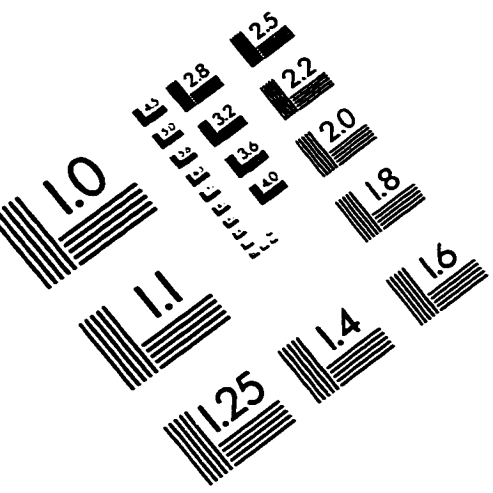
(108) Hersh, W. H.; Xu, P.; Simpson, C. K.; Wood, T.; Rheingold, A. L. *Inorg. Chem.* **1998**, *37*, 384.

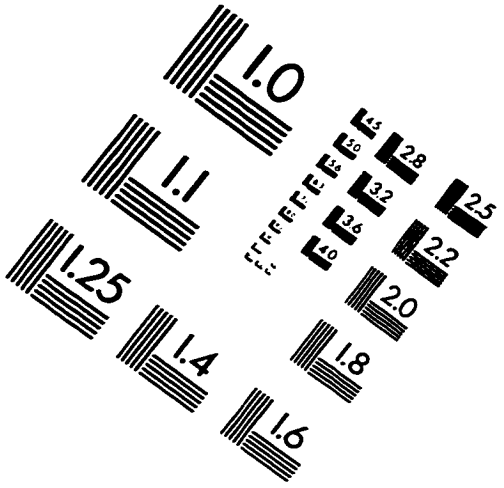
(109) Bonningue, C.; Houalla, D.; Wolf, R.; Jaud, J. *J. Chem. Soc., Perkin Trans II* **1983**, 773.

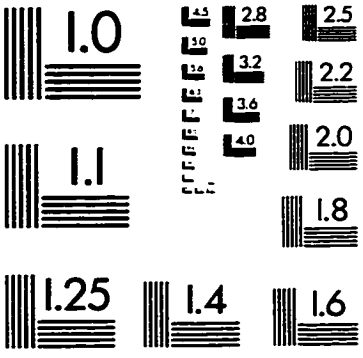
(110) Hoffman, H.; Schellenbeck, P. *Chem. Ber.* **1966**, *99*, 1134.

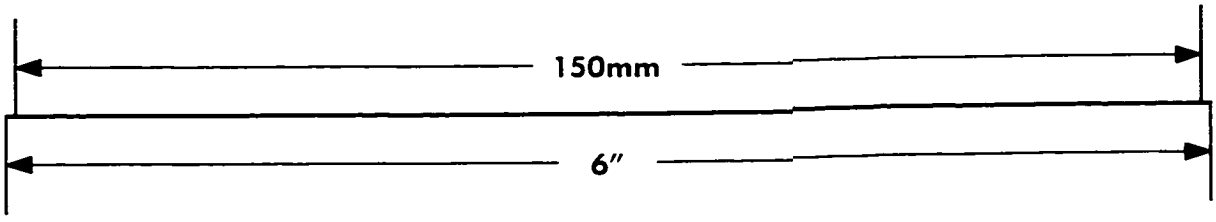
(111) Colton, R.; Commons, C. J. *Aust. J. Chem.* **1973**, *26*, 1493.

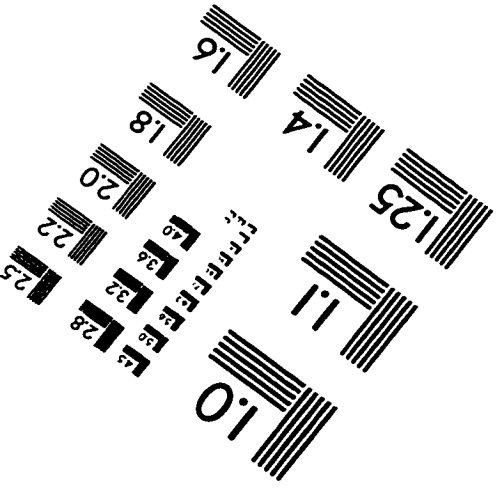
IMAGE EVALUATION TEST TARGET (QA-3)

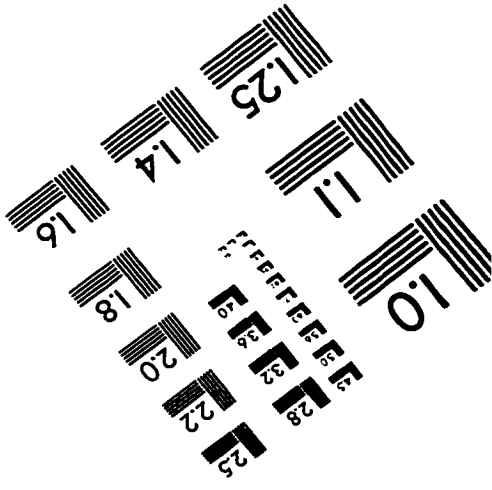












APPLIED IMAGE, Inc
1653 East Main Street
Rochester, NY 14609 USA
Phone: 716/482-0300
Fax: 716/288-5989