# CHIRAL MOLYBDENUM AND TUNGSTEN IMIDO ALKYLIDENE COMPLEXES AS CATALYSTS FOR ASYMMETRIC RING-CLOSING METATHESIS (ARCM)

by

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Submitted to the Department of Chemistry
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for the Degree of

DOCTOR OF PHILOSOPHY
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To my parents
and
Amanda

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## ABSTRACT

Chapter 1

The synthesis and resolution of sterically encumbered biphenols is presented. Oxidative coupling of either 2-*tert*-butyl-4,5-dimethylphenol or 2-(1-adamantyl)-4,5-dimethylphenol with potassium dichromate in acetic acid produced racemic (±)-3,3'-di-*tert*-butyl-5,5',6,6'-tetra-methyl-1,1-biphenyl-2,2'-diol {(±)-Biphen$H_2$} and (±)-3,3'-di-(1-adamantyl)-5,5',6,6'-tetra-methyl-1,1-biphenyl-2,2'-diol {(±)-Biad$H_2$} respectively. Treatment of the phosphoric acid derivative, (±)-Biphen$PO_2H$ with optically pure alkaloid base, (-)-cinchonidine, produced a diastereomeric mixture of phosphoric acid salts. Selective crystallization of the (S)-Biphen salt afforded optically pure (S)-Biphen$H_2$. Alternatively treatment of (±)-Biphen$H_2$ with triethyl amine and (-)-menthyldichlorophosphine (Men*$PCl_2$) followed by oxidation with 30% hydrogen peroxide produced a diastereomeric mixture of phosphates, (±)-BiphenP(O)Men*. The $^{31}P$ NMR resonances for the diastereomers are well resolved ((±)-BiphenPMen* $\Delta\delta$ = 5.7 and (±)-BiphenP(O)Men* $\Delta\delta$ = 1.52). (S)-BiphenP(O)Men* was selectively crystallized from refluxing acetic acid and (R)-BiphenP(O)Men* was isolated from methanol. Optically pure (R)- or (S)-Biphen$H_2$ were obtained by reduction of (R)- or (S)-BiphenP(O)Men* with Red-Al®. The resolution of (±)-Biad$H_2$ was similar to the phosphate technique used for (±)-Biphen$H_2$. The diastereomeric mixture of phosphates was prepared by addition of Men*$PCl_2$ to (±)-Biad$K_2$ in THF followed by oxidation with 30% hydrogen peroxide in methylene chloride. Due to the low solubility of (±)-BiadP(O)Men*, the diastereomeric mixture was dissolved in refluxing acetone using a Soxhlet extraction apparatus and optically-pure (S)-BiadP(O)Men* was precipitated from the refluxing acetone. Resolved (S)-Biad$H_2$ was recovered by Red-Al® reduction.

Chapter 2

The synthesis of molybdenum(VI) imido alkylidene complexes containing racemic and optically pure biphenoxides (Biphen and Biad) is reported. The *bis*(triflate) complexes Mo(NAr)(CHR)$(OTf)_2$•DME (**3b**, Ar = 2,6-$Et_2C_6H_3$, R = $CMe_2Ph$; **3f'**, Ar = 2,4-$^tBu_2$-6-$MeC_6H_2$, R = $^tBu$) were prepared in three steps from sodium molybdate. The neopentylidene complexes Mo(NR)($CH^tBu$)$(OTf)_2$•DME (**3g'**, R = 2-$CF_3C_6H_4$; **3h'**,1-adamantyl) were prepared from the corresponding Mo$(NR)_2Cl_2$•DME. The molybdenum(VI)*bis*(imido) dichloride complex, Mo(N-2,4-$^tBu_2$-6-$C_6H_2)_2Cl_2$, was isolated not as a DME adduct but as an ammonium chloride salt, [HBase][Mo(N-2,4-$^tBu_2$-6-$C_6H_2)_2Cl_3$] (Base = $NEt_3$, 2,6-lutidine). The $^1H$ NMR spectrum of the $C_2$-symmetric Mo(N-2,4-$^tBu_2$-6-$C_6H_2)_2(CH_2{}^tBu)_2$ exhibited diastereotopic neopentyl methylene protons at -40 °C at δ 3.10 and 1.54 which coalesce at room temperature presumably due to hindered rotation about the Mo-C bond. Deprotonation of (±)- or (S)-Biphen$H_2$ with excess KH in THF followed by addition of Mo(NAr)$(CHCMe_2Ph)(OTf)_2$•DME (Ar = 2,6-

$^{i}Pr_2C_6H_3$ (**3a**), 2,6-$Et_2$Ph (**3b**), 2,6-$Me_2$Ph (**3c**)) produced Mo(NAr)($CHCMe_2Ph$)((±)-Biphen) {(±)($R_2$)Mo(Neo) (R = $^{i}$Pr, Et, Me)} and (S)($R_2$)Mo(Neo) (R = $^{i}$Pr, Et, Me). Benzyl potassium was used to deprotonate (±)- and (S)-Biphen$H_2$ and (±)- and (S)-Biad$H_2$ to prepare Mo(N-2-$CF_3C_6H_4$)(CHR)(Biphen) (R = $^{t}$Bu, $CMe_2Ph$, 2-$MeOC_6H_4$) and Mo(NAr)(CHR)(Biad) (R = $CMe_2Ph$, Ar = 2,6-$^{i}Pr_2C_6H_3$, 2,6-$Et_2C_6H_3$, 2,6-$Me_2C_6H_3$, 3,5-$Me_2C_6H_3$; R = $^{t}$Bu, Ar = 2-$CF_3C_6H_4$). X-ray crystallographic studies of (S)($^{i}Pr_2$)Mo(Neo) and (S)'($CF_3$)Mo(Np)•py provided the absolute stereochemistry of (S)-Biphen$H_2$ and (S)-Biad$H_2$ and confirmed the *syn* configuration of the alkylidene ligand. In (S)($^{i}Pr_2$)Mo(Neo) one CNO face is blocked by one Biphen $^{t}$Bu group and an $^{i}$Pr from the arylimido ligand. The direct syntheses of molybdenum(VI) imido alkylidene biphenoxide complexes was attempted by activation of one arylimido group in Mo(NAr)$_2$((±)-Biphen) (Ar = 2,6-$^{i}Pr_2C_6H_3$, 2,6-$Me_2C_6H_3$) which were prepared from (±)-Biphen$K_2$ and Mo(NAr)$_2Cl_2$•DME. Addition of $AlEt_3$ induced decomposition, $NEt_3$•HCl protonated the (±)-Biphen ligand, and no reaction occurred when Mo(N-2,6-$Me_2C_6H_3$)$_2$((±)-Biphen) was heated in toluene with 20 equivalents of MeI at 80 °C for 7 days.

Chapter 3

The $^{1}$H NMR spectroscopic data for molybdenum(VI) imido alkylidene biphenoxide complexes prepared in Chapter 2 are presented. Neophylidene and neopentylidene complexes were predominantly *syn* based on the low $J_{CH}$ of 118-124 Hz. The neophylidene complex (±)($CF_3$)Mo(Neo) was predominantly *anti* ($K_{eq}$ = 0.26) as a result of arene coordination to molybdenum. The equilibrium constant for Mo(NAr)(CHR)(Biphen) increased in magnitude with decreasing size of the arylimido ligand ($^{i}Pr_2$ > 2,4-$^{t}Bu_2$-6-Me > $Et_2$ ~ $^{t}$Bu ~ $CF_3$ > $Me_2$). Reducing the steric bulk of the alkylidene increased the concentration of the *anti* rotamer ($K_{eq}$ = 2.0 for (±)($^{i}Pr_2$)Mo(CHMe), 3.1 for (±)($^{i}Pr_2$)Mo(CHEt) and 17.5 for (±)($^{i}Pr_2$)Mo(Neo)). The rate of rotamer exchange was measured for Mo(NAr)($CHCMe_2Ph$)(OAr')$_2$ (OAr' = O-2,6-$^{i}Pr_2C_6H_3$ (DIPP), 0.5 (±)-Biphen, 0.5 (±)-Biad) by single parameter line shape analysis and spin saturation transfer. Comparison of data for OAr' = DIPP with literature values suggested that the line shape analysis method was more accurate. The assumption that $T_1$(*syn*) = $T_1$(*anti*) was proposed to be a potential source of error in the spin saturation transfer method.

Chapter 4

The application of catalysts prepared in Chapter 2 in asymmetric ring-closing metathesis (ARCM) is described. Highly enantioselective kinetic resolutions ($k_{rel}$ = 58 for substrate **7**) of α,ω-dienes to give non-racemic linear α,ω-dienes and either carbocycles or dihydrofurans were carried out with (S)($R_2$)Mo(Neo) (R = $^{i}$Pr, Me). Kinetic resolution of substrates that contained a trisubstituted olefin such as 6-methyl-5-(triethylsiloxy)-1,6-octadiene, **7a**, generated cyclopentene **8a** (43% yield and >99% ee) and residual **7a** (19% yield and 93% ee). The slow reacting enantiomer was sequestered as dimer-**7a** by coupling two terminal olefins. Dimer formation was suppressed in substrates containing a 1,1-disubstituted olefin α to the stereogenic center without affecting the enantioselectivity (6-methyl-5-(triethylsiloxy)-1,6-heptadiene, **11**, $k_{rel}$ = 11). When the stereogenic center is α to the terminal olefin, such as **9**, no selectivity was observed. Kinetic resolution to form six-membered rings were not selective (7-methyl-6-(triethylsiloxy)-1,7-octadiene, **14**, $k_{rel}$ = 4). Achiral $CH_2$=$CHCH_2OCH(CMe$=$CHR)_2$ (**20**, R = H; **22**, R = Me) were desymmetrized to form enantiomerically enriched dihydrofurans with excellent stereoselectivity (up to 99% ee) with 1-2 mol% (S)($R_2$)Mo(Neo) (R = $^{i}$Pr, Me). Quaternary stereogenic centers were also set by ARCM. 3-Allyl-(3-phenyl-1,4-pentadienyl) ether, **30**, was desymmetrized by 5 mol% (S)($Me_2$)Mo(Neo) in toluene at -20 °C to **31** (91% yield and 82% ee). Substrates **20** and **22** were desymmetrized by 1-2 mol% (S)($Me_2$)Mo(Neo) in the absence of solvent to give dihydrofurans **21** and **23** in

excellent yield and enantiomeric excess. Substrates **20** and **22** were used as benchmark reactions to compare complexes containing (S)-Biphen and (S)-Biad ligands. The Biad complexes were slower and exhibited lower enantioselectivity than the corresponding Biphen complexes.

Chapter 5

Synthesis, characterization and reactivity of (±)($Me_2$)W(Neo) and (±)($^iPr_2$)W(Neo)•$PMe_2Ph$ is discussed. Addition of ethylene to (±)($Me_2$)W(Neo) produced the unsubstituted tungstacyclobutane, (±)($Me_2$)W($C_3H_6$), which was observed spectroscopically but could not be isolated. Addition of 1,6-heptadiene to a pentane suspension of (±)($Me_2$)W(Neo) followed by cooling to -25 °C afforded solid (±)($Me_2$)W($C_3H_6$). The unsubstituted tungstacyclobutane is stable as a solid but decomposes over several hours in solution by elimination of ethylene. (±)($Me_2$)W($C_3H_6$) is fluxional at room temperature on the NMR timescale exchanging between a square pyramidal and trigonal bipyramidal structures by a turnstile rotation of the Biphen ligand about the W(NAr)($C_3H_6$) fragment. At room temperature the $^1H$ NMR spectrum exhibits three aliphatic Biphen resonances (compared to six in (±)($Me_2$)W(Neo)) and six inequivalent tungstacyclobutane protons. On cooling to -40 °C, two sets of metallacycle β-$CH_2$ resonances were observed in a 3:1 ratio. RCM of simple achiral substrates was investigated. (±)($Me_2$)W(Neo) and (±)($Me_2$)W($C_3H_6$) cyclized 20 equivalents of *N,N*-diallyl-tosylsulfonamide and dimethyl diallylmalonate at room temperature over 16 h in benzene. The RCM of dimethyl diallylmalonate with 5 mol% of (±)($^iPr_2$)W(Neo)•$PMe_2Ph$ went to 60% conversion at 50 °C in 18 h. Allyl ether was not cyclized by (±)($Me_2$)W(Neo) even at extended reaction times or elevated temperature (50 °C).

Thesis Supervisor: Dr. Richard R. Schrock
Title: Frederick G. Keyes Professor of Chemistry

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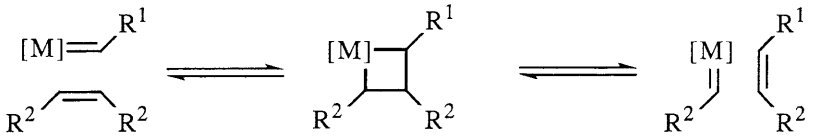
Abbreviations Used in Text

| | |
|---|---|
| Ac | acetate, $C(O)CH_3$ |
| Ad | 1-adamantyl |
| ADMET | acyclic diene metathesis |
| *anti* | alkylidene rotamer with hydrogen directed toward the imido group |
| Ar | aryl |
| ARCM | asymmetric ring-closing metathesis |
| $BiadH_2$ | 3,3'-di-(1-adamantyl)-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diol |
| BINO | 1,1'-binaphthyl-2,2'-diol |
| $BiphenH_2$ | 3,3'-di-*tert*-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diol |
| bp | boiling point |
| br | broad |
| conv | conversion |
| d | doublet |
| $\delta$ | chemical shift downfield from tetramethylsilane in ppm |
| de | diastereomeric excess |
| $\Delta\delta$ | difference between two chemical shifts |
| DME | 1,2-dimethoxyethane |
| Bu | butyl |
| $^tBu_4Me_2Biphen$ | 3,3',5,5'-tetra-*tert*-butyl-6,6'-dimethyl-1,1'-biphenyl-2,2'-diol |
| ee | enantiomeric excess |
| eq | equivalent |
| eqn(s) | equation(s) |
| Et | ethyl |
| h | hours |
| HRMS | high resolution mass spectroscopy |
| Hz | Hertz |
| J | coupling constant in Hertz |
| $k_{as}$ | rate constant for alkylidene rotation from *anti* to *syn* |
| $K_{eq}$ | equilibrium constant, [*syn*]/[*anti*] |
| $k_{rel}$ | ratio of reaction rates $k_R$ and $k_S$ |
| $k_{sa}$ | rate constant for alkylidene rotation from *syn* to *anti* |
| lut | 2,4-lutidine |
| m | multiplet |
| Me | methyl |

| | |
|---|---|
| $Me_2$Biphen | 6,6'-dimethyl-1,1'-biphenyl-2,2'-diol |
| Mes | mesityl, 2,4,6-$Me_3C_6H_2$ |
| min | minutes |
| MS | mass spectroscopy |
| Neo | neophylidene, $CHCMe_2Ph$ |
| NMR | nuclear magnetic resonance |
| Np | neopentylidene, $CH^tBu$ |
| OTf | $O_3SCF_3$, triflate, trifluoromethanesulfonate |
| Ph | phenyl |
| ppm | parts per million |
| Pr | propyl |
| py | pyridine |
| q | quartet |
| RCM | ring-closing metathesis |
| ROMP | ring-opening metathesis polymerization |
| rt | room temperature |
| s | singlet |
| sep | septet |
| Sty | *ortho*-methoxybenzylidene, CH-2-$MeOC_6H_4$ |
| *syn* | alkylidene rotamer with hydrogen directed away from imido group |
| t | triplet |
| TBDPS | *tert*-butyldiphenylsilyl |
| TBS | *tert*-butyldimethylsilyl |
| TES | triethylsilyl |
| THF | tetrahydrofuran |
| THT | tetrahydrothiophene |
| TMS | trimethylsilyl |
| tol | toluene |
| TRIP | 2,4,6-tri-*iso*-propylphenyl |
| Ts | tosyl |
| wt | weight |

## GENERAL INTRODUCTION

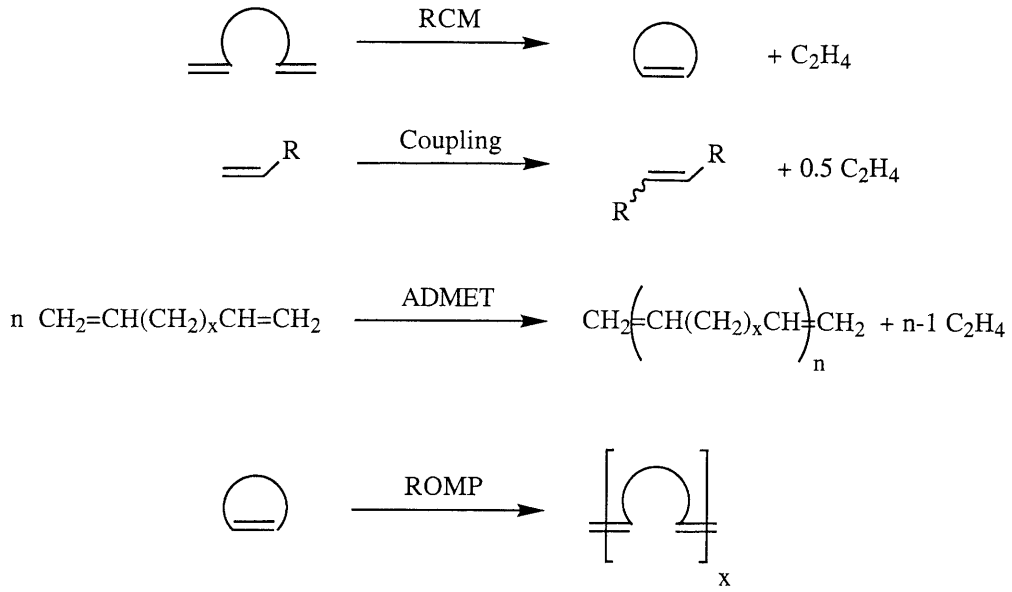
Olefin metathesis is a reaction which results in both the cleaving and the forming of C=C double bonds.[1-4] Addition of an olefin to a transition metal alkylidene complex (usually M=CHR or $M=CH_2$) in a 2+2 fashion generates an unstable metallacyclobutane intermediate.[5,6] Cycloreversion of the metallacycle usually is not selective and all possible olefinic products and metal alkylidene complexes result (Scheme I.1). The product mixture will contain a statistical mixture of alkene products each of which will be a mixture of *E/Z* isomers. For example, treating 3700 equivalents of *trans*-2-pentene with $W(NAr)(CH^tBu)(OCMe(CF_3)_2)_2$ produced a mixture of *cis* and *trans* isomers of 2-butene, 2-pentene and 3-hexene.[7,8]




**Scheme I.1.** Mechanism of Olefin Metathesis.

Several applications of olefin metathesis have been used recently with great effect in the preparation of a wide range of polymers and small organic molecules (Scheme I.2).[9-15] Perhaps the most promising of these reactions is ring-closing metathesis (RCM).[16-18] In this catalytic process, two intramolecular alkenyl functionalities are coupled to form a cycloalkene while a small olefin such as ethylene or propylene is eliminated. In a related process, the bimolecular coupling reaction combines two terminal alkenes forming an internal olefin and a low molecular weight alkene. In the related acyclic diene metathesis (ADMET), α,ω-dienes, which are unable to react via RCM, undergo two intermolecular coupling reactions to form oligomers or polymers.[19-24] Both ADMET and the intermolecular coupling reaction are potential competitive reaction pathways with RCM. The elimination of volatile olefin byproducts such as ethylene or propylene from the reaction mixture drives RCM, ADMET and coupling reactions to completion. In a fourth

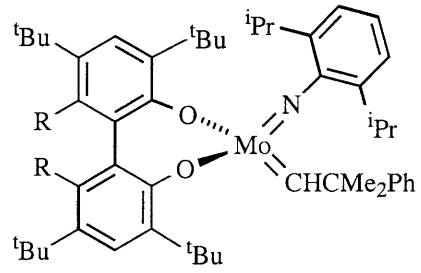
application of metathesis, some cyclic olefins can be opened to form oligomers or polymers by ring-opening metathesis polymerization (ROMP).[2,25,26] Norbornenes, cyclobutenes, and cyclooctenes are common ROMP substrates as the polymerization reaction is driven to completion by the release of ring strain.



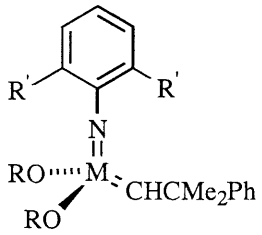

**Scheme I.2.** Olefin Metathesis Processes: Coupling, ADMET, RCM, and ROMP.

A variety of metathesis catalysts have been developed,[2,27-29] the vast majority of which are based on molybdenum(VI),[30-32] tungsten(VI)[7,8,33] and ruthenium(II).[34,35] Molybdenum(VI) and tungsten(VI) imido alkylidene *bis*(alkoxide) complexes, $M(NAr)(CHR)(OR')_2$, are extremely reactive metathesis catalysts. However, their sensitivity to oxygen, water and functionalities containing reactive protons requires that metathesis reactions be carried out under a dinitrogen or an argon atmosphere and that the solvents and substrate be pure and rigorously anhydrous. The related *bis*(aryloxide) complexes (Scheme I.3), $M(=E)(CHR)(OAr')_2$ (M = Mo, E = NAr;[31,36] M = W, E = O[37,38]), are active ROMP catalysts but have received less attention as catalysts for RCM.[39,40] In contrast, Ru-based metathesis catalysts, such as $Ru(PCy_3)_2Cl_2(CHR)$, are more robust in the presence of oxygen and water.[41] This increased tolerance is tempered

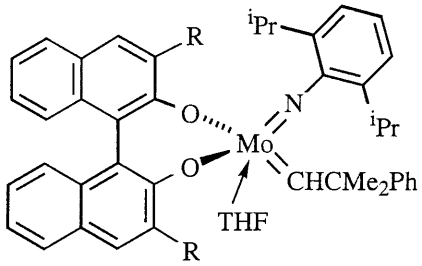
by the significantly lower activity when compared to the Mo catalysts. For example, sterically congested tri- and tetra-substituted olefins are not formed with $Ru(PCy_3)_2Cl_2(CHPh)$, yet they are readily prepared by the more reactive Mo catalyst, $Mo(NAr)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$.[42]



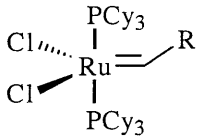
R = Me, H



M = Mo, W
R = $^t$Bu, $CMe_2(CF_3)$
$CMe(CF_3)_2$
R' = Me, $^i$Pr



R = $SiMe_2Ph$, $SiMe_2{}^tBu$
Ph, *o*-Tol, 2,6-$Me_2C_6H_3$
2,4,6-$^iPr_3C_6H_2$

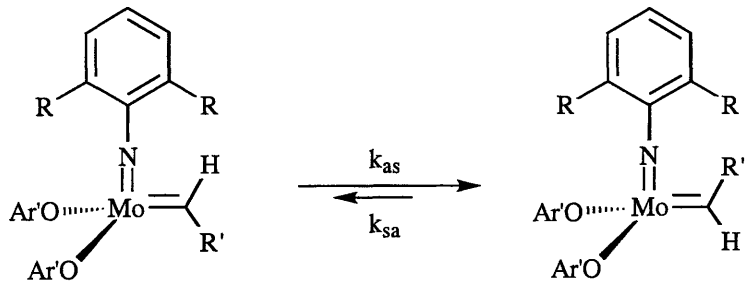


R = Ph, $CH{=}CPh_2$

**Scheme I.3.** Successful Metal Alkylidene Catalysts for Olefin Metathesis.

$Mo(NAr)(CHCMe_2Ph)(OR)_2$ (R = $CMe_x(CF_3)_{3-x}$ (x = 0-3), 2,6-$^iPr_2Ph$, 2-$^tBuC_6H_4$) complexes exist as a mixture of alkylidene rotamers as a result of the Mo-N $\pi$-bond lying in the N-Mo-C plane (Scheme I.4).[28,30,43,44] Consequently, the alkylidene lies in the N-Mo-C plane generating *syn* and *anti* rotamers. The *syn* rotamer has the alkylidene substituent directed toward the imido functionality and an $\alpha$-agostic bond arises from C-$H_\alpha$ donation to the 14-electron molybdenum center.[45] The *anti* rotamer has the alkylidene substituent directed away from the imido ligand. While both *syn* and *anti* rotamers are

present in solution, the *syn* rotamer is the lowest energy isomer.[43,44,46,47] Complexes with OR = O$^t$Bu or OCMe(CF$_3$)$_2$ are predominantly *syn*, $K_{eq}$ = 0.5-2 x $10^4$ at 298 K ($K_{eq}$ = [*syn*]/[*anti*]), and the rate of rotamer exchange is slow for R = CMe(CF$_3$)$_2$ ($k = k_{as} + k_{sa} \cong 10^{-4}$ sec$^{-1}$ at 298 K) and fast for R = $^t$Bu ($k \cong 500$ sec$^{-1}$). The related *bis*(aryloxide) complexes, Mo(NAr)(CHCMe$_2$Ph)(OAr')$_2$ (Ar' = 2,6-$^i$Pr$_2$C$_6$H$_3$, 2-$^t$BuC$_6$H$_4$), have a higher *anti* concentration ($K_{eq}$ = 10-20 at 298 K) and the rate of rotamer exchange is intermediate between OR = O$^t$Bu and OCMe(CF$_3$)$_2$ (k = 0.8 sec$^{-1}$ at 298 K for Mo(NAr)(CHCMe$_2$Ph(DIPP)$_2$).[44]



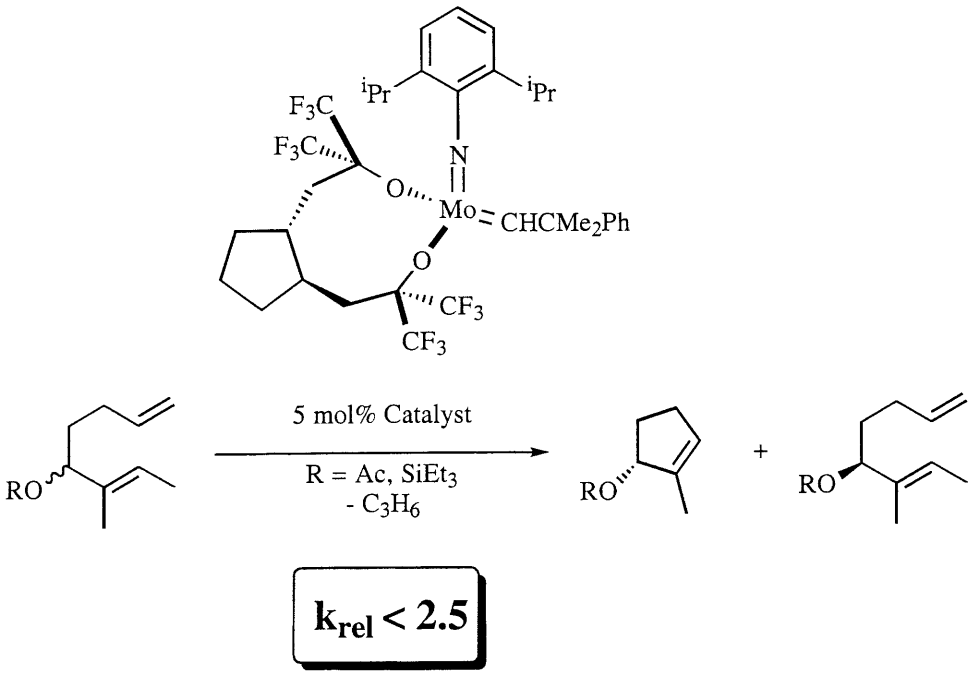

*anti* *syn*

**Scheme I.4.** Rotational Isomers of Mo(NAr)(CHR')(OAr')$_2$ Exchange with Rate Constants $k_{as}$ (*anti* → *syn*) and $k_{sa}$ (*syn* → *anti*).

Metal-catalyzed olefin metathesis has emerged as a powerful method in organic synthesis.[9,16,17,48] Mo-based[30,49-52] and Ru-based[35,53,54] complexes readily catalyze a range of ring-forming[55-58] or ring-opening[59-63] processes. Ring-closing metathesis is a formidable technology that is used in multi-step syntheses because the required transition metal-based precatalysts are tolerant of a number of polar functional groups such as amides, amines, esters, ethers, thioethers and phosphines. Mo-catalyzed reactions that give rise to macrocyclic trisubstituted olefins,[64] and Ru-based complexes that effect the formation of disubstituted olefins within large rings,[65,66] have been employed to fabricate an impressive array of complex molecules. In most - if not all - instances, without catalytic

RCM, such synthetic schemes would have been notably longer and less convergent, if not impossible.[67-69]

A chiral analog of $Mo(NAr)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$ containing a $C_2$-symmetric *trans*-1,2-cyclopentane backbone has been developed. The enantioselectivity in the kinetic resolution of simple α,ω-dienes was uniformly low ($k_{rel} \leq 2.5$, $k_{rel} = k_{fast}/k_{slow}$, all cases where $k_{fast}$ and $k_{slow}$ refer the rate constant for the RCM of the fast and slow reacting enantiomers). The low selectivity might be due to the "floppy" nature of the aliphatic ligand backbone and the 9-membered ring chelate.[70-72] The discovery and development of a chiral catalyst that promotes efficient *asymmetric* ring-closing metathesis (ARCM) thus remains as a significant and compelling research objective.



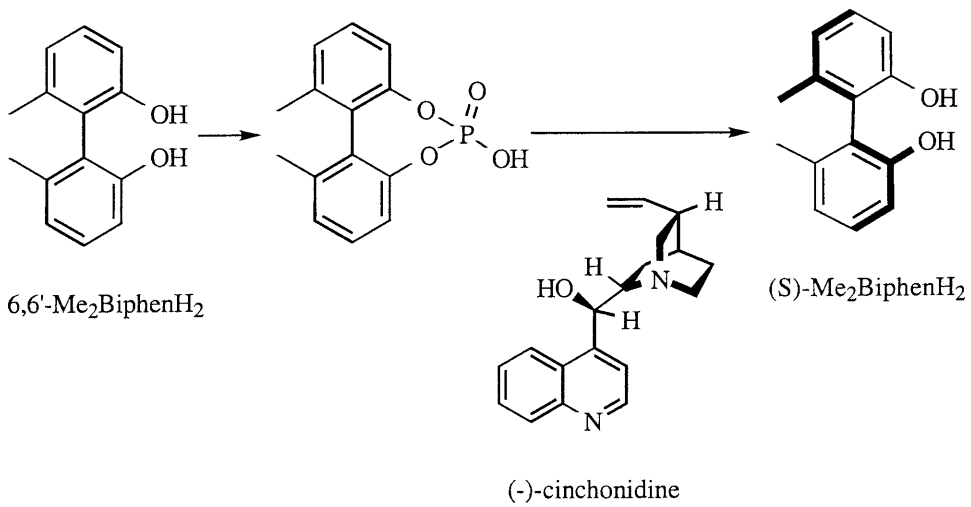

**Scheme I.5.** Recent Report of Kinetic Resolution via ARCM by Fujimura and Grubbs.

# CHAPTER 1

## Synthesis and Resolution of Sterically Demanding, Optically Pure Biphenols

## INTRODUCTION

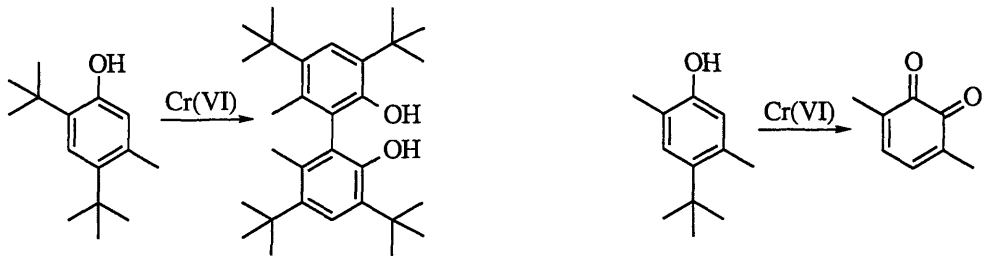
Multidentate chiral ligands based on $C_2$-symmetric backbones are the most prevalent class of chiral auxiliary in asymmetric catalysis.[73-75] In particular, binaphthol has been used in conjunction with a wide range of metals to effect enantioselective organic reactions.[73] Biphenols have received significantly less attention as chiral ligands in the literature. Racemic 6,6'-dimethyl-1,1'-biphenyl-2,2'-diol ($Me_2BiphenH_2$) has been prepared by an eight step synthesis[76] and resolved using the phosphoric acid derivative, (±)-$Me_2BiphenPO_2H$, and (-)-cinchonidine.[77] Alternatively, non-racemic $Me_2BiphenH_2$ was prepared by an eleven step asymmetric synthesis.[78,79] The resolved diol was then derivatized to a borane-amine adduct and used in the asymmetric reduction of ketones.[80] Because of the lengthy synthesis and resolution of this biphenol when compared with the two step preparation of optically pure binaphthol,[81,82] (S)-$Me_2BiphenH_2$ has not been investigated as a chiral auxiliary for other enantioselective processes.




**Scheme 1.1.** Resolution of (S)-$Me_2BiphenH_2$ via (±)-$Me_2BiphenPO_2H$ and (-)-Cinchonidine.

Sterically demanding hexa-alkylbiphenols have been prepared from two equivalents of phenol using oxidative coupling.[83,84] Although oxidation of either 2,5-dimethyl-4-*tert*-butyl phenol or 3,4-dimethyl-6-*sec*-butyl phenol with chromic acid led to exclusive quinone formation (see Figure 1.2), biaryl bond formation is in competition with quinone formation

for other trialkylphenols.[84] Formation of the biphenol product was maximized when the starting phenol contains an alkyl group at the *ortho-* and *para-* position and the *ortho* alkyl group contains an α quaternary center. In particular, (±)-$^{t}Bu_4Me_2$Biphen was prepared on a 70 g scale in 50% recrystallized yield.




(±)-$^{t}Bu_4Me_2BiphenH_2$

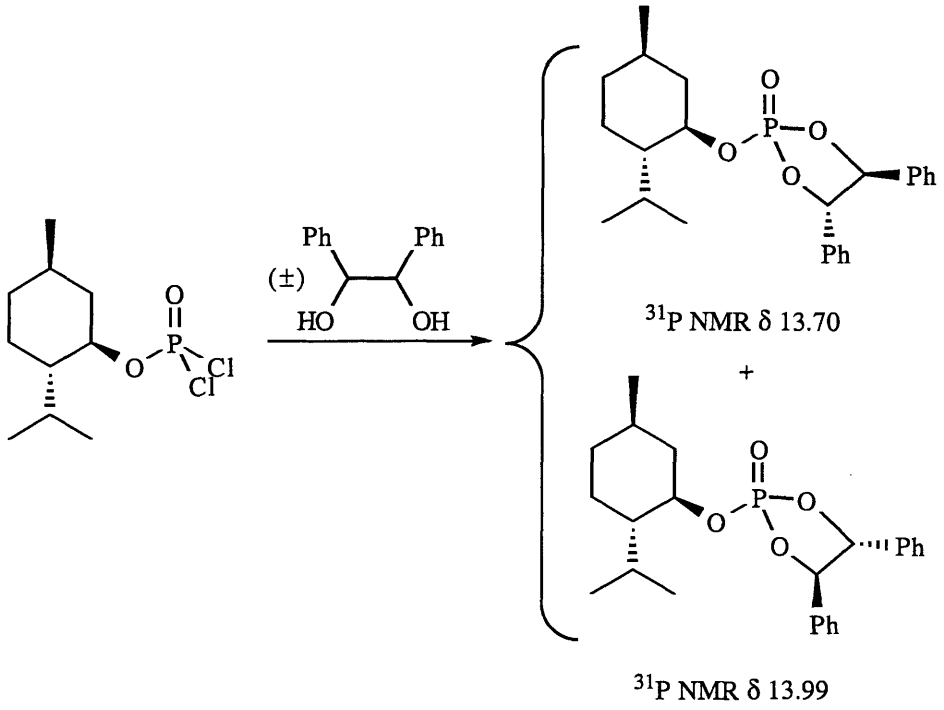
**Figure 1.1.** Oxidative Coupling of a Tri-substituted Phenol to (±)-$^{t}Bu_4Me_2$Biphen.

A variety of methods for the chemical resolution of binaphthol has been reported. Racemic binaphthol is readily resolved by crystallization of an inclusion complex of one diol enantiomer with a optically pure ammonium salt.[82,85-87] Resolving agents have been developed from amines in the chiral pool such as (-)-cinchonidine and amino alcohols. Unfortunately there are no reports of this method working for sterically hindered binaphthols or biphenols.

Another chemical resolution methodology is the derivatization of a racemic diol to the corresponding phosphoric acid followed by deprotonation by an optically pure amine. The diastereomeric salts are then separated by crystallization. For example, 6,6'-$Me_2BiphenH_2$[77] and 2,2'-vaulted binaphthol[88] have been resolved by this method using an optically pure chiral pool alkaloid such as (-)-cinchonidine or (-)-brucine. Alternatively, racemic diols have been separated by derivatization to a mixture of diastereotopic phosphites.[36]

Chiral phosphorus reagents have also been used as auxiliaries for determining the enantiomeric excess of alcohols and amines by $^{31}P$ NMR spectroscopy.[89,90] These

resolving agents frequently contain a chiral substituent bound to phosphorus and one or two reactive P-Cl bonds allowing for alcoholysis or aminolysis of the substrate to be studied. For example, (-)-menthylphosphorusoxydichloride has been used for a variety of *gem*-diols and *gem*-diamines. The $^{31}P$ NMR chemical shift separation ($\Delta\delta$) for the diastereomers range from 0.05 and 0.5 ppm.




**Scheme 1.2.** Determination of Enantiomeric Excess of *Gem*-Diols using (-)-Menthylphosphorusoxydichloride.

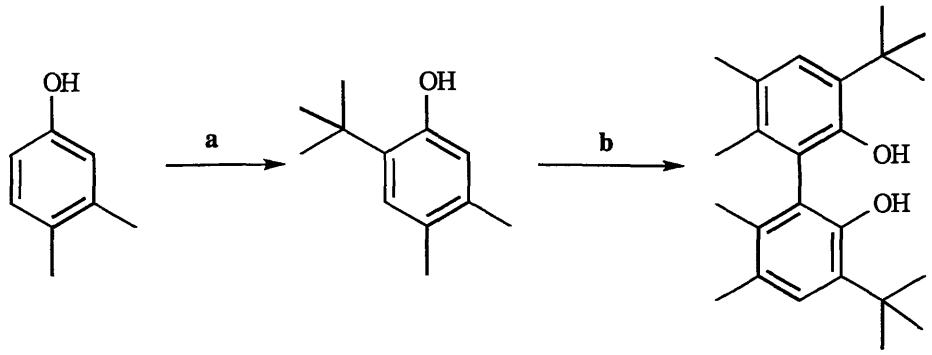
## RESULTS AND DISCUSSION

### 1.1. Synthesis of (±)-BiphenH$_2$ and (±)-BiadH$_2$

Racemic 3,3'-di-*tert*-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diol {(±)-BiphenH$_2$} was prepared from 3,4-dimethylphenol in two steps using modified literature procedures. Alkylation of 3,4-dimethylphenol was affected at 65 °C under two atmospheres of isobutylene with a catalytic amount of sulfuric acid.[91] The product was then oxidized to the biphenol with potassium dichromate in acetic acid and purified by washing with methanol to give (±)-BiphenH$_2$ as a white solid in 50% overall yield.[84]

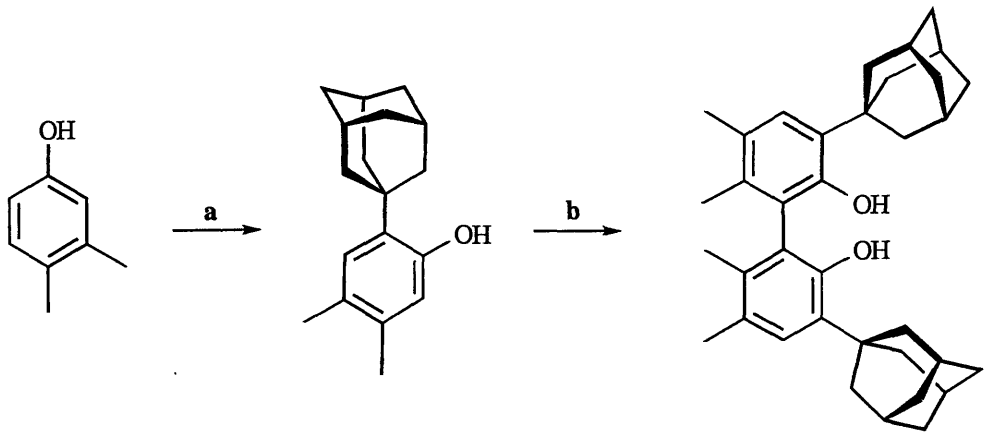
Synthesis of racemic 3,3'-di-(1-adamantyl)-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diol {(±)-BiadH$_2$} ligand paralleled that of (±)-BiphenH$_2$. 2-(1-Adamantyl)-4,5-

dimethylphenol was prepared by heating 1-bromoadamantane with a slight excess of 3,4-dimethylphenol at 130 °C under dinitrogen.[92,93] Oxidative coupling with chromic acid afforded (±)-Biad$H_2$ in 55% isolated yield on a 10 g scale.




**a)** Isobutylene, 22 psi, cat $H_2SO_4$, 65-70 °C. **b)** $K_2Cr_2O_7$, $H_2SO_4$, HOAc, 60 °C.

**Scheme 1.3.** Synthesis of (±)-Biphen$H_2$.



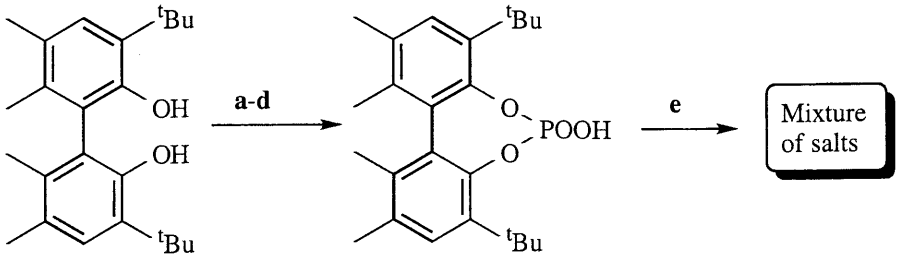

**a)** AdBr, 130°C, no solvent. **b)** $K_2Cr_2O_7$, $H_2SO_4$, HOAc, 60 °C.

**Scheme 1.4.** Synthesis of (±)-Biad$H_2$.

## 1.2. Resolution of (S)-Biphen$H_2$ via Phosphoric Acid Derivative

The initial method for the resolution of (±)-Biphen$H_2$ was achieved by four step derivatization to (±)-Biphen$PO_2H$. The diol was doubly deprotonated with potassium hydride and then treated with phosphorus oxychloride to give the corresponding chlorophosphate, (±)-BiphenP(O)Cl. The final P-Cl bond was then hydrolyzed by treatment with water and triethylamine in refluxing THF. The free biphenylphosphoric acid, (±)-Biphen$PO_2H$ ($^{31}P\{^1H\}$ NMR ($CD_3OD$) δ 2.4 ppm), was obtained by slurrying

the amine salt in refluxing 6 N hydrochloric acid. Deprotonation of the free acid with (-)-cinchonidine gave a diastereomeric mixture of salts with $^{31}P$ NMR resonances at δ -0.256 and -0.336 in ethanol.



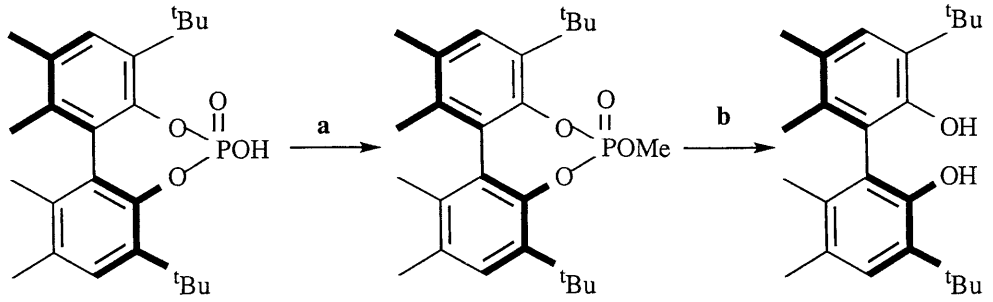

**a**) 2.1 eq KH, THF. **b**) 1.1 eq $P(O)Cl_3$. **c**) $H_2O$, $NEt_3$, refluxing THF. **d**) 6 N HCl, 100 °C. **e**) (-)-cinchonidine, EtOH.

**Scheme 1.5.** Resolution of (S)-Biphen$H_2$ via (±)-Biphen$PO_2H$ and (-)-Cinchonidine.

The [(S)-Biphen$PO_2$][HB*] (B* = (-)-cinchonidine) diastereomer was selectively crystallized by slowly boiling off methanol from a 1:1 methanol/ethyl acetate solution until the solution was nearly saturated and then slowly cooling to room temperature. The collected crystals had only one $^{31}P$ NMR resonance at -0.256 ppm. Based on the poor separation of $^{31}P$ NMR diastereomer resonances, the salt was judged to be at least 90% de. Crystallization of salts derived from (-)-cinchonidine, (-)-quinine, (-)-brucine and (-)-strychnine with enriched (R)-Biphen$PO_2H$ did not lead to optically pure (R)-Biphen$H_2$. The diastereomerically pure (S)-Biphen$PO_2H$ was obtained by refluxing a slurry of [(S)-Biphen$PO_2$][HB*] in 6 N HCl. After esterification of (S)-Biphen$PO_2H$ with dimethyl sulfate, (S)-Biphen$PO_2$Me was reduced with excess Red-Al® to give optically pure (S)-Biphen$H_2$.

The phosphoric acid resolution technique for preparing optically pure (S)-Biphen$H_2$ had several shortcomings. The preparation of the phosphoric acid derivative was time consuming, the fractional crystallization of one diastereomer was problematic, and (R)-Biphen$H_2$ could not be prepared optically pure by this method. Several of the chemicals employed in the resolution, such as (-)-cinchonidine and dimethyl sulfate, are extremely

toxic. An improved resolution technique was sought to permit the isolation of both (R)- and (S)-$BiphenH_2$ in high yield.

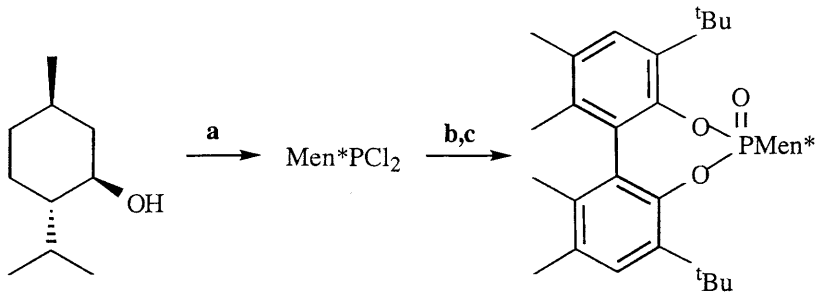



(S) $BiphenH_2$

**a**) 2 eq $Me_2SO_4$, $MeC(O)NMe_2$, 2.5 eq $NaHCO_3$, rt, 16h. **b**) 2.5 eq Red-Al®, toluene, rt, 12h.

## 1.3. Resolution via Diastereomeric Phosphates

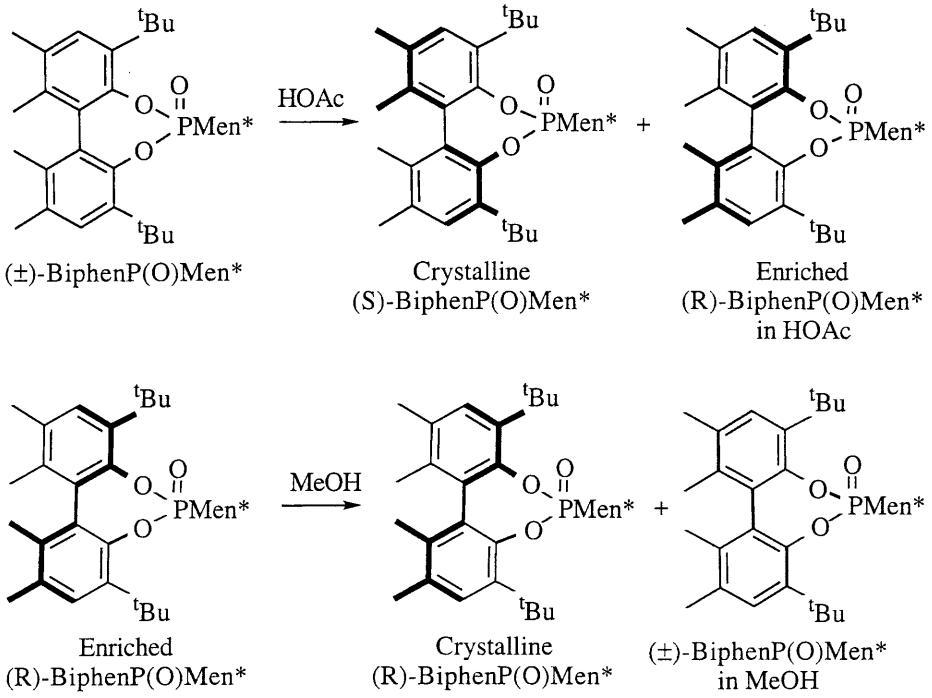
A resolution methodology based on using a mixture of diastereomeric phosphates containing a enantiomerically pure alcohol as the chiral auxiliary was targeted. There are a number of inexpensive, readily available enantiomerically pure alcohols. (-)-Menthyldichlorophosphite[36] (Men*$PCl_2$) was prepared by addition of (-)-menthol to a $CH_2Cl_2$ solution of excess $PCl_3$ followed by vacuum distillation to separate Men*$PCl_2$ from Men*$_2$PCl. Addition of a mixture of (±)-$BiphenH_2$ and triethylamine to a $CH_2Cl_2$ solution of Men*$PCl_2$ followed by treatment with 30% hydrogen peroxide afforded a diastereomeric mixture of phosphates, (±)-BiphenP(O)Men*.




**a**) excess $PCl_3$, $CH_2Cl_2$, distill. **b**) (±)-$BiphenH_2$, 2 eq $NEt_3$, $CH_2Cl_2$, filter. **c**) $H_2O_2$, $CH_2Cl_2$.

The (S)-BiphenP(O)Men* diastereomer was selectively crystallized from refluxing acetic acid. Two crops were collected and the combined precipitate was recrystallized from

refluxing acetic acid to give (S)-BiphenP(O)Men* in > 99% de. The acetic acid from the (R)-BiphenP(O)Men* enriched eluent was removed by vacuum distillation and the residue was crystallized from refluxing methanol. Diastereomerically pure (R)-BiphenP(O)Men* was obtained after two crystallizations from methanol. The phosphate remaining in methanol solution was approximately racemic.

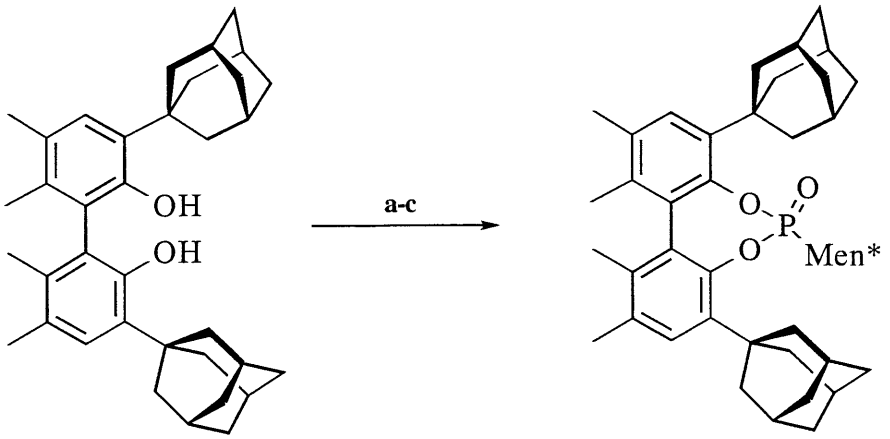



**Scheme 1.6.** Resolution of (S)- and (R)-Biphen$H_2$ via Diastereotopic Phosphates, (±)-BiphenP(O)Men*.

Treatment of resolved phosphate (S)-BiphenP(O)Men* with an excess of Red-Al® in toluene produced a mixture of (S)-Biphen$H_2$, (-)-menthol and low molecular weight PH compounds. The toluene solution was washed with Clorox® bleach to oxidize the phosphorus containing impurities and then concentrated to give a waxy white solid. Subsequent trituration with methanol removed (-)-menthol leaving enantiomerically pure (S)-Biphen$H_2$. (R)-Biphen$H_2$ was obtained similarly by reduction of (R)-BiphenP(O)Men*.

The phosphate resolution developed for Biphen$H_2$ also works for Biad$H_2$. Deprotonation of (±)-Biad$H_2$ with excess potassium hydride followed by addition of

Men*$PCl_2$ cleanly generates the diastereomeric mixture of phosphites, (±)-BiadPMen*. The $^{31}P$ NMR resonances at δ 143.6 and 138.8 were very sharp and provide a convenient method for the determination of enantiomeric excess. Oxidation of (±)-BiadPMen* with 30% hydrogen peroxide provided a mixture of diastereomeric phosphates with $^{31}P$ NMR resonances at δ -3.29 and -5.57 in benzene.




(±) $BiadH_2$
**a**) 2.5 eq KH, THF. **b**) (-) Men*$PCl_2$, $NEt_3$, $CH_2Cl_2$. **c**) $H_2O_2$, $CH_2Cl_2$.

**Scheme 1.7.** Preparation of (±)-BiadP(O)Men*.

(S)-BiadP(O)Men* ($^{31}P$ NMR δ -3.29 ppm) was selectively crystallized from acetone (96% de) on a small scale (< 100 mg). The low solubility of the phosphate in acetone prevented the use of acetone in a large scale crystallization (20 g (±)-BiadP(O)Men* did not dissolve in 1 L of refluxing acetone). Consequently a Soxhlet extraction apparatus was charged with solid (±)-BiadP(O)Men* in the cup and acetone was refluxed through the mixture of diastereomers until all of the solid in the cup had completely dissolved. As the amount of solid in the extraction cup diminished, a precipitate formed in the refluxing acetone solution. The acetone insoluble material was (S)-BiadP(O)Men* (98% de). Additional precipitate formed in the eluent during the filtration of the initial precipitate and this second crop was (±)-BiadP(O)Men* (0% de). The phosphate remaining in solution was enriched (R)-BiadP(O)Men* (~90% de). The diastereomeric excess of (R)-BiadP(O)Men* could not be increased. Reduction of (S)-

BiadP(O)Men* with Red-Al® was significantly slower (4 days) than the corresponding reduction of (S)-BiphenP(O)Men* (12 hours) presumably due to the increased steric demand of the 1-adamantyl groups.

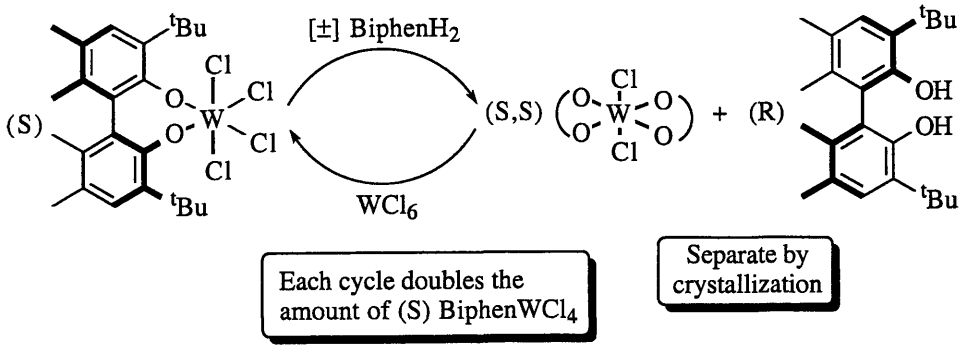
## 1.4. Attempted Resolution Using (R)-BiphenMX$_n$ as the Resolving Agent

Chiral resolution of compounds using the desired optically pure material as the template is uncommon. It was thought that an optically pure BiphenMX$_n$ complex could be used as the resolving agent for (±)-BiphenH$_2$. Modeling studies show that tetrahedral metal centers would preferentially form *meso* (R,S) Biphen$_2$M complexes while square planar and octahedral metal centers would selectively form only (R,R)- or (S,S)-Biphen$_2$MX$_n$ (n = 0, 2) complexes. The four *tert*-butyl groups are arrayed in a plane about the metal center with each group in one quadrant.

Square planar and octahedral complexes W(OAr)$_4$ and W(OAr)$_4$Cl$_2$ (Ar = 2,6-$^i$Pr$_2$Ph or 2,6-Me$_2$Ph) have been prepared from WCl$_4$•(SEt$_2$)$_2$ and WCl$_6$.[94,95] The four oxygen atoms and the metal are coplanar, and the four aryl rings are approximately orthogonal to the MO$_4$ plane. In addition, W(OAr)$_4$ is prepared by reduction of the six-coordinate W(OAr)$_4$Cl$_2$ with sodium metal.[94]

The proposed resolution would involve the initial synthesis of the resolution complex (R)-BiphenWCl$_4$ and two iterative steps. The resolution complex would be treated with two equivalents of (±)-BiphenH$_2$ and the resulting (R,R)-Biphen$_2$WCl$_2$ complex would be separated from optically pure (S)-BiphenH$_2$. Conproportionation of WCl$_6$ with (R,R)-Biphen$_2$WCl$_2$ would generate two equivalents of the resolving complex, (R)-BiphenWCl$_4$. The two step resolution cycle could then be repeated on a doubled scale (assuming > 95% yield for each step). Starting with one gram of (R)-BiphenH$_2$, it would be possible to generate one kilogram of (S)-BiphenH$_2$ and an equal amount of (R)-BiphenH$_2$ in the resolving complex after 10 iterations ($2^{10}$ = 1024; (1g (S)-BiphenH$_2$ * 1024) ≅ 1.0 kg (S)-BiphenH$_2$).

Unfortunately the preparation of (R)-BiphenWCl$_4$ and (R,R)-Biphen$_2$WCl$_2$ was not facile. Separation of the metal phenoxide complexes from free BiphenH$_2$ was problematic and the isolated yields of (R)-BiphenWCl$_4$ and (R,R)-Biphen$_2$WCl$_2$ were approximately 50%. Consequently this resolution methodology is not as efficient as the phosphate resolution discussed earlier.




**Scheme 1.8.** Proposed Method of Resolving (±)-BiphenH$_2$ using (R)-BiphenWCl$_4$ as the Chiral Auxiliary.

## CONCLUSIONS

The chromic acid synthesis of hexaalkylbiphenols developed by Albert was extended to (±)-BiadH$_2$ and the purification of the biphenols simplified by trituration with methanol instead of multiple crystallizations. Two resolution techniques based on phosphorus derivatives have been developed. The diastereomeric (-)-cinchonidine salts of (±)-BiphenPO$_2$H afforded optically pure (S)-BiphenH$_2$. Crystallization conditions were difficult to optimize and this methodology required large quantities of extremely toxic reagents. A more general phosphate resolution technique was developed based on the separation of diastereomeric (-)-menthyl phosphates. Both enantiomers of BiphenH$_2$ were isolated in good yield. Optically pure (S)-BiadH$_2$ was isolated in good yield and the (R)BiadP(O)Men was enriched to 90% de.

## EXPERIMENTAL

**General Procedures.** Ether, THF, and pentane were sparged with dinitrogen followed by passage through 2 1-gallon columns of activated alumina.[96] Toluene and

benzene were distilled from benzophenone ketyl. Reagent grade methylene chloride was used without purification. NMR spectra were taken on Varian instruments (75.4 or 125.8 MHz, $^{13}C$; 300 or 500 MHz, $^{1}H$; 202.5 MHz, $^{31}P$). $^{1}H$ spectra were referenced versus residual protons in the deuterated solvents as follows: $\delta = 7.16$ $C_6D_6$, $\delta = 7.27$ $CDCl_3$. $^{13}C$ spectra are referenced as follows: $\delta = 128.39$ $C_6D_6$. $^{31}P$ spectra were referenced versus an external standard of $PPh_3$ in $C_6D_6$ ($\delta = -4.78$). All NMR spectra were recorded at room temperature in $C_6D_6$ unless otherwise noted. Optical rotations were taken on a Perkin Elmer Model 241 polarimeter. (±)-BiphenH$_2$[84] and 2-*tert*-butyl-4,5-dimethylphenol[91] were prepared by modified literature procedures. 2-(1-Adamantyl)-4,5-dimethylphenol[93] was prepared by a literature procedure. Potassium hydride, 35% wt/wt in mineral oil was washed repeatedly with pentane and dried *in vacuo*. All other reagents were used as received from Lancaster Synthesis, Inc. or Aldrich Chemical Company, Inc. Optical rotations were obtained on a Perkin Elmer Model 241 Polarimeter. Elemental analyses were performed at H. Kolbe, Mikroanalytisches Laboratorium (Mühlheim an der Ruhr, Germany).

**3,3'-Di-*tert*-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diol ((±)-BiphenH$_2$)**

Potassium dichromate (54 g, 0.184 mol) in sulfuric acid (100 mL) and water (300 mL) was slowly added over 10 minutes to an acetic acid (550 mL) solution of 3,4-dimethyl-2-*tert*-butylphenol (137 g, 0.544 mol) at 60 °C. The color went from orange to green and a tan precipitate formed. The reaction was then heated for one hour at 60 °C and then cooled to room temperature. The reaction was filtered, and the brown solid was washed with water (2 x 250 mL) and methanol (3 x 200 mL). The remaining off-white solid was dried *in vacuo* to give (±)-BiphenH$_2$ (54.4 g, 50%): $^{1}H$ NMR ($CDCl_3$) $\delta$ 7.12 (s, 2H, Ar), 4.79 (s, 2H, OH), 2.24 (s, 6H, Me), 1.80 (s, 6H, Me), 1.38 (s, 18H, $^{t}Bu$); $^{13}C\{^{1}H\}$ NMR $\delta$ 151.24, 134.60, 134.13, 127.73, 128.79, 121.64, 35.15, 30.19. 20.46, 16.35.

**MenthylPCl$_2$[36] (Men*PCl$_2$)**

A solution of (-)-menthol (78 g, 0.50 mol) in $CH_2Cl_2$ (50 mL) was added dropwise to a solution of phosphorus trichloride (137.5 g, 1.0 mol) in $CH_2Cl_2$ (50 mL) over 30 minutes. The mixture was allowed to stir at room temperature for one hour under a nitrogen atmosphere before removing the volatile components by vacuum transfer (rt, 100 mTorr). Purification by short-path vacuum distillation yielded menthyldichlorophosphine (bp 62 °C/150 mTorr): $^{31}$P NMR (THF) δ 177.4.

**(±)-BiphenPMen***

Triethylamine (30 mg, 0.3 mmol) and (±) BiphenH$_2$ (35 mg, 0.1 mmol) were dissolved in THF (3 mL). Men*PCl$_2$ (26 mg, 0.1 mmol) was added, and the reaction stood at room temperature for 18 hours. The precipitate was removed by filtration, transferred to an NMR tube, and inserted directly into the NMR spectrometer: $^{31}$P NMR (THF) δ 143.7 ((R)-BiphenPMen*), 138.0 ((S)-BiphenPMen*).

**Resolution of (S) BiphenH$_2$ via BiphenPO$_2$H**

Potassium hydride (12.42 g, 0.310 mol) was added in portions over an hour to a THF solution (550 mL) of (±)-BiphenH$_2$ (54.4 g, 0.154 mol). Hydrogen gas evolved, and the solution turned brown. After two hours of stirring, phosphorusoxychloride (25.9 g, 0.169 mol) was slowly added, and the solution became opaque, bleaching to a pale yellow. After stirring at room temperature for one hour, the reaction was filtered through Celite to remove potassium chloride. Water (27 mL, 10 eq) and triethylamine (85 mL, 4 eq) were added and the mixture was heated to reflux for five hours in order to hydrolyze the P-Cl bond. After cooling to room temperature, the volatiles were removed on a rotary evaporator. The triethylamine salt was slurried in hydrochloric acid (6 N, 1 L) and heated to 110 °C for five hours, and the solid became bone white. The slurry was then filtered and washed with water (2 x 250 mL), and dried *in vacuo* (61.9 g, 97% from (±)-BiphenH$_2$). The crude acid was recrystallized twice from refluxing glacial acetic acid and dried under a stream of air. To remove residual acetic acid, the purified (±)-BiphenPO$_2$H was taken up

in $CH_2Cl_2$, washed with water (3 x 250 mL), dried over $MgSO_4$, and evaporated to dryness affording pure (±)-Biphen$PO_2H$ (35 g, 55%): $^{31}P$ NMR ($CD_3OD$) δ 2.5; $^1H$ NMR ($CD_3OD$) δ 7.18 (s, 2H, Ar), 5.37 (br s, 1H, $PO_2H$), 2.17 (s, 6H, Me), 1.72 (s, 6H, Me), 1.37 (s, 18H, $^tBu$).

The biphenyl phosphoric acid, (±)-Biphen$PO_2H$, (23.8 g, 57.2 mmol) and (-)-cinchonidine (16.8 g, 57.2 mmol) were dissolved in refluxing absolute ethanol (600 mL) and allowed to stand at room temperature for an hour. The ethanol was removed with a rotary evaporator, and the residue was redissolved in ethyl acetate (250 mL). The solution was concentrated to 200 mL, and acetone (50 mL) was added. Microcrystals of the racemic salt precipitated (25.9 g, 64%, $^{31}P$ NMR (EtOH) δ -0.257 and -0.366). A second crop was collected which was optically pure ($^{31}P$ NMR (EtOH) δ -0.257). The racemate was dissolved in 1:1 methanol:ethyl acetate (100 mL total). The solution was concentrated to 70 mL to remove some of the methanol and acetone (~ 50 mL) was then added. Optically pure microcrystals were collected (9.23 g): $^{31}P$ NMR (EtOH) δ -0.257 ppm.

The optically pure salt (9.23 g) was dissolved in refluxing ethanol (100 mL) and hydrochloric acid was added (6 N, 100 mL). A white powder immediately precipitated, but the reaction was maintained at 70 °C for one hour before filtering. The solid was washed with water and dried *in vacuo* for several hours to give pure (S)-Biphen$PO_2H$ (4.88 g, 90%).

The resolved acid (4.88 g, 11.7 mmol) was dissolved in *N,N*-dimethylacetamide (54 mL) and dimethyl sulfate (2.95 g, 23.4 mmol) was then added under an argon purge. After stirring for ten minutes, sodium bicarbonate (2.16 g, 25.8 mmol) was added as a solid to the reaction mixture and a gas evolved. The reaction was allowed to stir overnight. The solvent was then removed by vacuum distillation (60-70 °C, 500 mTorr), leaving a pale pink residue. The solid was dissolved in $CH_2Cl_2$ (100 mL) and washed with water (2 x 100 mL) and brine (100 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent evaporated to give the methyl ester, (S)-Biphen$PO_2Me$ (4.48 g, 89%).

The methyl ester (4.48 g, 10.4 mmol) was taken up in toluene (75 mL), and Red-Al® (65% wt in toluene, 7.4 mL, 24.4 mmol) was added slowly to the reaction mixture over 25 minutes by syringe. The solution turned yellow on full addition of the Red-Al® and a gas evolved. The mixture was stirred for ten hours and then ethyl acetate (100 mL) and hydrochloric acid (1 N, 100 mL) were added. The layers were separated and the organic phase was washed with aqueous sodium bicarbonate and water. The organic layer was dried over $MgSO_4$, the drying agent was then removed by filtration, and the solvent evaporated to give pure (S)-Biphen$H_2$ (3.1 g, 80%). Note that volatile phosphines were formed as byproducts in this reaction and all glassware should be washed with bleach after use. The optical rotation was determined to be ($[\alpha]_D$ = -53.0 (THF, c = 0.352)).

**Resolution of (R) and (S) Biphen$H_2$ via BiphenP(O)Men***

A solution of (1R, 2S, 5R)-(-)-menthol (44 g, 282 mmol) in $CH_2Cl_2$ (100 mL) was added to a 0 °C solution of phosphorus trichloride (1.5 eq, 58 g, 423 mmol) in $CH_2Cl_2$ (200 mL) over 30 minutes. The ice bath was removed. After one hour at room temperature, the volatiles were removed *in vacuo*. The oil was redissolved in $CH_2Cl_2$ (250 mL) and a $CH_2Cl_2$ (400 mL) solution of triethylamine (3 eq, 118 mL, 847 mmol) and (±)-Biphen$H_2$ (100 g, 282 mmol) was added over 30 minutes. After two hours the reaction mixture was filtered and hydrogen peroxide (30%, 200 mL) was added slowly with stirring (CAUTION: extremely vigorous reaction). The biphasic mixture was stirred rapidly for two hours and then the layers were separated. The organic phase was washed with water and brine (200 mL) and dried over $MgSO_4$. The drying agent was removed by filtration and the solution was concentrated by rotary evaporation to a white solid. The solid was dried *in vacuo* to afford (±)-BiphenP(O)Men* (124 g, 85%): $^{31}P$ NMR δ -3.37 ((S)-BiphenP(O)Men*), δ -4.89 ((R)-BiphenP(O)Men*).

The diastereomeric mixture of phosphates was dissolved in a minimum amount of refluxing acetic acid (~450 mL). After the solution was left at room temperature for 16 hours, white crystals formed. These were collected by filtration and washed with cold

acetic acid (2 x 50 mL). The solid was then dried *in vacuo* to give (S)-BiphenP(O)Men* (42 g, 97-99% de). This material was recrystallized from refluxing acetic acid to afford (S)-BiphenP(O)Men* (37.8 g, >99% de, corresponding to 61% of (S) diastereomer).

The liquor from the first crystallization was concentrated *in vacuo* to give a solid enriched with (R)-BiphenP(O)Men*. This solid was recrystallized from refluxing MeOH (300 mL). On cooling to 0 °C, white crystals formed (32 g, ~98% de). This solid was recrystallized a second time from refluxing MeOH to give (R)-BiphenP(O)Men* in two crops (26.8 g, >99% de, 43% (R) diastereomer).

The MeOH solution was concentrated to give approximately (±)-BiphenP(O)Men* which was reused in subsequent resolution processes. Consequently the effective yield of both (R) and (S)-BiphenP(O)Men* is higher than the 43% and 61% respective yields reported above.

Resolved (S)-BiphenP(O)Men* (37.83 g, 70.3 mmol) was dissolved in toluene (500 mL) in a 2 L round bottom Schlenk flask equipped with an addition funnel. Red-Al® (53 mL, 65% wt in toluene) was introduced into the addition funnel by cannula and then added dropwise at 0 °C onto the phosphate solution with effervescence. The reaction was stirred at room temperature for 16 hours and then carefully quenched with water (75 mL) and bleach (75 mL). The slurry was filtered through Celite, the pad was washed with toluene (250 mL), and the layers separated. The toluene layer was washed with bleach and brine (200 mL each) and then dried over $MgSO_4$. The drying agent was removed by filtration and the toluene was removed by vacuum distillation at 0 °C to give a white solid. The menthol was removed by repeated trituration with MeOH (50 mL/wash) until the minty odor disappeared. The resolved (S)-Biphen$H_2$ was collected by filtration and dried *in vacuo* (17.5 g, 70%, >99% ee). The optical purity of (S)-Biphen$H_2$ was tested by $^{31}P$ NMR of the (S)-BiphenPMen* derivative. The reduction of (R)-BiphenP(O)Men* to (R)-Biphen$H_2$ followed an identical procedure.

**(±)-3,3'-Di-(1-adamantyl)-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diol ((±)-BiadH$_2$)**

A solution of potassium dichromate (3.95 g, 13.4 mmol) in sulfuric acid (6.5 mL) and water (20 mL) was added dropwise over 20 minutes to an acetic acid (40 mL) slurry of 2-adamantyl-3,4-dimethylphenol (10.3 g, 40.2 mmol) at 65 °C. After stirring the reaction mixture for one hour at 65 °C, the green suspension was cooled to room temperature and filtered. The brown precipitate was washed with water (120 mL), triturated with methanol (3 x 75 mL), and the resulting white solid was dried *in vacuo* to afford (±)-BiadH$_2$ (5.6 g, 55% yield): $^1$H NMR ($CDCl_3$) δ 7.07 (s, 2H, m-Ar), 4.80 (s, 2H, OH), 2.25 (s, 6H, Me), 2.13 (br s, 12H, Ad-$CH_2$), 2.06 (br s, 6H, Ad-CH), 1.82 (s, 6H, Me), 1.76 (br s, 12 H, Ad-$CH_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 150.55, 134.04, 133.78, 128.71, 128.30, 121.11, 40.74, 37.43, 36.85, 29.38, 20.39, 16.29. Anal. Calcd for $C_{36}H_{46}O_2$: C 84.66, H 9.08. Found: C 84.78, H 9.18.

**(±)-BiadK$_2$**

Addition of benzyl potassium (13 mg, 0.1 mmol) to a THF-$d_8$ slurry of (±)-BiadH$_2$ resulted in a clear golden solution. No hydroxyl resonances were observed by $^1$H NMR, and the reaction mixture contained toluene (1.2 eq): $^1$H NMR (THF-$d_8$) δ 6.54 (s, 2H, Ar), 2.30 (s, 12H, Ad-$CH_2$), 2.10 (s, 6H, Me), 1.94 (br s, 6H, Ad-CH), 1.75 (br q, 12H, Ad-$CH_2$), 1.70 (s, 6H, Me).

**(±)-BiadPMen***

To a slurry of (±)-BiadH$_2$ (25 mg, 0.049 mmol) in THF (1 mL) was added potassium hydride (5 mg, 0.12 mmol) affording a blue solution. Men*$PCl_2$ (13 mg, 0.051 mmol) in THF (0.5 mL) was added, and the reaction became yellow with a white precipitate formed. The reaction was filtered through a Kimwipe® plug into an NMR tube and inserted directly into the NMR spectrometer: $^{31}P\{^1H\}$ NMR (THF) δ 143.6 ((S)-BiadPMen*), 138.8 ((R)-BiadPMen*).

**Resolution of $BiadH_2$ by (±)BiadP(O)Men***

(±)-$BiadH_2$ (29.9 g, 58.6 mmol) was dissolved in THF (500 mL) and solid potassium hydride (2.1 eq, 4.9 g, 123 mmol) was added in portions. The reaction mixture became dark green and evolved hydrogen gas. After one hour, Men*$PCl_2$ was added, the solution became brown and a white precipitate formed. Water was then added slowly to quench the excess potassium hydride. The volatiles were removed by rotary evaporation, and the brown residue was taken up in $CH_2Cl_2$ (400 mL). Hydrogen peroxide (30%, 50 mL) was added and the biphasic mixture was stirred vigorously for one hour. The layers were separated and the organic phase was washed with water (200 mL) and brine (200 mL) and then dried over $MgSO_4$. The drying agent was removed by filtration and the solution concentrated to an orange foam. The diastereomeric mixture of phosphates was purified by crystallization from refluxing heptane (3 crops, 25 g total, 60%): $^{31}P$ NMR ($C_6H_6$) δ -3.29 and -5.57.

A Soxhlet extraction apparatus was charged with the mixture of (±)-BiadP(O)Men* diastereomers (6 g). The pot was charged with acetone (75 mL) and heated to reflux until all of the material in the filter cup dissolved (3 days). Concurrently, a precipitate formed in the pot. After cooling the reaction mixture to room temperature, the precipitate was collected by filtration (2.52 g, 99% de (S)-BiadP(O)Men*). Additional white powder was precipitated from the mother liquor and collected by filtration (1.35 g, ~0% de). The remaining acetone solution was then concentrated to give enriched (+)-BiadP(O)Men* (0.91 g, 90% de).

The diastereomerically pure phosphate, (S)-BiadP(O)Men* (7.78 g, 10.96 mmol) was dissolved in toluene (125 mL). Red-Al® (13.3 mL, 44 mmol, 65% wt in toluene) was added by syringe. After stirring for 4 days at room temperature, water (50 mL) was added slowly to quench excess Red-Al®. The slurry was stirred for 10 minutes, filtered through Celite and the pad was washed liberally with toluene and bleach. The layers were separated and the organic phase was washed with bleach and brine (100 mL each) and then dried

over $Na_2SO_4$. The toluene solution was decanted from the drying agent and the volatiles were removed by vacuum distillation at room temperature. The waxy white solid was washed with hexane (3 x 50 mL) until the minty aroma of (-)-menthol disappeared. Optically pure (S)-Biad$H_2$ was dried *in vacuo* (3.11 g, 56%). Optical rotation was determined ($[\alpha]_D$ = -32.1 (THF, c = 0.033))

**W((S)-Biphen)$_2$Cl$_2$**

A 50 mL sealed reaction tube was charged with a $CH_2Cl_2$ (3 mL) suspension of $WCl_6$ (40 mg, 0.1 mmol). (S)-Biphen$H_2$ (106 mg, 0.3 mmol) in $CH_2Cl_2$ (2 mL) was then added and the solution turned purple. The flask was sealed and heated to 40 °C for one hour with vigorous stirring. After cooling to room temperature, the volatiles were removed and pentane (1 mL) was added. A dark purple precipitate formed which was collected by filtration (50 mg, 52%). The pentane extract contained (S)-Biphen$H_2$ and 5-10% paramagnetic impurities. $^1$H NMR δ 7.23 (s, 2H, Ar), 2.74 (s, 6H, Me), 1.61 (s, 18H, $^t$Bu), 1.255 (s, 6H, Me).

**W((R)-Biphen)Cl$_4$**

Tungsten hexachloride (2 eq, 336 mg, 0.847 mmol) was suspended in $CH_2Cl_2$ (5 mL), and (R)-Biphen$H_2$ (50 mg, 0,424 mmol) was added as a solid. The solution darkened in color from red to purple. After 75 minutes, the volatiles were removed *in vacuo* and the resulting solid contained two species according to the $^1$H NMR spectrum.

**MoCl$_4$•THF$_2$ with (R)-Biphen$H_2$ and MeLi**

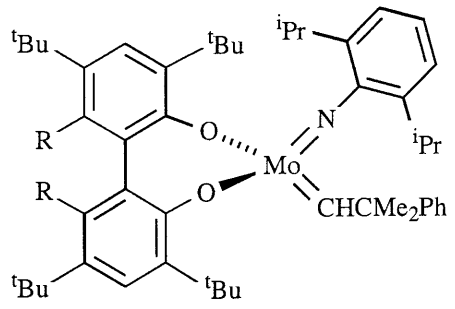
A solid mixture of $MoCl_4$•$THF_2$ (44 mg, 0.141 mmol) and (R)-Biphen$H_2$ (2 eq, 100 mg, 0.282 mmol) was suspended in THF (4 mL). Methyllithium (4 eq, 0.4 mL, 0.564 mmol, 1.4 M in diethyl ether) was added causing gas evolution and precipitation of a white solid. After 10 minutes, the solution was concentrated and extracted with a diethyl ether/pentane mixture (4 mL). The slurry was filtered and concentrated to give a white residue (180 mg). $^1$H NMR 7.38 (br s, 2H, Ar), 3.63 (br s, THF), 3.28 (q, $OEt_2$), 2.29 (br s, 6H, Me), 1.88 (br s, 6H, Me), 1.78 (br s, THF), 1.38 (br s, 18H, $^t$Bu), 1.12 (t, $OEt_2$).

# CHAPTER 2

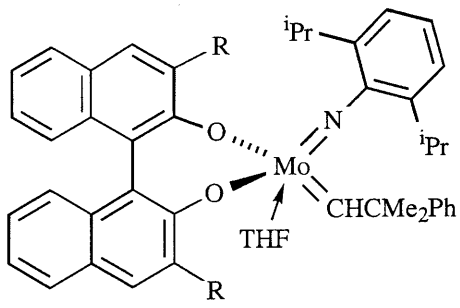
## Biphenoxides as Chiral Auxiliaries for Molybdenum(VI) Imido Alkylidene Complexes

## INTRODUCTION

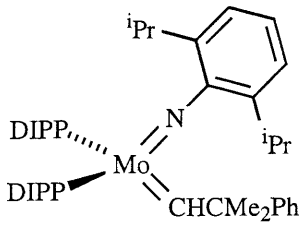
A number of achiral and racemic molybdenum imido alkylidene complexes containing phenoxide ligands have been prepared by Schrock and coworkers.[30,31,36,44,46,47,97] While optically pure binaphtholate complexes have been prepared and studied as catalysts in the ROMP of norbornadienes,[36] optically pure biphenoxide complexes have not been synthesized. The (S)-Biphen$H_2$ and (S)-Biad$H_2$ biphenol ligands discussed in Chapter 1 have been used to prepare a family of optically pure molybdenum(VI) imido alkylidene complexes. The modular structure of these complexes, Mo(NAr)(CHR)(biphenoxide), allows for a library of complexes with variable catalytic activity to be prepared. The precursor *bis*(triflate), Mo(NAr)(CHR)$(OTf)_2$•DME have been prepared with a wide range of arylimido substituents.[32,98-100] The biphenoxide ligand is introduced by substitution for the triflate ligands in the last synthetic step. As a result, any combination of arylimido and biphenoxide could theoretically be prepared.




R = Me, H




R = $SiMe_2Ph$, $SiMe_2{}^tBu$
Ph, *o*-Tol, 2,6-$Me_2C_6H_3$
2,4,6-$^iPr_3C_6H_2$



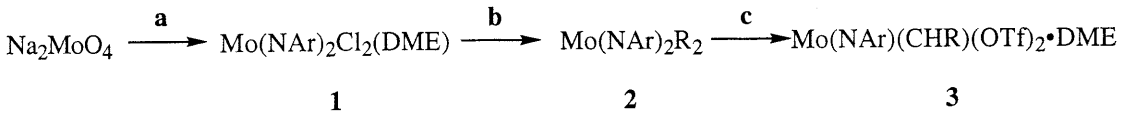

DIPP = O-2,6-$^iPr_2C_6H_3$

**Scheme 2.1.** Achiral and Racemic Molybdenum Imido Alkylidene Complexes Containing Phenoxide,[33,44] Biphenoxide[31,36,47,97] and Binaphtholate Ligands.[31,36]

## RESULTS AND DISCUSSION

### 2.1. New Molybdenum(VI) Imido Alkylidene *Bis*(triflate) Complexes

In the course of studying the ARCM of Mo(NAr)(CHR)(biphenoxide) complexes, *bis*(triflates) complexes containing new arylimido and alkylidene groups were prepared. The general synthetic strategy developed by Fox, Oskam and Schrock was employed except that sodium molybdate was substituted for ammonium dimolybdate as this reagent required significantly less chlorotrimethylsilane in the first step (8 *vs.* 17 equivalents for $NH_4Mo_2O_7$).[32,98-100] Catalyst precursors will be enumerated as $Mo(NAr)_2Cl_2$•DME (**1**), $Mo(NAr)_2(CH_2R)_2$ (**2**, R = $CMe_2Ph$; **2'**, R = $^tBu$), and Mo(NAr)(CHR)$(OTf)_2$•DME (**3**, R = $CMe_2Ph$; **3'**, R = $^tBu$). The imido substituent will be denoted by a lower case letter (**a** = 2,6-$^iPr_2C_6H_3$, **b** = 2,6-$Et_2C_6H_3$, **c** = 2,6-$Me_2C_6H_3$, **d** = 3,5-$Me_2C_6H_3$, **e** = 2-$^tBuC_6H_4$, **f** = 2,4-$^tBu_2$-6-$MeC_6H_2$, **g** = 2-$CF_3C_6H_3$, **h** = 1-adamantyl). For example, Mo(N-2-$CF_3C_6H_4)_2(CH_2{}^tBu)_2$ is denoted by **2g'**.




**a**) 2 eq $ArNH_2$, 4 eq $NEt_3$, 10 eq TMSCl, DME, 60-65 °C, 4-12 h **b**) 2 eq $RCH_2MgCl$, $OEt_2$, 12-24 h. **c**) 3 eq HOTf, DME, -25 °C → rt, 4-16 h

**Scheme 2.2.** Synthesis of Molybdenum(VI) Imido Alkylidene *Bis*(triflate) Complexes from Sodium Molybdate.

Imido alkylidene complexes containing Biphen will be denoted $(Z)(R_n)M(X)$ and complexes containing Biad will be denoted $(Z)'(R_n)M(X)$ where (Z) = (±) or (S), $R_n$ denotes the substituents on the arylimido ring ($^iPr_2$ = 2,6-$^iPr_2C_6H_3$, $Et_2$ = 2,6-$Et_2C_6H_3$, $Me_2$ = 2,6-$Me_2C_6H_3$, 3,5-$Me_2$ = 3,5-$Me_2C_6H_3$, $^tBu$ = 2-$^tBuC_6H_4$, $^tBu_2Me$ = 2,4-$^tBu_2$-6-$MeC_6H_2$, $CF_3$ = 2-$CF_3C_6H_3$), M is either molybdenum or tungsten, and X = Neo ($CHCMe_2Ph$), Np ($CH^tBu$) or Sty (CH-2-$MeOC_6H_4$). For complexes with substituents that are not *ortho* to nitrogen, the ring position of the groups will be included. For example, the shorthand for Mo(N-3,5-$Me_2C_6H_3$)($CHCMe_2Ph$)((S)-Biad) will be (S)'(3,5-

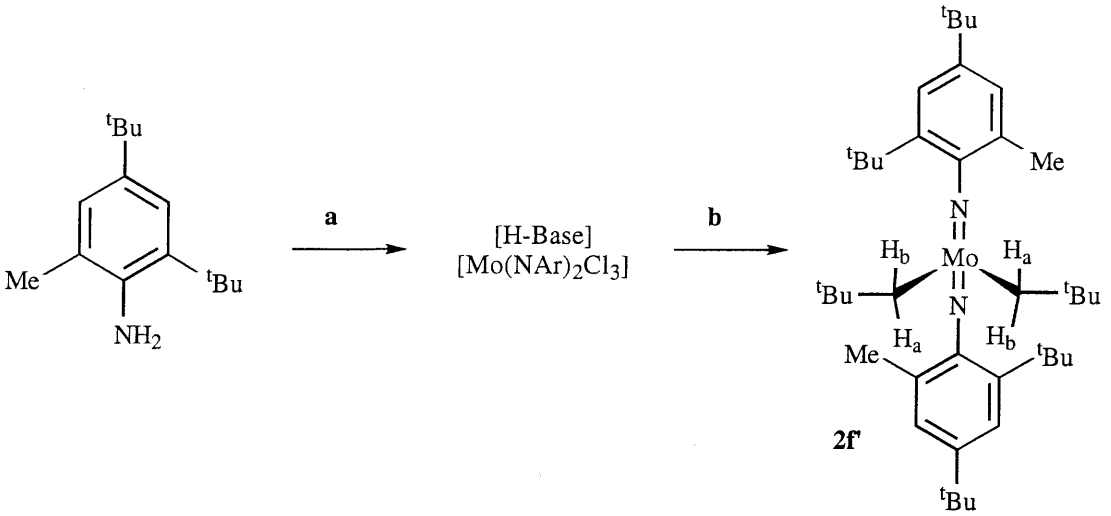
$Me_2$)Mo(Neo) and Mo(N-2,6-$Me_2C_6H_3$)($CHCMe_2Ph$)((±)-Biphen) will be (±)($Me_2$)Mo(Neo)

The synthesis of **3b** was carried out using methods developed by Fox[98,99] and Oskam.[32,100] Reaction of 2,6-diethylaniline with sodium molybdate, triethylamine and excess chlorotrimethylsilane (10 eq) at 60 °C in a sealed vessel generated **1b** in 40% isolated yield without prepurifying any of the starting materials. Alkylation of **1b** with neophylmagnesium chloride in ether afforded **2b** in 75% isolated yield after crystallization from ether. Treatment of **2b** with three equivalents of triflic acid in DME generated the *bis*(triflate), **3b**, in 44% yield isolated after trituration with cold ether.

2,4-Di-*tert*-butyl-6-methylaniline was prepared in two steps from 3,5-di-*tert*-butyltoluene by nitration with nitric acid in acetic acid/acetic anhydride, followed by hydrogenation over Raney nickel.[101] The reaction of the aniline with sodium molybdate, triethylamine and chlorotrimethylsilane did not generate the expected six-coordinate $Mo(NAr)_2Cl_2$•DME. Instead, the red triethylammonium salt $[HNEt_3][Mo(NAr)_2Cl_3]$ was isolated in 35% isolated yield from ether. The composition was substantiated by $^1H$ and $^{13}C$ NMR spectroscopy. The elemental analysis was low in carbon (6%), hydrogen (0.5%) and nitrogen (0.5%), but the impurity was not identified. The lutidinium salt, [H•lutidine][$Mo(NAr)_2Cl_3$], was prepared in a 81% crystallized yield under similar conditions. This complex was spectroscopically pure and combustion analysis agreed with this composition. These ionic complexes were the only members of the family of $Mo(NAr)_2Cl_2$ complexes that were not neutral DME adducts. Presumably the increased steric bulk of the arylimido ligand prevented DME coordination to generate an octahedral molybdenum center, but the four-coordinate $Mo(NAr)_2Cl_2$ was sufficiently electrophilic to bind an additional chloride from base•HCl generated in the reaction (Scheme 3.2).

The addition of three equivalents of neopentylmagnesium chloride to [HBase][$Mo(NAr)Cl_3$] (Base = $NEt_3$ or 2,6-lutidine) in ether deprotonated the ammonium or lutidinium cation and generated $Mo(NAr)_2(CH_2{}^tBu)_2$, **2f'**, in 68% yield as a viscous

red oil which crystallized upon cooling. The $^1$H NMR spectrum (Figure 2.1) indicated **2f'** was $C_2$-symmetric with the aryl rings stacked such that each *ortho-tert*-butyl group was adjacent to the *ortho*-methyl on the other arylimido ring. The solution structure was supported by the observation of only one neopentyl *tert*-butyl group by $^1$H NMR spectroscopy. At room temperature, the neopentyl methylene resonance was not observed. Cooling a toluene-$d_8$ solution to -40 °C resolved the diastereotopic methylene protons as an AB pattern with two broad doublets at δ 3.10 and 1.54 with $J_{HH}$ = 14 Hz. The temperature dependence of the $^1$H NMR spectra was a result of hindered rotation about the N-aryl bond. The diastereotopic methylene protons equilibrate via N-aryl bond rotation from a $C_2$-symmetric complex to a $C_s$-symmetric isomer that has the *ortho-tert*-butyl groups in a *syn* orientation and the neopentyl methylene protons, $H_a$ and $H_b$, are equivalent. Warming the sample to 60 °C did not produce a time averaged singlet for the neopentyl methylene resonances, presumably the lack of coalescence was due to the large separation of the diastereotopic methylene resonances (Δδ = 1.56).




**a**) 0.5 eq, $Na_2MoO_4$, 2 eq Base, 5 eq TMSCl, DME, 65 C, 12-14 h. **b**) 3 eq $^t$BuCH$_2$MgCl, ether, 16 h.

**Scheme 2.3.** Synthesis of [HBase][Mo(N-2,4-$^t$Bu$_2$-6-MeC$_6$H$_2$)$_2$Cl$_3$] (Base = NEt$_3$ or 2,6-lutidine) and Mo(N-2,4-$^t$Bu$_2$-6-MeC$_6$H$_2$)$_2$(CH$_2$$^t$Bu)$_2$, **2f'**.

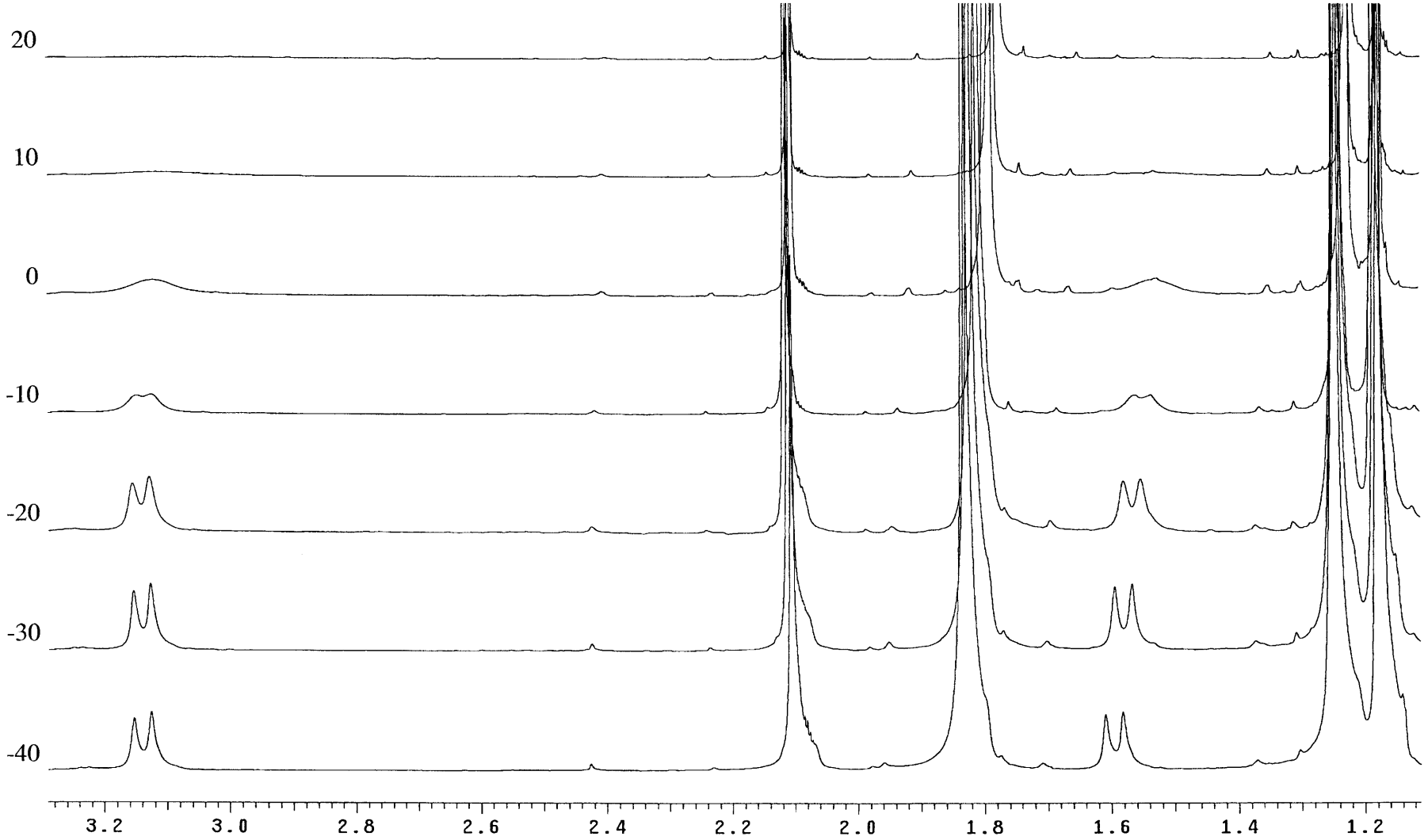



**Figure 2.1.** Variable Temperature $^1$H NMR Spectroscopy of Mo(N-2,4-$^t$Bu$_2$-6-MeC$_6$H$_3$)$_2$(CH$_2$$^t$Bu)$_2$, **2f'**, from 20 °C to -40 °C in Toluene-$d_8$.

The neophylidene complexes have been prepared for Mo(NR)($CHCMe_2Ph$)$(OTf)_2$•DME where R = 2-$CF_3C_6H_4$, Ad.[32] The neopentylidene complexes were prepared in order to improve catalyst crystallinity and to simplify the $^1H$ NMR spectra of Mo(NR)($CH^tBu$)(biphenoxide). Alkylation of $Mo(NAr)_2Cl_2$•DME with two equivalents of neopentylmagnesium chloride in ether generated the four-coordinate dialkyl complexes **2g'** (73%) and **2h'** (62%). Filtration of crude **2g'** to remove magnesium chloride and evaporation of the ethereal solvents gave a red oil which crystallized on standing at room temperature for several hours. The adamantyl imido analog, **2h'**, crystallized from a concentrated ether solution.

$$\underset{\textbf{2}}{Mo(NR)_2(CH_2R')_2} \xrightarrow{3\text{ eq HOTf}} \underset{\textbf{3}}{Mo(NR)(CHR')(OTf)_2\text{•DME}}$$

**Table 2.1.** Isolated Yields of Mo(NR)(CHR')$(OTf)_2$•DME from the Triflic Acid Reaction.

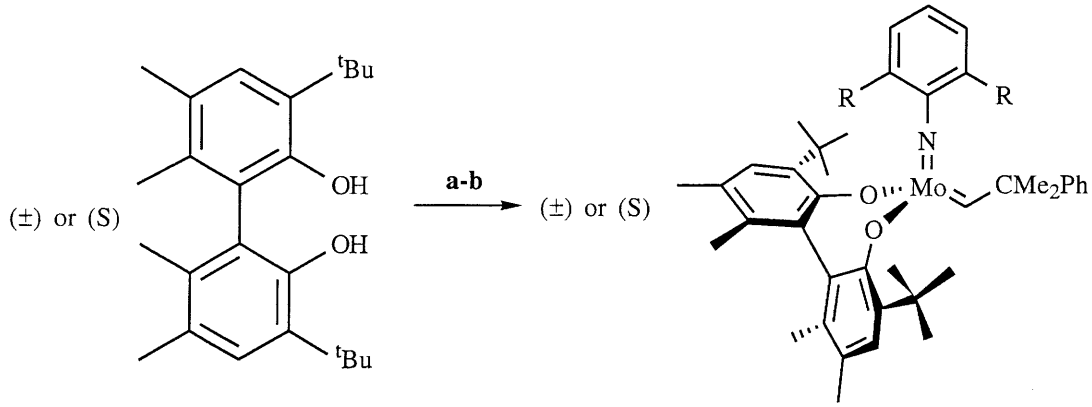
| Complex | R | R' | Yield (%) |
|---|---|---|---|
| **3b** | 2,6-$Et_2C_6H_3$ | $CMe_2Ph$ | 44 |
| **3f'** | 2,4-$^tBu_2$-6-$MeC_6H_2$ | $^t$Bu | 60 |
| **3g'** | 2-$CF_3C_6H_4$ | $^t$Bu | 65 |
| **3h'** | 1-Adamantyl | $^t$Bu | 52 |

The addition of three equivalents of triflic acid to dialkyls **2b**, **2f'-2h'**, generated the corresponding molybdenum(VI) imido alkylidene complexes, Mo(NR)(CHR)$(OTf)_2$•DME, **3b**, **3f'-3h'**. The arylimido *bis*(triflate) complexes **3b**, **3f'** and **3g'** were purified by removing the volatiles *in vacuo* and extracting the solid residue with cold toluene. The toluene suspension was filtered through Celite to remove the anilinium triflate and the eluent was concentrated to a yellow-brown solid. Trituration of the residue with ether gave **3b**, **3f'** and **3g'** as yellow powders. The 1-adamantylimido complex, **3h'**,

was sparingly soluble in hydrocarbon solvents. Consequently, copious benzene washes of the residue mixture from the reaction mixture were necessary to extract **3h'** from 1-adamantylammonium triflate. After removing the benzene *in vacuo*, the residue was triturated with ether to give **3h'** in 52% as a white powder.

## 2.2. Synthesis of Mo(NAr)(CHR)(Biphen) Complexes

Excess potassium hydride or stoichiometric benzyl potassium was employed to doubly deprotonate $BiphenH_2$ in THF. Addition of the appropriate triflate, **3a-c**, to a THF solution of (±)-$BiphenK_2$ or (S)-$BiphenK_2$ resulted in the formation of racemic (±)($R_2$)Mo(Neo) and optically pure (S)($R_2$)Mo(Neo) (Table 2.2). After removing the THF *in vacuo*, (±) and (S)($R_2$)Mo(Neo) were separated from KOTf by benzene extraction and filtration of the suspension through Celite. The complexes were then crystallized from ether. Due to its low solubility in ether, (±)($Me_2$)Mo(Neo) was triturated with ether to give the desired complex as a bright orange powder.




**a**) excess KH, THF, 18 h. **b**) Mo(NAr)($CHCMe_2Ph$)$(OTf)_2$•DME

**Table 2.2.** Isolated Yields for (±) and (S)($R_2$)Mo(Neo) Using Potassium Hydride to Deprotonate Biphen$H_2$.

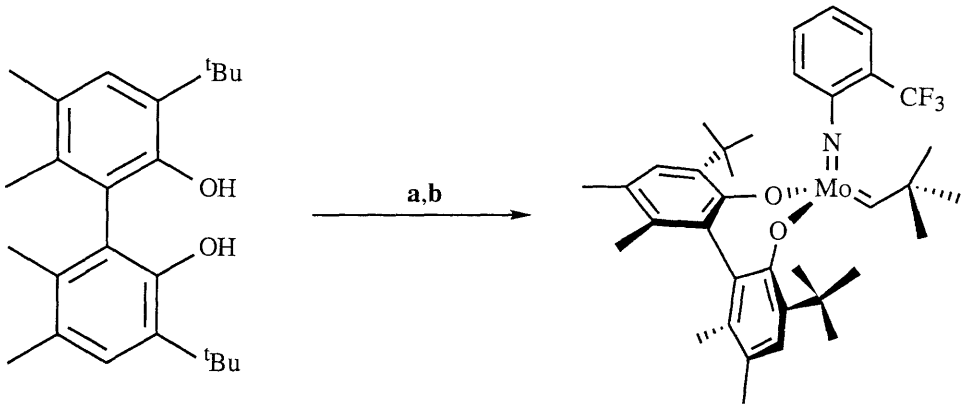
| Mo(N-2,6-$R_2C_6H_3$) (Neo)$(OTf)_2$•DME | Yield (%) (±)($R_2$)Mo(Neo) | Yield (%) (S)($R_2$)Mo(Neo) |
|---|---|---|
| R = Me | 77 | 43 |
| R = Et | 60 | 27 |
| R = $^i$Pr | 72 | 78 |

Racemic complexes with only one *ortho* aryl substituent, (±)(R)Mo(Neo) (R = $CF_3$, $^t$Bu), could not be prepared using potassium hydride as the deprotonating agent. The benzene extract of the reaction mixture contained significant amounts of (±)-Biphen$H_2$. When two equivalents of benzyl potassium were used instead of potassium hydride, spectroscopically pure (±)(R)Mo(Neo) (R = $CF_3$, $^t$Bu) was obtained. Both complexes were extremely soluble in hydrocarbon and ethereal solvents. Hence, unlike the 2,6-disubstituted arylimido complexes, (±)(R)Mo(Neo) did not precipitate from hydrocarbon or ethereal solvents. (±)($^t$Bu)Mo(Neo) was isolated as a four-coordinate THF-free complex by concentrating the benzene solution to a red powder. (±)($CF_3$)Mo(Neo) was prepared in THF and crystallized from a THF/ether mixture as a five-coordinate THF/ether base adduct, (±)($CF_3$)Mo(Neo)•$THF_{0.5}(OEt_2)_{0.5}$.

The optically pure (S)($CF_3$)Mo(Neo)•THF was prepared and observed by $^1$H NMR spectroscopy but could not be purified via crystallization. Solutions in ether, methylcyclohexane, hexamethyldisiloxane and toluene with and without 1-2 equivalents of THF did not induce precipitation at room temperature and viscous colloid suspensions were formed at -25 °C. Pentafluoropyridine was used as either a solvent or as an additive in ether or methylcyclohexane solutions without generating an isolable $NC_5F_5$ adduct. Addition of 2,4-lutidine afforded the five-coordinate adduct, (S)($CF_3$)Mo(Neo)•lut, but the lutidine base was not labile, and this adduct was not an active RCM catalyst. The

analogous (S)($^t$Bu)Mo(Neo) was not investigated due to the inability of (±)($^t$Bu)Mo(Neo) to effect RCM of ethereal substrates such as allyl ether.

A crystalline, optically pure (S)($CF_3$)Mo(CHR) complex was desired, consequently the neophylidene ligand was replaced with a neopentylidene group. Labile arene coordination to Mo in *anti*-(S)($CF_3$)Mo(Neo) reduced the rate of rotamer exchange relative to (±)($^i$Pr$_2$)Mo(Neo) (Chapter 3) and might hinder crystallization. Replacing the neophylidene group with neopentylidene prevented complications from arene coordination. Treatment of a toluene solution of (±)-Biphen$K_2$ (generated with benzyl potassium) at -25 °C with one equivalent of **3g'** followed by pentane extraction gave a dark red solution. Concentration of the pentane solution followed by cooling to -25 °C induced crystallization of base-free (±)($CF_3$)Mo(Np) in 38% yield (Scheme 2.4). The optically pure (S)($CF_3$)Mo(Np) was also be prepared by this route, however this complex could not be crystallized.



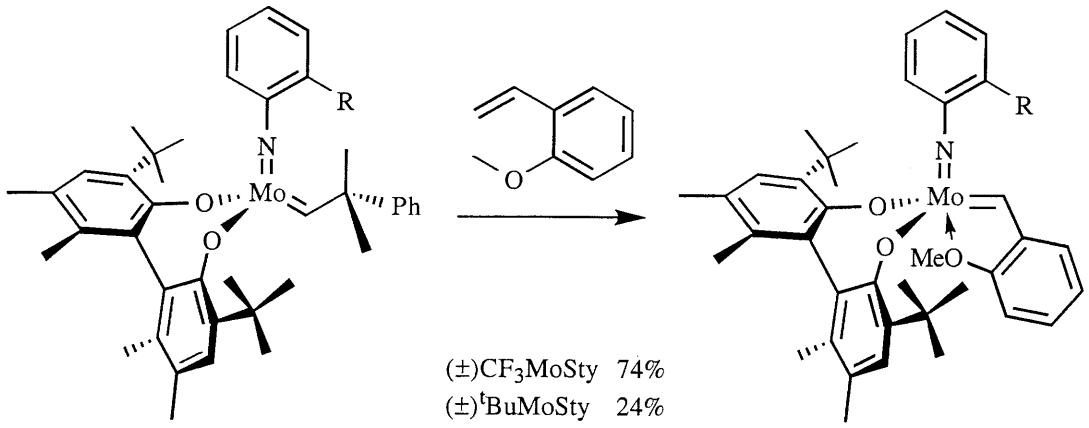

**a**) 2.1 eq $KCH_2Ph$, toluene, 5 h. **b**) Mo(N-2-$CF_3$Ph)(CH$^t$Bu)$(OTf)_2$• DME, -25 °C → rt, 45 min.

**Scheme 2.4.** Synthesis of (±)- and (S)($CF_3$)Mo(Np).

The purification of (±)($CF_3$)Mo(Neo)•base was not reproducible for bases that were sufficiently labile to permit RCM activity at room temperature. For example, crystallization of the racemic catalyst, (±)($CF_3$)Mo(Neo)•$THF_{0.5}(OEt_2)_{0.5}$, was extremely sensitive to the concentration of THF and ether. Replacing THF with 2,4-lutidine improved crystallinity but the tightly bound base arrested RCM activity. The alkylidene

substituent can be varied to alter the physical properties of the catalyst precursor without affecting the composition of the active RCM catalyst (±)($CF_3$)Mo($CH_2$). Cross-metathesis of (±)($CF_3$)Mo(Neo)•$THF_{0.5}$ $(OEt_2)_{0.5}$ with a slight excess of 2-methoxystyrene generated a benzylidene complex (±)($CF_3$)Mo(Sty) which precipitated from the ether reaction mixture in 74% yield (Scheme 2.5). The ether residue of 2-methoxystyrene generated in the first metathesis step should be a poor intermolecular base.

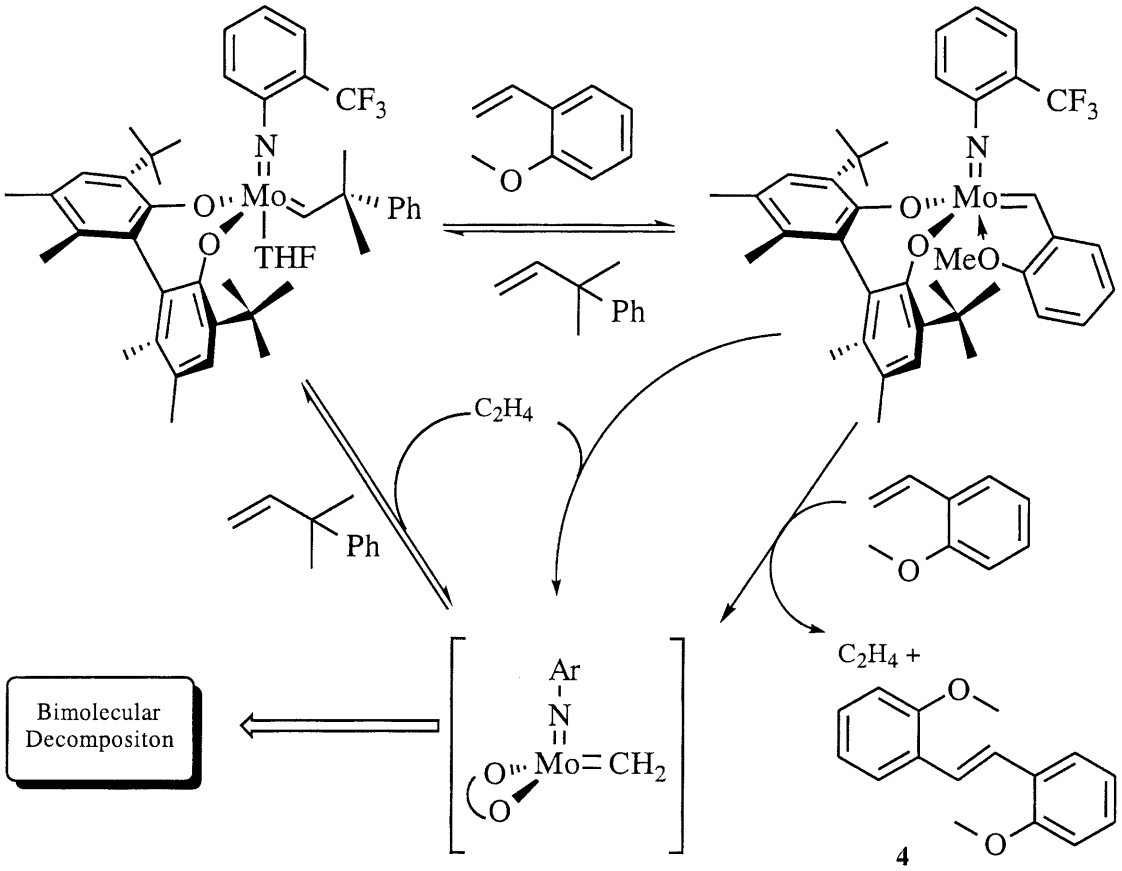
Addition of 2-methoxystyrene to (±)($^t$Bu)Mo(Neo) in ether generated (±)($^t$Bu)Mo(Sty) in low yield (24%) as a green powder (Scheme 2.5) . Presumably, the increased electron donating capacity of the 2-*tert*-butylphenylimido group compared with 2-trifluoromethylphenylimido reduced the electrophilicity of molybdenum in (±)($^t$Bu)Mo(Sty) relative to (±)($CF_3$)Mo(Sty). Without the methoxide residue tightly bound to molybdenum as in (±)($CF_3$)Mo(Sty), the benzylidene ligand may rotate more freely about both the Mo=$C_\alpha$ and $C_\alpha$-$C_\beta$ bonds. This conformational flexibility may hinder the precipitation of the five-coordinate base adduct and lower the yield compared to (±)($CF_3$)Mo(Sty).




**Scheme 2.5.** Synthesis of (±)($CF_3$)Mo(Sty) and (±)($^t$Bu)Mo(Sty).

Treatment of the optically pure neophylidene with 2-methoxystyrene in ether produced a mixture of *cis*- and *trans*-stilbene, **4**, as tan needles (Scheme 2.6).[102] The 2-methoxystyrene consumed in stilbene formation generated ethylene and the unstable methylidene, (S)($CF_3$)Mo($CH_2$). Unreacted (S)($CF_3$)Mo(Neo) reacted with ethylene to

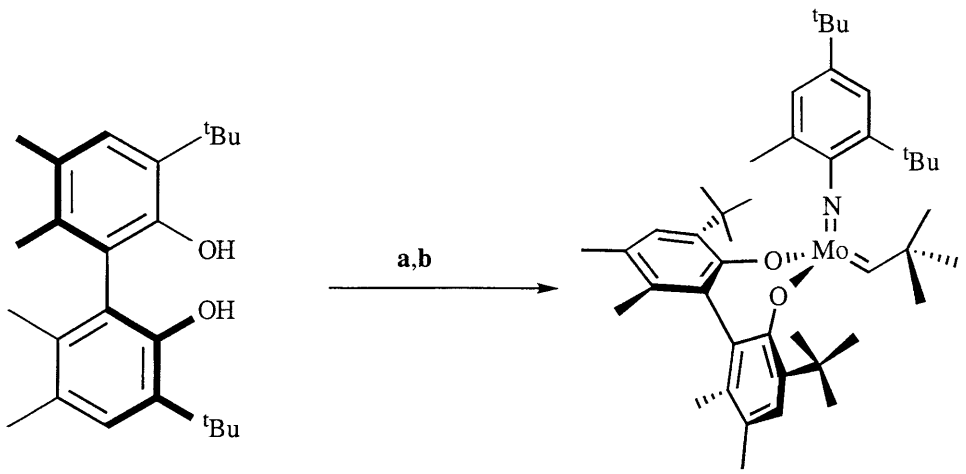
generate 3-methyl-3-phenyl-1-butene and additional (S)($CF_3$)Mo($CH_2$) which was susceptible to bimolecular decomposition processes. The low isolated yield of (S)($CF_3$)Mo(Sty) was attributed to the formation of **4** and decomposition of the unstable (S)($CF_3$)Mo($CH_2$).




**Scheme 2.6.** Competitive Formation of 2,2'-Dimethoxystilbene and (S)($CF_3$)Mo(Sty) from 2-Methoxystyrene and (S)($CF_3$)Mo(Neo)•$THF_{0.5}(OEt_2)_{0.5}$.

Due to the instability of (±)($^t$Bu)Mo(Neo) during RCM catalysis of ethereal substrates, complexes containing two different aliphatic *ortho*-arylimido substituents were prepared. Addition of **3f'** to a stirred THF solution of (±)-Biphen$K_2$ generated (±)($^t$Bu$_2$Me)Mo(Np) (Scheme 2.7, Table 2.3). This complex was observed spectroscopically but did not precipitate from a variety of hydrocarbon and ethereal solvents. The optically pure (S)($^t$Bu$_2$Me)Mo(Np) was prepared using similar conditions, and this complex crystallized from pentane. It should be noted that spectroscopically

pure (S)($^t$Bu$_2$Me)Mo(Np) was prepared on three occasions, but in only one case did the pentane solution yield a precipitate.




**a**) 2.1 eq $KCH_2Ph$, THF, rt, 10 minutes. **b**) **3f'**, rt, 30 minutes; pentane extraction.

**Scheme 2.7.** Synthesis of (S)($^t$Bu$_2$Me)Mo(Np).

**Table 2.3**. Reaction Solvent, Crystallization Solvent and Yields for the Synthesis of Hetero-2,6-Disubstituted Arylimido Complexes, (±) and (S)(RR')Mo(CHR)" (R ≠ R' and R" = $^t$Bu, $CMe_2Ph$, or 2-$MeOC_6H_4$).

| Complex | Solvent | Crystalline | Cryst. Solvent | Yield (%) |
|---|---|---|---|---|
| (±)($CF_3$)Mo(Neo) | toluene | No | -- | 51 |
| (±)($CF_3$)Mo(Neo)•$THF_{0.5}(OEt_2)_{0.5}$ | THF | Yes | ether/THF | 52 |
| (±)($CF_3$)Mo(Np) | toluene | Yes | pentane | 38 |
| (±)($CF_3$)Mo(Sty) | ether | Yes | ether | 74 |
| (S)($CF_3$)Mo(Neo)•lut | ether | Yes | ether | 45 |
| (S)($CF_3$)Mo(Np) | toluene | No | -- | 95 |
| (S)($CF_3$)Mo(Sty) | THF | Yes | ether | 12 |
| (±)($^t$Bu)Mo(Neo) | THF | No | -- | 90 |
| (±)($^t$Bu)Mo(Sty) | ether | Yes | ether | 24 |
| (S)($^t$Bu$_2$Me)Mo(Neo) | THF | Yes | pentane | 36 |

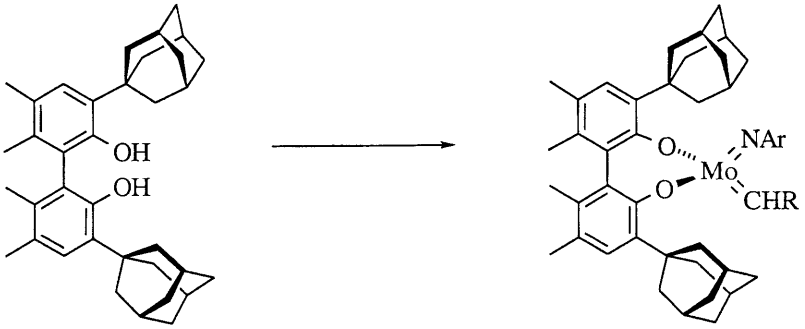
The enantioselectivity in ARCM with catalysts containing the spherical 1-adamantylimido instead of a planar arylimido group would be derived entirely from the Biphen ligand without projection through a planar arylimido ligand. These 1-adamantylimido catalysts would be ideal benchmarks for comparing the enantioselectivity

of chiral biphenoxide ligands. A mixture of complexes resulted from the addition of the *bis*(triflate), **3h**, to THF solutions of (±)-Biphen$K_2$ generated with either benzyl potassium or potassium hydride. Pale yellow powders were isolated from pentane. The $^1$H NMR spectra of these powders contained two resonances in the alkylidene region. There was a sharp resonance at δ 13.50 which was assigned to be the *anti* rotamer based on the large CH coupling ($J_{CH}$ = 143 Hz). In addition, there was a broad resonance at δ 12.23 (ω ≅ 300 Hz) which has not been unambiguously identified. The sum of the two resonances integrated to 0.6 H relative to the aryl and aliphatic regions. The broad resonance at δ 12.23 might correspond to an amido alkylidyne complex, Mo(NHAd)($CCMe_2Ph$)((±)-Biphen), which would arise from α-H migration from the neophylidene ligand to the 1-adamantylimido group. The reverse reaction, M(CR)(NHAr)$Cl_2$•DME → M(CHR)(NAr)$Cl_2$•DME, was used to prepare arylimido alkylidene complexes for molybdenum[103] and tungsten.[7] Presumably the increased basicity of the alkylimido relative to an arylimido ligand would shift the equilibrium towards the amido alkylidyne complex.

## 2.3. Synthesis of Mo(NAr)(CHR)(Biad) Complexes

A series of racemic and optically pure complexes containing the Biad ligand were prepared. (±)'(R)Mo(Neo) (R = $^i$Pr$_2$, $Me_2$) and (S)'(R)Mo(Neo) (R = $^i$Pr$_2$, $Et_2$, $Me_2$, 3,5-$Me_2$) were prepared by deprotonation of Biad$H_2$ with benzyl potassium in THF followed by addition of solid *bis*(triflate), **3a-d**, to the reaction mixture (Scheme 2.8, Table 2.4). Solid benzyl potassium was added to the THF solution of Biad$H_2$ until a pale orange color persisted, indicating complete coversion of Biad$H_2$ to Biad$K_2$. The reaction mixture was extracted with benzene, the suspension was filtered, and the eluent was crystallized from ether, diisopropyl ether or pentane. In a procedure similar to the method used to synthesize (±)($CF_3$)Mo(Np), toluene was employed as the reaction solvent for the preparation of (±) and (S)'($CF_3$)Mo(Np). Benzyl potassium was added as a solid to a toluene solution of (±)- or (S)-Biad$H_2$ and the mixture was stirred overnight. Addition of solid *bis*(triflate), **3g'**, to the stirred toluene suspension of (±)- or (S)-Biad$K_2$ generated

(±) or (S)'($CF_3$)Mo(Np). The complex was then extracted with pentane to remove potassium triflate and (±)'- and (S)'($CF_3$)Mo(Np) precipitated from concentrated pentane. All Biad complexes precipitated from pentane or an ethereal solvent ($OEt_2$ or $O^iPr_2$). Presumably, the rigid adamantyl substituents reduce the solubility of the complexes relative to the *tert*-butyl groups of the Biphen analogs.




**Scheme 2.8.** Synthesis of (±)- and (S)'($R_2$)Mo(Neo) and (±)- and (S)'($CF_3$)Mo(Np).

**Table 2.4.** Yields, Reaction Solvent and Crystallization Solvent for the Synthesis of Biad Complexes, (±) and (S)'($R_2$)Mo(Neo) and (±)- and (S)'($CF_3$)Mo(Np).

| Complex | Yield (±) | Yield (S) | Reaction Solvent | Crystallization Solvent |
|---|---|---|---|---|
| ($^iPr_2$)Mo(Neo) | 54% | 34% | THF | pentane |
| ($Et_2$)Mo(Neo) | -- | 30 | THF | pentane |
| ($Me_2$)Mo(Neo) | 33 | 44 | THF | $^iPr_2O$ |
| (3,5-$Me_2$)Mo(Neo) | -- | 38 | THF | pentane |
| ($CF_3$)Mo(Np) | 41 | 43 | toluene | pentane |

## 2.4. X-Ray Crystallography of (S)($^iPr_2$)Mo(Neo) and (S)'($CF_3$)Mo(Np)•py

Single crystals of (S)($^iPr_2$)Mo(Neo) and (S)'($CF_3$)Mo(Np)•py were grown and X-ray crystallographic studies were carried out by Dr. W. M. Davis to determine the molecular structure. Crystallographic data, collection parameters and refinement parameters for both complexes are given in Table 2.5 while selected bond lengths (Å),

angles (°), and torsion angles (°) are given in Table 2.6. The molecular structure of (S)($^{i}Pr_2$)Mo(Neo) along with the atom-labeling scheme is shown in Figure 2.2. The crystals of (S)($^{i}Pr_2$)Mo(Neo) suitable for X-ray crystallography were grown from concentrated diethyl ether at -25 °C. The catalyst crystallized in the $P2_1$ chiral monoclinic space group. This four-coordinate molybdenum imido alkylidene biphenoxide complex was related to a family of molybdenum and tungsten imido alkylidene *bis*(alkoxide) and biphenoxide complexes.[29,36,97] The *syn* rotamer of (S)($^{i}Pr_2$)Mo(Neo) selectively crystallized from solution which was similar to other Mo(NAr)(CHR)(OR')$_2$ complexes. The (S)-Biphen bite angle O(1)-Mo-O(2) was 127.0° which was similar to the biphenoxide bite angle of 123.5° in Mo(N-2,6-$Me_2C_6H_3$)(CHCMe$_2$Ph)((±)-$^{t}Bu_4Me_2$Biphen).[36] The torsion angle between the two aryl rings of the Biphen backbone was 102.2° which was identical to Mo(N-2,6-$Me_2C_6H_3$)(CHCMe$_2$Ph)($^{t}Bu_4Me_2$Biphen). The CNO(1) face was blocked by a Biphen *tert*-butyl group and one *iso*-propyl group of the arylimido ring and the CNO(2) face was relatively unobstructed by the ligand sphere. The arylimido ring was rotated approximately 40° relative to the Mo-C(1) alkylidene bond. The arylimido ring in Mo(N-2,6-$Me_2C_6H_3$)(CHCMe$_2$Ph)($^{t}Bu_4Me_2$Biphen) was orthogonal to the alkylidene bond.[36] Presumably the increased steric interaction of the *iso*-propyl substituents of the arylimido group and the *tert*-butyl substituents of the Biphen ligand caused the rotation of the arylimido ring.

Yellow blocks of (S)'($CF_3$)Mo(Np)•py (Figure 2.3) were grown from ether/pyridine and crystallized in the $P2_12_12_1$ space group. The unit cell contained two inequivalent (S)'($CF_3$)Mo(Np)•py molecules which were related by rotation about the arylimido group. Table 2.6 contains data for only one of the two inequivalent molecules. Table A.2 has the atomic coordinates for both inequivalent (S)'($CF_3$)Mo(Np)•py. The five-coordinate pyridine adduct was a distorted trigonal bipyramidal geometry with N(2A) (pyridine) and O(1A) (Biad) in the apical positions (N(2A)-Mo(1)-O(1A) = 165.1(4)°). The pyridine substituent was in the apical position after attack from the CNO(2A) face.[44]

**Table 2.5.** Crystallographic Data, Collection Parameters, and Refinement Parameters for (S)($^{i}Pr_2$)Mo(Neo) and (S)'($CF_3$)Mo(Np)•py.

| | **(S)($^{i}Pr_2$)Mo(Neo)** | **(S)'($CF_3$)Mo(Np)•py** |
|---|---|---|
| Identification Code | 97160 | 99079 |
| Empirical Formula | $C_{46}H_{61}MoNO_2$ | $C_{53}H_{63}F_3MoN_2O_2$ |
| Formula Weight | 755.90 | 912.99 |
| Crystal Dimensions (mm) | 0.20 x 0.20 x 0.20 | 0.15 x 0.15 x 0.30 |
| Crystal System | Monoclinic | Orthorhombic |
| Space Group | $P2_1$ | $P2_12_12_1$ |
| *a* (Å) | 10.7064(3) | 12.948(3) |
| *b* (Å) | 13.5262(5) | 28.452(6) |
| *c* (Å) | 14.8726(5) | 30.376(6) |
| α (°) | 90 | 90 |
| β (°) | 103.8060(10) | 90 |
| γ (°) | 90 | 90 |
| V (Å$^3$), Z | 2091.58(12), 2 | 11191(4), 8 |
| $D_{calc}$ (Mg/m$^3$) | 1.200 | 1.084 |
| Theta Range (°) | 1.41 to 23.24 | 1.34 to 20.00 |
| Diffractometer | Siemens SMART/CCD | Siemens SMART/CCD |
| λ($MoK_\alpha$) (Å) | 0.71073 | 0.71073 |
| Scan Type | ω | ω |
| Temperature (K) | 173(2) | 170(2) |
| Reflections collected | 8659 | 33558 |
| Independent Reflections | 5360 ($R_{int}$ = 0.0547) | 10427 ($R_{int}$ = 0.1033) |
| No. Parameters | 452 | 543 |
| $R_1$ (I>2σ(I), all data) | 0.0587, 0.0634 | 0.1119, 0.1312 |
| $wR_2$ (I>2σ(I), all data) | 0.1445, 0.1555 | 0.2789, 0.2991 |
| GooF | 1.191 | 1.199 |

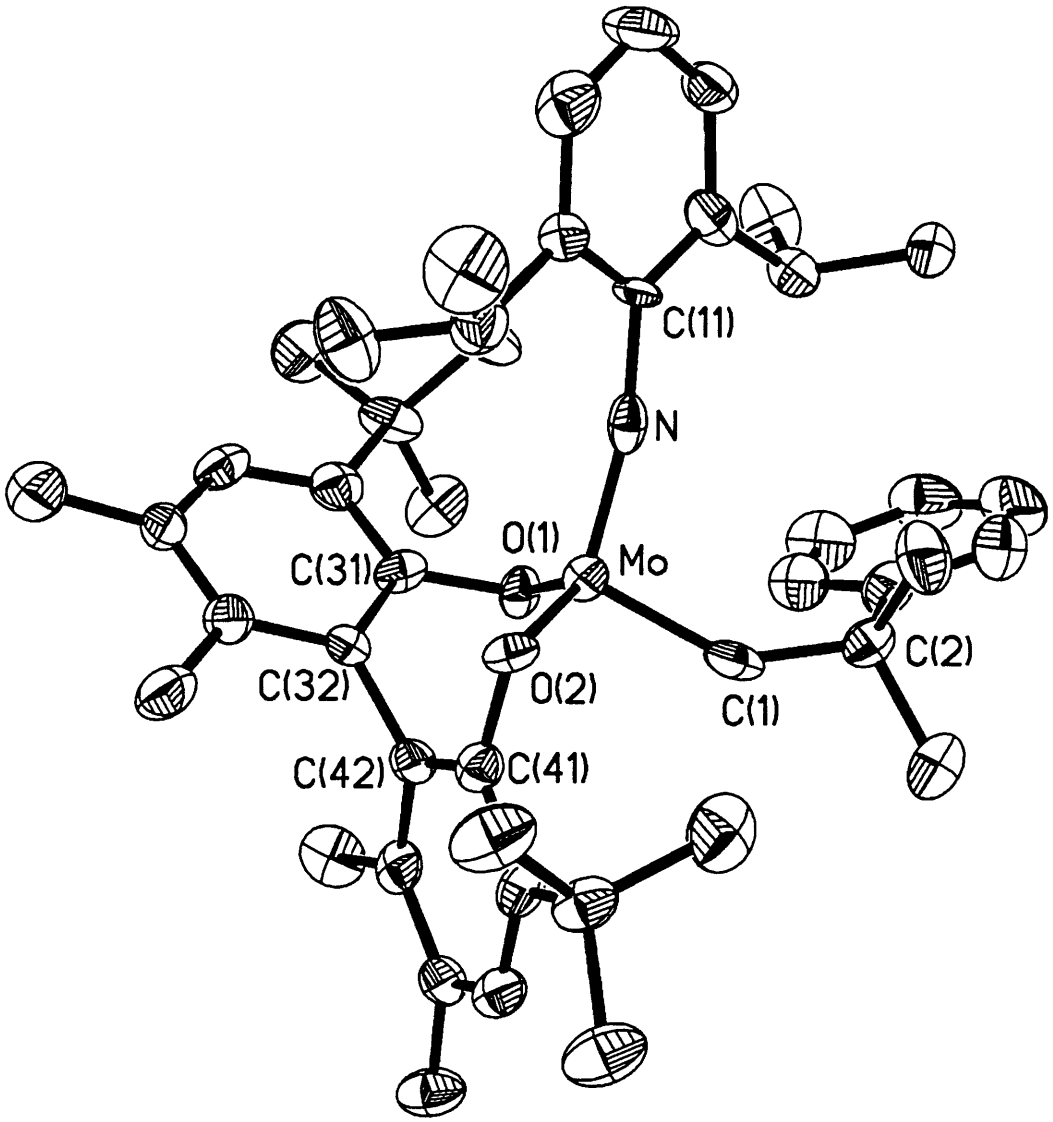



**Figure 2.2.** X-ray Crystal Structure of (S)($^{i}Pr_2$)Mo(Neo).

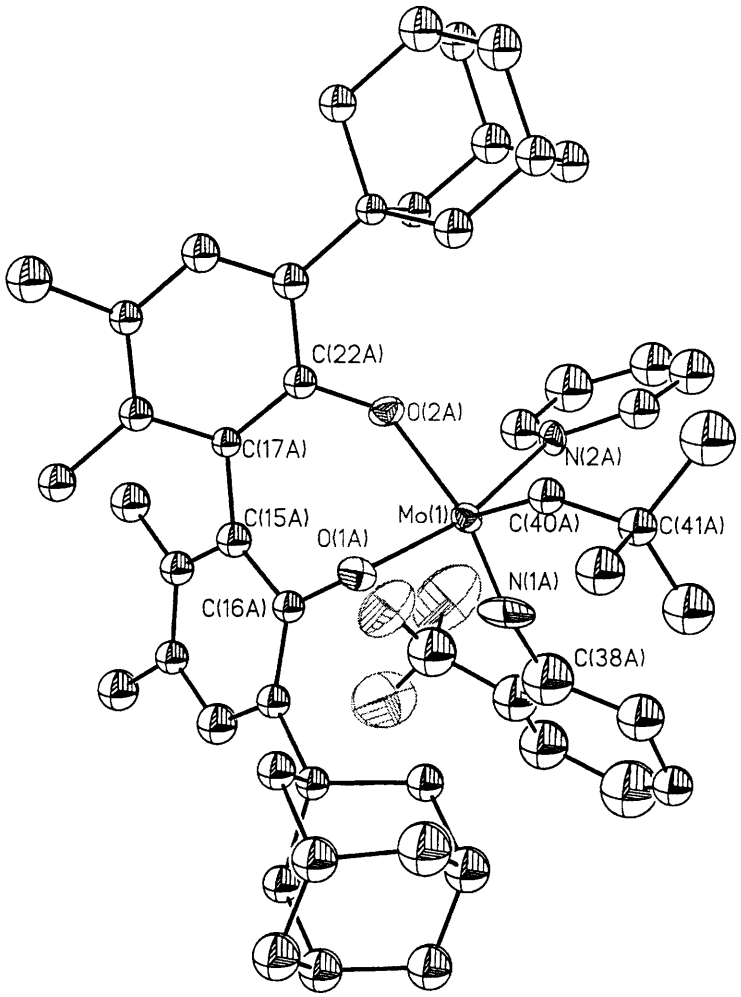



**Figure 2.3.** X-ray Crystal Structure of (S)'($CF_3$)Mo(Np)•py.

**Table 2.6.** Selected Interatomic Distances (Å) and Angles (°) for the Non-Hydrogen Atoms of (S)($^i$Pr$_2$)Mo(Neo) and (S)'($CF_3$)Mo(Np)•py.

**Bond Lengths (Å)**

| (S)($^i$Pr$_2$)Mo(Neo) | | (S)'($CF_3$)Mo(Np)•py | |
|---|---|---|---|
| Mo-O(1) | 1.999(5) | Mo(1)-O(1A) | 2.020(11) |
| Mo-O(2) | 2.006(5) | Mo(1)-O(2A) | 1.986(10) |
| Mo-C(1) | 1.885(10) | Mo-C(40A) | 1.90(2) |
| Mo-N | 1.738(6) | Mo-N(1A) | 1.70(2) |
| N-C(11) | 1.407(9) | Mo-N(2A) | 2.276(12) |
| C(1)-C(2) | 1.489(13) | C(40A)-C(41A) | 1.51(2) |
| O(1)-C(31) | 1.385(9) | O(1A)-C(16A) | 1.35(2) |
| O(2)-C(41) | 1.366(9) | O(2A)-C(22A) | 1.36(2) |

**Bond Angles (°)**

| (S)($^i$Pr$_2$)Mo(Neo) | | (S)'($CF_3$)Mo(Np)•py | |
|---|---|---|---|
| N-Mo-O(1) | 110.2(2) | N(1A)-Mo(1)-O(1A) | 101.2(6) |
| N-Mo-O(2) | 107.9(3) | N(1A)-Mo(1)-O(2A) | 136.7(7) |
| N-Mo-C(1) | 105.2(3) | N(1A)-Mo(1)-C(40A) | 107.1(8) |
| O(1)-Mo-O(2) | 127.0(2) | N(1A)-Mo(1)-N(2A) | 85.6(6) |
| Mo-O(1)-C(31) | 97.1(4) | N(2A)-Mo(1)-O(1A) | 165.1(4) |
| Mo-O(2)-C(41) | 96.8(4) | N(2A)-Mo(1)-O(2A) | 77.4(4) |
| Mo-C(1)-C(2) | 143.8(7) | N(2A)-Mo(1)-C(40A) | 95.3(6) |
| | | C(38A)-N(1A)-Mo(1) | 167.3(14) |
| | | C(41A)-C(40A)-Mo(1) | 148.0(13) |
| | | O(1A)-Mo(1)-O(2A) | 88.8(4) |
| | | O(1A)-Mo(1)-C(40A) | 95.3(6) |

**Dihedral Angles (°)**

| | | | |
|---|---|---|---|
| C(31)-C(32)-C(42)-C(41) | 102.2 | C(16A)-C(15A)-C(17A)-C(22A) | 72.3 |

(±)'($CF_3$)Mo(Np)•py was related to a family of molybdenum(VI) imido alkylidene *bis*(alkoxide) and binaphtholate base adducts. In particular, several X-ray structures have been obtained of five-coordinate molybdenum(VI) imido alkylidene binaphtholate base adducts. The Biad bite angle, O(1A)-Mo-O(2A), of 88.8(4)° (compared to 127° for pseudotetrahedral (S)($^i Pr_2$)Mo(Neo)). The biaryl torsion angle of 72.3° (C(16A)-C(15A)-C(17A)-C(22A)) was smaller than the torsion angle of 102.2° in (S)($^i Pr_2$)Mo(Neo). Five-coordinate, trigonal bipyramidal binaphtholate complexes, Mo(NAr)(CHCMe$_2$Ph)((R)-$R_2$BINO)•base (R = Ph, base = THF;[36] R = TRIP, base = py[104]) have similar bite angles (O-Mo-O), 87.8° and 86.5° respectively. The binaphthyl dihedral angle for Mo(NAr)(CHCMe$_2$Ph)((R)-$R_2$BINO)•base was 65.5° (R = Ph, base = THF) and 60.0° (R = TRIP, base = py). Presumably, the larger 1-adamantyl groups increase the biaryl dihedral angle of (S)'($CF_3$)Mo(Np)•py to minimize the steric repulsion of the Biad ligand with the other substituents around molybdenum. The arylimido ring was approximately coplanar with C(40A) and C(41A) of the neopentylidene ligand. The arylimido rings in the (S)-Biphen complex, (S)($^i Pr_2$)Mo(Neo), was twisted by approximately 40° and the arylimido ring in the related (±)$^t$Bu$_4$Me$_2$BiphenMe$_2$)Mo(Neo) was orthogonal to the neophylidene ligand. The arylimido ring in both Mo(NAr)(CHCMe$_2$Ph)((R)-$R_2$BINO)•base (R = Ph, base = THF; R = TRIP, base = py) were approximately coplanar with the neophylidene ligands.

The crystal structure of (S)($^i Pr_2$)Mo(Neo) provided the absolute stereochemistry of the Biphen ligand (Figure 2.4). With this information, it was possible to assign the resolved ligand as the (S) enantiomer. The chirality of the biaryl system was determined by examining the *ortho* substituents of both aryl rings and then ranking them as shown in Figure 2.4.[74,105] In this case, the oxygen substituents were ranked #1 and the methyl groups #2. Next the biaryl axis was oriented vertically on the page and the lower ring was placed in the plane of the paper with the #1' substituent of the ring perpendicular to the page above the plane of the paper. As with a chiral $sp^3$ stereogenic center, the three highest

ranked groups were connected by directional arrows in descending order (#1, #2, and #1') and the direction of orientation determines R (Clockwise) or S (Counterclockwise). The absolute stereochemistry of (-)-Biad$H_2$ was determined to be (S)-Biad$H_2$ from the structure of the (S)'($CF_3$)Mo(Np)•py.

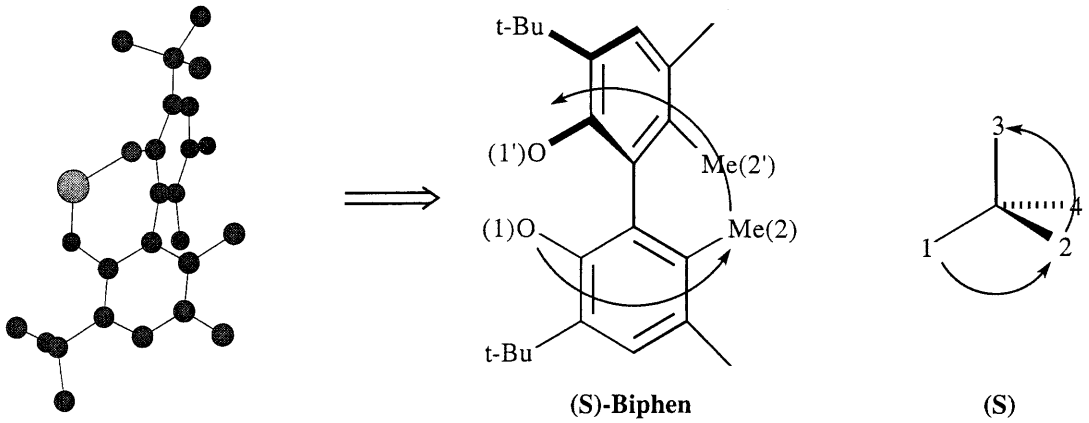


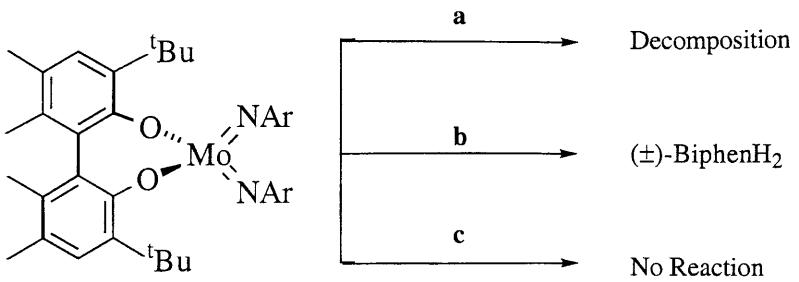

**Figure 2.4.** Determination of Absolute Stereochemistry for (S)-Biphen.

## 2.5. Approaches to Direct Catalyst Synthesis

A variety of Biphen$X_2$ (X = H, K, TMS) reagents were added to M(O)$Cl_4$ (M = W, Mo) and $Mo(O)_2Cl_2$ in hydrocarbon and ethereal solvents at both room temperature and -25 °C. In all cases, these reactions led to intractable, highly-colored, blue or purple solutions. The $^1$H NMR of the solid residue from these reactions contained several decomposition products of the Biphen ligand but there was never evidence for the formation of either M(O)$Cl_2$((±)-Biphen) or $Mo(O)_2$((±)-Biphen). Using the analogous imido complexes, W(N-2,6-$Me_2C_6H_3$)$Cl_4$•$OEt_2$ and Mo(NMes)$Cl_4$•THF (Mes = 2,4,6-$Me_3C_6H_2$), also led to the formation of intractable, highly colored solutions with Biphen$X_2$ (X = H, K).

Treatment of $Mo(NAr)_2Cl_2$•DME with (±)-Biphen$K_2$ in THF afforded $Mo(NAr)_2$((±)-Biphen) (Ar = 2,6-$^i$Pr$_2C_6H_3$, **5**; 2,6-$Me_2C_6H_3$, **6**). It was proposed that one arylimido group could be transformed into an alkylidene by direct alkylation or by a two step halogenation/alkylation. When triethyl aluminum was added to **5** and **6** in

pentane, the (±)-Biphen ligand was destroyed and in the case of **5** several isopropyl methine resonances were observed. Treatment of **5** and **6** with triethylamine hydrochloride in THF selectively deprotonated the (±)-Biphen ligand instead of an arylimido group. There was no reaction observed when **6** was treated with a 20-fold excess of methyl iodide at 80 °C for one week in toluene.




**a**) $AlEt_3$, toluene, 1h. **b**) $NEt_3$•HCl, THF, 1h. **c**) 20 eq MeI, toluene, 80 °C, 7 days.

**Scheme 2.9.** Reaction of **5** and **6** with $AlEt_3$, $NEt_3$•HCl, and MeI.

## CONCLUSIONS

Two series of optically pure molybdenum(VI) imido alkylidene biphenoxide complexes based on $C_2$-symmetric (S)-Biphen and (S)-Biad were prepared. Complexes containing (S)-Biphen with 2,6-heterodisubstituted arylimido ligands were difficult to precipitate. In only one case, (S)($^tBu_2$Me)Mo(Np), was an optically pure complex isolated as a crystalline solid. Replacing (S)-Biphen with the more sterically demanding (S)-Biad improved the crystallinity of Mo(NAr)(CHR)(biphenoxide) complexes. In particular, optically pure (S)($CF_3$)Mo(Neo) and (S)($CF_3$)Mo(Np) were not crystalline, but the Biad analog, (S)'($CF_3$)Mo(Np), readily precipitated from concentrated pentane. X-ray crystallographic studies of (S)($^iPr_2$)Mo(Neo) and (S)'($CF_3$)Mo(Np)•py proved the absolute stereochemistry of both biphenoxides. In addition, both complexes were structurally similar to other four- and five-coordinate molybdenum imido alkylidene catalysts.

## EXPERIMENTAL

**General Procedures.** Unless otherwise noted, all experiments were performed under rigorous exclusion of oxygen and moisture in a dinitrogen-filled glove-box or using standard Schlenk procedures. Ether, THF, and pentane were degassed with dinitrogen and passed through 2 1-gallon columns of activated alumina.[96] Toluene and benzene were distilled from sodium metal/benzophenone ketyl. Methylene chloride was distilled from calcium hydride. NMR spectra are taken on Varian instruments (75.4 or 125.8 MHz, $^{13}C$; 300 or 500 MHz, $^{1}H$). $^{1}H$ NMR spectra were referenced using residual protons in the deuterated solvents as follows: $\delta = 7.16$ $C_6D_6$, $\delta = 2.09$ toluene-$d_8$ ($CD_2H$); $^{13}C\{^{1}H\}$ NMR spectra were referenced as follows: $\delta = 128.4$ $C_6D_6$. All NMR spectra were taken at room temperature in $C_6D_6$ unless otherwise noted. Temperatures during variable temperature NMR studies were not calibrated. Benzyl potassium,[106] 2-methoxystyrene,[107] 2,4-di-*tert*-butyl-6-methylaniline,[101] $^{t}BuCH_2MgCl$,[108] $PhMe_2CCH_2MgCl$,[108] and the molybdenum bis(triflates) (**3a**, **3c**, **3e**, **3g** and **3h**)[30,32,98-100] were prepared according to literature procedures. Potassium hydride was purchased from Aldrich as a 35% dispersion in mineral oil, washed repeatedly with pentane and dried *in vacuo*. Isopropyl ether (Aldrich) was distilled from sodium and stored over 4Å molecular sieves for 1 day prior to use. All other reagents were used as received. $C_6D_6$ and toluene-$d_8$ (Cambridge Isotope Laboratories) were degassed with dinitrogen and dried over 4Å molecular sieves for approximately 1 day prior to use. Elemental analyses were performed in our laboratories on a Perkin Elmer 2400 CHN analyzer or at H. Kolbe, Mikroanalytisches Laboratorium (Mühlheim an der Ruhr, Germany).

### $Mo(N\text{-}2,6\text{-}Et_2C_6H_3)_2Cl_2 \cdot DME$ (1b)

Sodium molybdate (5 g, 24.3 mmol) was suspended in DME (200 mL). Triethylamine (4 eq, 9.8 g, 97.2 mmol) and 2,6-diethylaniline (2 eq, 7.24 g, 48.6 mmol) were added sequentially with rapid stirring over 5 minutes. Chlorotrimethylsilane (8 eq, 21 g, 194 mmol) was then introduced, the reaction vessel was sealed, and heated at 60 °C for

5 hours. The solution became brick red, and copious amounts of salt precipitated. The suspension was filtered through Celite, and the pad was washed with dimethoxyethane until only a pale orange color persisted in the pad. The volume was reduced to ~75 mL *in vacuo,* and the solution was stored overnight at -25 °C. Analytically pure dark red blocks were recovered from the DME solution (3.71 g). A second crop (1.6 g) was collected from diethyl ether (30 mL). The total yield was 5.3 g (40%): $^1$H NMR δ 6.90 (d, $J_{HH}$ = 7.2 Hz, 4 H, *m*-Ar), 6.81 (t, $J_{HH}$ = 7.2 Hz, 2 H, *p*-Ar), 3.40 (s, 6 H, $OCH_3$), 3.23 (q, $J_{HH}$ = 7.8 Hz, 8 H, $CH_2CH_3$), 3.32 (s, 4 H, $OCH_2$), 1.27 (t, $J_{HH}$ = 7.8 Hz, 8 H, $CH_2CH_3$); $^{13}C\{^1H\}$ δ 155.74, 140.79, 127.46, 126.52, 71.29, 63.06, 25.19, 16.57. Anal. Calcd for $C_{24}H_{36}Cl_2MoN_2O_2$: C 52.28, H 6.58, N 5.08. Found C 52.21, H 6.61, 5.08.

**[HNEt$_3$][Mo(N-2,4-$^t$Bu-6-MeC$_6$H$_2$)$_2$Cl$_3$]**

A 1 L pear shaped Schlenk flask was charged sequentially with sodium molybdate (10.3 g, 50 mmol), triethylamine (20.2 g, 200 mmol), 2,4-di-*tert*-butyl-6-methylaniline (21.9 g, 100 mmol) and DME (400 mL). The reaction vessel was sparged with nitrogen and chlorotrimethylsilane (54.2 g, 500 mmol) was added. A ground glass stopper was firmly attached with copper wire, and the sealed system was heated to 65 °C for 12 hours. The brick red solution was then filtered through Celite, and the precipitate was washed with DME until the pad was colorless. The red solution was concentrated *in vacuo* to give an oily residue. The red oil was taken up in diethyl ether (100 mL), and red needles precipitated (13 g, 35%): $^1$H NMR δ 8.30 (br s, 1H, *H*NEt$_3$), 7.46 (d, 2H, J = 1.8 Hz, Ar), 7.12 (d, 2H, J = 1.8 Hz, Ar), 3.06 (s, 6H, Me), 2.65 (d q, 6H, $CH_2$Me), 1.92 (s, 18H, $^t$Bu), 1.20 (s, 18H, $^t$Bu), 0.83 (t, 9H, $CH_2Me$); $^{13}C\{^1H\}$ NMR δ 155.04, 150.21, 144.80, 141.73, 127.21, 120.88, 46.89, 37.31, 35.38, 32.85, 31.91, 21.35, 9.08. Anal. Calcd for $C_{36}H_{62}Cl_3MoN_3$: C 58.46, H 8.45, N 5.68. Found C 52.90/52.95, H 8.15/8.10, N 5.24/5.26.

**[H-2,6-lutidine][Mo(N-2,4-$^t$Bu-6-MeC$_6$H$_2$)$_2$Cl$_3$]**

A 1 L pear shaped Schlenk flask was charged sequentially with sodium molybdate (11.29 g, 54.8 mmol), 2,6-lutidine (35.2 g, 329 mmol), 2,4-di-*tert*-butyl-6-methylaniline (28 g, 109.6 mmol) and DME (400 mL). The reaction vessel was sparged with nitrogen and chlorotrimethylsilane (59.4 g, 550 mmol) was added. A ground glass stopper was firmly attached with copper wire, and the sealed system was heated to 65 °C for 14 hours. The brick red solution was then filtered through Celite, and the precipitate was washed with ether until the pad was colorless. The red solution was concentrated *in vacuo* to a foam which was crushed to a powder, slurried in ether (400 mL) and cooled to -25 °C overnight. A bright red solid was collected by filtration, washed with pentane (100 mL) and dried *in vacuo* (33.3 g, 81%): $^1$H NMR δ 14.55 (br s, 1H, Hlut), 7.48 (d, 2H, J = 2.1 Hz, Ar), 7.13 (d, 2H, J = 2.7 Hz, Ar), 6.86 (t, 1H, J = 8.1 Hz, *p*-lut), 6.30 (d, 2H, J = 7.8 Hz, *m*-lut), 3.08 (s, 6H, Me), 2.46 (s, 6H, Me), 1.934 (s, 18H, $^t$Bu), 1.22 (s, 18H, $^t$Bu); $^{13}$C{$^1$H} NMR δ 155.11, 153.07, 150.30, 145.29, 144.84, 141.79, 127.23, 124.97, 120.90, 37.18, 35.22, 32.68, 31.73, 21.20, 20.15. Anal. Calcd for $C_{35}H_{56}Cl_3MoN_3$: C 59.64, H 7.57, N 5.64. Found (Kolbe) C 59.78, H 7.69, N 5.61.

**Mo(N-2,6-Et$_2$C$_6$H$_3$)$_2$(CH$_2$CMe$_2$Ph)$_2$ (2b)**

Mo(N-2,6-Et$_2$Ph)$_2$Cl$_2$•DME, **1b**, (5.02 g, 9.11 mmol) was dissolved in ether (100 mL) and precooled to -25 °C. Neophylmagnesium chloride (18.9 mL, 0.99 M in ether, 18.68 mmol) was added over 5 minutes with rapid stirring. The solution went from red to orange and a precipitate formed. After stirring at room temperature for 2 hours, the reaction was filtered through Celite, and the pad was washed with ether until it was pale yellow. The red solution was concentrated to 10 mL and orange blocks formed on standing at room temperature for one hour. The solution was then cooled to -25 °C for 3 hours. The supernatant was decanted, and the crystals of Mo(N-2,6-Et$_2$Ph)$_2$(CH$_2$CMe$_2$Ph)$_2$ were dried *in vacuo* (4.47 g, 75%): $^1$H NMR δ 7.41 (d, 4 H, *m*-Ar), 7.18 (t, $J_{HH}$ = 2 H, *p*-Ph), 7.05 (t, 2 H, *p*-Ar), 6.95-6.85 (m, 6 H, *o*-,*m*-Ph), 2.66

(q, 8 H, $CH_2CH_3$), 1.81 (s, 4 H, $MoCH_2R$), 1.46 (s, 12 H, $C(CH_3)_2Ph$), 1.07 (t, 12 H, $CH_2CH_3$). $^{13}C\{^1H\}$ NMR δ 155.25, 151.15, 138.42, 128.99, 126.93, 126.62, 126.05, 125.83, 78.90, 40.35, 32.72, 25.26, 14.92. Anal Calcd for $C_{40}H_{52}MoN_2$: C 73.15, H 7.98, N 4.27. Found C 73.29, H 8.38, N 4.24.

**Mo(N-2,4-$^t$Bu-6-Me$C_6H_2$)$_2$($CH_2{}^t$Bu)$_2$ (2f')**

A slurry of [$HNEt_3$][Mo(N-2,4-$^t$Bu-6-Me$C_6H_2$)$_2Cl_3$] (13 g, 17.58 mmol) in ether (250 mL) was cooled to -25 °C. Neopentylmagnesium chloride (24 mL, 2.27 M in ether, 54.5 mmol) was added over 5 minutes and the reaction was stirred at room temperature for 16 hours. The suspension was filtered and the precipitate washed with ether until the pad was colorless. The red solution was concentrated *in vacuo* and the residue was crystallized from ether (50 mL) at -25 °C. Orange crystals were collected by filtration (8.00 g, 68%): $^1H$ NMR 20 °C: δ 7.46 (br d, 2H, NAr), 7.01 (br d, 2H, NAr), 2.16 (s, 6H, Me), 1.82 (s, 18H, $^t$Bu), 1.24 (s, 18H, $^t$Bu), 1.19 (s, 18H, $^t$Bu). $^1H$ NMR ($C_7D_8$) -40 °C: δ 7.44 (br s, 2H, Ar), 6.96 (br s, 2H, Ar), 3.10 (br d, 2H, J = 14.4 Hz, $CH_aH_b{}^t$Bu), 2.07 (s, 6H, Me), 1.79 (s, 18H, $^t$Bu), 1.54 (br d, 2H, J = 13.5 Hz, $CH_aH_b{}^t$Bu), 1.21 (s, 18H, $^t$Bu), 1.14 (s, 18H, $^t$Bu); $^{13}C\{^1H\}$ NMR δ 154.46, 147.50, 140.28, 136.59, 126.47, 121.49, 84.96, 36.78, 35.22, 34.78, 34.22, 31.97, 31.35, 22.36. Anal. Calcd for C 71.39, H 10.19, N 4.16. Found (Kolbe) C 71.46, H 10.28, N 4.07.

**Mo(N-2-$CF_3C_6H_4$)$_2$($CH_2{}^t$Bu)$_2$ (2g')**

Neopentylmagnesium chloride (52 mL, 2.27 M in ether, 117.7 mmol) was added over 30 minutes to a cooled ether (500 mL) solution of Mo(N-2-$CF_3$Ph)$_2Cl_2$•DME, **1g**, (33.68 g, 58.6 mmol). The reaction mixture was stirred at room temperature for 12 hours and was then filtered through Celite. The pad was washed with ether until colorless. The clear red solution was then concentrated *in vacuo* to an oil. On standing overnight at -25 °C, the oil crystallized as red blocks (29 g, 73%): $^1H$ NMR δ 7.31 (d, 2H, Ar), 7.18 (d, 2H, Ar), 6.79 (t, 2H, Ar), 6.55 (t, 2H, Ar), 2.33 (s, 4H, $CH_2{}^t$Bu), 1.16 (s, 18H, $^t$Bu); $^{13}C\{^1H\}$ NMR δ 153.96, 132.85, 128.42, 126.42 (q, $J_{CF}$ = 5.7 Hz), 125.15, 124.93

(q, $J_{CF}$ = 294.4 Hz), 121.15 (q, $J_{CF}$ = 29.0 Hz), 86.49, 35.90, 33.52. Anal. Calcd for C 51.80, H 5.43, N 5.03. Found (Kolbe) C 51.65, H 5.53, N 4.92.

**Mo(N-1-adamantyl)$_2$($CH_2{}^tBu$)$_2$ (2h')**

Neopentylmagnesium chloride (22.1 mL, 2.27 M in ether, 50.25 mmol) was added over 5 minutes to a cold (-25 °C) solution of Mo(NAd)$_2$Cl$_2$•DME (13.875 g, 25 mmol), **1h** in ether (250 mL). The reaction was then stirred at room temperature for 24 hours and filtered through Celite. The pad was washed with ether (300 mL) and toluene (100 mL). The eluent was concentrated to a dark yellow residue which was dissolved in ether (50 mL). After the solution was left at -25 °C overnight, a tan powder was collected by filtration and dried *in vacuo* (8.3 g, 62%): $^1$H NMR δ 2.13 (br d, 12H, Ad-$CH_2$), 2.02 (br s, 6H, Ad-CH), 1.88 (s, 4H, $CH_2{}^tBu$), 1.58 (br q, 12 H, Ad-$CH_2$), 1.28 (s, 18H, $^t$Bu); $^{13}$C{$^1$H} NMR δ 74.92, 68.80, 46.76, 36.96, 34.56, 33.98, 30.64. Anal. Calcd for C 67.14, H 9.77, N 5.22. Found (Kolbe) C 67.24, H 9.77, N 5.29.

**Mo(N-2,6-$Et_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$•DME (3b)**

Triflic acid (3 eq, 2.925 g, 19.5 mmol) was dissolved in cold (-25 °C) DME (10 mL) and then added to a precooled DME (50 mL) solution of Mo(N-2,6-$Et_2$Ph)$_2$($CH_2CMe_2$Ph)$_2$, **2b**, (4.264 g, 6.5 mmol). After stirring at room temperature for 18 hours, the solution color went from orange to dark yellow. The volatiles were removed *in vacuo*, the yellow residue was extracted with cold toluene (~175 mL), and then filtered through Celite. The toluene was removed *in vacuo* and the solid extracted with ether (50 mL) to give a pale yellow powder (1.5 g) which was pure by $^1$H NMR. The ether eluent was then concentrated to 7 mL to give additional yellow powder (700 mg, total yield 44%): $^1$H NMR δ 14.28 (s, 1H, )Mo(CHR)), 7.62 (d, $J_{HH}$ = 8.4 Hz, 2H, *o*-Ph), 6.98 (t, $J_{HH}$ = 7.6 Hz, 1H, *p*-Ph), 6.80-6.66 (m, 5H, *m*-Ph+*m*-,*p*-Ar), 3.83 (s, 3H, OC$H_3$), 3.24 (br t, $J_{HH}$ = 5.1 Hz, 2H, OC$H_2$), 2.95-2.67 (m, 4H, diastereotopic C$H_2$CH$_3$), 2.82 (br t, $J_{HH}$ = 5.1 Hz, 2H, OC$H_2$), 2.67 (s, 3H, OC$H_3$), 1.77 (s, 6H, C$Me_2$Ph), 1.22 (t, 6H, $CH_2CH_3$); $^{13}$C{$^1$H} NMR δ 327.99, 153.05, 148.54, 146.88, 129.94, 128.50, 127.37,

126.84, 125.84, 120.33, 73.24, 70.18, 65.83, 61.74, 58.84, 30.69, 25.21, 13.89. Anal. Calcd for $C_{26}H_{35}F_6MoNO_8S_2$: C 40.90 H 4.62, N 1.83. Found: C 40.95, H 4.55, N 1.77.

**Mo(N-2,4-$^t$Bu-6-Me$C_6H_2$)(CH$^t$Bu)(OTf)$_2$•DME (3f')**

Triflic acid (5.25 g, 35 mmol) was dissolved in cold (-25 °C) DME (10 mL) and then added to a cold (-25 °C) suspension of Mo(N-2,4-$^t$Bu-6-Me$C_6H_2$)$_2$($CH_2{}^t$Bu)$_2$, **2f'**, (7.84 g, 11.67 mmol) in DME (125 mL). The reaction was stirred for 16 hours at room temperature and then concentrated *in vacuo* to a light brown solid. The product was extracted with benzene (100 mL) and filtered through Celite. The pad was washed with additional benzene until colorless and the solution was then concentrated *in vacuo* to a tan foam which was dissolved in ether (30 mL). A yellow powder precipitated which was collected by filtration, washed with ether until the solid was bright yellow and dried *in vacuo* (5.4 g, 60%): $^1$H NMR δ 14.16 (s, 1H, C*H*$^t$Bu), 7.38 (d, 1H, J = 1.8 Hz, Ar), 7.06 (d, 1H, J = 1.8 Hz, Ar), 3.97 (s, 3H, OC*H*$_3$), 3.60 (br t, 1H OC*H*$_2$), 2.98 (br t, 2H, OC*H*$_2$), 1.74 (br s, 7H, overlapped ArMe, OC*H*$_3$, and 1 OC*H*$_2$), 1.60 (s, 9H, $^t$Bu), 1.43 (s, 9H, $^t$Bu), 1.14 (s, 9H, $^t$Bu); $^{13}$C{$^1$H} δ 329.06, 153.19, 153.14, 150.66, 145.29, 127.20, 121.95, 72.98, 70.67, 66.69, 61.83, 53.84, 37.07, 35.60, 31.47, 30.92, 22.93. Anal. Calcd for C 40.47, H 5.62, N 1.82. Found (Kolbe) C 40.68, H 5.75, N 1.76.

**Mo(N-2-$CF_3C_6H_4$)(CH$^t$Bu)(OTf)$_2$•DME (3g')**

Triflic acid (15.9 g, 105.9 mmol) was dissolved in cold DME (50 mL) and then added to a cold (-25 °C) solution of Mo(N-2-$CF_3$Ph)$_2$($CH_2{}^t$Bu)$_2$, **2g'**, (19.63 g, 35.3 mmol) in DME (200 mL) . The reaction was stirred at room temperature for 16 hours and then concentrated *in vacuo* to a brown solid. Toluene (50 mL) was added and the solution was concentrated again *in vacuo* to remove residual DME. The brown residue was then extracted with toluene (250 mL) and benzene (200 mL) and filtered through Celite. The solution was concentrated *in vacuo*. The resulting brown solid was triturated with ether to give a yellow powder that was collected by filtration (16.3 g, 65%): $^1$H NMR (4:1 Mixture

of rotamers) Major δ 14.02 (s, 1H, C*H*$^t$Bu), 8.38 (d, 2H, Ar), 7.04 (d, 2H, Ar), 6.82 (t, 2H, Ar), 6.52 (t, 2H, Ar), 3.65 (br s, 3H, OC$H_3$), 3.22 (br s, 2H, OC$H_2$), 2.82 (br s, 5H, OC$H_3$ and OC$H_2$), 1.44 (s, 9H, $^t$Bu). Minor δ 15.03 (s, 1H, C*H*$^t$Bu), 8.38 (d, 2H, Ar), 7.04 (d, 2H, Ar), 6.82 (t, 2H, Ar), 6.52 (t, 2H, Ar), 3.59 (s, 3H, OC$H_3$), 3.42 (br t, 1H, OC$H_2$), 3.15 (s, 4H, OC$H_3$ and one OC$H_2$), 2.64 (br t, 1H, OC$H_2$), 1.21 (s, 9H, $^t$Bu); $^{13}C\{^1H\}$ δ 329.53, 151.78, 133.88, 133.54, 133.48, 133.41, 129.85, 129.54, 126.45, 126.22, 124.99, 124.48, 124.25, 122.82, 122.29, 121.72, 119.20, 116.67, 78.16, 77.58, 74.23, 70.56, 70.33, 65.40, 62.17, 61.44, 54.42, 53.92, 31.27, 30.91. Anal. Calcd for C 30.30, H 3.39, N 1.96. Found (Kolbe) C 30.36, H 3.37, N 2.00.

**Mo(N-1-adamantyl)(CH$^t$Bu)(OTf)$_2$•DME (3h')**

Triflic acid (1.679 g, 11.2 mmol) was dissolved in cold DME (5 mL) and then added to a cold (-25 °C) solution of Mo(NAd)$_2$(CH$_2$$^t$Bu)$_2$, **2h'**, (2.00 g, 3.7 mmol) in DME (30 mL) and toluene (30 mL). The reaction was stirred for 4 hours at room temperature and concentrated *in vacuo* to a tan solid. The product was extracted with benzene (50 mL), the suspension was filtered trough Celite and the pad was washed with additional benzene (50 mL). The solution was concentrated *in vacuo*, triturated with ether (10 mL) and collected as an off-white powder by filtration (1.35 g, 52%): $^1H$ NMR (3:1 Mixture of rotamers) Major δ 13.79 (s, 1H, C*H*$^t$Bu), 3.18 (br s, 6H, OC$H_3$), 3.02 (br s, 4H, OC$H_2$), 2.34 (br s, 6H, Ad-C$H_2$), 1.83 (br s, 3H, Ad-C*H*), 1.54 (s, 9H, $^t$Bu), 1.53 (s, 9H, $^t$Bu), 1.39 (br AB q, 6H, Ad-C$H_2$). Minor 14.85 (br s, 1H, C*H*$^t$Bu), 3.29 (br s, 4H, OC$H_2$), 3.24 (s, 6H, OC$H_3$), 2.07 (br AB q, 6H, Ad-C$H_2$), 1.86 (br s, 3H, Ad-C*H*), 1.31 (s, 9H, $^t$Bu), 1.286 (br s, 6H, Ad-C$H_2$); $^{13}C\{^1H\}$ NMR Mixture of rotamers: δ 322.02, 321.85, 120.58 ($J_{CF}$ = 319 Hz), 80.44, 78.50, 71.34 (br s), 70.02, 62.78, 60.91, 48.35, 48.12, 43.93, 43.52, 40.57, 35.91, 35.88, 35.19, 31.61, 31.38, 29.86, 29.73, 29.29. Anal. Calcd for C 35.85, H 5.01, N 1.99. Found (Kolbe) C 35.95, H 5.12, N 2.10.

**Mo(N-2,6-$^{i}Pr_2C_6H_3$)(CHCMe$_2$Ph)((±)-Biphen) ((±)($^{i}Pr_2$)Mo(Neo))**

Potassium hydride (2.2 eq, 440 mg, 11 mmol) was added in portions to a stirred THF (40 mL) solution of (±)-BiphenH$_2$ (1.77 g, 5 mmol). After 3 hours, solid Mo(N-2,6-$^{i}Pr_2$Ph)(CHCMe$_2$Ph)(OTf)$_2$•DME, **3a**, (3.955 g, 5 mmol) was added. The red solution was stirred for 2 hours and then concentrated *in vacuo*. The residue was extracted with benzene (10 mL), the suspension was filtered trough Celite, and the pad was washed with benzene until colorless. The benzene was removed *in vacuo*, the residue was taken up in diethyl ether (18 mL) and transferred to a 20 mL vial. On standing for 12 hours uncapped in a well purged glovebox, the volume had decreased to ~5 mL. The red solution was decanted, the red blocks were washed with cold ether and dried *in vacuo* (2.71 g, 72%): $^{1}$H NMR (Mixture of rotamers, $K_{eq}$ = 17.5) *syn* δ 10.98 (s, 1H, $J_{CH}$ = 123 Hz, )Mo(CHR)), 7.42 (m, 3H, Biphen and *o*-Ph), 7.16 (m, 3H, Biphen and *m*-Ph), 7.05 (br t, J=7.6 Hz, 1H, *p*-Ph), 6.92 (s, 3H, Ar), 3.70 (heptet, $J_{HH}$ = 7.0 Hz, 2H, C*H*Me$_2$), 2.13 (s, 3H, Biphen), 2.15 (s, 3H, Biphen), 1.85 (s, 3H, Biphen), 1.74 (s, 3H, Biphen), 1.66 (s, 3H, C(C*H*$_3$)(MePh), 1.59 (s, 9H, $^{t}$Bu), 1.54 (s, 9H, $^{t}$Bu), 1.14 (d, J = 7.0 Hz, 6H, CH(C*H*$_3$)(Me), 1.13 (s, 3H, C(C*H*$_3$)(MePh), 0.90 (d, J = 7.0 Hz, 6H, CH(C*H*$_3$)(Me). *anti* δ 12.77 (s, 1H, Mo(C*H*R)); $^{13}$C{$^{1}$H} NMR δ 277.1 (d, $J_{CH}$=123 Hz), 155.4, 154.5, 154.3, 151.3, 146.8, 140.0, 138.0, 136.5, 135.7, 132.0, 131.1, 130.9, 130.6, 129.6, 128.2, 127.9, 126.3, 123.8, 53.7, 34.0, 35.7, 34.7, 33.1, 33.0, 30.9, 30.4, 29.2, 24.6, 23.0, 20.8, 20.7, 17.2, 16.7, 14.6. Anal. Calcd for $C_{46}H_{61}MoNO_2$: C 73.09, H 8.13, N 1.85. Found C 72.98, H 8.44, N 1.66.

**Mo(N-2,6-Et$_2$C$_6$H$_3$)(CHCMe$_2$Ph)((±)-Biphen) ((±)(Et$_2$)Mo(Neo))**

Potassium hydride (3 eq, 190 mg, 3 mmol) was added in portions to a stirred THF (10 mL) solution of (±)-BiphenH$_2$ (561 mg, 1.58 mmol). After stirring for 18 hours at room temperature, solid Mo(N-2,6-Et$_2$Ph)(CHCMe$_2$Ph)(OTf)$_2$•DME, **3b**, (1.21 g, 1.6 mmol) was added, and the solution became ruby red. After stirring for 3 hours, the solution was concentrated *in vacuo*. The red solid was extracted with benzene (10 mL), the

suspension was filtered trough Celite, and the pad was washed with additional benzene until colorless. The benzene was removed *in vacuo,* and the residue was crystallized from ether (5 mL). Red crystals of (±)($Et_2$)Mo(Neo) formed on standing for 1 hour at room temperature (550 mg). Reducing the volume of the liquor afforded additional precipitate (180 mg, 60% combined yield). $^1$H NMR (Mixture of rotamers, $K_{eq}$ = 110) *syn* δ 11.04 (s, 1H, $J_{CH}$ = 121 Hz, )Mo(CHR)), 7.45 (s, 1H, Biphen), 7.39 (br s, 2H, *o*-Ph), 7.36 (s, 1H, Biphen), 7.16 (t, 2H, $J_{HH}$ = 6.7 Hz, *m*-Ph), 7.00 (t, 1H, $J_{HH}$ = 6.7 Hz, *p*-Ph), 6.83 (br s, 3 H, Ar), 2.80 (q, 4H, $J_{HH}$ = 7.4 Hz, $CH_2CH_3$), 2.14 (s, 3H, Biphen), 2.03 (s, 3H, Biphen), 1.78 (s, 3H, Biphen), 1.76 (s, 3H, Biphen), 1.68 (s, 3H, $C(CH_3)$(MePh), 1.60 (s, 9H, Biphen), 1.54 (s, 9H, Biphen), 1.20 (s, 3H, $C(CH_3)$(MePh), 1.06 (t, 6H, $J_{HH}$ = 7.4 Hz, $CH_2CH_3$). *anti* δ 12.94 (s, 1H, )Mo(CHR)); $^{13}C\{^1H\}$ NMR δ 277.51, 155.62, 155.00, 153.74, 151.17, 142.55, 140.25, 138.48, 136.62, 135.70, 132.12, 131.11, 130.95, 130.74, 130.61, 129.80, 128.56, 127.83, 127.35, 126.29, 126.00, 53.82, 36.02, 35.73, 32.69, 30.79, 30.47, 25.67, 20.85, 20.73, 17.30, 16.77, 14.62. Anal. Calcd for $C_{44}H_{57}Cl_2MoNO_2$: C 72.61, H 7.89, N 1.92. Found (Kolbe) C 72.50, H 7.80, N 2.13.

**Mo(N-2,6-$Me_2C_6H_3$)(CHC$Me_2$Ph)((±)-Biphen) ((±)($Me_2$)Mo(Neo))**

To a THF (50 mL) solution of (±)-Biphen$H_2$ (708 mg, 2 mmol) was added potassium hydride (3 eq, 120 mg, 3 mmol). After stirring for 18 hours, solid Mo(N-2,6-$Me_2$Ph)(CHC$Me_2$Ph)(OTf)$_2$•DME, **3c**, (1.446 g, 2 mmol) was added and the red solution was stirred for 3 hours. The solution was then concentrated *in vacuo*. The residue was extracted with benzene (40 mL), the suspension was filtered trough Celite, and the pad was washed with benzene until the eluent was colorless. After removing the benzene *in vacuo*, the residue was triturated with ether (10 mL). The resulting orange powder was collected by filtration, washed with ether (5 mL) and dried *in vacuo* (1.06 g, 77%): $^1$H NMR (Mixture of rotamers, $K_{eq}$ = 244) *syn* δ 11.01 (s, 1H, $J_{CH}$ = 121 Hz, )Mo(CHR)), 7.39 (s, 1H, Biphen), 7.25 (d, 2H, *o*-Ph), 7.11 (s, 1H, Biphen), 7.05 (t, 2H, *m*-Ph), 6.88 (t,

1H, *p*-Ph), 6.63 (s, 3H, Ar), 2.22 (s, 6H, ArC*H*$_3$), 2.10 (s, 3H, Biphen), 1.97 (s, 3H, Biphen), 1.72 (s, 3H, Biphen), 1.61 (s, 3H, Biphen), 1.56 (s, 3H, C(C*H*$_3$)(MePh), 1.53 (s, 9H, $^t$Bu), 1.50 (s, 9H, $^t$Bu), 1.20 (s, 3H, C(C*H*$_3$)(MePh). *anti* δ 13.03 (s, 1H, Mo(C*H*R)); $^{13}$C{$^1$H} NMR δ 278.94 (d, $J_{CH}$ = 120.6 Hz), 155.97, 155.10, 154.18, 150.94, 140.16, 138.28, 137.16, 136.82, 135.65, 132.10, 131.04, 130.91, 130.82, 130.47, 130.05, 128.51, 128.31, 127.38, 127.25, 236.35, 54.16, 36.00, 35.76, 32.83, 31.93, 30.92, 30.56, 20.84, 20.73, 19.80, 17.34, 16.82. Combustion analysis was performed on the pyridine adduct, (±)(Me$_2$)Mo(Neo)•py Anal. Calcd for $C_{47}H_{58}MoN_2O_2$: C 72.47, H 7.51, N 3.60. Found C 72.06, H 7.74, N 3.49.

**Mo(N-2-$^t$BuC$_6$H$_4$)(CHCMe$_2$Ph)((±)-Biphen) ((±)($^t$Bu)Mo(Neo))**

Benzyl potassium (2.1 eq, 280 mg, 2.1 mmol) was added to a stirred solution of (±)-BiphenH$_2$ (354 mg, 1 mmol) in THF (10 mL). After 15 minutes, solid Mo(N-2-$^t$BuC$_6$H$_4$)(CHCMe$_2$Ph)(OTf)$_2$•DME, **3e**, (763 mg, 1 mmol) was added and the solution became dark red. After stirring at room temperature for two hours, the reaction was concentrated *in vacuo* and the residue was extracted with benzene (10 mL). The benzene solution was filtered through Celite and the pad was washed with benzene (20 mL) until colorless. The benzene was removed *in vacuo* and the residue taken up in ether and cooled to -25 °C. No precipitate formed overnight and the ether was removed *in vacuo* (650 mg, 90%). A portion of the red solid was taken up in $C_6D_6$ and the $^1$H NMR spectrum was collected. $^1$H NMR Mixture of rotamers $K_{eq}$ = 104: *Syn*: δ 10.98 (s, 1H, $J_{CH}$ = 120 Hz, C*H*R), 7.43 (d, 2H), 7.40 (s, 1H), 7.22 (t, 2H), 7.05-6.85 (m, 2H), 6.80 (br t, 1H), 2.15 (s, 3H, Biphen), 2.10 (s, 3H, Biphen), 1.80 (s, 3H, Biphen), 1.75 (s, 3H, Biphen), 1.73 (s, 3H, C(C*H*$_3$)(MePh), 1.68 (s, 9H), 1.63 (s, 9H), 1.35 (s, 9H), 1.20 (s, 3H, C(C*H*$_3$)(MePh); *Anti* δ 12.13 (s, 1H, C*H*R); $^{13}$C{$^1$H} NMR δ 276.53, 156.05, 154.67, 152.67, 152.57, 155.25, 145.50, 140.07, 139.41, 136.28, 135.71, 133.44, 131.75, 131.14, 131.07, 130.76, 130.39, 129.76, 129.66, 128.90, 128.78, 127.49, 127.40, 126.46, 126.35, 126.17, 54.63, 36.05, 35.74, 35.71, 33.23, 32.50, 30.73, 30.42,

30.10, 20.88, 20.71, 17.20, 16.73. Anal Calcd for $C_{44}H_{57}MoNO_2$: C 72.61, H 7.89, N 1.92. Found C 72.46, H 7.96, N 7.93.

**Mo(N-2-$^t$BuC$_6$H$_4$)(CH-2-MeOC$_6$H$_4$)((±)-Biphen) ((±)($^t$Bu)Mo(Sty))**

Benzyl potassium (546 mg, 4.2 mmol) was added in portions to a THF (15 mL) solution of (±)-BiphenH$_2$ (708 mg, 2 mmol). After stirring for 15 minutes, solid Mo(N-2-$^t$BuC$_6$H$_4$)(CHCMe$_2$Ph)(OTf)$_2$•DME, **1e**, (1.526 g, 2 mmol) was added and the reaction became dark red. After stirring for one hour, the solution was concentrated *in vacuo*, the residue was extracted with toluene (10 mL) and the suspension was filtered through Celite. The pad was washed with additional toluene until it was colorless. The toluene solution was concentrated *in vacuo* to afford a brown residue which was dissolved in ether (10 mL). 2-Methoxystyrene was added with vigorous stirring and the reaction became heterogeneous after 15 minutes. An olive green powder was isolated by filtration, washed with ether (5 mL) and dried *in vacuo* (340 mg, 24%): $^1$H NMR δ 12.84 (s, 1H, $J_{CH}$ = 151.5 Hz, C*H*Ar), 7.77 (dd, 1H, $J_{HH}$ = 7.5, 1.5 Hz, Ar), 7.28 (s, 1H, Biphen), 7.16 (s, 1H, Biphen), 7.14 (dd, 1H, $J_{HH}$ = 8.0, 1.0 Hz, Ar), 7.08 (td, 1H, $J_{HH}$ = 7.5, 1.0 Hz, Ar), 6.89 (td, 1H, $J_{HH}$ = 7.5, 1.5 Hz, Ar), 6.85 (td, 1H, $J_{HH}$ = 7.5, 0.5 Hz, Ar), 6.58 (td, 1H, $J_{HH}$ = 8.0, 1.5 Hz, Ar), 6.43 (td, 1H, $J_{HH}$ = 7.5, 1.0 Hz, Ar), 3.23 (s, 3H, OC*H*$_3$), 2.19 (s, 3H, Biphen), 2.10 (s, 3H, Biphen), 1.81 (s, 3H, Biphen), 1.67 (s, 3H, Biphen), 1.50 (s, 9H, $^t$Bu), 1.36 (s, 9H, $^t$Bu), 1.23 (s, 9H, $^t$Bu); $^{13}$C{$^1$H} NMR δ 256.19, 160.91, 158.74, 155.26, 154.99, 145.20, 139.43, 137.28, 136.86, 136.76, 135.59, 135.08, 131.28, 130.99, 130.74, 130.43, 129.54, 128.48, 127.44, 126.45, 125.68, 122.50, 120.24, 109.88, 58.72, 36.02, 35.81, 35.75, 30.69, 30.46, 30.30, 20.99, 20.83, 17.26, 17.08. Anal. Calcd for $C_{40}H_{53}MoNO_3$: C 69.45, H 7.72, N 2.02. Found C 69.54, H 7.77, N 1.96.

**Mo(N-2-$CF_3C_6H_4$)(CHCMe$_2$Ph)((±)-Biphen)•$THF_{0.5}(OEt_2)_{0.5}$**

**((±)($CF_3$)Mo(Neo)•$THF_{0.5}(OEt_2)_{0.5}$)**

Solid benzyl potassium (2.02 eq, 1.29 g, 10.32 mmol) was added in portions over 10 minutes to a stirred THF (50 mL) solution of (±)-Biphen$H_2$ (1.827 g, 5.16 mmol) at room temperature. After stirring for 15 minutes, solid Mo(N-2-$CF_3$Ph)(CHCMe$_2$Ph)$(OTf)_2$•DME, **3g**, (4.00 g, 5.16 mmol) was added to the reaction and the solution became dark red. The solution was stirred for two hours and then concentrated *in vacuo* to a red-brown solid. The residue was extracted with benzene (25 mL), the suspension was filtered through Celite, and the pad was washed with toluene until it was colorless. The eluent was then concentrated *in vacuo* and the residue was dissolved in ether (10 mL). The ethereal solution was filtered through a Kimwipe and the volume halved. Addition of THF (1 eq, 371 mg, 5.16 mmol) and vigorous scoring of the vial wall with a spatula induced precipitation of a dark yellow solid that was collected by filtration, washed with ether (2 mL), and dried *in vacuo* (2.01 g, 52%): $^1$H NMR δ 11.07 (s, 1H, C*H*R), 7.46 (d, $J_{HH}$ = 5.6 Hz, 2H, Ph), 7.45 (s, 1H, Biphen), 7.19 (t, $J_{HH}$ = 8.1 Hz, 2H, Ph), 7.17 (s, 1H, Biphen), 7.09 (d, $J_{HH}$ = 8.1 Hz, 1H, Ph), 7.02 (t, $J_{HH}$ = 7.5 Hz, 1H, Ar), 6.79 (m, 1H, Ar), 6.49 (t, $J_{HH}$ = 7.5 Hz, 1H Ar), 3.58 (THF), 3.27 ($OEt_2$), 2.13 (s, 3H, Biphen), 2.06 (s, 3H, Biphen), 1.73 (s, 3H, Biphen), 1.72 (s, 3H, Biphen), 1.70 (s, 3H, C(C*H*$_3$)(MePh), 1.66 (s, 9H, $^t$Bu), 1.57 (s, 9H, $^t$Bu), 1.39 (THF), 1.25 (s, 3H, C(C*H*$_3$)(MePh), 1.13 ($OEt_2$); $^{13}$C{$^1$H} NMR δ 281.14, 154.71, 153.71, 151.80, 139.67, 139.30, 136.20, 135.83, 132.01, 131.69, 131.36, 131.05, 130.69, 130.59, 130.46, 129.97, 128.82, 127.46, 126.42, 126.03 (q, $J_{CF}$ = 5.5 Hz), 68.97 (br), 66.26, 55.09, 36.14, 35.78, 32.99, 31.92, 30.77, 30.63, 26.13, 20.87, 20.73, 17.26, 16.92, 15.94.

**Mo(N-2-$CF_3$Ph)(CHCMe$_2$Ph)((±)-Biphen) ((±)($CF_3$)Mo(Neo))**

Solid benzyl potassium (2.2 eq, 58 mg, 0.44 mmol) was added in portions to a solution of (±)-Biphen$H_2$ (71 mg, 0.2 mmol) in toluene (5 mL). After 2 hours, solid

Mo(N-2-$CF_3C_6H_4$)(CHCMe$_2$Ph)(OTf)$_2$•DME, **3g**, (155 mg, 0.2 mmol) was added to the reaction and the resulting red solution was stirred for 45 minutes. The volatiles were removed *in vacuo* and the residue extracted with pentane (15 mL). The suspension was passed through Celite, and the pentane was removed *in vacuo* affording (±)($CF_3$)Mo(Neo) as a red powder (75 mg, 51%): $^1$H NMR Mixture of rotamers $K_{eq}$ = 0.26: *syn:* δ 11.69 (br s, *anti* C*H*R), 10.84 (s, *syn* C*H*R), 7.58 (dd), 7.52 (br d), 7.42 (s), 7.40 (dd), 7.30 (br s), 7.27 (d, $J_{HH}$ = 8 Hz), 7.2-6.85 (m), 6.79 (t, $J_{HH}$ = 8 Hz), 6.7-6.4 (m), 2.16 (s), 2.14-2.10 (m), 2.06 (s), 2.05 (s), 1.96 (s), 1.92 (s), 1.89 (s), 1.76 (s), 1.70-1.66 (m), 1.62 (s), 1.56-1.54 (two singlets), 1.53-1.49 (m), 1.45 (s), 1.44 (s), 1.43 (s), 1.39 (br d), 1.32 (s), 1.23 (s), 1.21 (s) 1.18-1.14 (m); $^{13}$C{$^1$H} NMR δ (Mixture of *syn* and *anti*) 316.15, 279.60, 161.83, 160.59, 156.70, 154.41, 154.13, 153.76, 153.20, 151.91, 151.25, 150.97, 148.85, 139.72, 139.56, 139.40, 138.22, 136.93, 136.28, 136.23, 135.94, 135.75, 135.65, 135.62, 135.43, 134.91, 134.76, 134.60, 134.14, 133.25, 133.22, 132.70, 132.42, 132.00, 131.96, 131.87, 131.64, 131.53, 131.28, 131.25, 131.14, 130.85, 130.67, 130.56, 130.23, 130.14, 129.94, 129.87, 129.72, 129.66, 129.32, 129.30, 129.00, 128.90, 128.80, 128.26, 127.52, 126.98, 126.83, 126.65, 126.43, 126.39, 82.67, 71.99, 68.18, 66.27, 62.56, 60.92, 59.06, 55.17, 42.50, 36.21, 36.18, 35.77, 35.54, 35.50, 35.29, 35.15, 33.55, 33.25, 33.01, 32.66, 32.04, 31.39, 31.02, 30.76, 30.71, 30.69, 30.60, 30.54, 30.20, 29.85, 29.52, 29.17, 28.87, 23.08, 21.78, 21.03, 20.92, 20.88, 20.76, 20.64, 20.46, 20.20, 17.41, 17.27, 17.09, 17.06, 16.91, 16.65, 16.56, 16.53, 16.34, 15.95. Anal. Calcd for $C_{41}H_{48}F_3MoNO_2$: C 66.47, H 6.54, N 1.89. Found C 66.55, H 6.65, N 2.01.

**Mo(N-2-$CF_3$Ph)(CH$^t$Bu)((±)-Biphen) ((±)($CF_3$)Mo(Np))**

Solid benzyl potassium (286 mg, 2.2 mmol) was added in portions to a toluene (20 mL) solution of (±)-Biphen$H_2$ (354 mg, 1 mmol) at room temperature. After stirring for 5 hours, the reaction was cooled to -25 °C and solid Mo(N-2-$CF_3$Ph)(CH$^t$Bu)(OTf)$_2$•DME, **3g'**, (714 mg, 1 mmol) was added. The reaction was stirred at room temperature for 45

min and then concentrated *in vacuo*. The residue was extracted with pentane (40 mL), the suspension was filtered through Celite, and the pad was washed with pentane until the eluent was very pale red. The eluent volume was reduced to 4 mL, and the solution was cooled to -25 °C overnight. The red precipitate of (±)($CF_3$)Mo(Np) was collected by filtration, washed with cold pentane (1 mL), and dried *in vacuo* (260 mg, 38%): $^1$H NMR (Mixture of rotamers, $K_{eq}$ = 31.4) δ *syn*: 10.61 (s, 1H, C*H*$^t$Bu), 7.59 (d, 1H, J = 8.1 Hz, Ar), 7.48 (s, 1H, Biphen), 7.16 (s, 1H, Biphen), 7.12 (d, 1H, J = 6.9 Hz, Ar), 6.91 (t, 1H, J = 7.5, Ar), 6.52 (t, 1H, J = 7.5 Hz, Ar), 2.15 (s, 3H, Biphen), 2.01 (s, 3H, Biphen), 1.73 (s, 3H, Biphen), 1.67 (s, 9H, $^t$Bu), 1.64 (s, 3H, Biphen), 1.59 (s, 9H, $^t$Bu), 1.14 (s, 9H, $^t$Bu); *Anti*: δ 11.84 (br s, 1H, C*H*$^t$Bu); $^{13}$C{$^1$H} NMR δ 281.18, 154.60, 154.22, 153.47, 139.69, 139.23, 136.22, 135.79, 132.15, 131.92, 131.30, 131.11, 130.77, 130.67, 130.18, 130.12, 126.80 (q, $J_{CF}$ = 30.3 Hz), 126.63, 126.48 (q, $J_{CF}$ = 5.2 Hz), 124.64 (q, $J_{CF}$ = 273.6 Hz), 49.09, 36.16, 35.84, 32.59, 30.80, 30.54, 20.89, 20.77, 17.30, 16.89. Anal. Calcd for $C_{36}H_{46}F_3MoNO_2$: C 63.80, H 6.84, N 2.07. Found (Kolbe) C 63.84, H 6.80, N 2.22.

**Mo(N-2-$CF_3C_6H_4$)(CH-2-$MeOC_6H_4$)((±)-Biphen) ((±)($CF_3$)Mo(Sty))**

A toluene (2 mL) solution of 2-methoxystyrene (241 mg, 1.8 mmol) was added in one portion to a toluene (6 mL) solution of (±)($CF_3$)Mo(Neo)•(THF/$OEt_2$) (1.217g, 1.5 mmol), and the reaction was stirred for 10 minutes. The red solution was concentrated *in vacuo*, triturated with ether (5 mL) and collected by filtration. The red powder was washed with ether and dried *in vacuo* (800 mg, 74%): $^1$H NMR δ 12.85 (s, 1H, $J_{CH}$ = 151 Hz, C*H*Ar), 7.29 (d, 1H, $J_{HH}$ = 7.5 Hz, Ar), 7.28 (s, 1H, Biphen), 7.20 (s, 1H, Biphen), 7.11 (br d, 1H, $J_{HH}$ = 8.0 Hz, Ar), 6.93 (br t, 1H, $J_{HH}$ = 7.5 Hz, Ar), 6.88 (br t, 1H, $J_{HH}$ = 7.5 Hz, Ar), 6.61 (br t, 1H, $J_{HH}$ = 7.5 Hz, Ar), 6.51 (br t, 1H, $J_{HH}$ = 7.5 Hz, Ar), 6.42 (br d, 1H, $J_{HH}$ = 8.5 Hz, Ar), 3.26 (s, 3H, OC*H*$_3$), 2.20 (s, 6H, 2 Me), 1.91 (s, 3H, Me), 1.65 (s, 3H, Me), 1.48 (s, 9H, $^t$Bu), 1.39 (s, 9H, $^t$Bu); $^{13}$C NMR δ 255.66, 161.57, 158.96, 154.05, 152.90, 139.36, 137.53, 136.64, 136.26, 135.53, 132.56,

131.12, 130.91, 130.56, 130.38, 130.11, 129.70, 126.34, 126.30 (q, $J_{CF}$ = 5.3 Hz), 123.99 (q, $J_{CF}$ = 274.5 Hz), 123.37 (q, $J_{CF}$ = 29.4 Hz), 122.46, 120.70, 109.96, 107.72, 104.54, 58.78, 35.90, 35.84, 30.54, 30.49, 20.97, 20.86, 17.27, 17.03. Anal. Calcd for $C_{39}H_{44}F_3MoNO_3$: C 64.37, H 6.09, N 1.92. Found (Kolbe) C 64.25, H 6.15, N 1.74.

**Mo(N-1-Adamantyl)(CHCMe$_2$Ph)((±)-Biphen) ((±)(Ad)Mo(Neo))**

Benzyl potassium (267 mg, 2.05 eq, 2.05 mmol) was added in portions to a stirred THF (10 mL) of (±)-Biphen$H_2$ (354 mg, 1 mmol). After 15 minutes, solid Mo(NAd)(CHCMe$_2$Ph)(OTf)$_2$•DME, **3h**, (765 mg, 1 mmol) was added to the reaction, and the solution became dark yellow. After stirring for one hour at room temperature, the volatiles were removed *in vacuo*. The residue was taken up in pentane, the suspension was filtered through Celite, and a pale yellow powder precipitated from the light brown eluent. The yellow powder was collected by filtration and dried *in vacuo* (435 mg): $^1$H NMR (Mixture of *anti*-(±)Ad)Mo(Neo) and an unidentified decomposition byproduct) δ 13.50 (s, 1H, $J_{CH}$ = 143 Hz, *anti* C*H*R), 12.23 (br s), 7.50 (br s, 2H, *anti*), 7.41 (br s, 1H from both impurity and *anti*), 7.33 (br d, 2H, $J_{HH}$ = 3 Hz, *anti*), 7.31 (br s, 1H, *anti*), 7.28 (s), 7.26-7.16 (m, 3H), 7.12-7.05 (m, 5H), 6.99 (br t, 1H, $J_{HH}$ = 2 Hz, *anti*), 5.17 (br s, 1H, *syn*), 3.26 (d, 1H, $J_{HH}$ = 12 Hz, *anti* AdC*H*H), 2.83 (d, 1H, $J_{HH}$ = 12 Hz, *anti* AdCH*H*), 2.43 (s, 3H, *anti* BiadC$H_3$), 2.40-2.24 (m, 12H), 2.21 (s, 3H, *anti*), 2.20 (s, 3H, *anti*), 2.18 (s), 1.97 (s), 1.94 (br s), 1.88 (br s), 1.84 (s), 1.78 (s), 1.77 (s), 1.61 (s), 1.46 (br s), 1.42-1.25 (m) 1.19 (s), 1.16 (br d, 2H, $J_{HH}$ = 10 Hz, *anti*); $^{13}$C{$^1$H} NMR 300.03, 164.77, 160.08, 150.66, 149.81, 135.68, 134.76, 134.49, 133.08, 132.52, 132.38, 130.74, 129.59, 129.25, 126.96, 126.83, 126.36, 126.28, 125.31, 74.88, 51.80, 50.58, 45.40, 45.21, 44.75, 43.96, 36.79, 36.67, 36.54, 36.38, 36.18, 36.02, 35.35, 35.04, 33.53, 32.21, 32.01, 31.70, 30.51 27.62, 23.38, 21.37, 20.84, 17.84, 17.66, 17.53, 14.96. Anal. Calcd for $C_{39}H_{44}F_3MoNO_3$: C 72.41, H 8.15, N 1.92. Found (Kolbe) C 72.36/72.38, H 9.54/9.54, N 2.95/2.94.

**Mo(N-2,6-$^{i}Pr_2C_6H_3$)(CHCMe$_2$Ph)((S)-Biphen) ((S)($^{i}Pr_2$)Mo(Neo))**

Potassium hydride (3 eq, 1.2 g, 30 mmol) was added in portions to a THF (100 mL) solution of (S)-BiphenH$_2$ (3.54 g, 10 mmol). After stirring for 18 hours at room temperature, solid Mo(N-2,6-$^{i}Pr_2$Ph)(CHCMe$_2$Ph)(OTf)$_2$•DME, **3a**, (0.99 eq, 7.83 g, 9.9 mmol) was added to the reaction mixture and the solution became ruby red. The solution was stirred for 3 hours and then concentrated *in vacuo*. The red solid was extracted with benzene (30 mL), the suspension was filtered through Celite, and the pad was washed with benzene until colorless. The benzene was removed *in vacuo,* and the residue dissolved in ether (30 mL). The volume was reduced to ~10 mL and allowed to stand at 20 °C for 2 hours. (S)($^{i}Pr_2$)Mo(Neo) was collected as red microcrystals in four crops and dried *in vacuo* (5.81 g, 78%):

**X-Ray Crystallographic Data Collection Parameters for (S)($^{i}Pr_2$)Mo(Neo)**

The data for (S)($^{i}Pr_2$)Mo(Neo) were collected on a Siemens SMART/CCD diffractometer with graphite monochromated MoK$\alpha$ radiation ($\lambda$ = 0.71073) and a 12 kW rotating anode generator. The data for (S)($^{i}Pr_2$)Mo(Neo) were collected using a red block having the dimensions 0.20 x 0.20 x 0.20 mm. The crystal system was monoclinic ($\alpha = \gamma$ = 90°) with $a$ = 10.7064(3) Å, $b$ = 13.5262(5) Å, $c$ = 14.8726(5) Å, and $\beta$ = 103.8060(10)°. This led to a cell volume $V$ = 2091.58(12) Å$^3$ with $Z$ = 2. The space group was found to be $P2_1$. The calculated density $\rho$ = 1.200 Mg/m$^3$, and F(000) = 804. The data were obtained at 173(2) K with 2$\theta$ being 23.24°. Of the 8659 reflections collected 5360 were independent ($R_{int}$ = 0.0547). Least squares refinement based on $F^2$ with 5358 data, one restraint and 452 parameters converged with final residuals: $R_1$ = 0.0547, 0.0634 (I>2$\sigma$(I), all data), w$R_2$ = 0.1445, 0.1555 (I>2$\sigma$(I), all data), and GooF = 1.191 based upon I > 3$\sigma$(I).

**Mo(N-2,6-Et$_2$C$_6$H$_3$)(CHCMe$_2$Ph)((S)-Biphen) ((S)(Et$_2$)Mo(Neo))**

Potassium hydride (3.1 eq, 250 mg, 6.1 mmol) was added in portions to a stirred THF (30 mL) solution of (S)-BiphenH$_2$ (708 mg, 2 mmol). After stirring for 12 hours,

solid Mo(N-2,6-$Et_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$•DME, **3b**, (1 eq, 1.526 g, 2 mmol) was added. The red solution was stirred for 4 hours, and the volatiles were then removed *in vacuo*. The solid was extracted with benzene (20 mL), the suspension was filtered through Celite and the pad was washed with benzene until the eluent was colorless. The benzene was then removed *in vacuo* and the residue dissolved in ether/isopropyl ether (1:1, 4 mL). Two crops of dark orange (S)($Et_2$)Mo(Neo) were collected by filtration (390 mg, 27%):

**Mo(N-2,6-$Me_2$Ph)(CHCMe$_2$Ph)((S)-Biphen) ((S)($Me_2$)Mo(Neo))**

Potassium hydride (3 eq, 360 mg, 9 mmol) was added in portions to a stirred solution of (S)-Biphen$H_2$ (1.062 g, 3 mmol) in THF (100 mL). After stirring for 18 hours, solid Mo(N-2,6-$Me_2$Ph)(CHCMe$_2$Ph)(OTf)$_2$•DME, **3c**, (0.94 eq, 2.235 g, 2.83 mmol) was added. After stirring for 3 hours, the solution was concentrated *in vacuo*. The residue was extracted with benzene, the suspension was filtered trough Celite, and the pad was washed with benzene until colorless. After removing the benzene *in vacuo*, the residue was dissolved in ether (6 mL). Red crystals formed at room temperature over 1 hour and they were collected by filtration (600 mg, 43%):

**Mo(N-2,4-$^t$Bu$_2$-6-MePh)(CH$^t$Bu)((±)-Biphen) ((S)($^t$Bu$_2$Me)Mo(Np))**

Benzyl potassium (2.2 eq, 286 mg, 2.2 mmol) was added in portions to a stirred THF (25 mL) solution of (S)-Biphen$H_2$ (354 mg, 1 mmol) until a pale orange color persisted. After stirring for 10 minutes, solid Mo(N-2,4-$^t$Bu-6-MePh)(CH$^t$Bu)(OTf)$_2$•DME, **3g'**, (772 mg, 1 mmol) was added and the reaction became red. After stirring for 30 minutes, the volatiles were removed *in vacuo*. The residue was dissolved in benzene (30 mL), the suspension was filtered trough Celite, and the pad was washed with benzene until the eluent was colorless. The benzene was removed *in vacuo* and the red powder was dissolved in pentane (2 mL). On transferring the solution to a vial, small orange crystals formed. The crystals were collected by filtration, washed with cold pentane (1 mL), and dried *in vacuo* (266 mg, 36%): The crystallization conditions could not be reproduced and the source of the inconsistencies could not be identified. $^1$H NMR

(Mixture of rotamers $K_{eq}$ = 51) *syn*: δ 10.63 (s, 1H, $J_{CH}$ = 126 Hz, C*H*R), 7.478 (s, 1H, Biphen), 7.323 (d, 1H, $J_{HH}$ = 1.8 Hz, Ar), 7.22 (d, 1H, $J_{HH}$ = 1.8 Hz, Ar), 7.16 (s, 1H, Biphen), 2.95 (s, 3H, ArC*H*$_3$), 2.18 (s, 3H, Biphen), 2.00 (s, 3H, Biphen), 1.81 (s, 3H, Biphen), 1.60 (s, 3H, Biphen), 1.64 (s, 9H, $^t$Bu), 1.55 (s, 9H, $^t$Bu), 1.53 (s, 9H, $^t$Bu), 1.18 (s, 9H, $^t$Bu), 1.13 (s, 9H, $^t$Bu); *anti*: δ 12.86 (s, 1H, C*H*R); $^{13}C\{^1H\}$ NMR δ 278.64, 156.02, 154.37, 149.76, 146.28, 139.97, 137.81, 137.62, 136.65, 135.47, 131.85, 130.65, 130.58, 130.55, 130.24, 125.89, 131.40, 119.77, 113.87, 48.43, 36.61, 36.14, 3591, 35.43, 32.04, 31.82, 31.23, 31.01, 30.83, 22.00, 21.04, 20.95, 17.67, 16.96. Anal. Calcd for $C_{44}H_{65}MoNO_2$: C 71.81, H 8.10, N 1.90. Found C 71.83, H 8.16, N 1.84.

**Mo(N-2-$CF_3$Ph)(CHCM$e_2$Ph)((S)-Biphen)•(2,4-lut) ((S)($CF_3$)Mo(Neo)•lut)**

Benzyl potassium (2 eq, 520 mg, 4 mmol) was added in portions over 10 minutes to a stirred toluene (20 mL) solution of (S)-Biphen$H_2$ (708 mg, 2 mmol). After 15 minutes, solid Mo(N-2-$CF_3$Ph)(CHC$Me_2$Ph)(OTf)$_2$•DME, **3f**, (1.550 g, 2 mmol) was added and the solution became dark red. The solution was stirred for 90 minutes and then concentrated *in vacuo* to a red-brown solid. The residue was extracted with benzene (10 mL), the suspension was filtered trough Celite, and the pad was washed with benzene (2 x 10 mL) until colorless. The extract was concentrated *in vacuo* and dissolved in methylcyclohexane (2 mL). No precipitate was observed on standing overnight at -25 °C. Layering the solution with pentafluoropyridine did not induce the formation of a precipitate. The solvents were removed *in vacuo,* and the residue was dissolved in pure methylcyclohexane (2 mL). The addition of 2,4-lutidine (231 μL, 2 mmol) generated an orange precipitate that was collected by filtration, washed with ether (2 mL) and dried *in vacuo* to afford a yellow powder (760 mg, 45%): $^1H$ NMR δ 13.61 (br s, 1H), 7.83 (br s, 1H), 7.54 (d, $J_{HH}$ = 7.8 Hz, 2H), 7.27 (s, 2H), 7.23-6.95 (m), 6.50 (br t, $J_{HH}$ = 7.8 Hz, 1H), 6.04 (br m, 2H), 2.45 (br s, 3H), 2.41 (br s, 3H), 2.20 (s, 3H), 2.14 (br s,

3H), 2.09 (br s, 3H), 1.78 (s, 3H), 1.77 (s, 3H), 1.68 (s, 9H), 1.44 (s, 3H), 1.32 (s, 9H).

**Mo(N-2-$CF_3$Ph)(CH$^t$Bu)((S)-Biphen) ((S)($CF_3$)Mo(Np))**

Benzyl potassium (2.2 eq, 355 mg, 2.75 mmol) was added to a toluene (40 mL) solution of (S)-Biphen$H_2$ (442 mg, 1.25 mmol). After stirring at room temperature for one hour, the reaction mixture was cooled to -25°C and solid Mo(N-2-$CF_3$Ph)(CH$^t$Bu)(OTf)$_2$•DME, **3g**, (892 mg, 1.25 mmol) was added. The reaction was stirred for one hour at room temperature and the volatiles were then removed *in vacuo*. The red solid was dissolved in pentane, the suspension was filtered trough Celite and the pad was washed with pentane until the eluent was colorless. The pentane was removed *in vacuo,* and the resulting foam was crushed to give spectroscopically pure (S)($CF_3$)Mo(Np) as a red powder (804 mg, 95%): Recrystallization conditions for (S)($CF_3$)Mo(Np) have not been developed.

**Mo(N-2-$CF_3C_6H_4$)(CH-2-$MeOC_6H_4$)((S)-Biphen) ((S)($CF_3$)Mo(Sty))**

Benzyl potassium (2.1 eq, 546 mg, 4.2 mmol) was added in portions to a THF (40 mL) solution of (S)-Biphen$H_2$ (708 mg, 2 mmol) until a pale orange color persisted. After stirring for 20 minutes, solid Mo(N-2-$CF_3C_6H_4$)(CHCMe$_2$Ph)(OTf)$_2$•DME (1.550 g, 2 mmol) was added and the red solution was stirred for one hour. The volatiles were removed *in vacuo*. The solid was extracted with benzene (20 mL), the suspension was filtered trough Celite, and the pad was washed with benzene until the eluent was colorless. 2-Methoxystyrene (1.2 eq, 326 mg, 2.4 mmol) was added and the solution stirred for 15 minutes. The volatiles were removed *in vacuo*. The dark red residue was dissolved in ether (15 mL) and filtered through Celite. The eluent was then concentrated to 5 mL and stored at -25°C overnight. Colorless plates of a mixture of *cis*- and *trans*-2,2'-dimethoxystilbene were collected by filtration (60 mg).[102] The liquor was then concentrated to 3 mL, and a brick red powder precipitated on standing for 2 hours at room

temperature. (±)($CF_3$)Mo(Sty) was collected by filtration, washed with pentane and dried *in vacuo* (174 mg, 12%).

**Mo(N-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$((±)-Biphen)**

Potassium hydride (2.5 eq, 220 mg, 5.5 mmol) was added in portions to a THF (40 mL) solution of (±)-Biphen$H_2$ (760 mg, 2.15 mmol). After stirring for 12 hours, the solution was filtered through Celite, solid Mo(N-2,6-$^i$Pr$_2$C$_6$H$_3$)$_2$Cl$_2$•DME, **1a**, (1.31 g, 2.15 mmol) was added and the solution became dark red. After stirring for 2.5 hours, the red solution was concentrated *in vacuo*. The residue was extracted with ether/pentane and filtered through Celite. The eluent volume was reduced and then cooled to -25 °C. The orange powder that precipitated was collected by filtration and dried *in vacuo* (1.00 g, 58%): $^1$H NMR δ 7.27 (s, 2H, Biphen), 6.96 (d, $J_{HH}$ = 7.5 Hz, 4H, *m*-Ar), 6.89 (t, $J_{HH}$ = 7.5 Hz, 2H, *p*-Ar), 3.62 (heptet, $J_{HH}$ = 6.8 Hz, 4H, C*H*Me$_2$), 2.05 (s, 6H, Biphen), 1.64 (s, 6H, Biphen), 1.56 (s, 18H, $^t$Bu), 1.25 (d, $J_{HH}$ = 7 Hz, 6H, CH(C*H*$_3$)(Me), 0.99 (d, $J_{HH}$ = 7 Hz, 6H, CH(C*H*$_3$)(Me); $^{13}$C{$^1$H} NMR δ 155.52, 154.60, 142.96, 138.81, 135.93, 131.60, 131.45, 129.09, 126.83, 123.30, 35.77, 30.96, 29.20, 24.67, 24.01, 16.71. Anal. Calcd for $C_{48}H_{66}MoN_2O_2$: C 72.16, H 8.33, N 3.51. Found C 72.50, H 8.09, N 3.48.

**Mo(N-2,6-Me$_2$Ph)$_2$((±)-Biphen)**

Potassium hydride (2.7 eq, 220 mg, 5.5 mmol) was added in portions to a THF (40 mL) solution of (±)-Biphen$H_2$ (720 mg, 2.03 mmol). After stirring for 12 hours, the solution was filtered, solid Mo(N-2,6-Me$_2$Ph)$_2$Cl$_2$•DME, **1c**, (1 g, 2.02 mmol) was added and the solution became dark red. After stirring for 3 hours, the solution was concentrated *in vacuo*. The residue was extracted with ether and filtered through Celite. The eluent volume was reduced and the solution cooled to -25 °C. An orange powder was collected by filtration (831 mg, 60%): $^1$H NMR δ 7.30 (s, 2H, Biphen), 6.78 (d, $J_{HH}$ = 7.5 Hz, 4H, *m*-Ar), 6.70 (t, $J_{HH}$ = 7.5 Hz, 2H, *p*-Ar), 2.25 (s, 12H, ArC*H*$_3$), 2.0 (s, 6H, Biphen), 1.70 (s, 6H, Biphen), 1.53 (s, 18H, $^t$Bu); $^{13}$C{$^1$H} NMR 157.31, 152.70,

139.38, 135.37, 132.43, 131.66, 131.45, 129.64, 127.81, 125.41, 35.52, 30.28, 20.52, 18.63, 16.63. Anal. Calcd for $C_{40}H_{50}MoN_2O_2$: C 69.95, H 7.34, N 4.08. Found C 69.64 H 7.49, N 3.98.

**Mo(N-2,6-$^i$Pr$_2$Ph)(CHCMe$_2$Ph)((±)-Biad) ((±)'($^i$Pr$_2$)Mo(Neo))**

Benzyl potassium (2.07 eq, 269 mg, 2.07 mmol) was added in portions to a THF (30 mL) solution of (±)-Biad$H_2$ (510 mg, 1 mmol) until a pale orange color persisted. After stirring for 10 minutes, solid Mo(N-2,6-$^i$Pr$_2$Ph)(CHCMe$_2$Ph)(OTf)$_2$•DME (791 mg, 1 mmol) was added, and the solution became red. After stirring for one hour, the volatiles were removed *in vacuo,* and the residue was taken up in benzene (15 mL). The suspension was filtered through Celite, and the pad was washed with benzene until the eluent was colorless. The benzene was removed *in vacuo,* and the orange powder was triturated with pentane (15 mL) overnight. Orange (±)'($^i$Pr$_2$)Mo(Neo) was collected by filtration, washed with cold pentane and dried *in vacuo* (495 mg, 54%): $^1$H NMR (Mixture of rotamers $K_{eq}$ = 12) *Syn*: δ 10.94 (s, 1H, $J_{CH}$ = 119.5 Hz, C*H*R), 7.47 (d, 2H, $J_{HH}$ = 7.5 Hz, *o*-Ph), 7.34 (s, 1H, Biad), 7.25 (t, 2H, $J_{HH}$ = 8 Hz, *m*-Ph), 7.11 (s, 1H, Biad), 7.06 (t, 1H, $J_{HH}$ = 7.5 Hz, *p*-Ph), 6.91 (s, 3H, m,*p*-Ar), 3.65 (sept, 2H, $J_{HH}$ = 7.0 Hz, C*H*Me$_2$), 2.37 (AB q, 6H, Ad-C*H*$_2$), 2.28 (AB q, 6H, Ad-C*H*$_2$), 2.21 (s, 3H, Biad), 2.14 (br d, 6H, Ad-C*H*), 2.13 (s, 3H, Biad), 1.90 (s, 3H, CH(C*H*$_3$)(MePh), 2.1-1.82 (m, 12H, Ad), 1.78 (s, 3H, Biad), 1.74 (s, 3H, Biad), 1.16 (d, 6H, $J_{HH}$ = 7.0 Hz, CH(C*H*$_3$)(Me), 1.15 (s, 3H, C(C*H*$_3$)(Me)Ph), 0.94 (d, 6H, $J_{HH}$ = 7.0 Hz, CH(C*H*$_3$)(Me). *Anti* δ 12.88 (s, 1H, C*H*R), 7.75 (d, 2H, $J_{HH}$ = 7.5 Hz, *o*-Ph), 7.29 (t, 2H, $J_{HH}$ = 8.0 Hz, *m*-Ph), 7.12 (s, 1H, Biad), 3.48 (sept, 2H, C*H*Me$_2$), 1.42 (d, 6H, CH(C*H*$_3$)(Me), 1.03 (d, 6H, CH(C*H*$_3$)(Me); $^{13}$C{$^1$H} NMR δ 274.88, 155.61, 154.41, 154.23, 151.48, 146.48, 139.78, 138.68, 135.97, 135.70, 131.80, 131.12, 130.97, 130.45, 130.43, 128.70, 127.77, 127.30, 126.60, 126.36, 123.64, 53.61, 41.64, 41.51, 38.30, 38.12, 37.97, 37.90, 37.82, 33.42, 33.26, 29.97, 29.93, 29.27, 24.55, 25.52, 23.09, 20.97, 20.76,

17.00, 16.66, 14.65. Anal. Calcd For $C_{58}H_{73}MoNO_2$: C 76.37, H 8.07, N 1.54. Found C 76.45, H 8.14, N 1.47.

**Mo(N-2,6-$Me_2C_6H_3$)(CHC$Me_2$Ph)((±)-Biad) ((±)'($Me_2$)Mo(Neo))**

Benzyl potassium (2.2 eq, 286 mg, 2.2 mmol) was added in portions to a solution of (±)-Biad$H_2$ (510 mg, 1 mmol) in THF (25 mL). After stirring for one hour, solid Mo(N-2,6-$Me_2C_6H_3$)(CHC$Me_2$Ph)(OTf)$_2$•DME (735 mg, 1 mmol) was added and the resulting dark red solution was stirred for 75 minutes. The reaction was then concentrated *in vacuo* to a red film. The product was extracted with benzene (10 mL), the suspension was filtered trough Celite and the pad was washed with benzene until colorless. The benzene was removed *in vacuo* and the residue dissolved in ether (4 mL). Orange crystals began to form at room temperature. After standing at room temperature for 20 minutes, the solution was cooled to -25 °C to promote additional precipitation. Two crops were collected by filtration and dried *in vacuo* (297 mg, 33%): The product may be further purified, if necessary, by crystallization from refluxing isopropyl ether. $^1$H NMR δ 11.04 (s, 1H, C*H*R), 7.37 (s, 1H, Biad), 7.31 (d, 2H, *o*-Ph), 7.13 (t, 2H, *m*-Ph), 7.10 (s, 1H, Biad), 6.98 (t, 1H, *p*-Ph), 6.69 (s, 3H, Ar), 2.34 (br AB pattern, 12 H, Ad-C$H_2$), 2.31 (s, 6H, Ar(C$H_3$)$_2$), 2.22 (s, 3H, Biad), 2.14 (br s, 6H, Ad-C*H*), 2.08 (s, 3H, Biad), 1.86 (br AB pattern, 12H, Ad-C$H_2$), 1.80 (s, 3H, Biad), 1.71 (s, 3H, Biad), 1.65 (s, 3H, C(C$H_3$)(MePh), 1.24 (s, 3H, C(C$H_3$)(MePh); $^{13}$C{$^1$H} NMR δ 278.09, 125.89, 154.98, 154.13, 151.11, 140.26, 138.55, 137.27, 136.43, 135.34, 132.16, 131.14, 131.04, 130.90, 130.42, 129.64, 128.50, 128.27, 127.42, 127.20, 126.28, 54.21, 41.67, 41.56, 38.33, 38.15, 38.10, 3799, 32.94, 32.26, 30.10, 21.10, 20.96, 19.92, 17.43, 17.01. Anal. Calcd for $C_{54}H_{65}MoNO_2$: C 74.12, H 8.00, N 1.76. Found C 74.20, H 8.04, N 1.74.

**Mo(N-2-$CF_3$Ph)(CH$^t$Bu)((±)-Biad) ((±)'($CF_3$)Mo(Np))**

Benzyl potassium (2.2 eq, 56 mg, 0.44 mmol) was added in portions to a solution of (±)-Biad$H_2$ (102 mg, 0.2 mmol) in toluene (6 mL). The reaction was stirred at room

temperature for 20 hours and solid Mo(N-2-$CF_3$Ph)(CH$^t$Bu)(OTf)$_2$•DME, **1g'**, (142 mg, 0.2 mmol) was added. After stirring for 45 minutes, the red solution was concentrated *in vacuo*. The dark red residue was extracted with pentane (5 mL), the suspension was filtered trough Celite and the pad was washed with pentane until the eluent was colorless. The solution was then concentrated to 2 mL and red microcrystals began to form. The solution was stored at -25 °C overnight and red-orange microcrystals were collected by decanting the liquor and drying *in vacuo* (68 mg, 41%): $^1$H NMR δ 10.64 (s, 1H, C*H*$^t$Bu), 7.62 (d, 1H, J = 7.8 Hz, Ar), 7.42 (s, 1H, Biad), 7.11 (d, 1H, J = 7.5 Hz, Ar), 7.06 (s, 1H, Biad), 6.92 (t, 1H, J = 7.8 Hz, Ar), 6.53 (t, 1H, J = 7.8 Hz, Ar), 2.45 (br q, 6H, Ad-C*H*$_2$), 2.31 (br s, 6H, Ad-C*H*$_2$), 2.22 (s, 3H, Biad), 2.17 (br q, 6H, Ad-C*H*), 2.06 (s, 3H, Biad), 2.02-1.82 (multiple signals, 12H, Ad), 1.76 (s, 3H, Biad), 1.68 (s, 3H, Biad), 1.16 (s, 9H, $^t$Bu); $^{13}$C{$^1$H} NMR δ 281.75, 154.53, 154.34, 153.68, 139.86, 139.47, 136.02, 135.49, 132.09, 131.98, 131.48, 131.18, 130.96, 130.62, 130.47, 130.26, 126.93 (q, $J_{CF}$ = 29.5 Hz), 126.74, 126.52 (q, $J_{CF}$ = 5.1 Hz), 124.23 (q, $J_{CF}$ = 272.8 Hz) 46.10, 41.59, 38.47, 38.05, 37.92, 32.70, 30.05, 30.02 23.10, 21.01, 20.86, 17.32, 16.95, 14.66. Anal. Calcd for $C_{48}H_{58}F_3MoNO_2$: C 69.13, H 7.01, N 1.68. Found C 68.95, H 6.91, N 1.70.

**Mo(N-2,6-$^i$Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)((S)-Biad) ((S)'($^i$Pr$_2$)Mo(Neo))**

Solid benzyl potassium (2.04 eq, 53 mg, 4.08 mmol) was added in portions to a solution of (S)-Biad$H_2$ (102 mg, 0.2 mmol) in THF (6 mL). After 10 minutes, Mo(N-2,6-$^i$Pr$_2$Ph)(CHCMe$_2$Ph)(OTf)$_2$•DME, **3a**, (158 mg, 0.2 mmol) in THF (2 mL) was added and the reaction became dark red. After one hour, the volatiles were removed *in vacuo*. The residue was then dissolved in toluene (2 mL) and concentrated again *in vacuo* to remove residual THF. The solid was then extracted with pentane (10 mL), the suspension was filtered trough Celite and the eluent volume reduced to ~1 mL. On standing for one hour at room temperature, a golden precipitate formed which was collected by filtration and dried *in vacuo* (62 mg, 34%).

**Mo(N-2,6-$Et_2C_6H_3$)(CHC$Me_2$Ph)((S)-Biad) ((S)'($Et_2$)Mo(Neo))**

Benzyl potassium (2.08 eq, 146 mg, 1.12 mmol) was added in portions to a stirred solution of (S)-Biad$H_2$ (275 mg, 0.54 mmol) in THF (30 mL). After stirring for 30 minutes, solid Mo(N-2,6-$Et_2C_6H_3$)(CHC$Me_2$Ph)(OTf)$_2$•DME, **3b**, (412 mg, 0.54 mmol) was added and the reaction became dark red. After one hour, the volatiles were removed *in vacuo* and the residue was dissolved in pentane (5 mL). The red slurry was filtered through Celite and orange microcrystals precipitated at room temperature. Two crops were collected by filtration and dried *in vacuo* (145 mg, 30%): $^1$H NMR (Mixture of rotamers $K_{eq}$ = 100) *Syn*: δ 11.03 (s, 1H, C*H*$^t$Bu), 7.37 (d, 2H, J = 7.0 Hz, *o*-Ph), 7.37 (s, 1H, Biad), 7.19 (t, 2H, J = 8.0 Hz, *m*-Ph), 7.08 (s, 1H, Biad), 7.02 (t, 1H, J = 7.5 Hz, *p*-Ph), 6.86-6.79 (m, 3H, m,*p*-Ar), 2.93 (ABX$_3$ sextet, 2H, C$H_a$H$_b$Me), 2.74 (ABX$_3$ sextet, 2H, CH$_a$$H_b$Me), 2.37 (AB q, 6H, Ad-C$H_2$), 2.28 (AB q, 6H, Ad-C$H_2$), 2.21 (s, 3H, Biad), 2.16 (br s, 3H, Ad-C*H*), 2.11 (br s, 3H, Ad-C*H*), 2.10 (s, 3H, Biad), 1.93-1.80 (2 overlapping AB q, 12H, 2 Ad-C$H_2$), 1.97 (s, 3H, Me), 1.769 (s, 3H, Biad), 1.73 (s, 3H, C(C$H_3$)(MePh), 1.20 (s, 3H, C(C$H_3$)(MePh), 1.01 (t, 6H, J = 7.5 Hz, CH$_a$H$_b$C$H_3$). *Anti*: δ 12.91 (s, 1H, C*H*$^t$Bu), 3.35 (ABX$_3$ m, 4H, C$H_a$$H_b$Me), 0.95 (t, 6H, CH$_2$C$H_3$); $^{13}$C{$^1$H} NMR: 276.84, 155.76, 155.13, 153.82, 151.27, 142.37, 140.21, 138.70, 136.32, 135.49, 132.11, 131.19, 131.00, 130.80, 130.52, 129.37, 128.68, 127.76, 127.40, 126.27, 125.69, 53.77, 41.56, 41.49, 38.25, 38.02, 37.96, 37.85, 32.94, 32.92, 30.01, 29.98, 25.60, 20.95, 20.79, 17.95, 16.79, 14.30. Anal. Calcd for $C_{56}H_{69}MoNO_2$: C 76.08, H 7.87, N 1.58. Found C 75.92, H 7.96, N 1.51.

**Mo(N-2,6-$Me_2C_6H_3$)(CHC$Me_2$Ph)((S)-Biad) ((S)'($Me_2$)Mo(Neo))**

Benzyl potassium (2.08 eq, 146 mg, 1.04 mmol) was added in portions to a stirred solution of (S)-Biad$H_2$ (255 mg, 0.5 mmol) in THF (30 mL). After stirring for 30 minutes, solid Mo(N-2,6-$Me_2C_6H_3$)(CHC$Me_2$Ph)(OTf)$_2$•DME (368 mg, 0.5 mmol) was added and the reaction became dark red. After stirring for one hour, the volatiles were removed *in vacuo* and benzene (10 mL) was added. The slurry was filtered through Celite

and the eluent was concentrated *in vacuo*. The residue was dissolved in isopropyl ether (4 mL). An orange-red precipitate formed on standing at room temperature. The orange-red powder was collected by filtration, washed with cold isopropyl ether and dried *in vacuo* (190 mg, 44%).

**Mo(N-3,5-$Me_2C_6H_3$)(CHCMe$_2$Ph)((S)-Biad) ((S)'-3,5-$Me_2$)Mo(Neo))**

Benzyl potassium (2.04 eq, 53 mg, 0.41 mmol) was added to a stirred solution of (S)-Biad$H_2$ (102 mg, 0.2 mmol) in THF (10 mL). After stirring for 15 minutes, a solution of Mo(N-3,5-$Me_2C_6H_3$)(CHCMe$_2$Ph)(OTf)$_2$•DME, **3d**, (147 mg, 0.2 mmol) in THF (4 mL) was added and the reaction became dark red. After one hour, the volatiles were removed *in vacuo* and the residue was dissolved in pentane (5 mL). The slurry was filtered through Celite and the eluent was concentrated *in vacuo*. The residue was dissolved in pentane (4 mL) and the solution volume was reduced to 2 mL. A yellow precipitate formed on standing at room temperature and the powder was collected by filtration (65 mg, 38%): $^1$H NMR δ 11.10 (s, 1H, $J_{CH}$ = 122.6 Hz, C*H*R), 7.46 (d, 2H, J = 7.0 Hz, *o*-Ph), 7.40 (s, 1H, Biad), 7.24 (t, 2H, J = 7.5 Hz, *m*-Ph), 7.12 (s, 1H, Biad), 7.06 (t, 1H, J = 7.5 Hz, *p*-Ph), 6.53 (s, 2H, *o*-Ar), 6.40 (s, 1H, *p*-Ar), 2.43 (AB q, 6H, Ad-C$H_2$), 2.30 (br t, 6H, Ad-C$H_2$), 2.20 (s, 3H, Biad), 2.14 (br s, 6H, Ad-C$H_2$), 2.07 (s, 3H, Biad), 1.93-1.86 (m, 12H, Biad + Ad-C$H_2$ + Ad-C*H*), 1.83 (s, 6H, ArC$H_3$), 1.82 (m, 3H, Ad-C*H*), 1.78 (s, 3H, Biad), 1.75 (s, 3H, C(C$H_3$)(MePh), 1.25 (s, 3H, C(C$H_3$)(MePh); $^{13}$C{$^1$H} δ 278.15, 157.28, 154.39, 152.81, 152.41, 140.53, 139.81, 137.95, 136.24, 135.56, 131.96, 131.38, 131.02, 130.87, 129.88, 129.55, 128.75, 128.68, 127.40, 126.19, 125.56, 54.50, 41.69, 41.67, 38.41, 38.09, 37.97, 37.95, 33.33, 32.77, 30.04, 29.96, 21.27, 20.99, 20.84, 17.26, 16.95. Anal. Calcd for $C_{54}H_{65}MoNO_2$: C 75.75, H 7.65, N 1.64. Found C 75.86, H 7.75, N 1.59.

**Mo(N-2-$CF_3C_6H_4$)(CH$^t$Bu)((S)-Biad) ((S)'($CF_3$)Mo(Np))**

Solid benzyl potassium (2.08 eq, 135 mg 1.04 mmol) was added in portions to a stirred solution of (S)-Biad$H_2$ (254 mg, 0.5 mmol) in toluene (40 mL). Solid Mo(N-2-

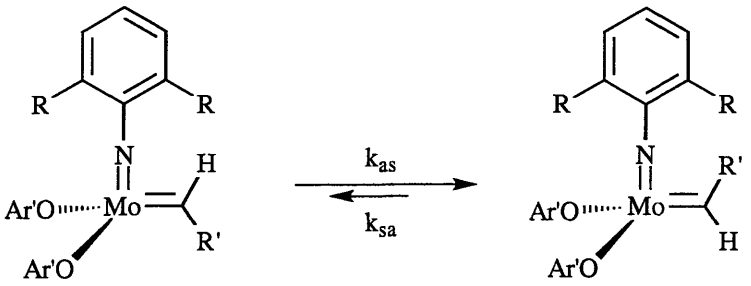
$CF_3C_6H_4)(CH^tBu)(OTf)_2$•DME, **3g'**, (356 mg, 0.5 mmol) was added and the reaction became dark red. After stirring at room temperature for 1.5 hours, the solution was concentrated *in vacuo* and the residue dissolved in pentane (75 mL). The suspension was filtered through Celite and the volume reduced to approximately 5 mL. Red-orange microcrystals formed and were collected by decanting the solution. A second crop of red-orange powder was collected by filtration and dried *in vacuo*. (180 mg, 43%).

# CHAPTER 3

# $^1$H NMR Spectroscopy of Molybdenum(VI) Imido Alkylidene Biphenoxide Complexes

## INTRODUCTION

Complexes such as Mo(NAr)(CHR)(OR')$_2$ exist as a mixture of rotational isomers due to the accessibility of only one $\pi$ orbital for the formation of the metal-alkylidene $\pi$ bond in the presence of the strong $\pi$ bonding imido group.[2,28,109,110] Equilibrium constants ($K_{eq}$ = [*syn*]/[*anti*]) and interconversion rates (k = $k_{as}$ + $k_{sa}$; $k_{as}$ = *anti* → *syn*; $k_{sa}$ = *syn* → *anti*) have been measured for complexes of the type Mo(NAr)(CHR)(OAr')$_2$.[31,36,44,46,47,97] The kinetics of rotamer exchange have been studied by $^1$H NMR complete band shape analysis for a number of phenoxide complexes (Ar = 2,6-$^i$Pr$_2$C$_6$H$_3$; Ar' = 2,6-$^i$Pr$_2$C$_6$H$_3$, 2-$^t$BuC$_6$H$_4$; R = TMS, CMe$_2$Ph) where both *syn* and *anti* rotamers are readily observable ($K_{eq} \cong 15$).[44] The overall rate of interconversion, k, is on the order of 1-10 sec$^{-1}$.




*anti* *syn*

**Scheme 3.1.** Rotational Isomers of Mo(NAr)(CHR') (OAr')$_2$ Exchange with Rate Constants $k_{as}$ (*anti* → *syn*) and $k_{sa}$ (*syn* → *anti*).

The importance of alkylidene rotamers of Mo(NAr)(CHR)(OR')$_2$ (Ar = 2,6-$^i$Pr$_2$C$_6$H$_3$; R = $^t$Bu, CMe$_2$Ph; R' = $^t$Bu, CMe(CF$_3$)$_2$) in determining polymer structure in the ROMP of 2,3-bis(trifluoromethyl) norbornadiene, (NBDF6) has been addressed by Oskam.[46] The *anti* rotamer, which selectively forms *trans*-C=C bonds, is estimated to react approximately $10^5$ faster than the *syn* rotamer with NBDF6, which forms only *cis*-C=C bonds. Monomer insertion into either the *syn* or the *anti* rotamer results in the formation of a new *syn* alkylidene complex. Consequently, poly(NBDF6) prepared with

catalysts with negligible rotamer isomerization rates ($k = 2.26 \times 10^{-4}$ $sec^{-1}$ and $k_{sa} = 1.1 \times 10^{-7}$ $sec^{-1}$ for R' = $CMe(CF_3)_2$) contained exclusively *cis*-C=C bonds because the *anti* rotamer is not accessible on the polymerization timescale. Poly(NBDF6) containing exclusively *trans*-C=C bonds is produced by catalysts with fast rotamer exchange rates (R' = $^tBu$; $k \sim 500$ $sec^{-1}$).

Rotational isomers of molybdenum(VI) imido alkylidene biphenoxide complexes exhibit different reactivity in ROMP polymerizations and in THF binding studies. For example, the base-free four-coordinate Mo(N-2-$^tBuC_6H_4$)(CHCMe$_2$Ph)((±)-3,3',5,5'-$^tBu_4$Biphen) is chiral on the $^1H$ NMR timescale since rotation about the biaryl bond is slow, preventing epimerization.[31,47,97] Only one alkylidene resonance is observed at δ 10.87 ($J_{CH}$ = 120 Hz) at room temperature. One THF adduct each for both the *syn* and *anti* rotamers are observed by $^1H$ NMR spectroscopy after addition of excess THF and cooling the sample to -60 °C. The THF adduct of the *syn* rotamer is more labile than the *anti* adduct. As a result, the tacticity and stereochemistry of poly(NBDF6) prepared by ROMP with racemic molybdenum biphenoxide, Mo(N-2-$^tBuC_6H_4$)(CHCMe$_2$Ph)((±)-3,3',5,5'-$^tBu_4$Biphen), is highly dependent on polymerization solvent and temperature.[47] At low temperature (T < -10 °C) in THF, the polymerization is extremely sluggish (~5% yield, 48 h) and the polymer produced contains exclusively *cis*-double bonds. At room temperature and above, the *trans*-olefin content increases from 42% (T = 23 °C) to 76% (T = 65 °C). At higher temperatures, the *anti* base adduct is labile and the *anti* rotamer competes more effectively with the *syn* rotamer in the propagation step. The related Mo(N-2,6-$^iPr_2$Ph)(CHCMe$_2$Ph)((±)-3,3',5,5'-$^tBu_4$Biphen) is a 3:1 mixture of the base-free *syn* rotamer and the THF adduct of the *anti* rotamer at room temperature.[31] This complex forms exclusively (99%) *cis*-NBDF6 since the *anti* rotamer is sequestered as an unreactive THF adduct. Table 3.1 contains $^1H$ NMR data and equilibrium constants for Mo(NAr)(CHR)(OAr')$_2$ complexes.

The concentration and accessibility of *syn* and *anti* alkylidene rotamers can have a profound effect on the outcome of a metathesis reaction. The *cis/trans* composition of ROMP polymers was controlled by modifying the concentration of the more reactive *anti* alkylidene rotamer. The *anti* rotamer has been excluded by reducing the rate of rotamer exchange as in Mo(NAr)(CHR)[OCMe$(CF_3)_2$]$_2$, or by sequestering the *anti* rotamer as a five-coordinate base adduct as in *anti* Mo(N-2-$^t$BuC$_6$H$_4$)(CHCMe$_2$Ph)((±)-3,3',5,5'-$^t$Bu$_4$Biphen)•THF.

**Table 3.1.** Literature $^1$H NMR Data for Mo(NAr)(CHR)(OAr')$_2$ Complexes.[44]

| Complex | δ(*anti*) | δ(*syn*) | Δδ | $K_{eq}$*a* |
|---|---|---|---|---|
| Mo(NAr)(CH$^t$Bu)(DIPP)$_2$ | 12.64 | 11.42 | 1.22 | 15.7 |
| Mo(NAr)(CHCMe$_2$Ph)(DIPP)$_2$ | 12.74 | 11.77 | 0.97 | 11.5 |
| Mo(NAr)(CHCMe$_2$Ph)(DIPP)$_2$ (in tol-$d_8$) | 12.69 | 11.72 | 0.97 | 9.6 |
| Mo(NAr)(CHTMS)(DIPP)$_2$ | 13.10 | 13.00 | 0.10 | 1.9 |
| Mo(NAr)(CHCMe$_2$Ph)(O-2-$^t$BuC$_6$H$_4$)$_2$ | 13.36 | 11.79 | 1.57 | -- |
| Mo(NAr)(CHTMS)(O-2-$^t$BuC$_6$H$_4$)$_2$ | 13.24 | 12.65 | 0.59 | 0.33 |
| Mo(NAr)(CHCMe$_2$Ph)(O-2,6-Cl$_2$C$_6$H$_3$)$_2$•py | 14.31 | 14.46 | 0.15 | -- |

*a*. Equilibrium constants measured at 25 °C.

The participation of the *anti* rotamer in the ROMP propagation step dramatically effects the regiochemistry of the C=C double bonds in the polymer backbone. The relative importance of *syn* and *anti* rotamers in determining the stereoselectivity of ARCM reactions is unknown. The *anti* rotamer is expected to be the faster reacting species based on the ROMP reactivities of Mo(NAr)(CHR)(OR)$_2$ with biphenoxide[47] and alkoxide ligands.[46] Information about *anti* concentration for the complexes prepared in Chapter 2 combined with rates for rotamer interconversion will help elucidate the enantioselectivity trends for the ARCM presented in Tables 4.4 and 4.5.

## RESULTS AND DISCUSSION

### 3.1 Syn/Anti Rotamers: Equilibrium and $^1$H NMR Studies

The $^1$H NMR spectroscopy data for molybdenum(VI) imido alkylidene biphenoxide complexes are listed in Table 3.2. The concentration of the *anti* rotamer appeared to be roughly proportional to the steric bulk of the arylimido group. In the series (±)($R_2$)Mo(Neo), the equilibrium constant ($K_{eq}$) decreased from 244 (R = Me) to 17 (R = $^i$Pr) at T = 20 °C. This change in $K_{eq}$ corresponds to an increase in the *anti* concentration from 0.4% for (±)($Me_2$)Mo(Neo) to 5.6% for (±)($^iPr_2$)Mo(Neo). The magnitude of the equilibrium constant increased as the size of the arylimido ring decreased in the order: $^iPr_2$ > 2,4-$^t$Bu$_2$-6-Me > $Et_2$ ~ $^t$Bu ~ $CF_3$ > $Me_2$. Changing the metal from molybdenum to tungsten in (±)($Me_2$)M(Neo) causes $K_{eq}$ to decrease from 244 (Mo) to 88 (W). The equilibrium constants for (±)'($R_2$)Mo(Neo) (R = $^i$Pr and Et) were similar to those of analogous Biphen complexes. The *anti* rotamer was not observable ($K_{eq}$ > 500) for the less sterically demanding arylimido complexes (±)'($R_2$)Mo(Neo) ($R_2$ = 2,6-$Me_2$ and 3,5-$Me_2$) and (±)'($CF_3$)Mo(Np). (±)($^t$Bu)Mo(Sty) ($J_{CH}$ = 155 Hz) and (±)($CF_3$)Mo(Sty) ($J_{CH}$ = 151 Hz) were exclusively *anti* in solution due to the coordination of the *ortho*-methoxy residue to molybdenum to give a five-membered ring chelate.

Reducing the steric bulk on the alkylidene increased the *anti* concentration. Addition of excess *cis*-2-butene or *trans*-3-hexene to toluene-$d_8$ solutions of (±)($^iPr_2$)Mo(Neo) produced ethylidene and propylidene complexes respectively which were in equilibrium with (±)($^iPr_2$)Mo(Neo). The equilibrium favored the neophylidene complex, as a ~20 fold excess of olefin was necessary to generate ~5% of (±)($^iPr_2$)Mo(CHMe) or (±)($^iPr_2$)Mo(CHEt). The equilibrium constant for ethylidene-neophylidene exchange was determined using eqn 1, K = 9.1 x $10^{-4}$ at 20 °C.

$$K = \frac{[(\pm)(^iPr_2)Mo(CHMe)]\,[PhMe_2CH = CHMe]}{[(\pm)(^iPr_2)Mo(Neo)]\,[MeCH = CHMe]} \quad (1)$$

**Table 3.2.** $^1$H NMR Data for *Syn* and *Anti* Rotamers for Biphenoxide Complexes.

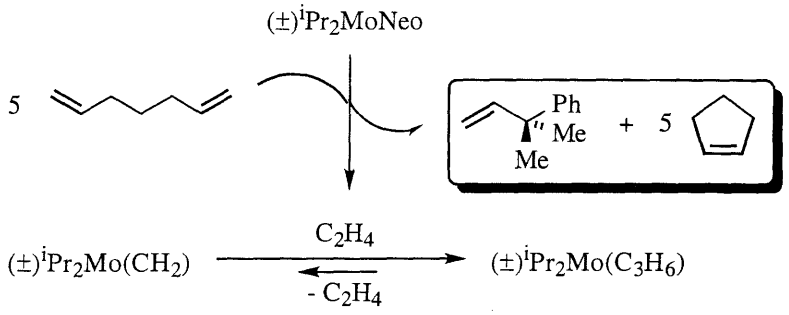
| Complex | δ(*syn*) | $J_{CH}$(*syn*) | δ(*anti*) | $J_{CH}$(*anti*) | Δδ | $K_{eq}$[c] |
|---|---|---|---|---|---|---|
| (±)($^i$Pr$_2$)Mo(Neo)[a] | 10.98 | 123 | 12.77 | 146 | 1.79 | 17.0 |
| (±)($^i$Pr$_2$)Mo(CHEt)[b] | 10.68 | -- | 12.15 | -- | 1.47 | 3.1 |
| (±)($^i$Pr$_2$)Mo(CHMe)[b] | 10.64 | -- | 12.37 | -- | 1.37 | 2.0 |
| (±)(Et$_2$)Mo(Neo)[a] | 11.04 | 121 | 12.94 | -- | 1.90 | 110 |
| (±)(Me$_2$)Mo(Neo)[a] | 11.01 | 121 | 13.03 | -- | 2.01 | 244 |
| (±)(Me$_2$)W(Neo)[a] | 7.99 | 115 | 9.06 | -- | 1.07 | 88 |
| (±)($^t$Bu)Mo(Neo)[a] | 10.98 | 120 | 12.13 | -- | 1.15 | 104 |
| (±)($^t$Bu)Mo(Sty)[a] | -- | -- | 12.84 | 155 | -- | ~0 |
| (S)($^t$Bu$_2$Me)Mo(Neo)[a] | 10.63 | 118 | 12.86 | -- | 2.23 | 51 |
| (±)(CF$_3$)Mo(Neo)[b] | 10.84 | 124 | 11.69 | -- | 0.85 | 0.26 |
| (±)(CF$_3$)Mo(Np)[a] | 10.61 | 120 | 11.85 | -- | 1.24 | 86 |
| (±)(CF$_3$)Mo(Sty)[a] | -- | -- | 12.85 | 151 | -- | ~0 |
| (±)'($^i$Pr$_2$)Mo(Neo)[a] | 10.94 | 121 | 12.88 | -- | 1.94 | 11.4 |
| (±)'(Et$_2$)Mo(Neo)[a] | 11.03 | 121 | 12.91 | -- | 1.88 | 100 |
| (±)'(Me$_2$)Mo(Neo)[a] | 11.04 | 122 | -- | -- | -- | -- |
| (±)'(3,5-Me$_2$)Mo(Neo)[a] | 11.10 | 122 | -- | -- | -- | -- |
| (±)'(CF$_3$)Mo(Neo)[a] | 10.64 | 120 | -- | -- | -- | -- |

*a.* ~15 mg of complex in benzene-$d_6$. *b.* ~15 mg of complex in toluene-$d_8$. *c.* $K_{eq}$ measured at 20 °C.

The ethylidene complex was a 2:1 mixture of *syn* and *anti* rotamers ($K_{eq}$ = 2), and the alkylidene resonances were quartets due to coupling with the β-$CH_3$. The *anti* rotamer had a larger β-$CH_3$ coupling ($J_{HH}$ = 8.5 Hz) than the *syn* rotamer ($J_{HH}$ = 6.5 Hz). The larger propylidene complex, (±)($^i$Pr$_2$)Mo(CHEt), had an equilibrium constant ($K_{eq}$ = 3.1) intermediate between (±)($^i$Pr$_2$)Mo(CHMe) and (±)($^i$Pr$_2$)Mo(Neo). The alkylidene $H_\alpha$ for both the *syn* and *anti* rotamers of the propylidene complex, (±)($^i$Pr$_2$)Mo(CHEt), was a doublet of doublets due to coupling with the two diastereotopic β-$CH_2$ protons. The

coupling to each diastereotopic β-$CH_2$ proton was similar for the *syn* rotamer ($J_{HH}$ = 6.8, 6.4 Hz), however, the *anti* rotamer exhibited two inequivalent coupling constants between the two β-$CH_2$ protons and the alkylidene proton ($J_{HH}$ = 11.9, 7.0 Hz).

Addition of 1,6-heptadiene to (±)($^i$Pr$_2$)Mo(Neo) produced cyclopentene, 3-methyl-3-phenyl-1-butene and ethylene (Scheme 3.2). The (±)-Biphen ligand remained bound to molybdenum, but no alkylidene resonances were observed in the $^1$H NMR spectrum and the ethylene resonance was broad. Several broad resonances were observed between δ 3-4 which could be the α-$CH_2$ resonances of (±)($^i$Pr$_2$)Mo($C_3H_6$). However, β-$CH_2$ resonances at δ < 0.8 were not observed. The broad ethylene and proposed α-$CH_2$ resonances sharpened on cooling the sample to -20 °C. A transient metallacycle, (±)($^i$Pr$_2$)Mo($C_3H_6$), in rapid exchange with unobserved (±)($^i$Pr$_2$)Mo($CH_2$) was proposed to account for the absence of methylidene or β-$CH_2$ resonances by $^1$H NMR. Attempts to crystallize either (±)($^i$Pr$_2$)Mo($CH_2$) or (±)($^i$Pr$_2$)Mo($C_3H_6$) from pentane or ether were unsuccessful. A six-coordinate molybdenum methylidene complex, Mo(N-2,6-$^i$Pr$_2$$C_3H_6$)($CH_2$)[OCMe($CF_3$)$_2$]$_2$•DME was observed by $^1$H NMR spectroscopy and the related 2,2'-bipyridine (bipy) complex, Mo(NAr)($CH_2$)[OCMe($CF_3$)$_2$]$_2$•bipy was isolated as a crystalline solid.[111]




**Scheme 3.2.** Proposed Metallacycle/Methylidene Exchange (±)($^i$Pr$_2$)Mo($CH_2$) + $C_2H_4$ ↔ (±)($^i$Pr$_2$)Mo($C_3H_6$).

The neophylidene complex (±)($CF_3$)Mo(Neo) was predominantly *anti* ($K_{eq}$ = 0.26) in toluene-$d_8$. The neopentylidene complex, (±)($CF_3$)Mo(Np) was predominantly *syn* ($K_{eq}$ = 86) in benzene-$d_6$. Changing hydrocarbon solvent from benzene to toluene had a

minimal effect on the equilibrium constant for related $Mo(NAr)(CHR)(OR')_2$ complexes.[46] Therefore, the large shift in $K_{eq}$ was due to the change in the alkylidene substituent. At room temperature, the $^1H$ NMR spectrum of $(\pm)(CF_3)Mo(Neo)$ exhibited a broad *anti* alkylidene resonance ($\omega$ = 13 Hz) and a sharp signal for the *syn* rotamer (w < 2 Hz). Warming the sample to 50 °C did not affect the linewidth of the *syn* rotamer resonance, but the *anti* resonance broadened dramatically ($\omega$ = 59 Hz). Cooling the sample to 0 °C sharpened the *anti* resonance to $\omega$ = 7.0 Hz. The constant value for $K_{eq}$ and the sharp *syn* rotamer ($J_{CH}$ < 2 Hz) between 0 °C and 50 °C suggest that the rate of alkylidene rotation was much slower than it is in $(\pm)(iPr_2)Mo(Neo)$. The fluxional process which induced the temperature dependent line broadening is proposed to be a reversible $\pi$-coordination of the neophylidene arene ring to molybdenum via one or more distinct coordination modes.

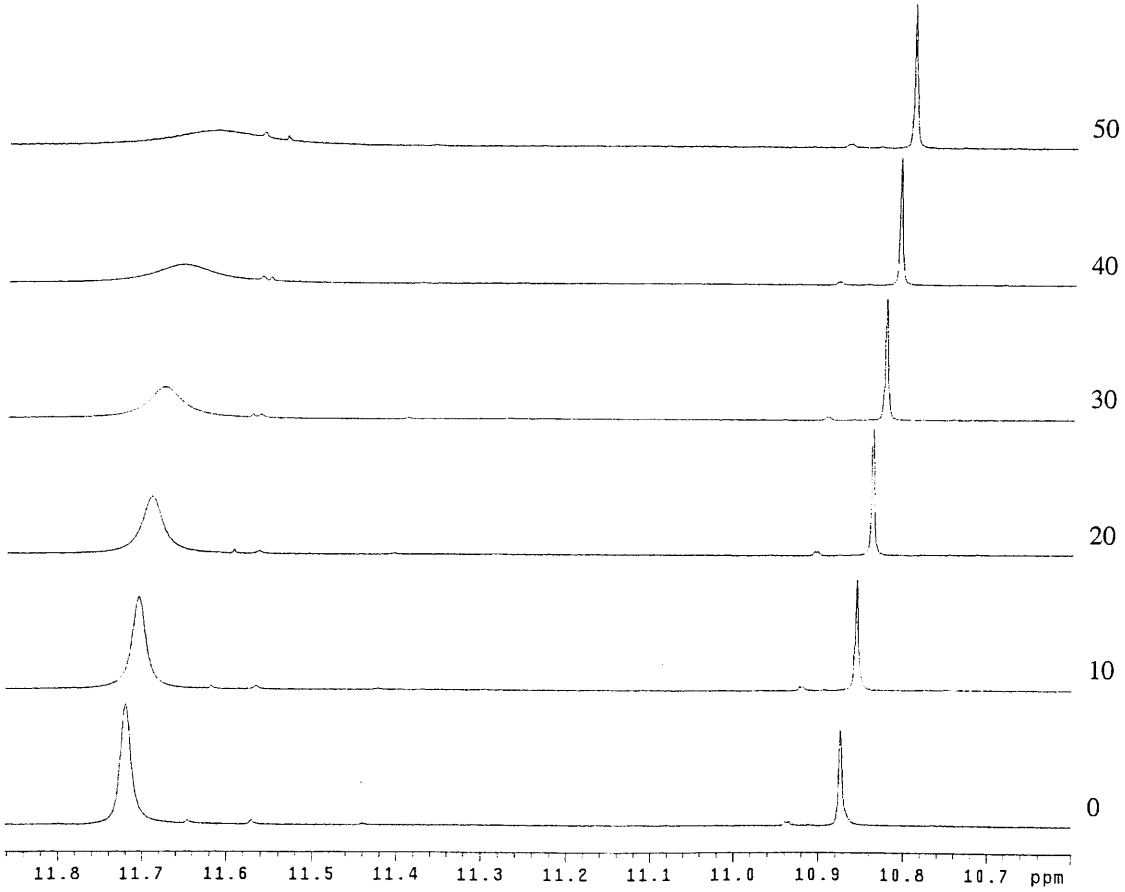



**Figure 3.1.** Variable Temperature $^1H$ NMR Spectroscopy of $(\pm)(CF_3)Mo(Neo)$ from 0 °C to 50 °C in Toluene-$d_8$.

## 3.2 Measurement of Thermodynamic Parameters for Rotamer Exchange

The thermodynamic parameters, $\Delta H^\circ$ and $\Delta S^\circ$, for rotamer exchange in (±)($^i$Pr$_2$)Mo(Neo), (±)'($^i$Pr$_2$)Mo(Neo) and Mo(NAr)(CHCMe$_2$Ph)(DIPP)$_2$ were measured by linear regression of the plot of ln($K_{eq}$) versus (1/T).[111] Integrals for both rotamers were cut to include only the $^{12}CHR$ singlets. Equilibrium measurements were collected at elevated temperature until the linewidth of the *anti* rotamer ~50 Hz. The room temperature equilibria for Mo(NAr)(CHCMe$_2$Ph)(OAr')$_2$ were similar (NAr = 2,6-$^i$Pr$_2$C$_6$H$_3$; OAr' = 0.5 Biphen, 0.5 Biad, DIPP), ranging from 9.6 to 17.5.

**Table 3.3.** Thermodynamic Parameters for Rotamer Exchange in (±)($^i$Pr$_2$)Mo(Neo), (±)'($^i$Pr$_2$)Mo(Neo) and Mo(NAr)(CHCMe$_2$Ph)(DIPP)$_2$.

| Complex[a] | $\Delta G^\circ_{298}$[b] | $\Delta H^\circ$[b] | $\Delta S^\circ$[c] |
|---|---|---|---|
| (±)($^i$Pr$_2$)Mo(Neo) | 2.7(0.2) | 2.2(0.1) | -1.6(0.3) |
| (±)'($^i$Pr$_2$)Mo(Neo) | 3.4(0.2) | 2.4(0.1) | -3.3(0.4) |
| Mo(NAr)(CHCMe$_2$Ph)(DIPP)$_2$ | 0.9(0.2) | 1.1(0.1) | 0.6(0.2) |

**a)** Experiments performed in toluene-$d_8$. **b)** Units in kcal/mol. **c)** Units in eu.

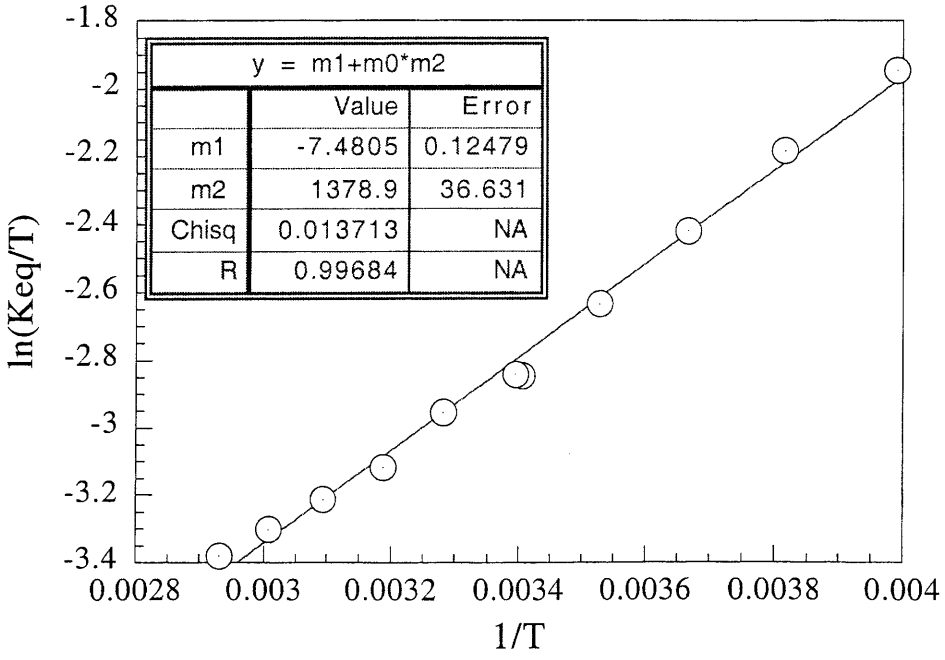



**Figure 3.2.** Calculation of $\Delta H^\circ$ and $\Delta S^\circ$ for (±)($^i$Pr$_2$)Mo(Neo) from the Plot of ln($K_{eq}$/T) versus 1/T.

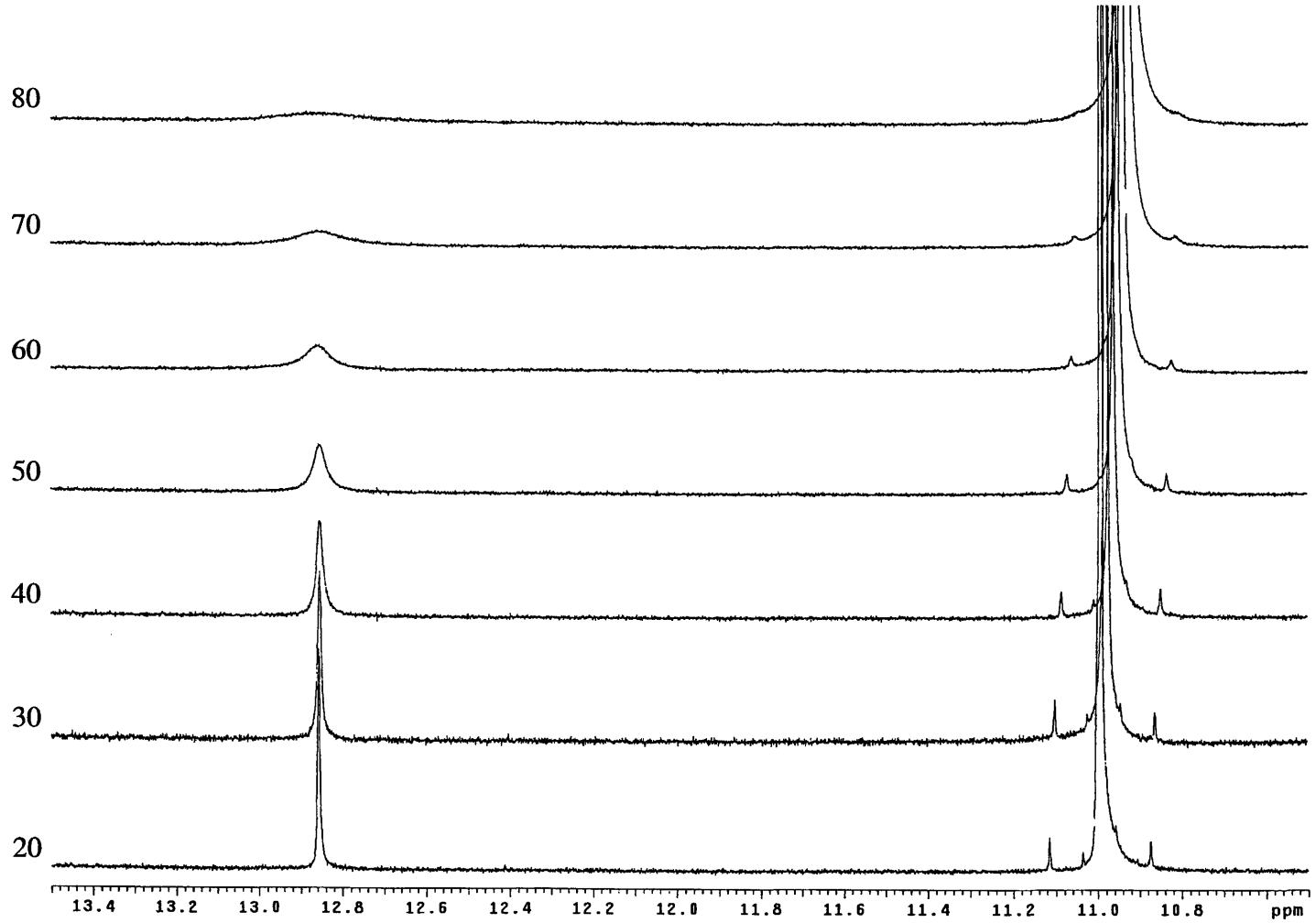



**Figure 3.3.** Variable Temperature $^1$H NMR Spectroscopy of (±)($^i$Pr$_2$)Mo(Neo) from 20 °C to 80 °C in Toluene-$d_8$.

## 3.3 Measurement of Activation Parameters by $^1$H NMR Spectroscopy

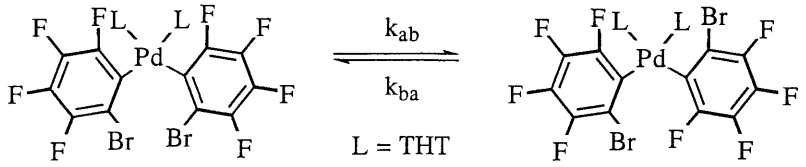
Rotational exchange between *syn* and *anti* rotamers can induce broadened NMR spectra depending on the chemical shifts, rate constants of exchange ($k_{as}$ and $k_{sa}$), transverse relaxation times ($T_2$) and the populations of the different sites.[112] Several techniques have been developed to determine rate constants for exchange processes. The complete band-shape method involves iteratively fitting a calculated band shape to the experimental shape by visual comparison. This procedure is not straightforward. Simplified one parameter techniques have been developed for measuring rate constants. For example, the line broadening of the *anti* resonance ($\omega_{anti}$) is a function of the transverse relaxation time ($T_2$), $\omega_{anti} = (\pi T_2(anti))^{-1}$. The observed relaxation time $(T_2(obs))^{-1}$ is a sum of the natural linebroadening $(T_2(nat))^{-1}$, broadening due to the spectrometer $(T_2(spect))^{-1}$, and broadening due to exchange $(T_2(exch)^{-1})$.

$$\frac{1}{T_2(obs)} = \frac{1}{T_2(nat)} + \frac{1}{T_2(spect)} + \frac{1}{T_2(exch)}$$

The sum of the natural and instrument line broadening was approximated as $(T_2)^{-1} \approx 1\ sec^{-1}$. This approximation could incorporate some systematic error into the calculation of the activation parameters. In order to minimize this error, data for temperatures where $\omega_{anti} < 5$ Hz were excluded from the calculation of the activation parameters (Table 3.4). The observed line broadening was then expressed as, $\omega_{anti} = (1+k_{as})/\pi$, and the rate constant expressed as $k_{as} = [(\pi\omega_{anti})-1]\ sec^{-1}$.

The rate of interconversion of *syn* and *anti* atropisomers in $Pd(C_6BrF_4)_2(THT)_2$ was investigated recently using spin saturation transfer methods to selectively irradiate the *ortho* fluorine of the *anti* isomer (Scheme 3.3).[113] The atropisomerization process in this complex is similar to rotamer exchange in imido alkylidene complexes. Both processes involve exchange between two unequally populated isomers via hindered rotation about a metal-carbon bond. A set of equations (eqn 2 and eqn 3) were developed based on earlier kinetic studies of metallacene vinyl hydride complexes.[114] The resonance for isomer **b**

was selectively inverted and then the $^{19}F$ NMR spectrum of **a** and **b** was recorded, varying the delay time, $t$ (in sec), between inversion and data acquisition. The equilibrium concentrations of atropisomers **a** and **b** were $a_\infty$ and $b_\infty$, and the integration areas for **a** and **b** at delay time, $t$, were $a_t$ and $b_t$. The relaxation time ($R_1$), also known as $T_1$, for the nuclei under investigation was obtained using eqn 2. The rate constant $k_{ab}$ was obtained by inserting the value for $R_1$ into eqn 3. The derivation of these equations assumed that the relaxation time ($R_1$) for **a** and **b** were the same.




*Syn* (**a**) *Anti* (**b**)

**Scheme 3.3.** Atropisomerization of $(THT)_2Pd(C_6BrF_4)_2$.

$$\ln\{(a_\infty + b_\infty) - (a_t + b_t)\} = -R_1 t + C \qquad (2)$$

$$\ln\left(a_t - \frac{a_\infty}{b_\infty}\right) = \left[-R_1 - k_{ab}\left(1 + \frac{a_\infty}{b_\infty}\right)\right]t + C \qquad (3)$$

Applying eqns 2 and 3 to alkylidene rotation generated eqns 4 and 5 substituting *anti* for **a** and *syn* for **b**. A $T_1$ measurement was attempted at room temperature for (±)($^i$Pr$_2$)Mo(Neo) to determine whether $T_1(syn) = T_1(anti)$. It was found that $T_1(syn)$ = 1.2 sec and $T_1(anti)$ = 1 sec (~20% difference). The accuracy of this measurement was dubious due to fast rotamer exchange at room temperature ($k_{as}$= 8.6 sec$^{-1}$ at T = 20 °C by line shape analysis). The delay time, d2 ($t$), was varied ($t$ = 0, 0.05, 0.1, ..., 0.5, 0.6, 0.7, 0.8, 0.9, 1, 2, 12 sec) and the integrated areas for $syn_t$ and $anti_t$ were collected (Figure 3.4). The values for $t$ = 12 were assigned to be $syn_\infty$ and $anti_\infty$ as both rotamers had sufficient time to completely relax to the ground state ($t \approx 10T_1$). Figure 3.5 contains the linear regression of eqn 4 and eqn 5 to give $k_{as}$ for (±)($^i$Pr$_2$)Mo(Neo) at 15 °C. A plot

of ln(k/T) versus 1/T afforded the activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, for the total rate of rotamer exchange (Figure 3.6, Table 3.5).

$$\ln\{(anti_{\infty} + syn_{\infty}) - (anti_t + syn_t)\} = -R_1 t + C \qquad (4)$$

$$\ln\left(syn_t - \frac{syn_{\infty}}{anti_{\infty}}\right) = \left[-R_1 - k_{as}\left(1 + \frac{syn_{\infty}}{anti_{\infty}}\right)\right]t + C \qquad (5)$$

The activation parameter, $\Delta H^{\ddagger}$ = 12.5 kcal/mol, for (±)($^{i}Pr_2$)Mo(Neo) obtained by line shape analysis (*lsa*) was smaller than the value obtained by spin saturation transfer (*sst*), $\Delta H^{\ddagger}$ = 15.1 kcal/mol. The entropy parameter, $\Delta S^{\ddagger}$ = -11.6 eu (*lsa*), was also more negative than the *sst* value ($\Delta S^{\ddagger}$ = -4.0 eu). The results obtained for Mo(NAr)(CHCMe$_2$Ph)(DIPP)$_2$ followed a similar trend, but the activation parameters calculated by line shape analysis were similar to those calculated in the literature by complete band shape analysis (Table 3.5) .[44] A redetermination of the overall rate constant at -42 °C using the line shape analysis data gave k = 3.81 x $10^{-4}$ $sec^{-1}$ which was faster than the literature values (k = 1.35 x $10^{-4}$ $sec^{-1}$ and 1.1 x $10^{-4}$ $sec^{-1}$)[44,46] by a factor of ~3. The rate constant calculated using the spin saturation transfer technique at -42 °C was k = 2.61 x $10^{-5}$ $sec^{-1}$ which was slower than the literature values by a factor of ~4. The activation parameters for (±)'($^{i}Pr_2$)Mo(Neo) were similar to the data collected for (±)($^{i}Pr_2$)Mo(Neo) using the same technique. The discrepancy between the line shape analysis and the spin saturation transfer experiments may, in part, be due to the assumption that the spin-lattice relaxation times ($T_1$) were the same for both rotamers. $T_1$ measurements were obtained for *syn* and *anti* rotamers of (±)($^{i}Pr_2$)Mo(Neo) at -10 °C, where rotamer exchange would be slow (k ~ 0.02 $sec^{-1}$). There was a 30% difference in $T_1$ measurements at this temperature ($T_1$(*syn*) = 1.00 sec and $T_1$(*anti*) = 0.72 sec). The large difference in $T_1$ relaxation times may invalidate eqns 4 and 5 as the assumption that $R_1$(*syn*) = $R_1$(*anti*) is clearly false.

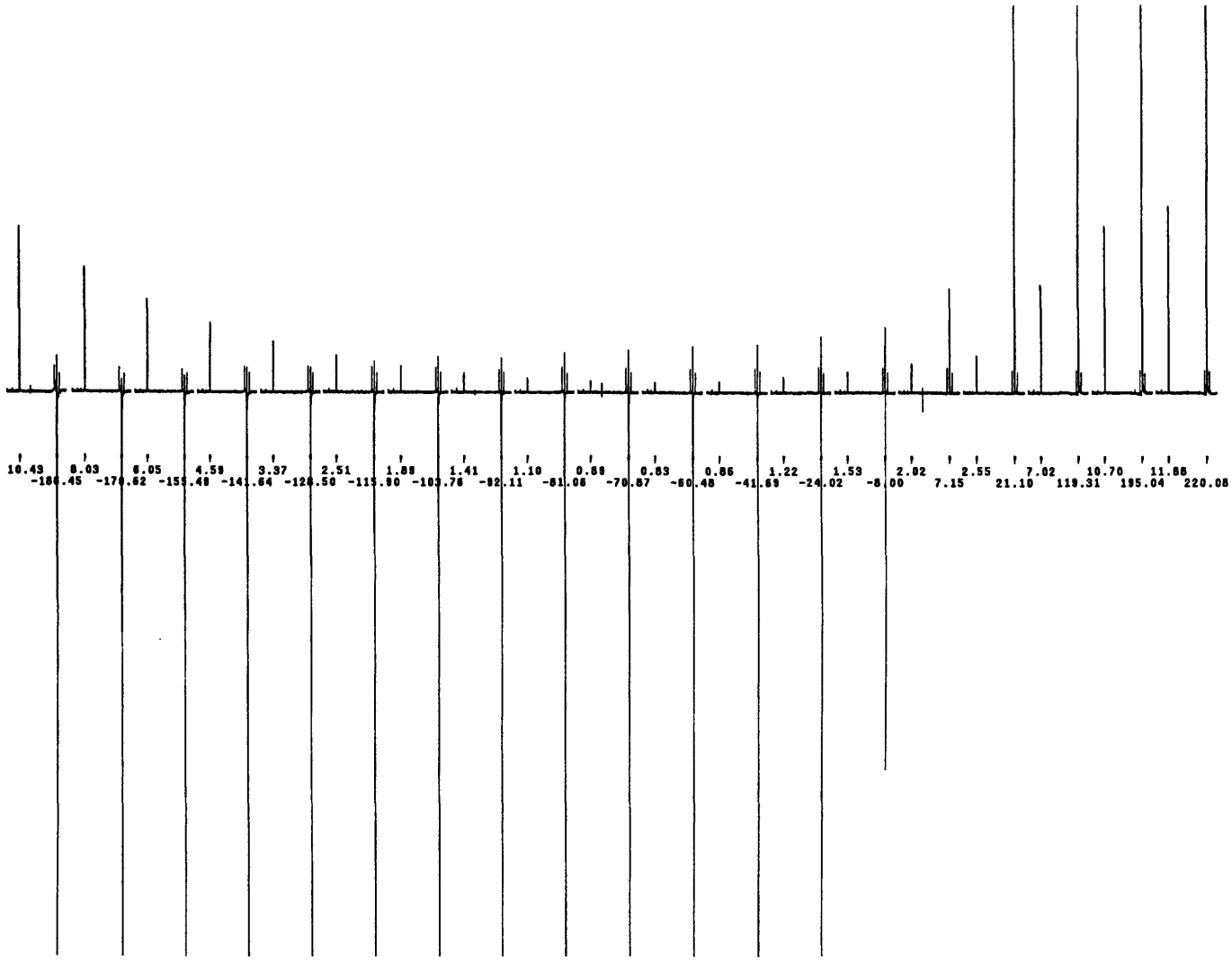



**Figure 3.4.** Spin Saturation Transfer Study for (±)($^{i}Pr_2$)Mo(Neo) at 15 °C in Toluene-$d_8$. The Delay Time ($t$ = d2) between the Selective Inversion of the*Syn* Rotamer and Data Acquisition Increased from Left ($t$ = 0 sec) to Right ($t$ = 12 sec).

**Table 3.4.** $^1$H NMR Linewidths of *Syn* and *Anti* Rotamers, Equilibrium Constants and Rate Constants, $k_{as}$ and $k_{sa}$, for (±)($^i$Pr$_2$)Mo(Neo) in Toluene-$d_8$ from -10.92 to 68.21 °C.

| Temp[a] | $\omega_{syn}$ [b] | $\omega_{anti}$ [b] | $k_{as}$[c] | $k_{sa}$[c] | $K_{eq}$[d] |
|---|---|---|---|---|---|
| -10.92 | 1.338 | 1.974 | 5.20 | 0.18 | 29.50 |
| -0.27 | 1.615 | 2.314 | 6.27 | 0.26 | 24.24 |
| 10.45 | 1.365 | 2.389 | 6.50 | 0.32 | 20.32 |
| 20.71 | 1.172 | 3.060 | 8.61 | 0.50 | 17.04 |
| 31.70 | 1.548 | 5.108 | 15.05 | 0.95 | 15.87 |
| 40.65 | 1.870 | 9.243 | 28.04 | 2.02 | 13.86 |
| 50.20 | 2.610 | 13.034 | 39.95 | 3.08 | 12.99 |
| 59.41 | 4.103 | 32.298 | 100.47 | 8.21 | 12.23 |
| 68.21 | 7.639 | 46.529 | 145.18 | 12.52 | 11.60 |

*a*. Temperature in °C. *b*. Units in Hz. *c*. Units in sec$^{-1}$. *d*. $K_{eq}$ measured at 20 °C.

**Table 3.5.** Activation Parameters for (±)($^i$Pr$_2$)Mo(Neo), (±)'($^i$Pr$_2$)Mo(Neo), Mo(NAr)(CHCMe$_2$Ph)(DIPP)$_2$ by Line Shape Analysis (*lsa*) and Spin Saturation Transfer (*sst*). Literature Values for Literature Values for Mo(NAr)(CHCMe$_2$Ph)(OAr')$_2$ by Complete Band Shape Analysis.

| Complex[a] | Technique | $\Delta G^{\ddagger}_{298}$[b] | $\Delta H^{\ddagger}$[b] | $\Delta S^{\ddagger}$[c] |
|---|---|---|---|---|
| (±)($^i$Pr$_2$)Mo(Neo) | *lsa* | 16.0(2.3) | 12.5(1.2) | -11.6(3.7) |
| (±)($^i$Pr$_2$)Mo(Neo) | *sst* | 16.2(1.6) | 15.1(0.8) | -4.0(2.8) |
| (±)'($^i$Pr$_2$)Mo(Neo) | *sst* | 16.7(3.6) | 14.4(1.8) | -7.4(6.2) |
| Mo(NAr)(CHCMe$_2$Ph)(DIPP)$_2$ | *lsa* | 17.2(1.5) | 16.2(0.8) | -3.4(2.4) |
| Mo(NAr)(CHCMe$_2$Ph)(DIPP)$_2$ | *sst* | 17.6(1.4) | 20.1(0.7) | 8.3(2.3) |
| Mo(NAr)(CHCMe$_2$Ph)(DIPP)$_2$[d] | *lsa* | 17.5(1) | 17.8(1.0) | 1.0(2.7) |
| Mo(NAr)(CHCMe$_2$Ph)(O-2-$^t$BuC$_6$H$_4$)$_2$[d] | *lsa* | 18.3(1) | 22.8(2.1) | 15(6) |

**a)** ~15 mg complex in toluene-$d_8$. **b)** Units in kcal/mol. **c)** Units in eu. **d)** Literature values[44]

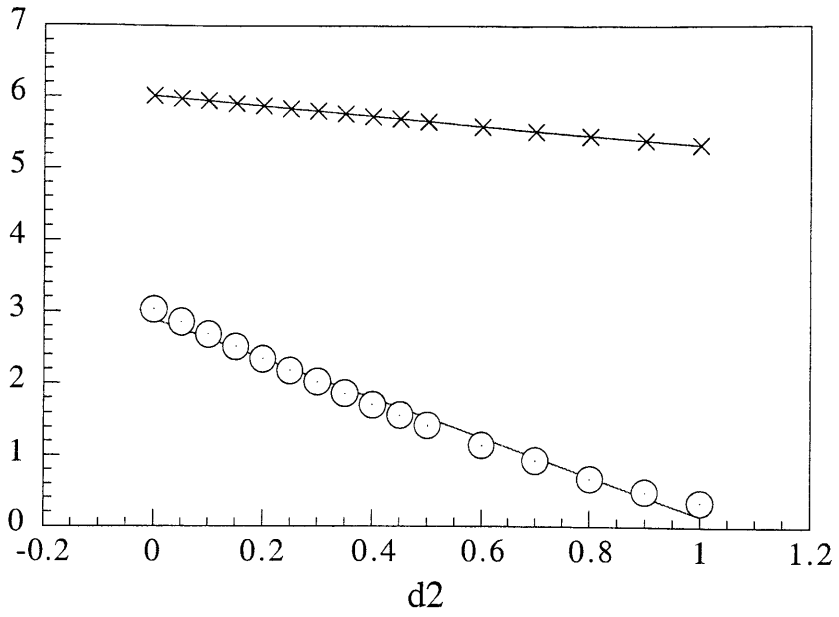



**Figure 3.5.** Linear Regression of eq 4 (×) and eq 5 (⊙) versus Relaxation Delay Time, d2 = *t*, for (±)($^{i}$Pr$_2$)Mo(Neo) at 15 °C.

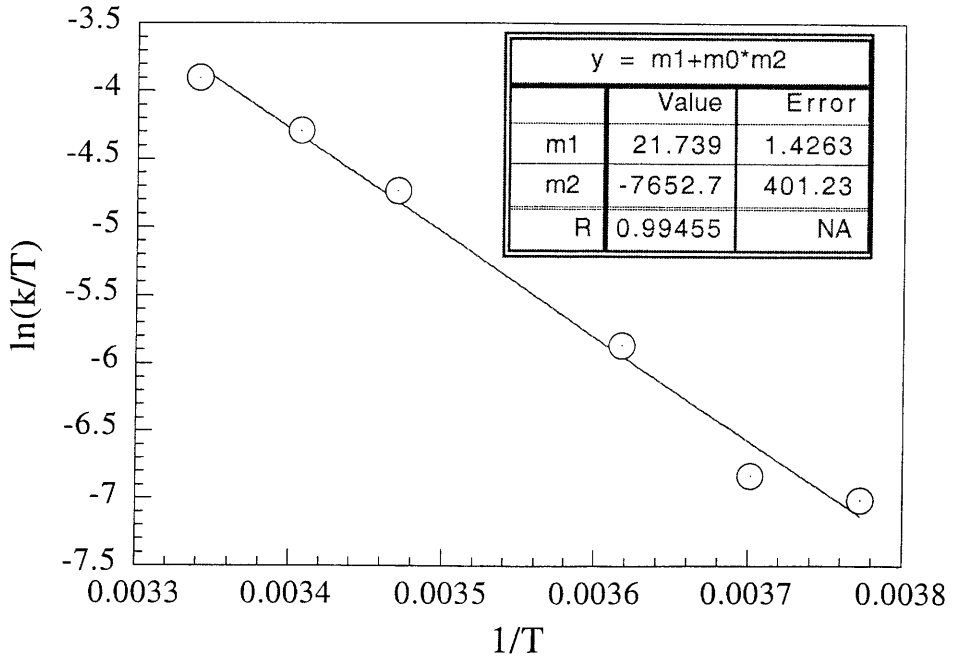



**Figure 3.6.** Determination of Activation Parameters for (±)($^{i}$Pr$_2$)Mo(Neo) from the Linear Regression of ln(k/T) versus 1/T.

## CONCLUSIONS

The *syn* rotamer is the major isomer in molybdenum imido alkylidene biphenoxide complexes. The *anti* rotamer was favored in complexes such as (±)($^t$Bu)Mo(Sty), (±)($CF_3$)Mo(Sty), and (±)($CF_3$)Mo(Neo) where the alkylidene ligand in the *anti* conformation was able to form an intramolecular chelating base adduct. The equilibrium constant in base-free four-coordinate complexes is inversely proportional to the size of the arylimido ligand and directly proportional to the size of the alkylidene substituent. Neophylidene complexes were the most stable species and addition of excess *cis*-2-butene or *trans*-3-hexene only partially converted the neophylidene to the more reactive ethylidene or propylidene complexes. Reaction with five equivalents of 1,6-hexadiene generated cyclopentene and ethylene, but neither the molybdacyclobutane, (±)($^i$Pr$_2$)Mo($C_3H_6$), nor the methylidene complex, (±)($^i$Pr$_2$)Mo($CH_2$) was observed at room temperature or at -20 °C. There was no evidence of complex decomposition, and a transient metallacycle-methylidene exchange was proposed to account for the lack of β-$CH_2$ and alkylidene resonances by $^1$H NMR. The thermodynamic parameters, $\Delta H^\circ$ and $\Delta S^\circ$, were calculated for (±)($^i$Pr$_2$)Mo(Neo), (±)'($^i$Pr$_2$)Mo(Neo), and Mo(NAr)($CHCMe_2Ph$)(DIPP)$_2$, for which $\Delta H^\circ$ = 1.1-2.4 kcal/mol and $\Delta S^\circ$ = -3.3-0.6 eu. Single parameter line shape analysis of rotamer exchange for Mo(NAr)($CHCMe_2Ph$)(DIPP)$_2$ gave similar $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values to those calculated by complete band shape analysis in the literature without having to use multiple iterations of visually fitting the theoretical and experimental band shapes. The difference in determining the activation parameters for Mo(NAr)($CHCMe_2Ph$)(DIPP)$_2$ by spin saturation transfer and line shape analysis was attributed to the incorrect assumption that $T_1$(*syn*) = $T_1$(*anti*).

## EXPERIMENTAL

**General Procedures.** All manipulations were performed under rigorous exclusion of oxygen and moisture in a dinitrogen-filled glove-box or using standard high-vacuum line procedures. NMR spectra were obtained on Varian instruments (500 MHz,

$^1$H). $^1$H NMR spectra were referenced versus residual protons in the deuterated solvents ($\delta$ = 7.16 $C_6D_6$ and $\delta$ = 2.09 toluene-$d_8$ ($CD_2H$)) or to an internal standard of hexamethylbenzene ($\delta$ = 2.11 in toluene-$d_8$). All NMR spectra were taken at room temperature unless otherwise noted. Temperatures during variable temperature NMR studies were calibrated with external ethylene glycol (T > 20 °C) or methanol (T < 20 °C) and the *tempcal* macro in the Varian software. *Trans*-3-hexene and *cis*-2-butene (Aldrich) were degassed and stored over 4Å molecular sieves. Benzene-$d_6$ (Cambridge Isotope Laboratories) was degassed with dinitrogen and dried over 4Å molecular sieves for approximately 1 day prior to use. Toluene-$d_8$ was degassed, stirred over sodium metal for 4 days and then vacuum distilled onto 4Å molecular sieves prior to use. Commands entered by keystroke for the NMR experiments are italicized and button commands are in quotations.

**Sealed Samples for NMR Spectroscopy**

Samples for room temperature NMR spectroscopy were prepared in a glove box under dinitrogen using 15-20 mg of the imido alkylidene complex in $C_6D_6$. The solution was then transferred to a Young valve NMR tube. Samples for variable temperature NMR or for kinetics experiments were prepared by charging an NMR tube with a 14/20 standard taper joint with 15-20 mg of the imido alkylidene complex and hexamethylbenzene (1-3 mg). The NMR tube was attached to a vacuum adapter and then connected to the high-vacuum line. The NMR tube was evacuated and toluene-$d_8$ (~0.7 mL) was introduced by trap-to-trap distillation. While the toluene-$d_8$ solution was frozen in liquid nitrogen, the NMR tube was sealed *in vacuo* with a propane torch.

**(±)($^i$Pr$_2$)Mo(Neo) with 5 equivalents of 1,6-hexadiene**

A sealed reaction flask was charged with 1,6-hexadiene (24 mg, 0.25 mmol) and an NMR tube with a 14/20 standard taper joint was charged with (±)($^i$Pr$_2$)Mo(Neo) (38 mg, 0.05 mmol) and hexamethylbenzene (~2 mg). Toluene-$d_8$ was introduced into the NMR tube by trap-to-trap distillation. The Schlenk flask containing 1,6-hexadiene was degassed

by two freeze-pump-thaw cycles, the 1,6-hexadiene transferred by trap-to-trap distillation into the NMR tube, and the NMR tube was then sealed. The tube was warmed to room temperature and the $^1$H NMR spectrum was recorded after two hours. No resonances were observed downfield of δ 7.6 and the ethylene resonance at δ 5.25 was broad. The ethylene resonance sharpened on cooling the sample to -20 °C but no methylidene resonances were observed.

**(±)($^i$Pr$_2$)Mo(Neo) with *Cis*-2-Butene**

*Cis*-2-butene (~20 mg) was added to a toluene-$d_8$ (0.7 mL) solution of (±)($^i$Pr$_2$)Mo(Neo) (25 mg, 0.033 mmol). The orange solution was transferred to an NMR tube with a 14/20 standard taper joint and a vacuum adapter was attached. The solution was degassed with two freeze-pump-thaw cycles and then sealed under an active vacuum. After 18 h, the $^1$H NMR spectrum was collected: $^1$H NMR (toluene-$d_8$; Mixture of (±)($^i$Pr$_2$)Mo(Neo) (16 eq), (±)($^i$Pr$_2$)Mo(CHMe) (1 eq), and *cis/trans*-2-butene (68 eq); Mixture of (±)($^i$Pr$_2$)MoN(CHMe) rotamers, $K_{eq}$ = 2.0) 13.37 (q, 1H, $J_{HH}$ = 8.5 Hz, *anti* C*H*Me), 10.64 (q, 1H, $J_{HH}$ = 6.5 Hz, *syn* C*H*Me).

**(±)($^i$Pr$_2$)Mo(Neo) with *Trans*-3-Hexene**

An NMR tube with a 14/20 standard taper joint was charged with (±)($^i$Pr$_2$)Mo(Neo) (38 mg, 0.05 mmol) and hexamethylbenzene (1-2 mg). A vacuum adapter was attached, the tube was evacuated and toluene-$d_8$ (0.7 mL) was condensed by trap-to-trap distillation. A sealed reaction tube was charged with 3-hexene (42 mg, 0.5 mmol) and degassed with two freeze-pump-thaw cycles. The hexene was transferred to the NMR tube which was then sealed with a torch *in vacuo*. After 2 days the $^1$H NMR spectrum was collected. $^1$H NMR (toluene-$d_8$) Mixture of (±)($^i$Pr$_2$)Mo(Neo) and (±)($^i$Pr$_2$)Mo(CHEt) 17.4:1 ratio. (±)($^i$Pr$_2$)Mo(CHEt) Mixture of rotamers ($K_{eq}$ = 3.1). 12.15 (dd, 1H, $J_{HH}$ = 11.9, 7.0 Hz, *anti* C*H*Et), 10.68 (dd, 1H, $J_{HH}$ = 6.8, 6.4 Hz, *syn* C*H*Et).

**Variable Temperature $^1$H NMR Spectroscopy to Determine Thermodynamic Parameters and Activation Parameters (Line Shape Analysis)**

A sealed NMR tube was inserted into the spectrometer (Inova 500 for T > -20 °C and Inova 501 for T < -20 °C). The temperature was set at the console, the sample was given 10-15 minutes to reach thermal equilibrium and the spectrometer was tuned, locked and shimmed. The spectrum was collected with an attenuation time of at least $5*T_1$ (generally *at = 6* sec was sufficient) and the data was saved. The spectrum was properly phased and integral cut for all resonances. Separate integrals were cut for the $^{13}$C satellites and for the central $^{12}$C singlet. The integral for the *anti* rotamer was cut to ensure exclusion of unobservable $^{13}$C satellites. The baseline correct command, *bc*, was used to insure flat baselines and accurate integrals. For complexes with $K_{eq} > 100$, the integrals for the *syn* and *anti* $^{12}$C singlets were used to determine the equilibrium constant. For larger $K_{eq}$, the $^{13}$C satellites of the *syn* rotamer were integrated against the *anti* rotamer. Carbon-13 has a 1.10% natural abundance. Linewidth at half-height measurements were made by placing the cursor on top of either the *syn* or *anti* rotamer and typing *nl* to place the cursor on the resonances maxima and then *dres* to display the linewidth (ω in Hz).

**Activation Parameters by Spin-Saturation Transfer**

A sealed NMR tube was inserted into the Inova-500 spectrometer and the machine was tuned, locked and shimmed. The sweep width (*sw=sw*2*) was doubled and the $^1$H NMR spectrum was recorded. The spectrometer frequency was centered on the *syn* alkylidene resonance by placing the left cursor on top of the signal and typing *nl movetof*. The $^1$H NMR spectrum was reacquired and the spectrum was phased. Integrals were cut for the entire spectrum and the baseline was corrected (*bc*).

**Instructions to create the pulse sequence for the selective inversion of the *syn* rotamer:** type *ds* then click "pbox" → "180". Place the cursors around the *syn* rotamer excluding the $^{13}$C satellites and click on "Iburp2" → "close" → "name". Enter the name for the pulse pattern (such as *s180*) then click on "close." The console then asks for

values for pw and pw90. This information was available in the text box by typing *dg*. The console will print values for the pulse width (pw) and pulse power (pwr) in the text box. Record the values for pw and pwr. To set up the pulse sequence enter *selsupMIT selpw=pw selpwr=pwr pwpat='s180'*. To display the pulse sequence enter *dps*. The attenuation time was entered to be at least $5*T_1$ (generally *at=6* was sufficient) and the number of transients set to 16 (*nt=16*). The d2 delay time (in sec) was arrayed (generally enter: *d2=0,.05,.1,.15,.2,.25,.3,.35,.4,.45.,5,.6,.7,.8,.9,1,2,12*). To check that the array was properly entered type *da*. To start the acquisition enter *ss=1 au ai*. The *ai* command sets the integration to absolute intensity to avoid integration errors between d2 delay times. The *time* command will display the experiment run time (generally 40-50 min). After data collection was complete, the arrayed spectra were viewed using the *dssh* command. To print the results with integrals, expand the window to include only the *syn* and *anti* rotamers. Type *dssh*. Then type *r1=0* to prime the variable r1. Next enter *ds(r1) aph bc pl pir* to print the arrayed spectrum for d2 = 0. Then enter *r1=r1+1 sc=sc-wc-0.5 ds(r1) aph bc pl pir*. The last entry was repeated until the entire array had been processed then enter *page* to print. The output for (±)($^{i}Pr_2$)Mo(Neo) at T = 15 °C is displayed in Figure 3.4 with d2 = 0 on the left and d2 = 12 on the far right.

# CHAPTER 4

## Asymmetric Ring-Closing Metathesis Catalyzed by Molybdenum(VI) Imido Alkylidene Biphenoxide Complexes

The research covered in this chapter was conducted in collaboration with Professor Amir H. Hoveyda, Daniel S. La and Dustin R. Cefalo at Boston College and much of it has appeared in print elsewhere:

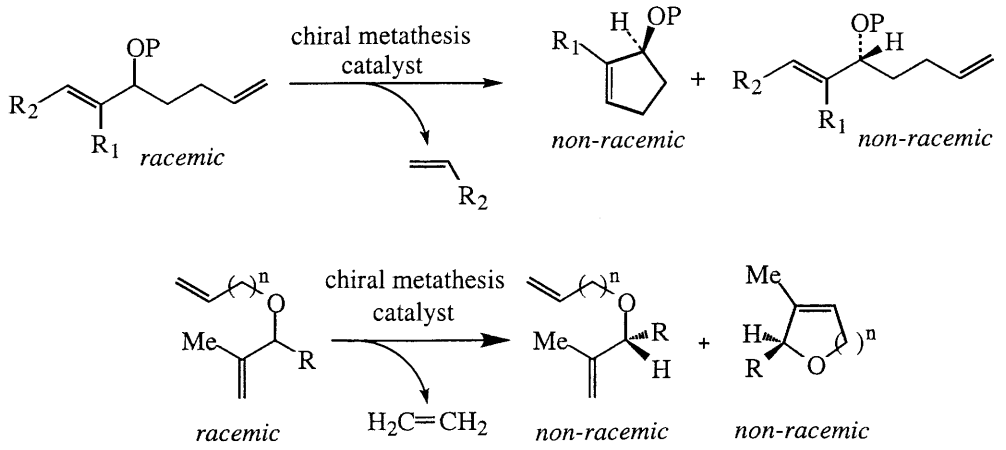
La, D. S.; Alexander, J. B.; Cefalo, D. R.; Graf, D. D.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1998**, *120*, 9720.

Alexander, J. B.; La, D. S.; Cefalo, D. R.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1998**, *120*, 4041.

## INTRODUCTION

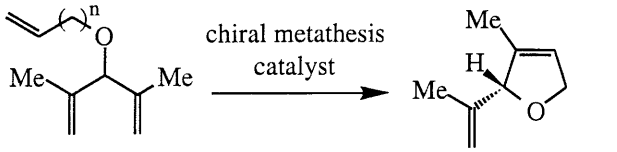
Asymmetric synthesis of enantiomerically enriched products has become a useful tool for practical organic synthesis. Both natural products and compounds of pharmaceutical interest frequently contain one or more stereogenic centers. The development of new enantioselective metal catalyzed C-C bond forming reactions is an important target in synthetic chemistry.

A kinetic resolution is a process whereby a chiral catalyst reacts faster with one enantiomer of a racemic compound. The relative rate difference causes the faster reacting substrate to be selectively consumed, leaving the unreacted starting material enriched in the slower reacting enantiomer. In a perfect kinetic resolution, only one enantiomer of the starting material reacts and the reaction mixture would contain a 1:1 mixture of enantiomerically pure starting material and product. The chiral molybdenum complex, (S)($R_2$)Mo(Neo), prepared in Chapter 2 was screened in the ARCM of racemic acyclic α,ω-dienes to give non-racemic cycloalkenes and acyclic dienes. Within this context one possible scenario involves reaction of an optically pure RCM catalyst with a racemic α,ω-diene giving rise to non-racemic cycloalkenes and acyclic dienes. In addition to the enantioselective synthesis of unsaturated carbocycles, ARCM offers unique opportunities for the preparation of enantiomerically enriched heterocycles.[9,10,17,18,48,109]




**Scheme 4.1.** Kinetic Resolution of α,ω-Dienes by ARCM.

A more attractive extension of this strategy is catalytic enantioselective desymmetrization,[115-119] which would deliver the derived heterocycles in high optical purity and with a maximum yield of 100% compared to 50% in a typical kinetic resolution (Scheme 4.2). The utility of molybdenum complexes containing the chiral biphenoxide ligands, (S)-Biphen and (S)-Biad, to catalytically desymmetrize triolefins by ARCM to give five-membered heterocycles will be discussed. Moreover, presented here are the first examples of efficient and enantioselective desymmetrization reactions that led to the formation of chiral dihydrofurans with high levels of optical purity; in certain cases, the absolute stereochemistry of quaternary carbon centers was controlled.




*achiral* *chiral, non-racemic*

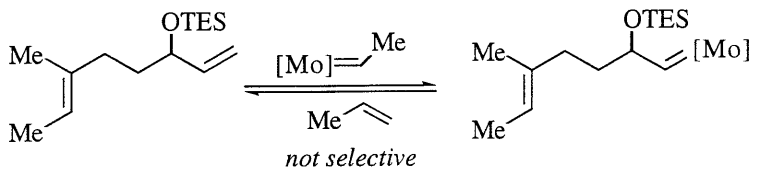
**Scheme 4.2.** Desymmetrization of Achiral Substrates to Non-Racemic Heterocycles.

## RESULTS AND DISCUSSION

### 4.1 Kinetic Resolution

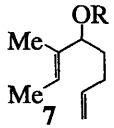
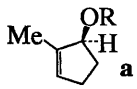
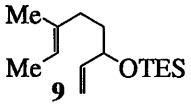
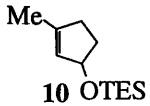
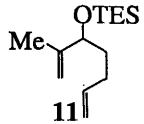
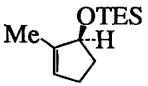
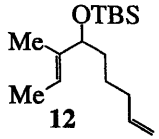
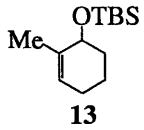
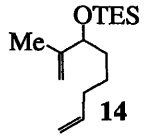
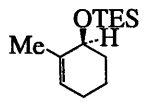
With (S)($^{i}Pr_2$)Mo(Neo), we began to explore the utility of optically pure biphenoxide complexes to effect ARCM. As illustrated in entry 1 of Table 4.1, when unsaturated TES ether **7a** was subjected to 5 mol% (S)($^{i}Pr_2$)Mo(Neo), (0.1 M benzene or toluene, Ar atmosphere, 22 °C), 43% **8a** and 38% of the corresponding dimeric product (from reaction of the terminal olefins) was formed after 10 minutes. Although not distinguishable through analysis of $^{1}H$ or $^{13}C$ NMR spectra, the dimer was likely a mixture of *cis* and *trans* isomers. Most importantly, cyclic product **8a** was obtained in 93% ee ($k_{rel}$ = 58) and the unreacted **7a** (19%) was isolated in >99% ee (chiral GLC analysis). The value for $k_{rel}$ was calculated by the equation reported by Kagan using the % ee of the residual starting material **7a**.[120,121] This calculation was only an approximation of the

relative rates of reaction for the enantiomers, as it was based on a first-order equation, where a simultaneous process that consumes both enantiomers (dimer formation) does not occur. Ring-closure was slower with lower catalyst loadings, but catalytic resolution remained effective: with 1 mol% (S)($^i$Pr$_2$)Mo(Neo), under otherwise identical conditions, after four hours, 33% **8a** and 33% dimer are formed. Chiral GLC analysis indicated that the RCM product **8a** was generated in 95% ee, whereas the recovered diene **7a** was a 5:1 mixture of enantiomers (70% ee). Entries 2 and 3 of Table 4.1 indicate that similarly high levels of enantioselectivity and reaction efficiency were obtained with bulkier silyl protecting groups (with **7b** and **7c** as substrates). When the smaller benzyloxy group was used as the alkoxy protecting unit, catalytic RCM proceeded smoothly (entry 4) and resolution efficiency remained high ($k_{rel}$ = 22).

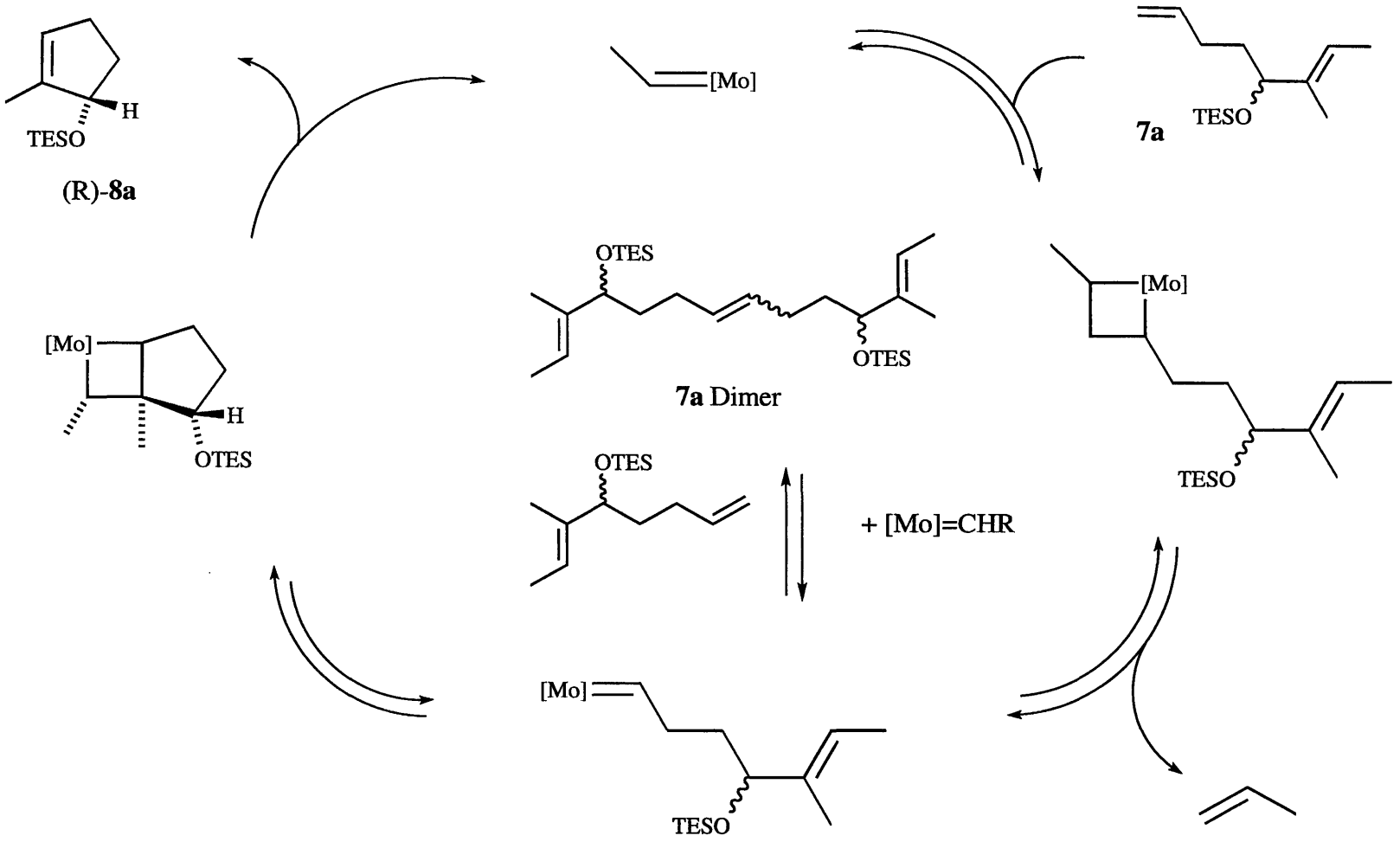



As entry 5 of Table 4.1 indicates, when the stereogenic center was positioned α to the terminal alkene, dimer formation was significantly diminished, but efficient catalytic kinetic resolution was not achieved (**9**→**10**). This result was mechanistically significant, as it suggested that formation of the Mo-alkylidene with the substrate terminal olefin, [Mo]=CHC(OR)H(CH$_2$)$_2$CMe=CHMe, did not occur with significant stereodifferentiation (that is, both enantiomers reacted with equal facility). It was the subsequent formation or decomposition of the metallacyclobutane that determined the identity of the faster reacting enantiomer. It was therefore plausible that with substrates such as **7a-c**, significant diastereotopic CNO face differentiation was achieved in the cyclic transition state for the addition of the terminal metal-carbene to the trisubstituted olefin to form the bicyclic metallacyclobutane due to the presence of the adjacent stereogenic site (Scheme 4.3).

**Table 4.1.** Kinetic Resolution of Acyclic Dienes Catalyzed by (S)$^{i}Pr_2$MoNeo.

| entry | substrate | product | reaction time (min); conv. (%) | percent product[b] | percent dimer[b] | unreacted substrate config., ee (%)[c] | product ee (%)[c] | $k_{rel}$ |
|---|---|---|---|---|---|---|---|---|
| 1[f] |  **7** |  **8** **a** R=TES | 10; 81 | 43 | 38 | *R*, >99 | 93 | 58[d] |
| 2[g] | | **b** R=TBS | 60; 75 | 42 | 33 | *R*, >99 | 93 | 56[d] |
| 3[g] | | **c** R=TBDPS | 120; 83 | 43 | 40 | *R*, 95 | 92 | 52[d] |
| 4[g] | | **d** R=Bn | 180; 76 | 41 | 35 | *R*, 91 | 85 | 22[d] |
| 5[g] |  **9** |  **10** | 120; 50 | 40 | 10 | <5 | <5 | -- |
| 6[g] |  **11** |  **8a** | 5; 59 | 55 | <5 | *R*, 97 | 65 | 11[e] |
| 7[g] |  **12** |  **13** | 120; 50 | <5 | 50 | -- | -- | -- |
| 8[g] |  **14** |  **15** | 30; 58 | 47 | 11 | *R*, 57 | 45 | 4[e] |

*a.* Reaction Conditions: 5 mol % (S)$^{i}Pr_2$MoNeo, $C_6H_6$, Ar atm., 22 °C. Mass Balance >90% in all cases. *b.* Conversion determined by analysis of the 400 MHz $^1$H NMR spectrum of the unpurified mixture. *c.* Enantioselectivity determined by GLC analysis (CHIRALDEX-GTA by Alltech) of the derived acetates in comparison with authentic racemic material. *d.* Relative rate measured based on formation and selectivity of RCM product. *e.* Relative rate measured based on the recovered starting material. *f.* Performed at M.I.T. *g.* Performed at Boston Collegeby Daniel La and Dustin Cefalo.




**Scheme 4.3.** Mechanism for Kinetic Resolution by ARCM Including Dimer Formation.

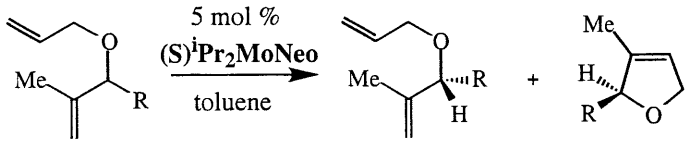
When RCM of **7a** was carried out under an atmosphere of ethylene, the rate of ring closure was reduced, but the relative amount of dimeric product and enantioselectivity were unaffected. In order to minimize dimer formation,[122] while maintaining high asymmetric induction, 1,1-disubstituted alkene substrate **11** was investigated. Cyclization of the less substituted olefin would compete more efficiently with dimerization to lead to a more efficient ARCM. As shown in entry 6 of Table 4.1, diene **11** afforded 55% yield of cyclic product **8a** and < 5% of the corresponding dimeric product after only 5 minutes with standard RCM conditions. The recovered starting material was obtained in 97% ee (chiral GLC analysis; $k_{rel}$ = 11), and **8a** was isolated in 65% ee. This result, together with the data in entry 1, indicated that both the starting diene and the product cycloalkene could be isolated in excellent optical purity and good yield, depending on whether the trisubstituted (*e.g.*, **7a**) or the 1,1-disubstituted olefin (*e.g.*, **11**) was utilized as the starting material. The notable difference in resolution efficiency between substrates **7a** and **11** ($k_{rel}$ = 58 and 11, respectively) may be partly due to the transition state energy differences involved in reactions of lower and higher substituted olefinic substrates. In light of the data in entry 5 of Table 4.1, it is also feasible that, with **11** as the substrate, resolution efficiency suffers because the chiral (S)($^{i}Pr_2$)Mo(CHR) (R = H, Me) no longer selects the terminal alkene as its initial site of reaction. That product enantioselection was higher in the reaction of **7a** than in ARCM of **11** is intriguing. It is tenable that, in the former instance, concomitant dimerization enhanced product enantioselectivity because the slow-reacting enantiomer concentration was simultaneously diminished through this coupling pathway. As a result, since the relatively slower substrate enantiomer was sequestered at a higher rate through dimerization as the reaction proceeded, cyclization of this enantiomer was expected to occur less frequently than expected for a first order kinetic resolution.[120]

Attempted catalytic RCM of 1,7-diene **12** (entry 7) resulted only in the formation of the corresponding dimer. As before, dimerization was minimized in the ARCM of the lesser substituted **14**. After 30 min, 47% product and 11% dimer were obtained. The

resolution efficiency represented an improvement to previous related results on similar substrates,[72] but was lower than that observed for **11**. The recovered starting material was obtained in 57% ee ($k_{rel}$ = 4).[72] A chiral binaphtholate complex, Mo(NAr)(CHCMe$_2$Ph)((R)-3,3'-(TRIP)$_2$-BINO) (Ar = 2,6-Me$_2$Ph, 2,6-$^i$Pr$_2$Ph) has been developed by Zhu and Schrock[104] where the large 2,4,6-tri-*iso*-propylphenyl groups projected the binaphthyl chirality toward the alkylidene active site. The planar nature of the TRIP group also produces a larger asymmetric pocket immediately around the alkylidene than the *tert*-butyl groups of the Biphen ligand. As a result, the selectivity of the TRIP-binaphthyl complexes complements that of (S)(R$_2$)Mo(Neo) (R = Me, $^i$Pr). Binaphthyl complexes are less selective at ARCM of substrates that generate cyclopentenes or dihydrofurans and are much more selective in six-membered ring forming reactions ($k_{rel}$ up to 56 for kinetic resolutions).[104]

As illustrated in entry 1 of Table 4.2, treatment of diene ether **16a** with 5 mol% (S)($^i$Pr$_2$)Mo(Neo) in toluene at -25 °C led to the formation of dihydrofuran (S)-**17**. After 63% conversion, the unreacted starting material, (R)-**16**, was obtained in 92% ee ($k_{rel}$ = 10).[120] Although diene **16d** was resolved with slightly lower enantioselectivity, entries 2 and 3 of Table 4.2 indicated that increasing the size of the α substituent can lead to notable enhancement in resolution. With **16a**, **16b** and **16d**, when ARCM was performed at 22 °C, the reactions reached >80% conversion within one minute. ARCM of **16c** was also carried out at ambient temperature (64% conv in 8 min) without significant reduction in enantioselectivity (entry 3). It is worth noting that although the ARCM processes in Table 4.2 were performed with 5 mol% catalyst, lower loadings are effective; for example, in the presence of 2.5 mol% (S)($^i$Pr$_2$)Mo(Neo), (±)-**16a** was resolved with $k_{rel}$ = 10 (58% conv, 23 h).

**Table 4.2.** Kinetic Resolution of Allylic Ethers with (S)($^i$Pr$_2$)Mo(Neo).[a,b]

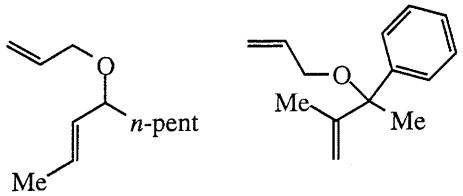



(±)-**16** (R)-**16** (S)-**17**

| entry | substrate | temp (°C), time | conv.[c] (%) | unreacted subs. ee (%)[d] | $k_{rel}$ |
|---|---|---|---|---|---|
| 1 | (±)-**16a**, R = *n*-Pent | -25, 6 h | 63 | 92 | 10 |
| 2 | (±)-**16b**, R = $^i$Bu | -25, 10 h | 56 | 95 | 23 |
| 3 | (±)-**16c**, R = Cy | -25, 7 h | 62 | 98 | 17 |
| | | 22, 8 min | 64 | 97 | 13 |
| 4 | (±)-**16d**, R = Ph | -25, 6 h | 56 | 75 | 8 |

*a*. Performed at Boston College by Dustin Cefalo. *b*. Conditions: 5 mol% (S)($^i$Pr$_2$)Mo(Neo), toluene, Ar atm. *c*. Conversion determined by GLC analysis in comparison with dodecane as the internal standard. *d*. Enantioselectivity determined by chiral GLC (CHIRALDEX-GTA by Alltech) in comparison with authentic racemic material.

In contrast to dienes that bear a 1,1-disubstituted alkene (**16a-d**), 1,2-disubstituted substrates such as **18** were not resolved.[123] Thus, after the treatment of diene **18** to standard conditions with (S)($^i$Pr$_2$)Mo(Neo), recovered starting material was obtained in only 27% ee after 54% conversion ($k_{rel}$ = 1.5). In addition, chiral catalysts (S)($R_2$)Mo(Neo) (R = $^i$Pr, Me) were ineffective in resolving the related tertiary ethers, such as **19** (<10% ee after 20% conversion in 24 h).[123]




(±)-**18** (±)-**19**

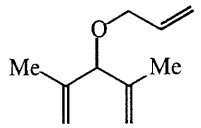
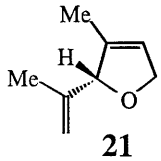
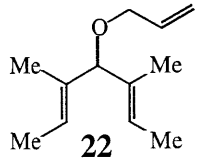
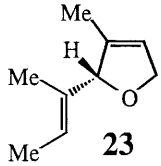
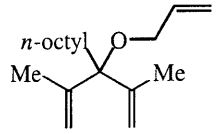
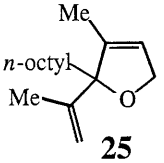
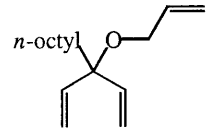
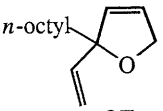
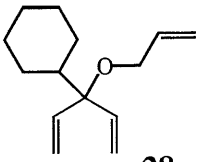
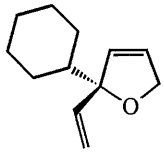
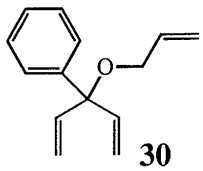
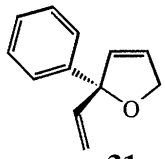
## 4.2 Desymmetrization with (S)($R_2$)Mo(Neo) (R = Me, $^i$Pr)

Catalytic enantioselective desymmetrization processes were investigated. As illustrated in Table 4.3, when triene **20** was subjected to 1 mol% (S)($^i$Pr$_2$)Mo(Neo)

(toluene or benzene, 22 °C), ARCM proceeds to 94% conversion after 6 h; dihydrofuran (R)-**21** was obtained in 93% ee (chiral GLC) and 82% yield after silica gel chromatography. Similar results were obtained with (S)($Me_2$)Mo(Neo) as the catalyst. With the more substituted triene **22** as the substrate and (S)($^iPr_2$)Mo(Neo) as the catalyst, enantioselectivity remained high (94% ee) but the rate of formation of **23** decreased significantly (32% conversion after 9 h). With 5 mol% (S)($Me_2$)Mo(Neo), ARCM proceeds to 95% conversion after only 4 h and **23** was obtained in 99% ee and 83% isolated yield.

The ability to control the absolute stereochemistry of quaternary carbon stereogenic centers by metathesis was also investigated.[124] Attempts to effect the ARCM of triene **24** were thwarted by <2% reaction with (S)($^iPr_2$)Mo(Neo) as the initiator; when (S)($Me_2$)Mo(Neo) was used, the reaction proceeded to 42% conversion affording **25** in 50% ee. Higher conversions were obtained with the less substituted triene **26**, but selectivity suffered, presumably due to partial initial reaction at an alkene adjacent to the prochiral center. Because our preliminary studies indicated that it was the formation of the intermediate metallabicyclobutane that was likely the stereochemistry-determining step (versus the initial formation of the metal-alkylidene), higher levels of enantioselectivity were expected with larger alkyl substituents (allowing for more effective steric differentiation between vinyl units). These considerations led us to examine the ARCM of triene **28**. With them more sterically demanding cyclohexyl unit, the initial Mo-alkylidene formation probably occurred primarily at the less hindered terminal olefin, causing metallabicycle formation to occur adjacent to the quaternary site. As the data in entries 5 and 6 of Table 4.3 indicate, in the presence of 5 mol% (S)($Me_2$)Mo(Neo), ARCM of tertiary ethers **28** and **30** afforded **29** and **31** in 73 and 82% ee and 84 and 91% yield, respectively. The absolute stereochemistry has not been definitively assigned. It is important to note that, as depicted in entry 5, reactions with (S)($^iPr_2$)Mo(Neo) were less efficient and not as selective.

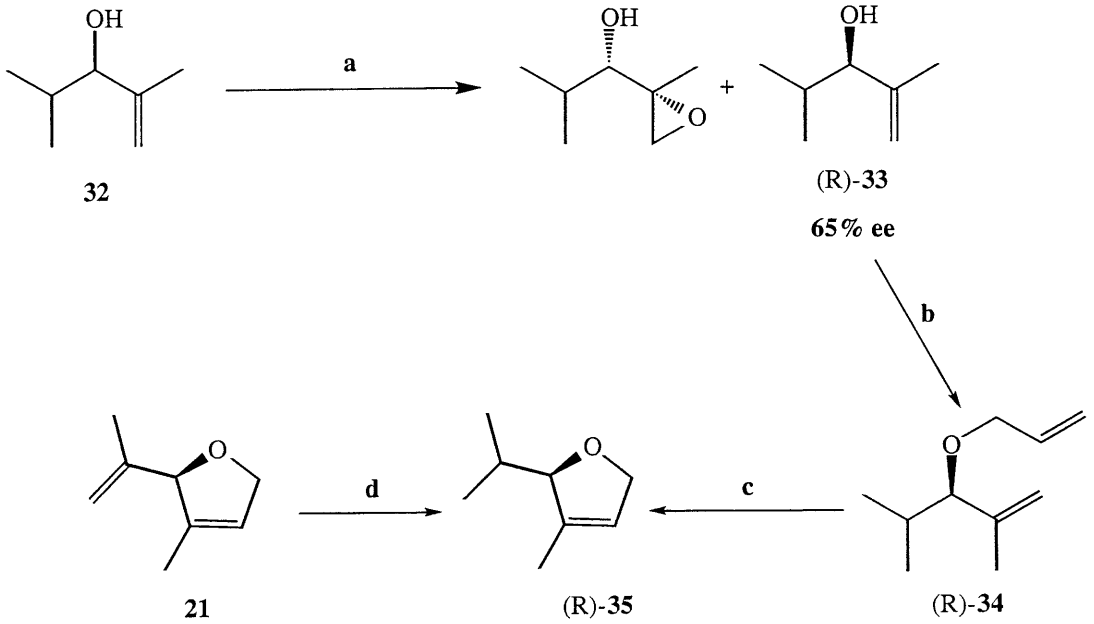
**Table 4.3.** Enantioselective Synthesis of Dihydrofurans by (S)($R_2$)Mo(Neo) (R = $^i$Pr, Me) Catalyzed Desymmetrization.[a]

| entry | substrate | (S)$R_2$MoNeo | temp (°C), time | product | product ee (%), config.[b] | conv.[c], yield (%)[d] |
|---|---|---|---|---|---|---|
| 1[e] |  **20** | R = $^i$Pr<br>R = Me | 22, 6 h<br>22, 6 h |  **21** | 93, *R*<br>93, *R* | 94, 82<br>93, 86 |
| 2[e] |  **22** | R = $^i$Pr<br>R = Me | 22, 9 h<br>22, 4 h |  **23** | 94, *R*<br>99, *R* | 32, --<br>95, 83 |
| 3[f] |  **24** | R = $^i$Pr<br>R = Me | 22, 9 h<br>22, 4 h |  **25** | --<br>50, | NO REACTION<br>42, 42 |
| 4[f] |  **26** | R = $^i$Pr<br>R = Me | 22, 15 h<br>22, 15 h |  **27** | 10<br>10 | 76, 73<br>>98, 88 |
| 5[f] |  **28** | R = $^i$Pr<br>R = Me | 22, 18 h<br>-20, 18 h |  **29** | 17<br>73 | 87, 85<br>93, 84 |
| 6[f] |  **30** | R = $^i$Pr<br>R = Me | 22, 18 h<br>-20, 18 h |  **31** | 16<br>82 | 36, 34<br>93, 91 |

*a*. Conditions: 5 mol% catalyst (1 mol%, entry 1), toluene or benzene, Ar atm. *b*. Selectivity determined by chiral GLC (CHIRALDEX-GTA by Alltech for entries 1-4; BETADEX-120 by Alltech for entries 5-6) in comparison with authentic racemic material. *c*. Conversion determined by GLC analysis in comparison with dodecane as the internal standard (entries 1-2) or by $^1$H NMR analysis (400 MHz). *d*. Isolated yields after silica gel chromatography or distillation. *e*. Performed at M.I.T. *f*. Performed at Boston College by Daniel La.

The absolute stereochemistry of dihydrofuran **21** was determined[125] using Sharpless epoxidation to set the stereochemistry of enriched (R)-2,4-dimethyl-pent-1-en-3-

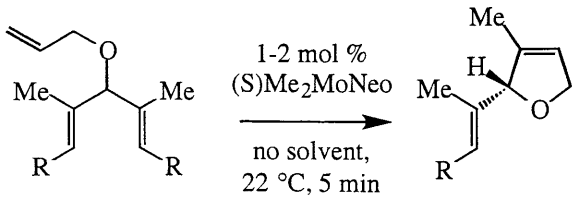
ol (65% ee), (R)-**33** (Scheme 4.4). Etherification similar to the preparation of **20** generated the α,ω-diene (R)-**34** which was then cyclized by Mo(NAr)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ to give dihydrofuran (R)-**35**.[50] Non-racemic **21** was hydrogenated with Wilkinson's catalyst to afford **35** which was compared with authentic (R)-**35** by chiral GLC, indicating that (S)(R$_2$)Mo(Neo) produced (R)-**21** by ARCM of **20**. The absolute stereochemistry of (R)-**23** was thus assigned by inference from (R)-**21**.




**a**) Ti(O$^i$Pr)$_4$, (+)-DCHT, $^t$BuOOH, CH$_2$Cl$_2$, -20 °C. **b**) NaH, BrCH$_2$CH=CH$_2$, THF. **c**) 5 mol% Mo(NAr)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$, benzene. **d**) Rh(PPh)$_3$Cl, H$_2$ atmosphere.

**Scheme 4.4.** Determination of Absolute Stereochemistry for **21** by Comparison with Optically Enriched Dihydrofuran Generated by Sharpless Epoxidation.

Most noteworthy is the remarkable efficiency of the Mo-catalyzed enantioselective desymmetrization process, where we find that ARCM reactions can be performed in solvent-free conditions. For example, as shown in Scheme 4.5, catalytic ARCM of **20** and **22** can be carried out in the absence of solvent with 1-2 mol% (S)(Me$_2$)Mo(Neo) to afford – within five minutes – (R)-**21** and (R)-**23** in 85% and 99% isolated yield and 93% and 99% ee after distillation (>99% conversion in both cases), respectively. In both reactions, there is <5% dimer formed (GLC analysis).




**20** R=H (1 mol %) (R)-**21** *93% ee, 85% yield*
**22** R=Me (2 mol %) (R)-**23** *99% ee, 93% yield*

**Scheme 4.5.** ARCM of Substrates **20** and **22** in the Absence of Solvent with (S)($Me_2$)Mo(Neo).

## 4.3 ARCM of Substrates 20 and 22 with (S)-Biphen and (S)-Biad Complexes

Desymmetrization of substrates **20** and **22** was used as a benchmark reaction to test the enantioselectivity of optically pure (S)-Biphen and (S)-Biad complexes. The conversion of starting material to furan product was measured by integration of the olefinic region of the $^1H$ NMR spectrum. The enantioselectivity of the desymmetrization process was readily obtained by trap to trap distillation of the volatile substrate/product mixture and separation of product enantiomers by chiral GLC. The stereoselectivity ($k_{rel}$) of the desymmetrization reaction was not dependent on the conversion level as was the case for kinetic resolutions. Consequently, the enantiomeric excess (% ee) of the desymmetrized product was as accurate a measure of selectivity as $k_{rel}$ was for kinetic resolutions. The relative rate for the desymmetrization reaction is calculated directly from the enantiomeric excess {$k_{rel}$ = (%ee + 100)/(100 - %ee}. In addition, the desymmetrization process was not prone to substrate dimerization, whereas this process had complicated the determination of the enantioselectivity ($k_{rel}$) for kinetic resolutions in Section 4.1.

(S)-Biad complexes were found to be slower and less selective than the corresponding (S)-Biphen complexes. The increased reaction times and catalyst loading for (S)-Biad complexes was necessary due to the increased shielding of the alkylidene functionality by the 1-adamantyl groups of (S)-Biad compared to the *tert*-butyl groups of

(S)-Biphen. The reduced selectivity of the (S)-Biad complexes relative to (S)-Biad complexes might be due to a combination of factors. The *anti* rotamer of (S)($Me_2$)Mo(Neo), (S)3,5-$Me_2$)Mo(Neo) and (S)($CF_3$)Mo(Np) were not observed by $^1H$ NMR spectroscopy. (S)'($^iPr_2$)Mo(Neo) and (S)'($Et_2$)Mo(Neo) had similar concentrations of *anti* rotamer as (S)($^iPr_2$)Mo(Neo) and (S)($Et_2$)Mo(Neo) respectively. The equilibrium concentrations of neophylidene complexes does not necessarily correlate to the concentration of *syn* and *anti* rotamers of intermediate alkylidenes such as [Mo]$CHCH_2OCH(CMe{=}CHR)_2$ (R = H or Me) which are involved in the stereodetermining metathesis step.

**Table 4.4**. Desymmetrization of **20** with (S)-Biphen and (S)-Biad Catalysts in Benzene at Room Temperature.

| Entry | Catalyst | Time (h) | Loading (mol%) | Conversion (%) | ee (%) |
|---|---|---|---|---|---|
| 1 | (S)($^iPr_2$)Mo(Neo) | 6 | 1 | 94 | 93 |
| 2 | (S)($Et_2$)Mo(Neo) | 6 | 1 | >95 | 93 |
| 3 | (S)($Me_2$)Mo(Neo) | 6 | 1 | 93 | 93 |
| 4 | (S)($CF_3$)Mo(Sty) | 1 | 1 | >95 | 26 |
| 5 | (S)($^tBu_2Me$)Mo(Neo) | 24 | 5 | 40 | 31 |
| 6 | (S)'($^iPr_2$)Mo(Neo) | 23 | 5 | 16 | 51 |
| 7 | (S)'($Et_2$)Mo(Neo) | 2 | 5 | >95 | 64 |
| 8 | (S)'($Me_2$)Mo(Neo) | 1 | 5 | >95 | 78 |
| 9 | (S)'(3,5-$Me_2$)Mo(Neo) | 1 | 5 | >95 | 64 |
| 10 | (S)'($CF_3$)Mo(Np) | 1 | 5 | >95 | 7 |

**Table 4.5**. Desymmetrization of **22** with (S)-Biphen and (S)-Biad Catalysts in Benzene at Room Temperature.

| Entry | Catalyst | Time (h) | Loading (mol%) | Conversion (%) | ee (%) |
|---|---|---|---|---|---|
| 1 | (S)($^{i}Pr_2$)Mo(Neo) | 9 | 1 | 32 | 94 |
| 2 | (S)($Et_2$)Mo(Neo) | 6 | 1 | >95 | 99 |
| 3 | (S)($Me_2$)Mo(Neo) | 4 | 1 | >95 | 99 |
| 4 | (S)($CF_3$)Mo(Sty) | 1 | 1 | >95 | 94 |
| 5 | (S)($^{t}Bu_2Me$)Mo(Neo) | 24 | 5 | 20 | 99 |
| 6 | (S)'($^{i}Pr_2$)Mo(Neo) | 24 | 5 | 10 | 33 |
| 7 | (S)'($Et_2$)Mo(Neo) | 20 | 5 | 50 | 77 |
| 8 | (S)'($Me_2$)Mo(Neo) | 18 | 5 | >95 | 86 |
| 9 | (S)'(3,5-$Me_2$)Mo(Neo) | 2.5 | 5 | >95 | 94 |
| 10 | (S)'($CF_3$)Mo(Np) | 1 | 5 | >95 | 90 |

The enantioselectivity and reactivity of (S)($Et_2$)Mo(Neo) was similar to (S)($Me_2$)Mo(Neo) for both **20** and **22**. The heterodisubstituted (S)($^{t}Bu_2Me$)Mo(Np) was much slower than the other (S)-Biphen complexes in the ARCM of both **20** and **22**. The desymmetrization of **20** with 5 mol% (S)($^{t}Bu_2Me$)Mo(Np) was only 40% complete after 24 hours and the enantioselectivity (31% ee) was poor. For comparison, RCM of **20** with the largest symmetrically substituted arylimido complex, (S)($^{i}Pr_2$)Mo(Neo), went to completion (93% conv) in 6 hours with only 1 mol% catalyst loading and the enantioselectivity was excellent (93% ee). The reactivity of (S)($^{t}Bu_2Me$)Mo(Np) and (S)($^{i}Pr_2$)Mo(Neo) was similar with the trisubstituted substrate **22**. Neither reaction went to completion: 5 mol% (S)($^{t}Bu_2Me$)Mo(Np) completed only 4 turnovers within 24 hours (20% conversion) and 1 mol% (S)($^{i}Pr_2$)Mo(Neo) completed 32 turnovers in 9 hours (32% conversion). The enantioselectivity of (S)($^{i}Pr_2$)Mo(Neo) remained high (94% ee) while the selectivity of (S)($^{t}Bu_2Me$)Mo(Np) was low (33% ee). (S)($CF_3$)Mo(Sty) was the fastest

catalyst in the desymmetrization reaction. With 1 mol% catalyst loading, (S)($CF_3$)Mo(Sty) completely cyclized both **20** and **22** in one hour. (S)($Me_2$)Mo(Neo) required 4-6 h at the same catalyst loading. The increased reaction rate was offset however by reduced enantioselectivity. With the trisubstituted substrate **22**, the dihydrofuran, **23**, was formed in 90% ee and $k_{rel}$ = 19 (compared to >99% ee and $k_{rel} \cong 200$ for (S)($Me_2$)Mo(Neo)). The stereoselectivity of (S)($CF_3$)Mo(Sty) with the smaller 1,1-disubstituted substrate **20** was only 26% ee which was significantly lower than the 93% ee obtained with (S)($R_2$)Mo(Neo) (R = $^i$Pr, Et, Me).

## CONCLUSIONS

The chiral molybdenum-based metathesis complexes developed in Chapter 2 effected ARCM with outstanding levels of enantioselectivity and with high efficiency in general. The chiral molybdenum complex, (S)($^i Pr_2$)Mo(Neo), promoted the formation of cyclopentenes and dihydrofurans in high optical purity by the kinetic resolution of racemic starting materials; in most instances, the recovered substrate was also obtained in excellent enantiomeric excess. Racemic substrates containing a trisubstituted olefin proximal to the stereogenic center were prone to dimerization of the slower cyclizing enantiomer via a coupling reaction of the terminal olefins. Sequestering of the slower reacting enantiomer by dimer formation increased the enantiomeric excess of cyclized product.

A series of achiral triolefinic substrates were cyclized by ARCM with (S)($Me_2$)Mo(Neo) and (S)($^i Pr_2$)Mo(Neo) to generate chiral non-racemic dihydrofuran products. Substrates **20** and **22** were cyclized with (S)($Me_2$)Mo(Neo) without solvent to give the corresponding dihydrofuran product within five minutes with excellent enantioselectivity. In some cases, quaternary stereogenic centers were obtained with good enantioselectivity (up to 84% ee) and in high yield. The enantioselectivity of (S)-Biphen and (S)-Biad complexes in ARCM were compared using the desymmetrization of **20** and **22** as benchmark reactions. The (S)-Biad complexes were slower and less stereoselective

than the corresponding (S)-Biphen complexes. The source of the lower enantioselectivity for (S)-Biad molybdenum complexes has not been identified.

## EXPERIMENTAL

**General Procedures.** Unless otherwise noted all manipulations were performed under rigorous exclusion of oxygen and moisture in a dinitrogen-filled glove-box or using standard Schlenk procedures. Benzene, THF and toluene were distilled from sodium metal/benzophenone ketyl. Dichloromethane was distilled from calcium hydride. Infrared (IR) spectra were recorded on Perkin Elmer 781 and 1608 spectrophotometers, $\nu_{max}$ in $cm^{-1}$. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). $^1H$ NMR spectra were recorded on Varian GN-400 (400 MHz), Unity 300 (300 MHz), and Varian VXR 500 (500 MHz) spectrometers. Chemical shifts are reported in ppm from tetramethylsilane with the residual protonated solvent resonance as the internal standard ($CHCl_3$: $\delta$ 7.26). $^{13}C$ NMR spectra were recorded on Varian GN-400 (100 MHz), Unity 300 (75.4 MHz), and Varian VXR 500 (125 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal reference ($CDCl_3$: $\delta$ 77.7 ppm). Enantiomer ratios were determined by chiral GLC analysis (Alltech Associates Chiraldex GTA column (30m x 0.25mm)) or Betadex 120 column (30m x 0.25mm) in comparison with authentic materials. 2,4-Dimethyl-1,4-pentadien-3-ol and 3,5-dimethyl-1,6-heptadien-4-ol were prepared using a modified literature procedure.[126,127] All other reagents were used as received. $C_6D_6$ and toluene-$d_8$ (Cambridge Isotope Laboratories) were degassed with dinitrogen and dried over 4Å molecular sieves for approximately 1 day prior to use. Spectroscopic characterization and microanalysis for substrates and products were performed at the institute where the ARCM was carried out (for example, **7b** was studied and characterized at Boston College while **20** was studied and characterized at M.I.T.). Elemental analyses were performed at Robertson Microlit Laboratories (Madison, New Jersey) and Microlytics Analytical Laboratories

(Deerfield, Massachusetts). High resolution mass spectrometry was performed by the University of Illinois and Massachusetts Institute of Technology Mass Spectrometry Laboratories.

**Representative procedure for Mo-catalyzed kinetic resolution of silyl ether substrates.**

Unsaturated silyl ether **7a** (58 mg, 0.228 mmol) was dissolved in anhydrous benzene (2.3 mL). The vessel was then charged with (S)($^{i}Pr_2$)Mo(Neo) (8.6 mg, 0.011 mmol, 5 mol%) and the flask sealed with a Teflon cap. After 30 min, the reaction was opened to air and MeOH was added (1 mL). The volatiles were removed on a rotary evaporator providing a dark brown residue which was passed through a plug of silica gel using 10:1 hexane:$OEt_2$. Organic solvents were then evaporated to yield a yellow oil (55.1 mg, 95% mass balance: assuming 78% conversion and all (S)-Biphen$H_2$). The percent conversion was determined by analysis of the $^1$H NMR spectrum (400 MHz, $CDCl_3$; recovered **7a** showed a signal at δ 5.82 ppm (1H), **8a** showed signals at δ 5.47 (1H) and δ 4.63 (1H), and the dimer showed signals at δ 5.35 (4H) and δ 3.94 (2H). The starting material **7a** and ring-closed product **8a** were purified by silica gel chromatography (distilled hexanes as the solvent) to afford pure (*R*)-**7a** (15.3 mg, 25% yield), (*S*)-**8a** (15.9 mg, 31% yield) and dimer of **7a** (7.53 mg, 13% yield). The stereochemical identity of the recovered starting material, **7a**, was determined by comparison with authentic non-racemic material obtained from RCM of the non-racemic allylic ethers. Non-racemic parent allylic alcohols were prepared by the method of Sharpless.[128]

**(6*E*)-6-Methyl-5-triethylsiloxy-1,6-octadiene (7a).** IR (NaCl) 2962 (s), 2917 (s), 2880 (s), 1640 (w), 1237 (m), 1073 (s), 1004 (m), 910 (m), 740 (s) cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 5.82 (dddd, $J_{HH}$ = 16.8, 10.0, 6.4, 6.4 Hz, 1H, *H*C=$CH_2$), 5.36 (q, $J_{HH}$ = 6.4 Hz, 1H, $CH_3$*H*C=C), 5.00 (dd, $J_{HH}$ = 12.0, 2.0 Hz, 1H, CH=C*H*H), 4.93

(d (br), $J_{HH}$ = 10.4 Hz, 1H, HC=CH*H*), 3.96 (t, $J_{HH}$ = 6.4 Hz, 1H, C*H*OSi), 2.08-1.90 (m, 2H, C*H*$_2$HC=CH$_2$), 1.65-1.47 (m, 2H, C*H*$_2$CH$_2$HC=CH$_2$), 1.58 (d, $J_{HH}$ = 6.8 Hz, 3H, C*H*$_3$HC=C), 1.55 (s, 1H, C*H*$_3$C=CH), 0.93 (t, $J_{HH}$ = 8.0 Hz, 9H, (C*H*$_3$CH$_2$)$_3$SiO), 0.55 (q, $J_{HH}$ = 8.0 Hz, 6H, (CH$_3$C*H*$_2$)$_3$SiO), $^{13}$C NMR (100 MHz, $CDCl_3$) δ 139.6, 138.8, 120.5, 114.9, 78.7, 36.1, 30.8, 13.6, 11.3, 7.6, 5.5. HRMS Calcd for $C_{15}H_{30}OSi$ (M+H) 255.2146. Found: 255.2151. Anal. Calcd for $C_{15}H_{30}OSi$: C, 70.79; H, 11.88. Found: C, 71.03; H, 11.96.

**(2*E*-12*E*)-4,11-Bis(triethylsiloxy)-3,12-dimethyl-2,7,12-tetradecatriene (7a Dimer).** IR (NaCl) 2949 (s), 2880 (s), 1464 (w), 1250 (w), 1073 (m), 1004 (m), 853 (w), 740 (m) cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 5.39-5.32 (m, 4H, CH$_3$C*H*=C, CH$_2$*H*C=C*H*CH$_2$), 3.94 (t, $J_{HH}$ = 7.2 Hz, 2H, C*H*OSi), 2.00-1.82 (m, 4H, C*H*$_2$CH=CHC*H*$_2$), 1.57 (d, $J_{HH}$ = 6.4 Hz, 6H, C*H*$_3$CH=C), 1.54 (s, 6H, C*H*$_3$C=CH), 1.51-1.41 (m, 4H, C*H*$_2$CH$_2$CH), 0.92 (t, $J_{HH}$ = 8.0 Hz, 18H, (C*H*$_3$CH$_2$)$_2$SiO), 0.54 (q, $J_{HH}$ = 8.0 Hz, 12H, (CH$_3$C*H*$_2$)$_2$SiO), $^{13}$C NMR (100 MHz, $CDCl_3$) δ 130.8, 130.4, 120.4, 78.8, 36.8, 29.6, 13.6, 11.3, 7.6, 5.6. HRMS Calcd for $C_{28}H_{56}O_2Si_2$ (M+H) 481.3898. Found: 481.3892.

**2-Methyl-1-triethylsiloxy-2-cyclopentene (8a).** IR (NaCl) 2955 (s), 2873 (s), 1464 (w), 1350 (w), 1237 (w), 1080 (m), 1004 (m), 727 (m) cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 5.47 (s, 1H, C*H*=CCH$_3$), 4.63 (s, 1H, C*H*OSi), 2.40-2.34 (m, 1H, CH$_2$CH*H*), 2.27-2.19 (m, 1H, CH$_2$C*H*H), 2.17-2.09 (m, 1H, CH*H*CH$_2$), 1.72 (s, 3H, C*H*$_3$C=CH), 1.69-1.65 (m, 1H, C*H*HCH$_2$), 0.98 (t, $J_{HH}$ = 8.0 Hz, 9H, (C*H*$_3$CH$_2$)$_3$SiO), 0.63 (q, $J_{HH}$ = 8.0 Hz, 6H, (CH$_3$C*H*$_2$)$_3$SiO), $^{13}$C NMR (100 MHz, $CDCl_3$) δ 142.6, 127.7, 80.4, 35.0, 30.4, 14.4, 7.5, 5.5. HRMS Calcd for $C_{12}H_{24}OSi$: 212.1596. Found: 212.1596. Anal. Calcd for $C_{12}H_{24}OSi$: C, 67.86; H, 11.39. Found: C, 67.66; H, 11.36.

**(6*E*)-6-Methyl-5-*tert*-butyldimethylsiloxy-1,6-octadiene (7b).** IR (NaCl) 2962 (s), 2955 (s), 2860 (s), 1476 (m), 1262 (m), 1080 (s), 910 (m), 841 (s), 778 (s) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.82 (dddd, $J_{HH}$ = 16.8, 10.0, 6.4, 6.4 Hz, 1H, *H*C=$CH_2$), 5.35 (q, $J_{HH}$ = 6.4 Hz, 1H, $CH_3$*H*C=C), 5.00 (dd, $J_{HH}$ = 16.0, 2.0 Hz, 1H, HC=C*H*H), 4.93 (d (br), $J_{HH}$ = 10.0 Hz, 1H, HC=CH*H*), 3.95 (t, $J_{HH}$ = 6.4 Hz, 1H, C*H*OSi), 2.00-1.91 (m, 2H, C*H*$_2$HC=$CH_2$), 1.66-1.45 (m, 2H, C*H*$_2$$CH_2$HC=$CH_2$), 1.58 (d, $J_{HH}$ = 6.4 Hz, 3H, C*H*$_3$HC=C), 1.54 (s, 1H, C*H*$_3$C=CH), 0.87 (s, 9H, (C*H*$_3$)$_3$CSiO), 0.02 (s, 3H, C*H*$_3$SiO), -0.03 (s, 3H, C*H*$_3$SiO), $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 139.6, 138.9, 114.9, 78.8, 36.2, 30.8, 26.6, 18.9, 13.6, 11.4, -4.0, -4.3. HRMS Calcd for $C_{15}H_{30}OSi$ (M-H) 253.1987. Found: 253.1992.

**(2*E*-12*E*)-4,11-Bis(*tert*-butyldimethylsiloxy)-3,12-dimethyl-2,7,12-tetradecatriene (7b dimer).** IR (NaCl) 2962 (m), 2936 (s), 2855 (m), 1464 (w), 1256 (m), 1067 (s), 834 (s), 784 (s) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.39-5.33 (m, 4H, $CH_3$*H*C=C, $CH_2$*H*C=C*H*$CH_2$), 3.93 (t, $J_{HH}$ = 6.4 Hz, 2H, C*H*OSi), 2.00-1.82 (m, 4H, C*H*$_2$HC=CHC*H*$_2$), 1.56 (d, $J_{HH}$ = 6.4 Hz, 6H, C*H*$_3$HC=C), 1.53 (s, 6H, C*H*$_3$C=CH), 0.86 (s, 18H, (C*H*$_3$)$_3$CSiO), 0.01 (s, 6H, C*H*$_3$SiO), -0.05 (s, 6H, C*H*$_3$SiO), $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 139.0, 130.8, 120.2, 78.9, 36.9, 29.6, 26.6, 20.8, 13.6, 11.4, -4.0, -4.3. HRMS Calcd for $C_{28}H_{56}O_2Si_2$: 480.3819. Found: 480.3819.

**2-Methyl-1-*tert*-butyldimethylsiloxy-2-cyclopentene (8b).** IR (NaCl) 2949 (s), 2855 (s), 1470 (m), 1357 (m), 1250 (s), 1086 (s), 992 (m), 885 (s), 847 (s), 778 (s) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.46 (s, 1H, *H*C=C$CH_3$), 4.64 (s (br), 1H, C*H*OSi), 2.40-2.32 (m, 1H, $CH_2$C*H*H), 2.28-2.20 (m, 1H, $CH_2$CH*H*), 2.18-2.10 (m, 1H, CH*H*$CH_2$), 1.71 (s, 3H, C*H*$_3$C=CH), 1.69-1.62 (m, 1H, C*H*H$CH_2$), 0.91 (s, 9H, (C*H*$_3$)$_3$CSiO), 0.09 (s, 3H, C*H*$_3$SiO), 0.08 (s, 3H, C*H*$_3$SiO), $^{13}C$ NMR (100 MHz,

$CDCl_3$) δ 142.7, 127.5, 80.8, 35.0, 30.4, 26.6, 14.5, -3.8, -4.1. HRMS Calcd for $C_{12}H_{24}OSi$: 212.1596. Found: 212.1593.

**(6*E*)-6-Methyl-5-*tert*-butyldiphenylsiloxy-1,6-octadiene (7c).** IR (NaCl) 3096 (m), 2936 (s), 2861 (s), 1476 (m), 1432 (m), 1111 (s), 1067 (m), 998 (w), 822 (m), 702 (s) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.70-7.63 (m, 4H, Ar*H*), 7.44-7.33 (m, 6H, Ar*H*), 5.67 (dddd, $J_{HH}$ = 16.8, 10.0, 6.4, 6.4 Hz, 1H, *H*C=$CH_2$), 5.10 (q, $J_{HH}$ = 6.4 Hz, 1H, $CH_3$*H*C=C), 4.90-4.85 (m, 2H, HC=C$H_2$), 4.04 (t, $J_{HH}$ = 6.4 Hz, 1H, C*H*OSi), 1.84 (q, $J_{HH}$ = 7.2 Hz, 2H, C$H_2$HC=$CH_2$), 1.64-1.53 (m, 2H, C$H_2$$CH_2$HC=$CH_2$), 1.57 (s, 3H, C$H_3$C=CH), 1.47 (s, 3H, C$H_3$HC=C), 1.07 (s, 9H, (C$H_3$)$_3$CSiO), $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 139.4, 136.7, 136.6, 135.4, 135.0, 130.1, 130.0, 129.0, 128.0, 127.9, 121.7, 114.8, 79.6, 35.5, 30.3, 27.7, 20.1, 13.5, 11.4. HRMS Calcd for $C_{25}H_{34}OSi$ (M+H) 379.2458. Found: 379.2449.

**(2*E*-12*E*)-4,11-Bis(*tert*-butyldiphenylsiloxy)-3,12-dimethyl-2,7,12-tetradecatriene (7c dimer).** IR (NaCl) 3075 (w), 2930 (s), 2861 (s), 1476 (w), 1432 (m), 1111 (s), 1067 (m), 702 (s) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.65-7.59 (m, 8H, Ar*H*), 7.39-7.29 (m, 12H, Ar*H*), 5.06-5.00 (m, 4H, $CH_3$*H*C=C, $CH_2$*H*C=C*H*$CH_2$), 3.95 (t, $J_{HH}$ = 6.4 Hz, 2H, C*H*OSi), 1.68-1.64 (m, 4H, C$H_2$HC=CHC$H_2$), 1.55 (s, 6H, C$H_3$HC=C), 1.49-1.40 (m, 4H, C$H_2$$CH_2$CH), 1.43 (d, J=6.4 Hz, 6H, C$H_3$HC=C), 1.03 (s, 18H, (C$H_3$)$_3$CSiO), $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 137.3, 136.7, 136.6, 135.4, 135.1, 130.5, 130.0, 130.0, 128.0, 127.9, 121.6, 79.7, 36.2, 29.1, 27.7, 20.1, 13.5, 11.3. HRMS Calcd for $C_{48}H_{64}O_2Si_2$ (M+H) 729.4524. Found: 729.4519.

**2-Methyl-1-*tert*-butyldiphenylsiloxy-2-cyclopentene (8c).** IR (NaCl) 3043 (m), 2962 (s), 2930 (s), 2861 (s), 1426 (s), 1117 (s), 1079 (s), 998 (m), 878 (m), 702 (s) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.81-7.76 (m, 4H, Ar*H*), 7.50-7.41 (m, 6H, Ar*H*),

5.49 (s, 1H, *H*C=CCH$_3$), 4.78 (s (br), 1H, C*H*OSi), 2.38-2.32 (m, 1H, CH$_2$C*H*H), 2.11-2.07 (m, 1H, CH$_2$C*H*H), 1.97 (m, 1H, CH*H*CH$_2$), 1.81-1.76 (m, 1H, C*H*HCH$_2$), 1.73 (s (br), 3H, C*H*$_3$C=CH), 1.17 (s, 9H, (C*H*$_3$)$_3$CSiO), $^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.0, 136.7, 135.5, 135.1, 130.1, 130.1, 128.2, 128.1, 127.5, 81.6, 35.0, 30.3, 27.8, 20.0, 14.9. HRMS Calcd for $C_{22}H_{28}OSi$ (M-H) 335.1830. Found: 335.1823.

**(6*E*)-5-Benzyloxy-6-methyl-1,6-octadiene (7d).** IR (NaCl) 2930 (m), 2867 (m), 1451 (w), 1099 (m), 910 (m), 740 (m), 664 (m) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38-7.30 (m, 5H, Ar*H*), 5.79 (dddd, $J_{HH}$ = 17.2, 13.2, 6.8, 6.8 Hz, 1H, *H*C=CH$_2$), 5.44 (q, $J_{HH}$ = 6.4 Hz, 1H, CH$_3$*H*C=C), 4.97 (dd, $J_{HH}$ = 17.2, 1.6 Hz, 1H, HC=C*H*H), 4.92 (d (br), $J_{HH}$ = 6.0 Hz, 1H, HC=CH*H*), 4.40 (d, J=12.0 Hz, 1H, PhC*H*HO), 4.20 (d, $J_{HH}$ = 12.0 Hz, 1H, PhCH*H*O), 3.65 (t, $J_{HH}$ = 6.4 Hz, 1H, C*H*OBn), 2.10-1.96 (m, 2H, C*H*$_2$CH=CH$_2$), 1.81-1.50 (m, 2H, C*H*$_2$CH$_2$HC=CH$_2$), 1.66 (d, $J_{HH}$ = 6.4 Hz, 3H, C*H*$_3$HC=C), 1.58 (s, 3H, C*H*$_3$C=CH), $^{13}$C NMR (100 MHz, CDCl$_3$) δ 140.2, 139.7, 136.2, 129.3, 128.9, 128.4, 124.2, 115.5, 85.6, 70.7, 34.0, 31.3, 14.2, 11.4. HRMS Calcd for $C_{16}H_{22}OSi$: 230.1671. Found: 230.1668.

**1-Benzyloxy-2-methyl-2-cyclopentene (8d).** IR (NaCl) 3031 (w), 2930 (m), 2855 (s), 1451 (m), 1350 (w), 1099 (s), 1080 (s), 734 (m), 696 (s) cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38-7.25 (m, 5H, Ar*H*), 5.57 (s, 1H, C*H*=CCH$_3$), 4.58 (d, $J_{HH}$ = 12.0 Hz, 1H, PhC*H*HO), 4.46 (d, $J_{HH}$ = 12.0 Hz, 1H, PhCH*H*O), 4.43 (s, 1H, C*H*OBn), 2.46-2.37 (m, 1H, CH$_2$C*H*H), 2.25-2.20 (m, 1H, CH$_2$CH*H*), 2.19-2.12 (m, 1H, CH*H*CH$_2$), 1.92-1.83 (m, 1H, C*H*HCH$_2$), 1.78 (s, 3H, C*H*$_3$C=CH), $^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.7, 140.7, 129.6, 129.0, 128.3, 128.0, 87.3, 71.0, 30.9, 30.7, 14.8. HRMS Calcd for $C_{12}H_{14}O$: 174.1045. Found: 188.1201.

**(6E)-6-Methyl-3-triethylsiloxy-1,6-octadiene (9).** IR (NaCl) 2955 (s), 2911 (s), 2879 (s), 1464 (w), 1419 (w), 1092 (m), 1016 (m), 922 (m), 746 (s) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.81 (ddd, $J_{HH}$ = 16.8, 10.0, 5.6 Hz, 1H, *H*C=$CH_2$), 5.20 (q, $J_{HH}$ = 6.4 Hz, 1H, $CH_3$*H*C=C), 5.13 (dd, $J_{HH}$ = 16.0, 2.0 Hz, 1H, HC=C*H*H), 5.02 (d (br), $J_{HH}$ = 6.4 Hz, 1H, HC=CH*H*), 4.05 (q, $J_{HH}$ = 6.4 Hz, 1H, C*H*OSi), 2.06-1.92 (m, 2H, C$H_2$$CH_2$), 1.64-1.50 (m, 2H, $CH_2$C$H_2$), 1.59 (s, 3H, C$H_3$C=CH), 1.56 (d, $J_{HH}$ = 6.4, 3H, C$H_3$HC=C), 0.95 (t, J=8.0 Hz, 9H, (C$H_3$$CH_2$)$_3$SiO), 0.59 (q, J=8.0 Hz, 6H, ($CH_3$C$H_2$)$_3$SiO), $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 142.8, 136.7, 119.3, 114.8, 74.7, 37.6, 36.3, 16.8, 14.4, 7.9, 6.0. HRMS Calcd for $C_{15}H_{30}OSi$: 254.2066. Found: 254.2062.

**3-Methyl-1-triethylsiloxy-2-cyclopentene (10).** IR (NaCl) 2955 (s), 2917 (s), 2879 (m), 1072 (m), 1652 (s), 1237 (w), 1073 (m), 1010 (m), 840 (w) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.34 (s, 1H, *H*C=$CCH_3$), 4.85 (s (br), 1H, C*H*OSi), 2.42-2.36 (m, 1H, $CH_2$CH*H*), 2.29-2.20 (m, 1H, $CH_2$C*H*H), 2.14-2.07 (m, 1H, CH*H*$CH_2$), 1.74 (s, 3H, C$H_3$C=CH), 1.73-1.67 (m, 1H, C*H*H$CH_2$), 0.96 (t, $J_{HH}$ = 8.0 Hz, 9H, (C$H_3$$CH_2$)$_3$SiO), 0.60 (q, $J_{HH}$ = 8.0 Hz, 6H, ($CH_3$C$H_2$)$_3$SiO), $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 144.9, 128.7, 78.8, 35.3, 30.4, 17.5, 7.5, 5.5. HRMS Calcd for $C_{12}H_{24}OSi$ (m-1) 211.1517. Found: 211.1518.

**6-Methyl-5-triethylsiloxy-1,6-heptadiene (11).** IR (NaCl) 3081 (w), 2962 (s), 2911 (s), 2880 (s), 1640 (m), 1457 (m), 1420 (m), 1243 (m), 1092 (s), 1010 (s), 897 (m), 746 (s) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.82 (dddd, $J_{HH}$ = 16.8, 10.0, 6.4, 6.4 Hz, 1H, *H*C=$CH_2$), 5.01 (dd, $J_{HH}$ = 12.0, 2.0 Hz, 1H, HC=C*H*H), 4.94 (d (br), $J_{HH}$ = 8.0 Hz, 1H, HC=CH*H*), 4.86 (s, 1H, $CH_3$C=C*H*H), 4.77 (s, 1H, $CH_3$C=CH*H*), 4.05 (t, $J_{HH}$ = 6.4 Hz, 1H, C*H*OSi), 2.07-1.99 (m, 2H, C$H_2$HC=$CH_2$), 1.68 (s, 3H, C$H_3$C=$CH_2$), 1.66-1.52 (m, 2H, C$H_2$$CH_2$HC=$CH_2$), 0.94 (t, $J_{HH}$ = 8.0 Hz, 9H, (C$H_3$$CH_2$)$_3$SiO), 0.58 (q, $J_{HH}$ = 8.0 Hz, 6H, ($CH_3$C$H_2$)$_3$SiO), $^{13}C$ NMR (100 MHz,

$CDCl_3$) δ 148.3, 139.4, 115.0, 111.5, 76.8, 36.0, 30.5, 17.7, 7.6, 5.5. Anal. Calcd for $C_{14}H_{28}OSi$: C, 69.93; H, 11.74. Found: C, 79.97; H, 11.66.

**(7*E*)-7-Methyl-6-tert-butyldimethylsiloxy-1,7-nonadiene (12).** IR (NaCl) 2962 (s), 2924 (s), 2861 (s), 1652 (w), 1483 (s), 1363 (w), 1256 (s), 1092 (s), 1004 (m), 910 (m), 847, (s), 778 (s) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.79 (dddd, $J_{HH}$ = 16.8, 10.0, 6.4, 6.4 Hz, 1H, *H*C=$CH_2$), 5.33 (q, $J_{HH}$ = 6.4 Hz, 1H, $CH_3$*H*C=C), 4.99 (dd, $J_{HH}$ = 12.0, 2.0 Hz, 1H, HC=C*H*H), 4.93 (d (br), $J_{HH}$ = 6.4 Hz, 1H, HC=CH*H*), 3.93 (t, $J_{HH}$ = 6.4 Hz, 1H, C*H*OSi), 2.03 (q, $J_{HH}$ = 6.4 Hz, 2H, $CH_2$HC=$CH_2$), 1.57 (d, $J_{HH}$ = 6.4 Hz, 3H, $CH_3$HC=C), 1.53 (s, 3H, $CH_3$C=CH), 1.44-1.23 (m, 4H, $CH_2CH_2$), 0.86 (s, 9H, $(CH_3)_3$CSiO), 0.09 (s, 3H, $CH_3$SiO), -0.41 (s, 3H, $CH_3$SiO), $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 139.8, 120.1, 114.9, 95.1, 79.2, 36.4, 34.4, 26.6, 25.9, 18.9, 13.6, 11.4, -4.0, -4.3. HRMS Calcd for $C_{15}H_{30}OSi$ (m-1) 253.1987. Found: 253.1985.

**(2*E*-14*E*)-4,13-Bis(triethylsiloxy)-3,14-dimethyl-2,8,14-hexadecatriene (12 dimer).** IR (NaCl) 2962 (s), 2924 (s), 2861 (s), 1470 (s), 1363 (w), 1256 (s), 1086 (s), 1004 (m), 834, (s), 778 (s) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.37-5.30 (m, 4H, $CH_2$*H*C=C*H*C$H_2$), 3.91 (t, $J_{HH}$ = 6.4 Hz, 2H, C*H*OSi), 1.97-1.93 (m, 4H, $CH_2$HC=CHC$H_2$), 1.56 (d, $J_{HH}$ = 6.4 Hz, 6H, $CH_3$HC=C), 1.52 (s, 6H, $CH_3$C=CH), 1.50-1.20 (m, 8H, $CH_2CH_2$), 0.86 (s, 18H, $(CH_3)_3$CSiO), 0.01 (s, 6H, $CH_3$SiO), -0.04 (s, 6H, $CH_3$SiO), $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 139.1, 131.0, 120.0, 79.3, 36.4, 33.2, 26.7, 18.9, 13.6, 11.4, -3.9, -4.3. HRMS Calcd for $C_{30}H_{60}O_2Si_2$: 508.4132. Found: 508.4128.

**7-Methyl-6-triethylsiloxy-1,7-octadiene (14).** IR (NaCl) 3081 (w), 2955 (s), 2911 (s), 2880 (s), 1646 (m), 1464 (w), 1413 (w), 1243 (w), 1086 (m), 1004 (s), 891 (m), 746 (s), 727 (s) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.80 (dddd, $J_{HH}$ = 17.2, 10.0,

6.4, 6.4 Hz, 1H, *H*C=$CH_2$), 5.00 (dd, $J_{HH}$ = 15.2, 1.6 Hz, 1H, HC=C*H*H), 4.94 (d (br), $J_{HH}$ = 8.0 Hz, 1H, HC=CH*H*), 4.86 (s, 1H, $CH_3C$=C*H*H), 4.75 (s, 1H, $CH_3C$=CH*H*), 4.03 (t, $J_{HH}$ = 6.4 Hz, 1H, C*H*OSi), 2.04 (q, $J_{HH}$ = 6.4 Hz, 2H, C*H*$_2$HC=$CH_2$), 1.67 (s, 3H, C*H*$_3$C=$CH_2$), 1.55-1.25 (m, 4H, C*H*$_2$C$H_2$), 0.94 (t, $J_{HH}$ = 8.0 Hz, 9H, (C*H*$_3$C$H_2$)$_3$SiO), 0.58 (q, $J_{HH}$ = 8.0 Hz, 6H, ($CH_3$C*H*$_2$)$_3$SiO), $^{13}$C NMR (100 MHz, $CDCl_3$) δ 148.5, 139.6, 115.1, 111.3, 77.2, 36.3, 34.4, 25.6, 17.7, 7.6, 5.5. Combustion analysis was performed on the derived alcohol (after deprotection) due to the instability of the TES ether. Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.31; H, 11.60.

**2-Methyl-1-triethylsiloxy-2-cyclohexene (15).** IR (NaCl) 2962 (s), 2873 (s), 1457 (m), 1243 (m), 1086 (m), 1004 (s), 897 (w), 734 (m) cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 5.50 (s, 1H, $CH_2$*H*C=C), 4.04 (s (br), 1H, C*H*OSi), 2.01 (d, $J_{HH}$ = 18.4 Hz, 1H, C*H*$_2$HC=$CH_2$), 1.88 (d, $J_{HH}$ = 18.4 Hz, 1H, C*H*$_2$HC=$CH_2$), 1.78-1.47 (m, 4H, C*H*$_2$C$H_2$), 1.71 (s, 3H, C*H*$_3$C=CH), 0.98 (t, $J_{HH}$ = 8.0 Hz, 9H, (C*H*$_3$C$H_2$)$_3$SiO), 0.64 (q, $J_{HH}$ = 8.0 Hz, 6H, ($CH_3$C*H*$_2$)$_3$SiO), $^{13}$C NMR (100 MHz, $CDCl_3$) δ 136.6, 125.5, 69.9, 33.7, 26.2, 21.5, 19.6, 7.6, 5.7. Anal. Calcd for $C_{13}H_{26}OSi$: C, 68.96; H, 11.57. Found: C, 68.76; H, 11.43.

**Representative procedure for Mo-catalyzed kinetic resolution of diallyl ether derivatives.** Unsaturated allyl ether **16a** (111 mg, 0.61 mmol) was dissolved in anhydrous toluene (6.1 mL). After cooling to –25 °C, the vessel was charged with (S)($^i$Pr$_2$)Mo(Neo) (23 mg, 0.03 mmol, 5 mol%) and the flask sealed with a Teflon cap. After 6 h, the reaction was opened to air and MeOH was added (1.0 mL). The volatiles were removed on a rotary evaporator providing a dark brown residue which was passed through a plug of silica gel using 10:1 pentane:$OEt_2$. Organic solvents were then removed to yield a yellow oil (103 mg, 98% mass balance: assuming 63% conversion and all (S)-

BiphenH$_2$). The percent conversion was determined by GLC analysis of the unpurified mixture in comparison to dodecane as an internal standard. The starting material **16a** and ring-closed product **17a** were purified by silica gel chromatography (distilled pentanes as the solvent) to afford pure (*R*)-**16a** (69 mg, 62% yield), (*S*)-**17a** (33 mg, 35% yield). The stereochemical identity of the recovered starting material was determined by comparison with authentic non-racemic material obtained from RCM of the non-racemic allylic ethers. Non-racemic parent allylic alcohols were prepared by the method of Sharpless.[128]

**3-Allyl-(2-methyl-1-octenyl) ether (16a).** IR (NaCl) 3069 (m), 2943 (s), 2867 (s), 1652 (m), 1464 (m), 1381 (m), 1319 (m), 1086 (s), 992 (m), 929 (m), 910 (s), 576 (w) cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 5.90 (dddd, $J_{HH}$ = 16.4, 15.6, 10.4, 5.2 Hz, 1H, *H*C=CH$_2$), 5.24 (dd, $J_{HH}$ = 15.6, 1.6 Hz, 1H, HC=CH*H*), 5.14 (dd, $J_{HH}$ = 10.0, 1.6 Hz, 1H, HC=C*H*H), 4.91-4.90 (m, 1H, C=CH*H*), 4.88-4.86 (m, 1H, C=CH*H*), 3.97-3.91 (m, 2H, OC*H*HCH=CH$_2$), 3.73 (dd, $J_{HH}$ = 4.8, 2.4 Hz, 1H, OCH*H*CH=CH$_2$), 3.65 (t, $J_{HH}$ = 2.8 Hz, 1H, OC*H*), 1.64 (d, $J_{HH}$ = 0.4 Hz, 3H, CH$_2$C*H*$_3$), 1.62-1.23 (m, 8H, (C*H*$_2$)$_4$), 0.87 (t, $J_{HH}$ = 2.8 Hz, 3H, (CH$_2$)$_4$C*H*$_3$), $^{13}$C NMR (100 MHz, $CDCl_3$) δ 145.5, 136.0, 117.2, 114.0, 84.1, 69.6, 34.2, 32.5, 26.2, 23.3, 17.1, 14.7. HRMS Calcd for $C_{12}H_{22}O$: 182.1671. Found: 182.1667. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.44; H, 11.92.

**3-Methyl-2-pentyl-2,5-dihydrofuran (17a).** IR (NaCl) 3075 (w), 2968 (s), 2936 (s), 2861 (s), 1457 (m), 1099 (m), 1036 (m), 935 (w), 778 (w) cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 5.44 (s (br), 1H, OCH$_2$*H*C=C), 4.59-4.49 (m, 3H, C*H*OC*H*$_2$), 1.66 (d, $J_{HH}$ = 0.8 Hz, 3H, HC=CC*H*$_3$), 1.64-1.58 (m, 2H, OCHC*H*$_2$), 1.44-1.24 (m, 6H, (C*H*$_2$)$_3$CH$_3$), 0.86 (t, $J_{HH}$ = 6.8 Hz, 3H, CH$_2$C*H*$_3$), $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.8, 121.0, 88.2, 75.1, 34.6, 32.7, 25.0, 23.3, 14.7, 13.1. HRMS Calcd for

$C_{10}H_{18}O$: 154.1358. Found: 154.1358. Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.45; H, 11.53.

**3-Allyl-(2,5-dimethyl-1-hexenyl) ether (16b).** IR (NaCl) 3081 (w), 2955 (s), 2924 (s), 2867 (s), 1652 (m), 1463 (m), 1367 (m), 1136 (m), 1092 (s), 922 (m), 910 (s), 570 (w) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.90 (dddd, $J_{HH}$ = 17.2, 15.6, 11.6, 6.0 Hz, 1H, *H*C=CH$_2$), 5.24 (ddd, $J_{HH}$ = 17.2, 3.6, 2.0 Hz, 1H, HC=C*H*H), 5.14 (ddd, $J_{HH}$ = 10.4, 3.2, 1.6 Hz, 1H, HC=CH*H*), 4.90 (dd, $J_{HH}$ = 3.6, 2.0 Hz, 1H, C=C*H*H), 4.88 (d, $J_{HH}$ = 0.8 Hz, 1H, C=CH*H*), 3.94 (ddt, $J_{HH}$ = 14.4, 5.2, 1.6 Hz, 1H, OC*H*), 3.77-3.70 (m, 2H, OC*H*$_2$), 1.71-1.63 (m, 1H, C*H*(CH$_3$)$_2$), 1.65 (t, $J_{HH}$ = 0.8 Hz, 3H, CC*H*$_3$), 1.54 (ddd, $J_{HH}$ = 9.6, 8.0, 6.8 Hz, 1H, OCHC*H*H), 1.29 (ddd, $J_{HH}$ = 13.2, 6.8, 5.6 Hz, 1H, OCHCH*H*), 0.89 (dd, $J_{HH}$ = 6.8, 1.2 Hz, 6H, CH(C*H*$_3$)$_2$), $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 145.8, 136.9, 117.3, 113.8, 82.2, 69.6, 43.6, 25.2, 23.6, 23.3, 17.2. HRMS Calcd for $C_{11}H_{20}O$: 168.1514. Found: 168.1513. Anal. Calcd for $C_{11}H_{20}O$: C, 77.09; H, 11.50. Found: C, 78.77; H, 11.80.

**2-*iso*-Butyl-3-methyl-2,5-dihydrofuran (17b).** IR (NaCl) 2962 (s), 2936 (s), 2861 (m), 1256 (m), 1080 (s), 1029 (s), 897 (w), 797 (m) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.43 (t, $J_{HH}$ = 1.6 Hz, 1H, C=C*H*), 4.65-4.49 (m, 3H, *H*$_2$COC*H*), 1.85 (tqq, $J_{HH}$ = 2.8, 2.8, 2.8 Hz, 1H, C*H*(CH$_3$)$_2$), 1.68 (d, $J_{HH}$ = 1.2 Hz, 3H, CC*H*$_3$), 1.35 (dd, $J_{HH}$ = 6.8, 6.8 Hz, 2H, OCHC*H*$_2$), 0.94 (d, $J_{HH}$ = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 139.6, 120.6, 86.6, 74.7, 44.1, 25.6, 24.7, 22.5, 13.1. Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.89; H, 11.20.

**3-Allyl-(3-cyclohexyl-2-methyl-1-propenyl) ether (16c).** IR (NaCl) 3069 (w), 2924 (s), 2855 (s), 1659 (m), 1451 (m), 1086 (m), 992 (w), 904 (m) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.92-5.82 (m, 1H, *H*C=CH$_2$), 5.22 (dq, $J_{HH}$ = 17.2, 3.2, 1.6 Hz, 1H,

HC=C*H*H), 5.13-5.10 (m, 1H, HC=CH*H*), 4.93-4.92 (m, 1H, C=C*H*H), 4.79 (dd, $J_{HH}$ = 1.2, 0.4 Hz, 1H, C=CH*H*), 3.92 (dddd, $J_{HH}$ = 14.4, 5.2, 1.6, 1.6 Hz, 1H, OC*H*H), 3.68 (dddd, $J_{HH}$ = 12.4, 6.0, 1.2, 1.2 Hz, 1H, OCH*H*), 3.26 (d, $J_{HH}$ = 8.8, 1H, OC*H*), 2.10-2.07 (m, 1H, OCHC*H*), 1.73-1.60 (m, 2H, CHC$H_2$), 1.60 (q, $J_{HH}$ = 2.4, 0.8 Hz, 3H, C$H_3$), 1.47-1.39 (m, 2H, CHC$H_2$), 1.22-1.09 (m, 4H, CHCH$_2$C$H_2$), 0.93-0.78 (m, 2H, CHCH$_2$CH$_2$C$H_2$), $^{13}$C NMR (100 MHz, $CDCl_3$) δ 144.3, 136.1, 117.1, 115.3, 89.2, 69.7, 40.1, 30.7, 30.1, 27.3, 26.9, 26.6, 17.3. HRMS Calcd for $C_{13}H_{22}O$: 194.1671. Found: 194.1676. Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.47; H, 11.64.

**2-Cyclohexyl-3-methyl-2,5-dihydrofuran (17c).** IR (NaCl) 3069 (w), 2924 (s), 2855 (s), 2666 (w), 1671 (w), 1451 (m), 1117 (m), 1042 (m), 935 (w) $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 5.49 (t, $J_{HH}$ = 1.6 Hz, 1H, OCH$_2$*H*C=C), 4.54-4.48 (m, 3H, C$H_2$OCH), 1.78-1.05 (m, 11H, C*H*(C$H_2$)$_5$), 1.67 (d, $J_{HH}$ = 1.6 Hz, 3H, C$H_3$), $^{13}$C NMR (100 MHz, $CDCl_3$) δ 137.4, 121.7, 92.6, 75.9, 41.7, 31.1, 27.6, 27.2, 27.0, 25.6, 13.4. HRMS Calcd for $C_{11}H_{18}O$: 166.1358. Found: 166.1361. Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.67; H, 10.90.

**3-Allyl-(2-methyl-3-phenyl-1-propenyl) ether (16d).** IR (NaCl) 3081 (m), 3031 (m), 2980 (m), 2855 (m), 1652 (m), 1495 (m), 1457 (s), 1137 (m), 1092 (s), 1073 (s), 903 (s), 752 (m), 696 (s) $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.40-7.26 (m, 5H, Ar*H*), 5.98 (dddd, $J_{HH}$ = 17.2, 10.4, 5.2, 5.2 Hz, 1H, *H*C=CH$_2$), 5.33 (dd, $J_{HH}$ = 17.2, 1.6 Hz, 1H, HC=C*H*H), 5.20 (dd, $J_{HH}$ = 10.4, 3.2 Hz, 1H, HC=CH*H*), 5.16 (t, $J_{HH}$ = 1.2 Hz, 1H, *H*HC=CH$_3$), 4.80 (s, 1H, OC*H*C), 3.99 (dddd, $J_{HH}$ = 18.0, 10.4, 5.2, 1.6 Hz, 2H, OC$H_2$HC=CH$_2$), 1.60 (d, $J_{HH}$ = 1.2 Hz, 3H, C$H_3$), $^{13}$C NMR (100 MHz, $CDCl_3$) δ 145.7, 141.2, 135.6, 128.8, 128.0, 127.3, 117.2, 113.6, 85.0, 69.8, 18.3.

HRMS Calcd for $C_{13}H_{16}O$ (M-H) 187.1123. Found: 187.1117. Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C,82.95; H, 8.28.

**3-Methyl-2-phenyl-2,5-dihydrofuran (17d)** IR (NaCl) 3062 (w), 3031 (w), 2848 (s), 1501 (m), 1457 (m), 1350 (w), 1067 (s), 841 (m), 752 (m), 696 (s), 639 (w) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.38-7.28 (m, 5H, Ar*H*), 5.65 (ddd, $J_{HH}$ = 3.2, 1.6, 1.6 Hz, 1H, OC*H*), 5.50 (s (br), 1H, $OCH_2HC$=C), 4.89-4.83 (m, 1H, OC*H*H), 4.76-4.70 (m, 1H, OCH*H*), 1.57 (t, $J_{HH}$ = 1.2 Hz, 3H, $CH_3$), $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 142.2, 139.2, 129.1, 128.6, 127.5, 121.4, 91.2, 76.2, 13.2. HRMS Calcd for $C_{11}H_{12}O$: 160.0888. Found: 160.0883. Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.21; H, 7.68.

**3-(2,4-Dimethyl-pentadienyl)-allyl-ether (20).** To a slurry of NaH (1.08 eq, 2.1 g, 87.5 mmol) in THF (125 mL) was added 2,4-dimethyl-1,4-pentadien-3-ol (9.06 g, 81 mmol) in THF (10 mL). After 10 minutes, allyl bromide (1.1 eq, 10.6 g, 7.6 mL) was introduced. A condenser was attached and the reaction heated to 60 °C for 16 h. Excess NaH was quenched carefully with water and the THF removed by rotary evaporation. The product was extracted with ether (2 x 100 mL) and dried over $MgSO_4$. The ether was removed by rotary evaporation affording a yellow liquid (10.7 g, 96% crude yield). The liquid was purified by vacuum distillation from $K_2CO_3$ (25 Torr, 49-51 °C) yielding a colorless liquid (6.88 g, 62%, 99% pure by GLC): IR(NaCl) 3074 (s), 2974 (s), 2941 (s), 2919 (s), 2855 (s), 1810 (w), 1647 (s), 1449 (s), 1427 (s), 1372 (s), 1330 (w), 1269 (w), 1236 (w), 1136 (s), 1086 (br s), 1015 (s), 997 (s), 903 (br s), 834 (w); $^1H$ NMR 5.85 (ddt, J = 17.3, 10.6, 5.4 Hz, 1H, $CH_2$=C*H*), 5.30 (dq, J = 17.2, 2 Hz, 1H, C$H_2$=CH), 5.15 (br m, J = 1 Hz, 2H, CMe=C$H_2$), 5.05 (dq, J = 10.3, 2 Hz, 1H, C$H_2$=CH), 4.94 (br m, J = 1 Hz, 2H, CMe=C$H_2$), 3.99 (s, 1H, OC*H*$R_2$), 3.82 (dt, J = 5.2, 2 Hz, 2H, OC$H_2$), 1.61 (s, 6H, C*Me*=$CH_2$); $^{13}C\{^1H\}$ NMR 143.24, 135.26,

116.38, 112.88, 85.92, 69.01, 18.13. HRMS (EI, M+) Calcd for $C_{10}H_{16}O$: 152.120115. Found 152.12014.

**(3,5-Dimethyl-(2*E*,5*E*)-heptadienyl)allyl ether (22).** To a 0 °C suspension of sodium hydride (5.3 g, 0.22 mol) in THF (200 mL) was added 3,5-dimethyl-(2*E*,5*E*)-heptadien-4-ol (12.3 g, 0.088 mol) in THF (20 mL) and then allyl bromide (13.8 g, 0.114 mole). The reaction was allowed to warm to room temperature and stirred for 18 h. The pale yellow suspension was cooled to 0 °C, water (100 mL) was slowly added and most THF was then removed by rotary evaporation. The aqueous mixture was extracted with ether (3 x 100 mL) and the combined extracts were dried over magnesium sulfate. The drying agent was removed by filtration and the solvent removed by rotary evaporation. The resulting viscous liquid was diluted with an equal volume of pentane and flashed with pentane on a silica column (15 cm x 5 cm) to obtain 9.95 g (63% yield) of (3,5-dimethyl-(2*E*,5*E*)-heptadienyl)allyl ether ($R_f$ = 0.25, pentane / silica) as a colorless liquid. The product was stored at -30 °C to avoid slow isomerization observed at room temperature. IR(NaCl) 2981 (s), 2918 (s), 2860 (s), 1668 (w), 1648 (w), 1445 (m), 1380 (m), 1060 (s), 1070(s), 999 (w), 919 (m), 864 (w), 839 (w), 806 (w), 784 (w). $^1$H NMR (300 MHz, $CDCl_3$) δ 5.91 (ddd, J = 18, 10, 5.2 Hz, 1H, $CH_2$=C*H*), 5.53 (qq, $J_{HH}$ = 6.8, 1.0 Hz, 1H, $CH_3$*H*C=C$CH_3$), 5.251 (dm, $J_{HH}$ = 17 Hz, 1H, C*H*H=CH), 5.12 (dm, $J_{HH}$ = 10 Hz, 1H, CH*H*=CH), 3.93 (br s, 1H, OC*H*(C=C)$_2$), 3.85 (ddd, $J_{HH}$ = 5.5, 1.3, 1.0 Hz, 2H, OC*H*$_2$CH=$CH_2$), 1.63 (dq, $J_{HH}$ = 6.8, 1.0 Hz, 3H, C*H*$_3$HC=C$CH_3$), 1.46 (dq, $J_{HH}$ = 3.0, 1.0 Hz, 3H, $CH_3$HC=CC*H*$_3$), $^{13}$C NMR (75.4 MHz, $CDCl_3$) 135.86, 134.53, 121.48, 116.48, 88.65, 69.07, 13.62, 12.54. Anal. Calcd for $C_{12}H_{20}O$; C, 79.94, H, 11.18. Found: C, 79.83, 11.22.

**Procedure for desymmetrization of trienes 20 and 22.** A 10 mL round bottom flask was charged with 3-allyl-(2,4-dimethyl-1,4-pentadienyl) ether, **20**, (1.22 g, 8.00

mmol) in a glove box under an atmosphere of argon. (S)($Me_2$)Mo(Neo) (1.0 mol%, 54.0 mg, 80.0 mmol) was added as a solid. The solution became dark red as the catalyst dissolved and vigorous gas evolution was observed. The flask was capped with a septum with an 18 gauge needle inserted as a vent. After 13 h, the flask was removed from the box, exposed to air and a short path distillation head was attached. The product was collected in 98.5% purity as a colorless liquid (850 mg, 86.0%) by distillation under nitrogen at 128 °C. Trace impurities may be removed via $SiO_2$ chromatography (99:1 pentane to ether), although the isolated yield dropped to 60-65% due to furan volatility.

**Determination of stereochemistry.** Alcohol **32**, obtained from the alkylation of isobutyraldehyde with 2-propenylmagnesiumbromide, was subjected to asymmetric epoxidation conditions of Sharpless[128] to provide optically enhanced alcohol (R)-**33**. Allylation followed by RCM resulted in optically enhanced dihydrofuran **35**. The stereochemical configuration of **35** was equivalent to that of the product of Wilkinson's catalyst hydrogenation of product **21**.

**2-*iso*-Propenyl-3-methyl-2,5-dihydrofuran (21).** IR (NaCl) 3074 (s), 2973 (s), 2946 (s), 2917 (s), 2845 (s), 2673 (w), 1802 (w), 1669 (w), 1648 (s), 1478 (w), 1447 (s (br)), 1381 (s), 1370 (s), 1346 (s), 1250 (s), 1184 (s), 1070 (s (br)), 1015 (s), 940 (s), 921 (s), 900 (s), 830 (s), 774 (w), 759 (w) $cm^{-1}$; $^1H$ NMR (300 MHz, $C_6D_6$) δ 5.17 (septet, $J_{HH}$ = 1.7 Hz, 1H, C=C*H*$CH_2$), 5.02 (t (br), $J_{HH}$ = 4.2 Hz, 1H, C=C*H*$CH_2$), 4.89 (t (br), $J_{HH}$ = 1.7 Hz, 1H, $CH_3C$=CH*H*), 4.82 (quintet, $J_{HH}$ = 1.7 Hz, 1H, $CH_3C$=C*H*H), 4.50 (d, $J_{HH}$ = 1.8 Hz, 2H, O*C*$H_2$CH=C), 1.64 (t (br), $J_{HH}$ = 1.3 Hz, C*H*$_3$C=$CH_2$), 1.38 (m, 1H, C*H*$_3$C=CHC$H_2$); $^{13}C$ NMR (125 MHz, $C_6D_6$) δ 146.2, 137.2, 122.4, 113.4, 93.5, 76.1, 16.4, 12.4. HRMS Calcd for $C_8H_{12}O$: 124.0888; Found: 124.0888.

**2-(2E-*sec*-butenyl)-3-methyl-2,5-dihydrofuran (23).** IR(NaCl) 2976 (s), 2917 (s), 2845 (s), 1762 (m), 1430 (m), 1380 (m), 1297 (w), 1250 (w), 1184 (w), 1054 (s), 935 (w), 920 (w), 818 (m) $cm^{-1}$; $^1H$ NMR (500 MHz, $CDCl_3$) δ 5.60 (dq, $J_{HH}$ = 3.0, 1.0 Hz, 1H, $OCH(C{=}C)_2$), 5.55 (m, 1H, $CH_3HC{=}CCH_3$), 4.91 (s (br), 1H, $OCH_2CH{=}C$), 4.64 (m, 2H, $OCH_2CH{=}C$), 1.66 (dq, $J_{HH}$ = 7.0, 1.0 Hz, 3H, $CH_3HC{=}CCH_3$), 1.60 (s (br), 3H, $CH_3HC{=}CCH_3$), 1.50 (dq, $J_{HH}$ = 3.0, 1.0 Hz, 3H, $OCH_2CH{=}CCH_3$), $^{13}C$ NMR (125.8 MHz, $CDCl_3$) δ 137.3, 135.7, 123.9, 121.6, 95.1, 75.7, 13.6, 12.6, 10.2. HRMS: Calcd for $C_9H_{14}O$: 138.1045; Found 138.1045

**Representative procedure for Mo-catalyzed desymmetrization of quaternary center-containing trienes.** Triene **24** (32.4 mg, 0.123 mmol) was dissolved in anhydrous benzene (1.23 mL). The vessel was then charged with (S)($^i$Pr$_2$)Mo(Neo) (4.29 mg, 0.006 mmol, 5 mol%) and sealed with a Teflon cap. After 24 h, the reaction was opened to air and MeOH was added (0.25 mL). The volatiles were removed on a rotary evaporator providing a dark brown residue. Purification by silica gel chromatography (500:1 hexane:$OEt_2$) afforded 8.20 mg of **25** (0.0347 mmol, 28.2% yield) and 2.30 mg of substrate dimer. The percent conversion was determined by $^1H$ NMR (400 MHz) analysis of the unpurified mixture.

**3-Allyl-(2-methyl-3-*iso*-propenyl-1-undecenyl) ether (24).** IR (NaCl) 3094 (w), 2930 (s), 2911 (s), 2855 (s), 1124 (m), 1067 (m), 1023 (m), 904 (s) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.93 (dddd, $J_{HH}$ = 17.2, 15.2, 10.8, 4.8 Hz, 1H, $CH_2HC{=}CH_2$), 5.32 (dd, $J_{HH}$ = 17.2, 1.6 Hz, 1H, $HC{=}CHH$), 5.14 (d, $J_{HH}$ = 1.2 Hz, 2H, $H_3CC{=}CHH$), 5.10 (dd, $J_{HH}$ = 10.4, 2.0, 1H, $HC{=}CHH$), 5.08 (dd, $J_{HH}$ = 10.4, 2.0, 1H, $HC{=}CHH$), 5.02 (d, $J_{HH}$ = 1.2 Hz, 2H, $H_3CC{=}CHH$), 3.69-3.67 (m, 1H, $OCH_2$), 1.71-1.67 (m, 2H, $OCH_2CH_2$), 1.56 (d, $J_{HH}$ = 0.4 Hz, 6H, $CH_3C{=}CH_2$), 1.32-1.15 (m, 12H, $(CH_2)_6CH_3$), 0.88 (t, $J_{HH}$ = 6.4 Hz, 3H, $(CH_2)_6CH_3$), $^{13}C$ NMR (100 MHz,

$CDCl_3$) δ 146.3, 136.4, 115.4, 113.7, 84.2, 63.3, 32.6, 30.8, 30.8, 30.3, 30.1, 23.5, 23.4, 19.5, 14.8. HRMS Calcd for $C_{18}H_{32}O$: 264.2453. Found: 264.2453. Anal. Calcd for $C_{18}H_{32}O$: C, 81.75; H, 12.20. Found: C, 81.72; H, 12.33.

**3-Methyl-2-octyl-2-*iso*-propenyl-2,5-dihydrofuran (25).** IR (NaCl) 3094 (w), 2924 (s), 2855 (s), 1457 (m), 1443 (m), 1055 (m), 904 (m), 784 (w) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.54 (d, $J_{HH}$ = 1.6 Hz, 1H, $OCH_2HC$=C), 4.87-4.86 (m, 2H, $CH_3C$=$CH_2$), 4.57 (t, $J_{HH}$ = 2.0 Hz, 2H, $OCH_2$), 1.74-1.70 (m, 2H, $CH_2(CH_2)_6CH_3$), 1.68 (d, $J_{HH}$ = 0.4 Hz, 3H, $OCH_2HC$=$CCH_3$), 1.55 (dd, $J_{HH}$ = 3.6, 2.0 Hz, 3H, $H_2C$=$CCH_3$), 1.39-1.10 (m, 12H, $CH_2(CH_2)_6CH_3$), 0.89-0.85 (m, 3H, $CH_2CH_3$), $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 149.2, 139.2, 122.0, 11.2, 95.6, 75.5, 35.9, 32.6, 30.8, 30.4, 30.0, 24.1, 23.4, 19.5, 14.8, 12.7. HRMS Calcd for $C_{16}H_{28}O$: 236.2140. Found: 236.2138. Anal, Calcd for $C_{16}H_{28}O$: C,81.29; H, 11.94. Found: 80.92; H, 11.79.

**Procedural Modifications for triene 26.** The procedure for triene **26** was akin to that of triene **24** with a few modifications. Triene **26** was dissolved in benzene to a concentration of 0.5 M and allowed to stir with the catalyst for 15 h. The enantiomeric excess was determined by chiral GLC analysis of the derived alcohol (Betadex 120 column) obtained through 9BBN hydroboration of product **27**.

**3-Allyl-(3-ethenyl-1-undecenyl) ether (26)** IR (NaCl) 3087 (w), 2924 (s), 2855 (s), 1464 (w), 1407 (w), 1130 (w), 1073 (m), 998 (m), 922, (s) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.92 (dddd, 17.2, 15.2, 10.4, 4.8 Hz, 1H, $OCH_2HC$=$CH_2$), 5.81 (dd, $J_{HH}$ = 17.6, 11.2 Hz, 2H, $CCH$=$CH_2$), 5.29 (dd, $J_{HH}$ = 17.2, 2.0 Hz, 1H, $OCH_2HC$=$CHH$), 5.24 (dd, $J_{HH}$ = 7.6, 1.2 Hz, 2H, CCH=$CHH$), 5.20 (s, 2H, CCH=$CHH$), 5.11 (dd, $J_{HH}$ = 10.4, 2.0 Hz, 1H, $OCH_2HC$=$CHH$), 3.84-3.82 (m, 2H, $OCH_2$), 1.65-1.61 (m, 2H, $CCH_2(CH_2)_6$), 1.25 (s (br), 12H, $CCH_2(CH_2)_6CH_3$), 0.87

(t, $J_{HH}$ = 6.8 Hz, 3H, C*H*$_3$), $^{13}$C NMR (100 MHz, $CDCl_3$) δ 141.2, 136.5, 116.1, 116.0, 81.2, 64.7, 38.9, 32.6, 30.8, 30.2, 30.0, 23.9, 23.4, 14.8. HRMS Calcd for $C_{16}H_{28}O$: 236.2140. Found: 236.2137. Anal. Calcd for $C_{16}H_{28}O$: C, 81.29; H,11.94. Found: C, 81.29; H, 11.84.

**2-Octyl-2-*iso*-ethenyl-2,5-dihydrofuran (27).** IR (NaCl) 3087 (w), 2930 (s), 2855 (s), 1640 (w), 1464 (w), 1092 (m), 1048 (m), 922 (m), 727 (w) cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 5.84 (dt, $J_{HH}$ = 6.0, 1.6 Hz, 1H, $OCH_2HC$=C*H*), 5.70 (dt, $J_{HH}$ = 6.0, 2.4 Hz, 1H, $OCH_2$*H*C=CH), 5.19 (dd, $J_{HH}$ = 17.2, 1.6 Hz, 1H, HC=CH*H*), 5.01 (dd, $J_{HH}$ = 10.8, 2.0 Hz, 1H, HC=C*H*H), 4.68-4.60 (m, 2H, O*CH*$_2$), 1.64-1.58 (m, 2H, C*CH*$_2$), 1.24 (s (br), 12H, (*CH*$_2$)$_6$CH$_3$), 0.85 (t, $J_{HH}$ = 6.8 Hz, 3H, C*H*$_3$), $^{13}$C NMR (100 MHz, $CDCl_3$) δ 142.3, 132.1, 126.6, 112.9, 93.0, 75.5, 40.1, 32.6, 30.7, 30.3, 33.0, 24.6, 23.3, 14.8. HRMS Calcd for $C_{14}H_{24}O$: 208.1827. Found: 208.1826. Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.93; H, 11.60.

**Procedural Modifications for trienes 28 and 30.** The procedure for trienes **28** and **30** was akin to that of triene **24** with a few modifications. Trienes **28** and **30** were dissolved in toluene to a concentration of 0.5M and cooled to –20 °C. The temperature remained at –20 °C for the duration of the reaction.

**3-Allyl-(3-cyclohexyl-1,4-pentadienyl) ether (28).** IR (NaCl) 3087 (w), 3012 (w), 2987 (w), 2930 (s), 2855 (s), 1646 (w), 1451 (m), 1407 (m), 1117 (m), 1042 (m), 922 (s) cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 5.89 (dddd, $J_{HH}$ = 16.8, 15.2, 10.0, 4.8 Hz, 1H, $OCH_2$*H*C=$CH_2$), 5.80 (dd, $J_{HH}$ = 17.6, 11.2 Hz, 2H, C*H*C=$CH_2$), 5.32-5.27 (m, 1H, $OCH_2HC$=C*H*H), 5.30 (dd, $J_{HH}$ = 11.2, 1.6 Hz, 2H, CHC=C*H*H), 5.20 (dd, $J_{HH}$ = 18.0, 1.6 Hz, 2H, CHC=CH*H*), 5.09 (dq, $J_{HH}$ = 10.4, 2.0, 1.6 Hz, 1H, $OCH_2C$=CH*H*), 1.84-1.48 (m, 5H, $CH_2CHCH_2$), 1.26-0.86 (m, 6H, $CH_2CH_2CH_2$), $^{13}$C NMR (100

MHz, $CDCl_3$) δ 138.8, 136.7, 117.5, 115.6, 83.8, 65.0, 49.1, 28.0, 27.4, 27.3. HRMS Calcd for $C_{14}H_{22}O$ (M-H) 205.1592. Found: 205.1595. Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.17; H, 10.57.

**2-Cyclohexyl-2-ethenyl-2,5-dihydrofuran (29).** IR (NaCl) 3087 (w), 2930 (s), 2855 (s), 1634 (w), 1457 (m), 1401 (m), 1092 (s), 1036 (s), 992 (m), 916 (m), 885 (w), 727 (m), 690 (m) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.91 (dd, $J_{HH}$ = 17.2, 10.4 Hz 1H, *H*C=$CH_2$), 5.84 (d, $J_{HH}$ = 6.0 Hz, 1H, $OCH_2HC$=C*H*), 5.75-5.73 (m, 1H, $OCH_2$*H*C=CH), 5.17 (dd, $J_{HH}$ = 17.2, 2.0 Hz, 1H, HC=C*H*H), 5.04 (dd, $J_{HH}$ = 10.8, 2.0 Hz, 1H, HC=CH*H*), 4.61 (t, $J_{HH}$ = 2.0 Hz, 2H, $OCH_2$), 1.78-1.44 (m, 5H, $CH_2CHCH_2$), 1.24-0.93 (m, 6H, $CH_2CH_2CH_2$), $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 141.3, 130.8, 126.7, 113.5, 95.8, 75.6, 47.0, 28.3, 28.0, 27.2. HRMS Calcd for $C_{12}H_{18}O$ (M-H) 177.1279. Found: 177.1282. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H,10.18. Found: C, 80.48; H, 9.99.

**3-Allyl-(3-phenyl-1,4-pentadienyl) ether (30).** IR (NaCl) 3087 (w), 3062 (w), 3018 (w), 2987 (w), 2924 (w), 2861 (w), 1652 (w), 1457 (m), 1407 (m), 1130 (m), 1155 (s), 998 (m), 929 (s), 696 (s) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, $J_{HH}$ = 7.6, 1.2 Hz, 2H, Ar*H*), 7.37-7.32 (m, 2H, Ar*H*), 7.26 (dd, $J_{HH}$ = 7.2-7.2 Hz, 1H, Ar*H*), 6.14 (dd, $J_{HH}$ = 17.6, 10.8 Hz, 2H, C*H*C=$CH_2$), 5.95 (dddd, $J_{HH}$ = 17.2, 15.2, 10.0, 6.0 Hz, 1H, $OCH_2$*H*C=$CH_2$), 5.35 (dd, $J_{HH}$ = 17.2,1.6 Hz, 1H, $OCH_2HC$=C*H*H), 5.32 (ddd, $J_{HH}$ = 10.4, 10.4, 1.2 Hz, 4H, CHC=C$H_2$), 5.15 (dd, $J_{HH}$ = 10.4, 1.6 Hz, 1H, $OCH_2HC$=CH*H*), 3.90-3.88 (m, 2H, $OCH_2$), $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 143.2, 140.6, 136.1, 128.8, 127.9, 127.8, 116.9, 116.2, 83.3, 65.5. HRMS Calcd for $C_{14}H_{16}O$ (M-H) 199.1123. Found: 199.1131. Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.11; H, 8.14.

**2-Ethenyl-2-phenyl-2,5-dihydrofuran (31).** IR (NaCl) 3087 (w), 3062 (w), 3024 (w), 2848 (m), 1640 (w), 1495 (w), 1445 (m), 1218 (w), 1061 (s), 991 (m), 922 (m), 702 (s) $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.41-7.24 (m, 5H, Ar*H*), 6.16 (dd, $J_{HH}$ = 17.2, 10.4 Hz, 1H, *H*C=$CH_2$), 6.07-6.04 (m, 1H, $OCH_2$HC=C*H*), 5.99-5.97 (m, 1H, $OCH_2$*H*C=CH), 5.28 (dd, $J_{HH}$ = 17.2, 1.2 Hz, 1H, HC=C*H*H), 5.18 (dd, $J_{HH}$ = 8.8, 1.6 Hz, 1H, HC=CH*H*), 4.80 (t, $J_{HH}$ = 2.4 Hz, 2H, $OCH_2$), $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 144.4, 141.6, 132.2, 128.9, 127.8, 126.9, 126.3, 114.3, 93.7, 75.5. HRMS Calcd for $C_{12}H_{12}O$: 172.0888. Found: 172.0887. Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.59; H, 7.06.

# CHAPTER 5

## Tungsten(VI) Imido Alkylidene Biphenoxide Complexes: Synthesis and Catalytic Activity in RCM

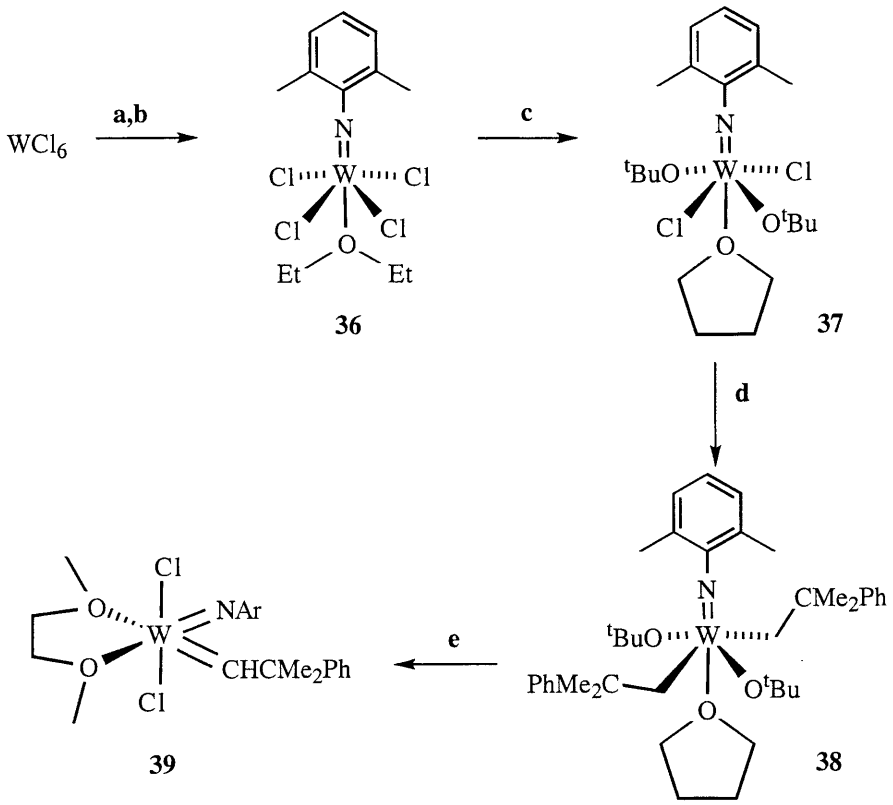
## INTRODUCTION

Tungsten imido alkylidene complexes of the type, $W(NAr)(CHR)(OR')_2$ have been used for ROMP polymerizations;[29,129,130] however, the application of these catalysts to the metathesis of acyclic olefins has been limited due to the formation of stable metallacyclobutanes. For example, $W(N\text{-}2,6\text{-}^iPr_2C_6H_3)(CH_2CH^tBuCH_2)(OR)_2$ (R = $CMe(CF_3)_2$, $^t$Bu, 2,6-$^i Pr_2C_6H_3$) were prepared by addition of excess *tert*-butylethylene and ethylene to pentane solutions of $W(NAr)(CH^tBu)(OR)_2$.[131] The unsubstituted metallacycles, $W(N\text{-}2,6\text{-}^iPr_2C_6H_3)(C_3H_6)(OR)_2$ were observed spectroscopically for (R = $^t$Bu and 2,6-$^i Pr_2C_6H_3$),[131] and were isolated for (R = $CMe(CF_3)_2$ and $C(CF_3)_2(CF_2CF_2CF_3)$.[8] Tungsten oxo alkylidene complexes containing aryloxide ligands have been used sparingly as catalysts for RCM reactions.[39,132]

## RESULTS AND DISCUSSION

### 5.1. Synthesis of (±)($R_2$)W(Neo)

A five-step synthesis of $W(N\text{-}2,6\text{-}^iPr_2C_6H_3)(CHCMe_2Ph)Cl_2$•DME starting from $WCl_6$ was developed by Schrock.[33] The related $W(N\text{-}2,6\text{-}Me_2C_6H_3)(CHCMe_2Ph)(Cl)_2$•DME, **39**, was prepared following their methodology (Scheme 5.1). The addition of $TMS_2O$ to $WCl_6$ in $CH_2Cl_2$ generated $W(O)Cl_4$ and two equivalents of TMSCl.[133] Refluxing a mixture of $W(O)Cl_4$ and 2,6-dimethylphenyl isocyanate in octane followed by an ether extraction afforded $W(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_4$•$OEt_2$, **36**. In the third step, two of the four chlorides in the green colored **36** were replaced with *tert*-butoxide ligands by slow addition of two equivalents of $LiO^tBu$ to a cold THF/ether solution of **36**. This dichlorobisalkoxide complex **37** was then alkylated with neophylmagnesium chloride to give the dineophylbisalkoxide **38**. The *tert*-butoxide ligands were then removed by addition of phosphorus pentachloride to give a proposed five-coordinate $W(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2(CH_2CMe_2Ph)_2$ intermediate which decomposed by α-elimination to generate the imido alkylidene **39**.

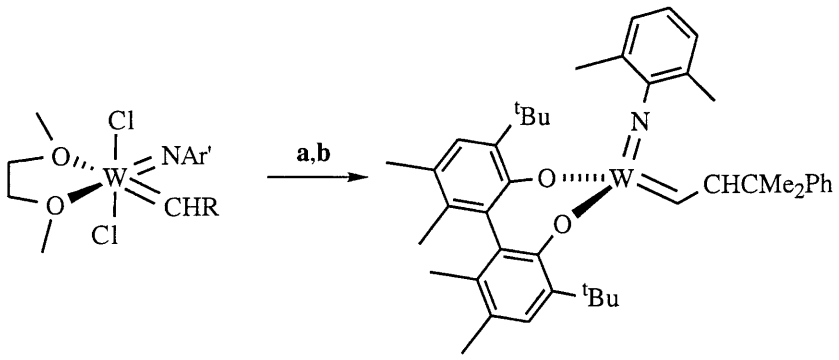



**a**) $TMS_2O$, $CH_2Cl_2$, rt, 1 h. **b**) Ar'NCO, octane, reflux, 8 h. **c**) 2 eq $LiO^tBu$, pentane, -25 °C → rt, 24 h. **d**) 2 eq $PhMe_2CCH_2MgCl$, $OEt_2$, rt, 12 h. **e**) $PCl_5$, DME, -25 °C → rt, 1 h.

**Scheme 5.1.** Synthesis of W(N-2,6-$Me_2C_6H_3$)(CHC$Me_2$Ph)$(Cl)_2$•DME, **39**.

Racemic W(N-2,6-$Me_2C_6H_3$)(CHC$Me_2$Ph)((±) Biphen), (±)$(Me_2)$W(Neo), was prepared by a method analogous to the method used to prepare (±)$(Me_2)$Mo(Neo). (±)-Biphen$H_2$ was deprotonated with excess potassium hydride in THF and then W(N-2,6-$Me_2C_6H_3$)(CHC$Me_2$Ph)$(Cl)_2$•DME was added as a solid (Scheme 5.2). After a benzene extraction, the resulting orange solid was triturated with ether to give (±)$(Me_2)$W(Neo) as a bright yellow powder. This complex existed as a mixture of *syn* and *anti* rotamers ($K_{eq}$ = 88) but the *anti* concentration was much larger than in (±)$(Me_2)$Mo(Neo) ($K_{eq}$ = 300). The *syn* alkylidene $^1H$ NMR chemical shift (7.99 ppm) was upfield by 3 ppm relative to (±)$(Me_2)$Mo(Neo) and $^{183}W$ and $^{13}C$ satellites were visible ($J_{WH}$ = 8.2 Hz; $J_{CH}$ = 115.6

Hz). The *anti* rotamer, δ 9.06, was also shifted upfield by 3.97 ppm relative to (±)($Me_2$)Mo(Neo) and the $^{183}W$ coupling was $J_{WH}$ = 7 Hz).




**a**) (±)-Biphen$K_2$, THF, 2 h. **b**) benzene extraction.

**Scheme 5.2.** Synthesis of (±)($Me_2$)W(Neo).

The 2,6-diisopropylphenylimido analog to (±)($Me_2$)W(Neo), W(N-2,6-$^{i}Pr_2C_6H_3$)(CHCMe$_2$Ph)((±)-Biphen), (±)$^{i}$Pr)W(Neo), was prepared by addition of W(NAr)(CHCMe$_2$Ph)(OTf)$_2$•DME[33] to a THF solution of (±)-Biphen$K_2$. The base-free four-coordinate complex was not crystalline. Addition of one equivalent of dimethylphenylphosphine induced precipitation from methylcyclohexane to give the five-coordinate phosphine adduct, W(N-2,6-$^{i}Pr_2C_6H_3$)(CHCMe$_2$Ph)((±)-Biphen)•PMe$_2$Ph, (±)$^{i}$Pr)W(Neo)•PMe$_2$Ph. The neophylidene resonance was observed as a doublet at δ 12.35 by $^1$H NMR spectroscopy with $J_{PH}$ = 6 Hz.

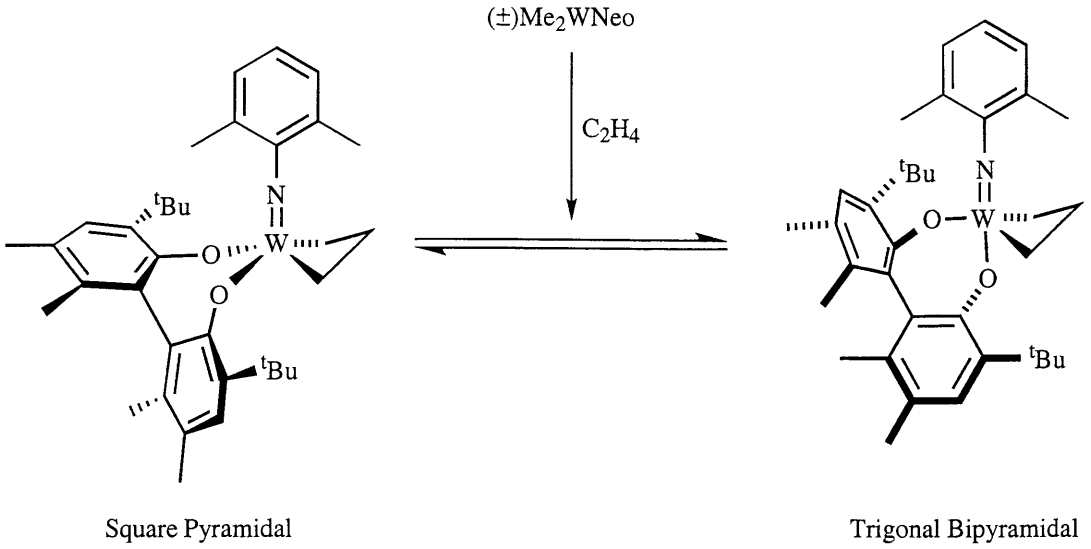
## 5.2. Tungsten Metallacyclobutane: Synthesis and NMR Studies

Addition of approximately three equivalents of ethylene to a benzene-$d_6$ solution of (±)($Me_2$)W(Neo) at room temperature generated 3-methyl-3-phenyl-1-butene and (±)($Me_2$)W($C_3H_6$). The room temperature $^1$H NMR spectrum of this reaction exhibited several interesting features. There were four resonances between δ 3.0 and 4.0 and two resonances between δ 0.0 and 1.0 that corresponded to the four $H_\alpha$ and two $H_\beta$ protons of an unsubstituted tungstacyclobutane (Figure 5.1).[8,131] Interestingly, the six aliphatic Biphen resonances (four Me and two $^{t}$Bu) in (±)($Me_2$)W(Neo) were observed as three averaged signals (two Me and one $^{t}$Bu). A similar sample prepared in toluene-$d_8$ was

cooled to -40 °C and the $^1H$ NMR spectrum was recorded. The aliphatic Biphen resonances were inequivalent (four Me and two $^tBu$) and there were resonances for two unsubstituted metallacycles in a 3:1 ratio. The major metallacycle exhibited two β-$CH_2$ $^1H$ NMR resonances at δ 0.10 and -0.42 ppm while the $H_\beta$ resonances of the minor metallacycle were at δ 0.81 and 0.54 ppm. In addition, four $H_\alpha$ resonances were clearly visible for the major metallacycle at δ 4.6, 4.08, 3.92 and 3.21 while several smaller signals are present in the same region which might correspond to the minor metallacycle $H_\alpha$ resonances. By comparison with W(N-2,6-$^i$Pr$_2$C$_6$H$_3$)(C$_3$H$_6$)(OR)$_2$ (R = CMe(CF$_3$)$_2$ and 2,6-$^i$Pr$_2$C$_6$H$_3$),[131] the major isomer was assigned to be square pyramidal (SP) with the arylimido group at the apical position based on similar chemical shifts for $H_\alpha$ and $H_\alpha$ (Scheme 5.3). The minor isomer was assigned to be trigonal bipyramidal (TBP) with the arylimido and one Biphen oxygen in the axial positions. The presence of two sets of metallacycle resonances at low temperature (-40 °C) which were averaged at elevated temperatures indicated that (±)(Me$_2$)W(C$_3$H$_6$) was a mixture of two tungstacyclobutanes which interconvert rapidly at room temperature. The isomerization between TBP and SP equilibrated the aliphatic Biphen resonances but did not cause the $H_\alpha$ or $H_\beta$ resonances to average. Fast rotation of the Biphen ligand relative to the rest of the molecule in either a turnstile or Berry pseudo-rotation mechanism caused the aliphatic Biphen resonances to average. Even with fast rotation of the Biphen ligand relative to the rest of (±)(Me$_2$)W(C$_3$H$_6$), the W(N-2,6-Me$_2$C$_6$H$_3$)((±)-Biphen) fragment was chiral and each metallacycle $H_\alpha$ and $H_\beta$ was unique. Consequently, ethylene dissociation from (±)(Me$_2$)W(C$_3$H$_6$) was slow on the NMR timescale.

The metallacycle, (±)(Me$_2$)W(C$_3$H$_6$), was moderately stable in solution when excess ethylene was present; however, concentrating a benzene or toluene solution of (±)(Me$_2$)W(C$_3$H$_6$) *in vacuo* induced decomposition. Presumably ethylene was extruded generating an unstable four-coordinate methylidene complex, (±)(Me$_2$)W(CH$_2$) which then decomposed by bimolecular pathways. The propylidene, W(N-2,6-Me$_2$C$_6$H$_3$)(CHEt)

$[OCMe(CF_3)_2]_2$, decomposed over 2 hours to the proposed $[W(N\text{-}2,6\text{-}Me_2C_6H_3)(OCMe(CF_3)_2)]_2$ with bridging arylimido ligands.[33]




**Scheme 5.3**. Formation of $(\pm)(Me_2)W(C_3H_6)$ and Isomerization between Trigonal Bipyramidal and Square Pyramidal Geometries.

In order to isolate solid $(\pm)(Me_2)W(C_3H_6)$, four equivalents of 1,6-heptadiene were added to a slurry of $(\pm)(Me_2)W(Neo)$ in pentane (Scheme 5.4). The reaction vessel was then sealed to prevent ethylene loss. The first cyclization generated 3-methyl-3-phenyl-1-butene and $(\pm)(Me_2)W(CH_2)$ which was a very active RCM catalyst. Full cyclization of 1,6-heptadiene produced 3.5 equivalents of ethylene which shifted the methylidene/metallacycle equilibrium towards $(\pm)(Me_2)W(C_3H_6)$. Cooling the reaction mixture induced precipitation of $(\pm)(Me_2)W(C_3H_6)$ from the pentane/cyclopentene solution. Solid $(\pm)(Me_2)W(C_3H_6)$ was stable under either a dinitrogen atmosphere or brief exposures to active vacuum. Dissolving $(\pm)(Me_2)W(C_3H_6)$ in benzene-$d_6$ caused ethylene loss and complex decomposition over 2-3 hours as the clear yellow solution became black and a dark solid precipitated. This ability to lose ethylene makes this a potential RCM catalyst precursor as $(\pm)(Me_2)W(CH_2)$ will be accessible during the course of the reaction.

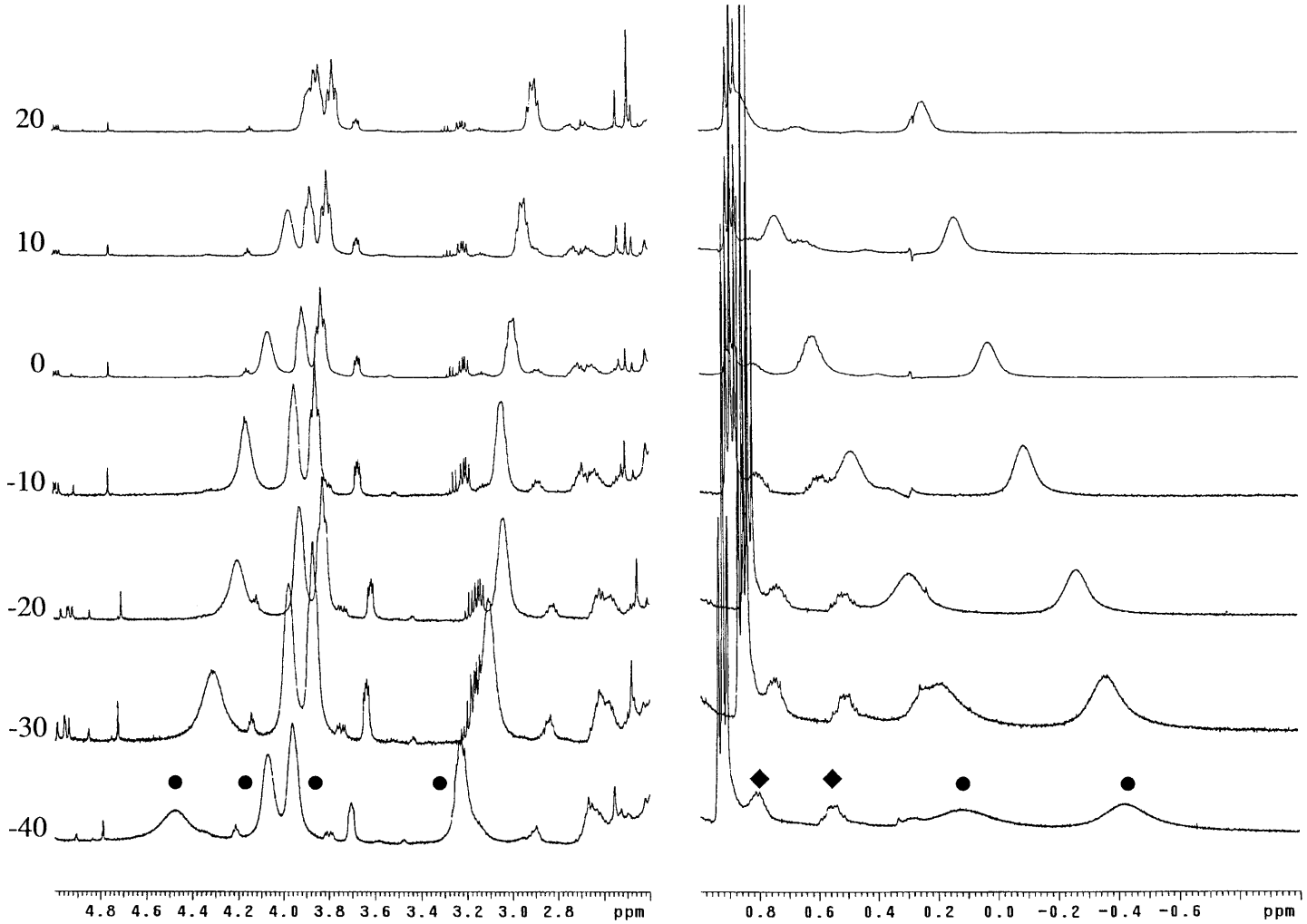
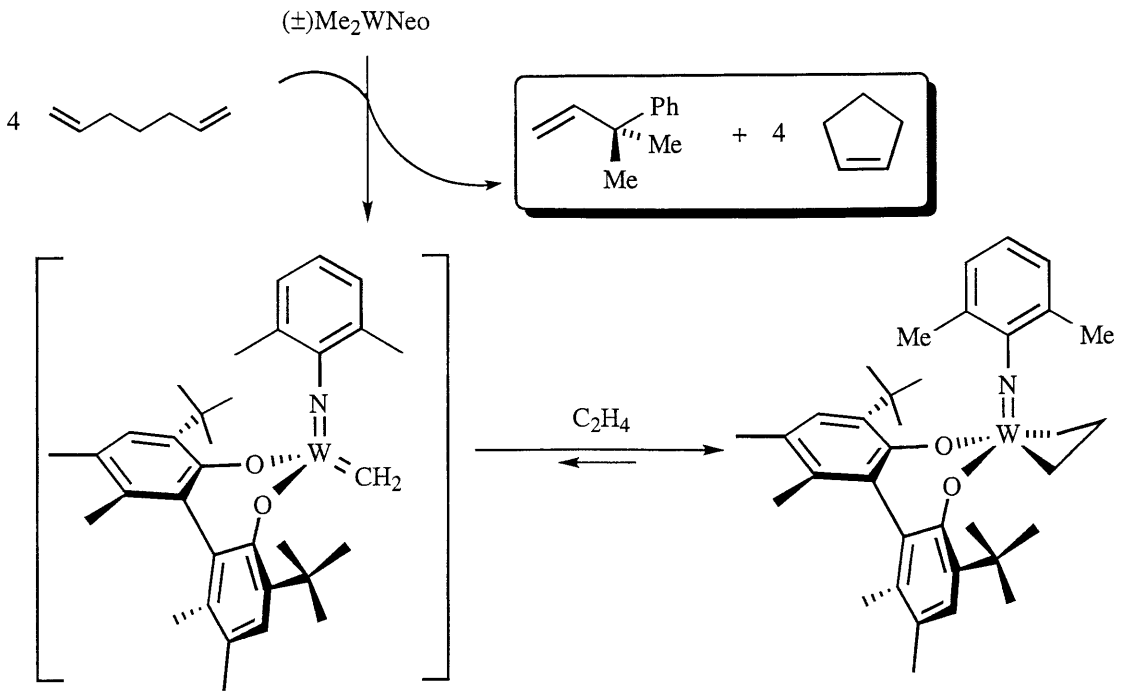



**Figure 5.1.** Variable Temperature $^1$H NMR Spectroscopy of (±)$(Me_2)W(C_3H_6)$ from 20 °C to -40 °C in Toluene-$d_8$ (Aliphatic Region from δ 2.5 to 1.0 Omitted for Clarity). (●) Square Pyramidal (±)$(Me_2)W(C_3H_6)$. (◆) Trigonal Bipyramidal (±)$(Me_2)W(C_3H_6)$.



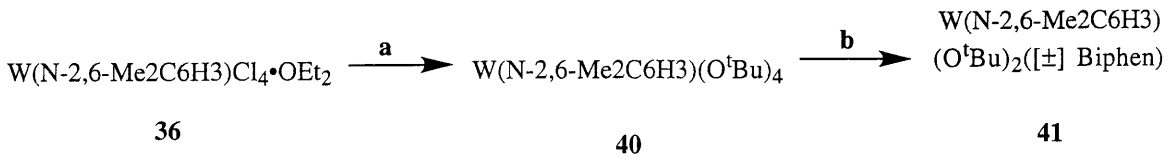

**Scheme 5.4.** Synthesis of (±)$(Me_2)W(C_3H_6)$ using 1,6-Heptadiene as the Ethylene Source.

## 5.3. Attempted Direct Synthesis: Preparation of W(N-2,6-$Me_2C_6H_3$)((±)-Biphen)($O^tBu$)$_2$

More direct or *in situ* routes to tungsten imido alkylidene biphenoxide complexes were investigated. W(O)(O-2,6-$Br_2C_6H_3)_2(Cl)_2$ was treated with two equivalents of $MEt_4$ (M = Pb or Sn) to generate a transient five-coordinate dialkyl, W(O)(O-2,6-$Br_2C_6H_3)_2Et_2$. The catalytically active ethylidene complex, W(O)(CHMe)(O-2,6-$Br_2C_6H_3)_2$, was generated *in situ* by α-elimination of ethane; this complex has been used previously for several RCM reactions.[37,40] The proposed target was the preparation of chiral molybdenum or tungsten complexes containing Biphen and an arylimido ligands. Addition of a cocatalyst, such as benzyl potassium or neopentyl lithium, would replace two reactive ligands (such as alkoxide or halide) with an alkylidene functionality. To this end, the

synthesis of metal complexes such as W(N-2,6-$Me_2C_6H_3$)(X)$_2$(Biphen) (X = Cl, O$^t$Bu) was investigated.

Phenylimido tungsten tetrakis-*tert*-butoxide was prepared by Pederson and Schrock in the early 1980's.[134] In addition, Herrmann prepared Mo(≡N)($CH_2CMe_3$)$_3$ by alkylation of Mo(N)(O$^t$Bu)$_3$.[135] With these precedents, it is reasonable to propose making W(NAr)($CHCMe_2Ph$)((±)-Biphen) by the synthesis outlined in Scheme 5.5. The tetra-*tert*-butoxide complex, **40**, could be prepared by addition of lithium *tert*-butoxide to W(N-2,6-$Me_2C_6H_3$)$Cl_4$•$OEt_2$. Introduction of the Biphen ligand could then be effected by alcoholysis with (±)-Biphen$H_2$, generating two equivalents of *tert*-butanol. Alternatively, heating W(N-2,6-$Me_2C_6H_3$)(O$^t$Bu)$_4$ with (±)-BiphenTMS$_2$ could give W(N-2,6-$Me_2C_6H_3$)((±)-Biphen)(O$^t$Bu)$_2$ and two equivalents of TMSO$^t$Bu. Alkylation with two equivalents of Grignard would then generate the five-coordinate dialkyl intermediate which would then form the alkylidene complex by α-elimination.




**a**) 4 eq LiO$^t$Bu, pentane, rt, 1.5h. **b**) (±)-BiphenTMS$_2$, xylenes, 110 °C, 18h.

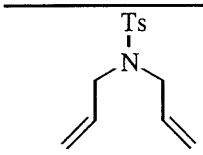
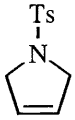
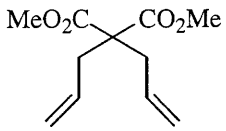
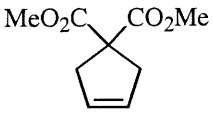
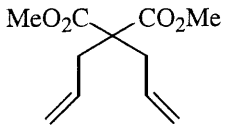
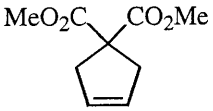
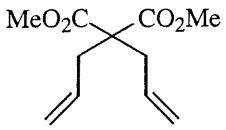
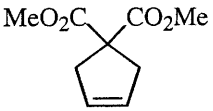
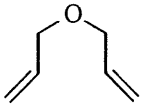
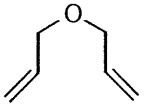
**Scheme 5.5.** Synthesis of W(N-2,6-$Me_2C_6H_3$)(O$^t$Bu)$_2$((±)-Biphen), **41**.

The preparation of W(N-2,6-$Me_2C_6H_3$)(O$^t$Bu)$_4$, **40**, was achieved by addition of LiO$^t$Bu to a pentane solution of W(N-2,6-$Me_2C_6H_3$)$Cl_4$•$OEt_2$ followed by filtration to remove lithium chloride. Treatment of **40** with (±)-Biphen$H_2$ did not generate W(N-2,6-$Me_2C_6H_3$)((±)-Biphen)(O$^t$Bu)$_2$ as expected. Instead addition of (±)-BiphenTMS$_2$ to **40** at 110 °C in xylene for 18 hours generated W(N-2,6-$Me_2C_6H_3$)((±)-Biphen)(O$^t$Bu)$_2$, **41**, in 43% yield after crystallization. Unfortunately, this high temperature could induce racemization of optically pure BiphenTMS$_2$. Consequently, the alkylation of **41** was not attempted and this approach to catalyst synthesis was not pursued.

## 5.4. RCM Activity of Tungsten Catalysts

The RCM activity of (±)($Me_2$)W(Neo) and (±)($^iPr_2$)W(Neo)•$PMe_2Ph$ was assayed with several substrates containing a variety of functional groups. Addition of 5 mol% (±)($Me_2$)W(Neo) to benzene-$d_6$ solutions of *N,N*-diallylsulfonamide, **42**, and dimethyl diallylmalonate, **43**, induced complete cyclization within 16 hours at room temperature. When the cyclization of allyl ether, **44**, was attempted under identical conditions no ring-closed product was observed after 16 hours. Repeating the allyl ether reaction with either higher catalyst loading (10 mol%) or elevated temperature (50 °C) did not generate 2,5-dihydrofuran. When an equimolar solution of (±)($Me_2$)W(Neo) and allyl ethyl ether are mixed in benzene-$d_6$, 3-methyl-3-phenyl-1-butene was observed by $^1H$ NMR but new alkylidene resonances were not observed. Clearly, W complexes (±)($R_2$)W(Neo) are not appropriate catalysts for ethereal substrates.

**Table 5.1.** RCM of Simple Achiral α,ω-Dienes with Tungsten Catalysts.

| Substrate | Product | Catalyst | Time | Temp | Conv. |
|---|---|---|---|---|---|
|  |  | (±)($Me_2$)W(Neo) | 18h | 20 °C | 100% |
|  |  | (±)($Me_2$)W(Neo) | 18h | 20 °C | 100% |
|  |  | (±)($Me_2$)W($C_3H_6$) | 18h | 20 °C | 100% |
|  |  | (±)($^iPr_2$)W(Neo) •$PMe_2Ph$ | 18h | 50 °C | 60% |
|  | -- | (±)($Me_2$)W(Neo) | 60h | 20 °C | 0% |
|  | -- | (±)($Me_2$)W(Neo) | 18h | 50 °C | 0% |

(±)($Me_2$)W(Neo) was much slower than (±)($Me_2$)Mo(Neo) (5 mol% catalyst led to complete conversion in < 10 min.) at catalyzing the RCM of malonate and sulfonamide substrates due to (±)($Me_2$)W($C_3H_6$) sequestering the active tungsten methylidene complex. Metallacycle formation was reversible with biphenoxide ligands based on the instability of (±)($Me_2$)W($C_3H_6$) in the absence of excess ethylene and the ability of (±)($Me_2$)W($C_3H_6$) to ring-close dimethyl diallylmalonate.

Unlike (±)($Me_2$)W(Neo), the RCM activity of (±)-($^iPr_2$)W(Neo)•$PMe_2Ph$ with dimethyl diallylmalonate is extremely slow. At 50 °C, the reaction went 60% to completion after 18 hours. Presumably, the combined inhibition from phosphine coordination and (±)($^iPr_2$)W($C_3H_6$) formation were responsible for the extremely sluggish RCM activity.

## CONCLUSIONS

Two chiral tungsten(VI) imido alkylidene biphenoxide complexes were prepared using the methodology developed for molybdenum in Chapter 2. A direct route to W(N-2,6-$Me_2C_6H_3$)(CHR)((±)-Biphen) was investigated, but the harsh thermal conditions necessary to generate W(N-2,6-$Me_2C_6H_3$)($O^tBu$)$_2$((±)-Biphen) made this approach impractical for optically pure catalyst synthesis due to the possibility of ligand racemization. The unsubstituted tungstacyclobutane, (±)($Me_2$)W($C_3H_6$) was observed spectroscopically by $^1$H NMR and then isolated as a solid using RCM to generate ethylene in the sealed reaction vessel. The metallacycle was fluxional at room temperature and two geometric isomers, square pyramidal and trigonal bipyramidal, were observed by $^1$H NMR at -30°C. The RCM activity of (±)($Me_2$)W(Neo), (±)($Me_2$)W($C_3H_6$), and (±)($^iPr_2$)W(Neo)•$PMe_2Ph$ were evaluated with simple achiral α,ω-dienes, **42**-**44**. The tungsten catalysts are less reactive than the corresponding molybdenum complexes. Presumably the stability of the unsubstituted tungstacyclobutane sequesters the most active form of the catalysts, (±)($Me_2$)W($CH_2$), reducing the effective concentration of active RCM catalysts.

## EXPERIMENTAL

**General Procedures.** Unless otherwise noted all manipulations were performed under rigorous exclusion of oxygen and moisture in a dinitrogen-filled glove-box or using standard Schlenk procedures. Ether, THF, and pentane were sparged with dinitrogen followed by passage through 2 1-gallon columns of activated alumina.[96] Toluene and benzene were distilled from sodium metal/benzophenone ketyl. Methylene chloride was distilled from $CaH_2$. NMR spectra are taken on Varian instruments (75.4 or 125.8 MHz, $^{13}C$; 300 or 500 MHz, $^{1}H$). $^{1}H$ NMR spectra are referenced versus residual protons in the deuterated solvents as follows: $\delta = 7.16$ $C_6D_6$, $\delta = 7.27$ $CDCl_3$, $\delta = 2.09$ toluene-$d_8$ ($CD_2H$). $^{13}C$ NMR spectra are referenced as follows: $\delta = 128.4$ $C_6D_6$ and $\delta = 137.9$ toluene-$d_8$. All NMR spectra were taken at room temperature in $C_6D_6$ unless otherwise noted. Temperatures during variable temperature NMR studies were not calibrated. $W(O)Cl_4$,[133] $W(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_4{\bullet}OEt_2$,[33,134] $W(N\text{-}2,6\text{-}^{i}Pr_2C_6H_3)(CHCMe_2Ph)(OTf)_2{\bullet}DME$,[33] $PhMe_2CCH_2MgCl$,[108] and **42**[136] were prepared according to literature procedures. **43** was prepared analogously to dimethyl dipropargylmalonate, $(MeO_2C)_2C(CH_2C{\equiv}CH)_2$.[137] $PMe_2Ph$ (Strem) and 1,6-heptadiene (Aldrich) were stored under dinitrogen over 4Å molecular sieves. Allyl ether (Aldrich) was distilled from $CaH_2$ under nitrogen and stored over 4Å molecular sieves. 2,6-Dimethylphenyl isocyanate was stirred over $P_2O_5$ for 24 hours, vacuum distilled and stored over 4Å molecular sieves at -25 °C. All other reagents were used as received. $C_6D_6$ and toluene-$d_8$ (Cambridge Isotope Laboratories) were degassed with dinitrogen and dried over 4Å molecular sieves for approximately 1 day prior to use. Elemental analyses were performed at H. Kolbe, Mikroanalytisches Laboratorium (Mühlheim an der Ruhr, Germany).

### $W(N\text{-}2,6\text{-}Me_2C_6H_3)(O^{t}Bu)_2(Cl)_2{\bullet}THF$

A slurry of lithium *tert*-butoxide (2 eq, 13.1 g, 164 mmol) in ether (100 mL) was added to a precooled solution (-25 °C) of $W(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_4{\bullet}OEt_2$ (42.5 g, 82 mmol) in diethyl ether (300 mL) and THF (100 mL) over 20 minutes. The solution bleached from

dark green to orange and a precipitate formed. After stirring for 20 hours, the mixture was filtered through Celite, and the pad was washed with diethyl ether (100 mL) until the solid residue was colorless. The solution was concentrated *in vacuo* to an orange solid. The solid was extracted with ether (250 mL) and the suspension was filtered again through Celite. The eluent volume was reduced to approximately 200 mL and then stored at -25 °C overnight. Orange crystals were collected by filtration and dried *in vacuo* (32.3 g, 66%): $^1$H NMR δ 6.90 (d, $J_{HH}$ = 7.8 Hz, 2H, m-Ar), 6.58 (t, $J_{HH}$ = 7.8 Hz, 1H, p-Ar), 4.20 (br t, 4H, THF), 3.02 (s, 6H, ArMe), 1.46 (s, 18H, O$^t$Bu), 1.42 (br t, 4H, THF); $^{13}$C{$^1$H} NMR δ 151.18, 140.29, 128.68, 128.04, 86.65, 71.21, 31.05, 25.79, 21.16. Anal. Calcd for $C_{20}H_{35}Cl_2NO_2W$: C 40.56, H 5.96, N 2.36. Found C 40.39, H 5.88, N 2.43.

**W(N-2,6-Me$_2$C$_6$H$_3$)(O$^t$Bu)$_2$(CH$_2$CMe$_2$Ph)$_2$**

To a precooled (-25 °C) ether (120 mL) solution of W(N-2,6-$Me_2C_6H_3$)(O$^t$Bu)$_2$(Cl)$_2$•THF (32.3 g, 54.6 mmol) was slowly added $PhMe_2CCH_2MgCl$ (2 eq, 95 mL, 109 mmol, 1.15 M in ether). The solution was stirred for 20 hours at room temperature and a white precipitate formed. The mixture was filtered through Celite and the pad was washed with ether (100 mL) until colorless. The eluent volume was reduced to ~50 mL and crystals formed when the solution was stored at -25 °C. The orange needles were collected by filtration and dried *in vacuo* (20 g, 51%): $^1$H NMR δ 7.55 (d, $J_{HH}$ = 7.5 Hz, 4H, o-Ph), 7.23 (t, $J_{HH}$ = 7.5 Hz, 4H, m-Ph), 7.05 (t, $J_{HH}$= 7.5 Hz, 2H, p-Ph), 6.92 (d, $J_{HH}$ = 7.5 Hz, 2H, m-Ar), 6.63 (t, $J_{HH}$ = 7.5 Hz, 1H, p-Ar), 2.45 (s, 6H, ArMe), 2.21 (br s, 4H, C*H*$_2$R), 1.66 (s, 12H, CH$_2$C*Me*$_2$Ph), 1.34 (s, 18H, O$^t$Bu); $^{13}$C{$^1$H} NMR δ 156.96, 152.99, 137.50, 128.74, 127.84, 126.29, 126.09, 125.78, 42.09, 33.36, 32.09, 19.98, 14.64. Anal. Calcd for $C_{36}H_{53}NO_2W$: C 60.42, H 7.46, N 1.96. Found C 60.58, H 7.54, N 2.04.

**W(N-2,6-$Me_2C_6H_3$)(CHC$Me_2$Ph)$(Cl)_2$•DME**

Phosphorus pentachloride (4.41 g, 21.2 mmol) was added to a rapidly stirred solution of W(N-2,6-$Me_2C_6H_3$)($O^tBu$)$_2$($CH_2CMe_2Ph$)$_2$ (14.7 g, 20.6 mmol) in cold (-25 °C) DME (125 mL). After one hour, the brown solution was concentrated *in vacuo*. The residue was extracted with ether (30 mL), and an orange precipitate formed. The orange powder was collected by filtration, triturated twice with ether (20 mL total), and dried *in vacuo* (5.4 g, 44%): $^1$H NMR δ 10.25 (s, 1H, C*H*R), 7.71 (d, $J_{HH}$ =7.7 Hz, 2H, o-Ph), 7.27 (t, $J_{HH}$ = 7.7 Hz, 2H, m-Ph), 7.05 (t, $J_{HH}$ = 7.7 Hz, 1H, p-Ph), 6.86 (d, $J_{HH}$ = 7.7 Hz, 2H, m-Ar), 6.76 (t, $J_{HH}$ = 7.7 Hz, 1H, p-Ar), 3.16 (s, 6H, OC$H_3$), 3.12 (s, 4H, OC$H_2$), 2.86 (s, 6H, Ar(C$H_3$)$_2$), 1.76 (s, 6H, CHC(C$H_3$)$_2$Ph); $^{13}$C{$^1$H} NMR δ 282.00, 155.32, 139.97, 128.92, 128.58, 127.13, 127.03, 126.44, 71.94, 62.64, 53.78, 33.00, 21.22.

**W(N-2,6-$Me_2C_6H_3$)($O^tBu$)$_4$**

A slurry of lithium *tert*-butoxide (4 eq, 197 mg, 2.19 mmol) in pentane (5 mL) was added to a pentane (10 mL) solution of W(N-2,6-$Me_2C_6H_3$)$(Cl)_4$•$OEt_2$ (284 mg, 0.547 mmol). After stirring for 90 minutes, the reaction mixture had become yellow. The solution was then filtered through Celite and concentrated *in vacuo* to afford 208 mg yellow powder (64%): $^1$H NMR δ 6.98 (d, 2H, m-Ar), 6.68 (t, 1H, p-Ar), 2.767 (s, 6 H, ArMe), 1.475 (s, 36H, $O^tBu$); $^{13}$C{$^1$H} NMR δ 138.61, 128.66, 127.77, 127.12, 80.78, 32.10, 19.02. Anal. Calcd for $C_{24}H_{45}NO_4W$: C 48.41, H 7.62, N 2.35. Found C 48.28, H 7.59, N 2.54.

**(±)-Biphen$(TMS)_2$**

Potassium hydride (176 mg, 4.4 mmol) was added in portions to a THF (10 mL) solution of (±)-Biphen$H_2$ (708 mg, 2 mmol). After 30 minutes, chlorotrimethylsilane (650 mg, 6 mmol) was added and the reaction stirred for 18 hours. The solution was then concentrated *in vacuo* and the residue was extracted with ether. The suspension was filtered through Celite and concentrated *in vacuo* to give a white powder (900 mg, 90%):

$^1$H NMR δ 7.08 (s, 2H, Aryl), 2.214 (s, 6H, Me), 1.686 (s, 6H, Me), 1.373 (s, 18H, $^t$Bu), 0.197 (s, 18H, TMS); $^{13}$C{$^1$H} NMR δ 151.60, 137.82, 135.33, 131.90, 129.44, 128.80, 35.12, 30.92, 20.85, 17.81, 2.49. Anal. Calcd for $C_{30}H_{50}O_2Si_2$: C 72.23, H 10.10. Found C 72.33, H 9.95.

**W(N-2,6-Me$_2$C$_6$H$_3$)(O$^t$Bu)$_2$((±)-Biphen)**

(±)-BiphenH$_2$ (66 mg, 0.186 mmol) and W(N-2,6-Me$_2$C$_6$H-3)(O$^t$Bu)$_4$ (114 mg, 0.192 mmol) were dissolved in xylenes (4 mL). The solution was heated to 110 °C in a sealed reaction flask for 18 hours. After cooling the reaction to room temperature, the volatiles were removed *in vacuo,* and the residue was dissolved in refluxing ether (5 mL). The ether solution was stored at -25 °C overnight and yellow microcrystals formed which were collected by filtration (64 mg, 43%): $^1$H NMR δ 7.35 (s, 1H, BiphenH), 7.05 (s, 1H, BiphenH), 6.82 (br d, 2H, m-Ar), 6.50 (t, 1H, p-Ar), 2.27 (s, 3H, BiphenMe), 2.17 (s, 3H, BiphenMe), 2.00 (s, 3H, BiphenMe), 1.78 (s, 9H, Biphen$^t$Bu), 1.74 (s, 3H, BiphenMe), 1.62 (s, 9H, Biphen$^t$Bu), 1.41 (s, 9H, O$^t$Bu), 1.30 (s, 9H, O$^t$Bu).

**W(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)((±)-Biphen) ((±)(Me$_2$)W(Neo))**

Benzyl potassium (2.05 eq, 533 mg, 4.1 mmol) was added to a THF (40 mL) solution of (±)-BiphenH$_2$ (708 mg, 2 mmol). After 15 minutes, W(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(Cl)$_2$•DME (1.191 g, 2 mmol) was added as a solid and the reaction was stirred for two hours at room temperature. The solution was concentrated to a yellow powder and extracted with benzene (20 mL). The suspension was filtered through Celite, and the pad was washed with additional benzene (30 mL) until colorless. The benzene was evaporated *in vacuo*, and the residue redissolved in ether (10 mL). A bright yellow powder precipitated and it was collected by filtration (1.09 g, 69%): $^1$H NMR (Mixture of rotamers, $K_{eq}$ = 88) *syn* δ 7.99 (s, $J_{WH}$ = 16.5 Hz, $J_{CH}$ = 115 Hz, 1H, C*H*R), 7.44 (s, 1H, BiphenH), 7.40 (d, $J_{HH}$ = 7.5 Hz, 2H, o-Ph), 7.17 (s, 1H, BiphenH), 7.14 (t, $J_{HH}$ = 7.5 Hz, 2H, m-Ph), 6.98 (t, $J_{HH}$ = 7.5 Hz, 1H, p-Ph), 6.83 (d, $J_{HH}$ = 7.5 Hz, 2H, m-Ar), 6.74 (t, $J_{HH}$ = 7.5 Hz, 1H, p-Ar), 2.31 (s, 6H, Ar*Me*), 2.12 (s, 3H,

BiphenMe), 2.00 (s, 3H, BiphenMe), 1.72 (s, 3H, BiphenMe/CHC*Me*$_2$Ph), 1.67 (s, 3H, BiphenMe/CHC*Me*$_2$Ph), 1.60 (s, 3H, BiphenMe/CHC*Me*$_2$Ph), 1.58 (s, 9H, Biphen$^t$Bu), 1.54 (s, 9H, Biphen$^t$Bu), 1.33 (s, 3H, CHC*Me*$_2$Ph). *syn* δ 9.06 (s, $J_{WH}$ = 15 Hz, 1H, C*H*R); $^{13}C\{^1H\}$ NMR 247.70, 155.12, 153.25, 152.67, 152.02, 140.29, 138.32, 136.58, 135.76, 135.48, 132.38, 131.95, 131.28, 130.89, 130.04, 129.86, 128.91, 128.10, 127.30, 126.19, 126.10, 51.75, 36.04, 35.45, 34.91, 33.92, 30.94, 30.85, 20.79, 20.71, 19.60, 17.30, 16.80. Anal. Calcd for $C_{42}H_{53}NO_2W$: C 64.04 H 6.78, N 1.78. Found C 64.12, H 6.71, N 1.74.

**W(N-2,6-$^i$Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)((±)-Biphen)•PMe$_2$Ph ((±)($^i$Pr$_2$)W(Neo)•PMe$_2$Ph)**

Potassium hydride (3 eq, 120 mg, 3 mmol) was added in portions to a THF (10 mL) solution of (±)-BiphenH$_2$ (354 mg, 1 mmol). After stirring for 3 hours, W(N-2,6-$^i$Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OTf)$_2$•DME (879 mg, 1 mmol) was added as a solid and the reaction stirred for an additional 3 hours. The volatiles were removed *in vacuo* and the residue extracted with benzene (10 mL). The red slurry was then filtered through Celite and washed with additional benzene (20 mL) until the pad was colorless. After concentrating the eluent to a red solid, methylcyclohexane (2 mL) was added and the resulting red solution was then cooled to -25 °C. A small amount of an unidentified white solid formed on the vial walls and the solution became viscous. The solution was filtered through glass wool and dimethylphenylphosphine (1 eq, 138 mg, 1 mmol) was added. The phosphine adduct, (±)($^i$Pr$_2$)W(Neo)•PMe$_2$Ph, precipitated as a dark yellow powder at -25 °C. The solid was collected by filtration and washed with cold methylcyclohexane to afford 750 mg (76%): $^1H$ NMR δ 12.35 (d, $J_{PH}$ = 6 Hz, 1H, C*H*R), 7.43 (d, $J_{HH}$ = 7.9 Hz, 2H, o-Ph), 7.25 (s, 1H, BiphenH), 7.23 (s, 1H, BiphenH), 7.14-6.88 (m, 10 H), 6.84 (m, 4H), 3.29 (heptet, $J_{HH}$ = 7.1 Hz, 2H, C*H*Me$_2$), 2.33 (s, 3H, BiphenMe/CHC*Me*$_2$Ph), 2.19 (s, 3H, BiphenMe/CHC*Me*$_2$Ph), 2.11 (s, 3H, BiphenMe/CHC*Me*$_2$Ph), 1.76 (br s, 3H, BiphenMe/CHC*Me*$_2$Ph), 1.72 (s, 9H,

Biphen$^t$Bu), 1.70 (s, 3H, BiphenMe/CHC*Me*$_2$Ph), 1.61 (d, $J_{PH}$ = 6.7 Hz, 3H, P*Me*$_2$Ph), 1.46 (d, $J_{PH}$ = 6.7 Hz, 3H, P*Me*$_2$Ph), 1.32 (s, 9H, Biphen$^t$Bu), 1.24 (d, 3H, CH*Me*$_2$), 1.04 (d, 3H, CH*Me*$_2$), 1.02 (d, 3H, CH*Me*$_2$), 0.88 (d, 3H, CH*Me*$_2$).

**Reaction of (±)(Me$_2$)W(Neo) with ethylene.**

An NMR tube with a Young valve was charged with a toluene-$d_8$ (0.6 mL) solution of (±)(Me$_2$)W(Neo) (25 mg, 0.032 μmol). The solution was frozen in liquid nitrogen, and the head space was evacuated. One atmosphere of ethylene (3.1 eq, 2.2 mL, 0.1 mmol) was then introduced into the tube. The Young valve was sealed and the reaction warmed to room temperature. The $^1$H NMR spectrum was recorded from room temperature to -85 °C. $^1$H NMR ($C_7D_8$) Excluding aryl resonances. (19 °C) δ 3.86 (br s, 1H, α-$CH_2$), 3.83 (br q, 1H, α-$CH_2$), 3.76 (br t, 1H, α-$CH_2$), 2.88 (br q, 1H, α-$CH_2$), 2.24 (br s, 6H, ArMe), 2.14 (s, 6H, BiphenMe), 1.74 (br s, 6H, BiphenMe), 1.49 (s, 18H, Biphen$^t$Bu), 0.84 (br s, 1H, β-$CH_2$), 0.24 (br s, 1H, β-$CH_2$). (-40 °C) 4.55 (br s, 1H), 4.08 (br s, 1H), 3.97 (br s, 1H), 3.25 (br s, 1H), 2.30 (br s, 6H, ArMe), 2.20 (s, 3H, BiphenMe), 2.13 (s, 3H, BiphenMe), 1.88 (s, 3H, BiphenMe), 1.71 (s, 3H, BiphenMe), 1.59 (s, 9H, Biphen$^t$Bu), 1.54 (s, 9H, Biphen$^t$Bu), 0.10 (br s, 1H), -0.49 (br s, 1H).

**W(N-2,6-Me$_2$C$_6$H$_3$)(C$_3$H$_6$)((±)-Biphen) (±)(Me$_2$)W(C$_3$H$_6$)**

To a slurry of W(N-2,6-$Me_2$-$C_6H_3$)(CHC$Me_2$Ph)([±] Biphen) (150 mg, 0.191 mmol) in pentane (1 mL) was added 1,6-heptadiene. The vial was quickly capped and the yellow suspension became a homogenous clear orange solution. The reaction was cooled to -25 °C. After 6 days, the yellow-orange precipitate was collected by decanting the solution and drying the precipitated *in vacuo* (125 mg, 95%): $^1$H NMR δ 7.17 (s, 2H, Biphen), 6.81 (d, 2H, m-NAr), 6.65 (t, 1H, p-NAr), 4.10-3.80 (three m, 1H each, three inequivalent α-$CH_2$), 3.03 (m, 1H, α-$CH_2$), 2.27 (s, 6H, NAr), 2.153 (s, 6H, Biphen), 1.78 (s, 6H, Biphen), 1.54 (s, 18H, Biphen), 0.64 (br s, 1H, β-$CH_2$), 0.03 (br s, 1H, β-$CH_2$); $^{13}$C{$^1$H} NMR δ 152.22, 136.69 (br s), 134.83, 129.55 (br s), 127.90, 126.14, 35.82 (br s), 34.76, 33.08, 31.74 (br s), 30.53, 28.71, 23.48, 23.06, 20.71, 19.76,

19.22, 17.18, 14.63, 3.51. Anal. Calcd for C 60.26, H 6.79, N 2.01. Found C 60.44, H 6.73, N 1.95.

**General conditions for room temperature RCM with (±)($Me_2$)W(Neo).**

Diallyl sulfonamide (51 mg, 0.203 mmol) was added to a benzene-$d_6$ solution of (±)($Me_2$)W(Neo) (0.05 eq, 8 mg, 0.010 mmol) and the mixture was transferred to an NMR tube. The $^1$H NMR spectrum was recorded after one hour and the conversion to ring-closed product determined by integration of the olefinic resonances (33% conversion). The NMR tube was then returned to the glove box to stand overnight and a second $^1$H NMR spectrum was collected after 16 hours. The reaction was complete at this time.

For high temperature RCM reactions, the benzene-$d_6$ or toluene-$d_8$ solutions are loaded into a NMR tube with a Young valve and heated in an oil bath.

# APPENDIX

Atomic Coordinates and Equivalent Isotropic Displacement Parameters for (S)($^{i}Pr_2$)Mo(Neo) and (S)'($CF_3$)Mo(Np)•py

**Table A.1.** Atomic Coordinates ( x $10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2$ x $10^3$) for (S)($^iPr_2$)Mo(Neo). U(eq) is Defined as One Third of the Trace of the Orthogonalized $U^{ij}$ Tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Mo | 2258(1) | 492(1) | 3126(1) | 26(1) |
| O(1) | 3372(5) | 987(4) | 2319(4) | 27(1) |
| O(2) | 2656(5) | -611(4) | 4053(4) | 26(1) |
| N | 689(6) | 335(5) | 2480(4) | 28(2) |
| C(1) | 2234(9) | 1672(7) | 3797(6) | 34(2) |
| C(2) | 1412(8) | 2521(6) | 3931(6) | 35(2) |
| C(11) | -491(7) | 37(6) | 1902(5) | 26(2) |
| C(12) | -1288(8) | 707(6) | 1313(5) | 36(3) |
| C(13) | -2403(8) | 330(7) | 721(6) | 40(2) |
| C(14) | -2726(9) | -640(8) | 730(7) | 53(3) |
| C(15) | -1928(10) | -1267(7) | 1328(7) | 44(2) |
| C(16) | -835(8) | -983(6) | 1927(5) | 30(2) |
| C(21) | 88(9) | 2111(8) | 4004(7) | 50(2) |
| C(22) | 2032(10) | 3075(7) | 4831(6) | 49(2) |
| C(23) | 1281(9) | 3274(6) | 3125(6) | 40(2) |
| C(24) | 2038(9) | 3225(6) | 2494(6) | 44(2) |
| C(25) | 1945(10) | 3938(8) | 1803(7) | 56(3) |
| C(26) | 1043(11) | 4679(7) | 1715(7) | 58(3) |
| C(31) | 3748(8) | 72(6) | 2058(5) | 26(2) |
| C(32) | 4270(7) | -582(6) | 2792(5) | 28(2) |
| C(33) | 4476(8) | -1575(6) | 2608(5) | 29(2) |
| C(34) | 4296(7) | -1871(6) | 1688(5) | 31(2) |
| C(35) | 3903(8) | -1167(6) | 996(5) | 34(2) |
| C(36) | 3610(8) | -205(6) | 1145(5) | 34(2) |
| C(37) | 301(11) | 4737(7) | 2322(7) | 58(3) |
| C(38) | 389(10) | 4046(7) | 3028(7) | 56(3) |
| C(41) | 3913(7) | -365(5) | 4415(5) | 27(2) |
| C(42) | 4686(8) | -211(5) | 3788(5) | 29(2) |
| C(43) | 5927(8) | 225(5) | 4078(5) | 31(2) |
| C(44) | 6387(7) | 429(9) | 5021(4) | 31(2) |
| C(45) | 5642(8) | 184(5) | 5643(5) | 32(2) |

| | | | | |
|---|---|---|---|---|
| C(46) | 4410(8) | -220(5) | 5388(5) | 28(2) |
| C(121) | -1024(8) | 1811(6) | 1333(6) | 33(2) |
| C(122) | -2069(9) | 2371(7) | 1705(6) | 39(2) |
| C(123) | -1009(10) | 2232(7) | 387(7) | 51(2) |
| C(161) | 14(9) | -1704(6) | 2588(6) | 39(2) |
| C(162) | 980(11) | -2162(8) | 2136(7) | 60(3) |
| C(163) | -755(12) | -2511(8) | 2940(7) | 64(3) |
| C(331) | 4904(10) | -2319(7) | 3379(6) | 47(2) |
| C(341) | 4492(10) | -2915(8) | 1447(6) | 51(2) |
| C(361) | 3153(7) | 566(10) | 337(4) | 36(2) |
| C(362) | 3995(10) | 1489(6) | 536(6) | 45(2) |
| C(363) | 3279(10) | 138(7) | -582(6) | 53(3) |
| C(364) | 1740(8) | 815(8) | 270(6) | 54(3) |
| C(431) | 6744(8) | 372(8) | 3394(5) | 41(2) |
| C(441) | 7702(9) | 897(6) | 5385(6) | 42(2) |
| C(461) | 3640(8) | -499(6) | 6085(5) | 35(2) |
| C(462) | 2454(9) | 162(7) | 5971(6) | 51(3) |
| C(463) | 4448(10) | -414(7) | 7080(6) | 51(2) |
| C(464) | 3199(10) | -1574(7) | 5923(6) | 50(2) |

**Table A.2.** Atomic Coordinates ( x $10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2$x $10^3$) for (S)'($CF_3$)Mo(Np)•py. U(eq) is Defined as One Third of the Trace of the Orthogonalized $U^{ij}$ Tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Mo(1) | -4615(1) | -8792(1) | -3552(1) | 29(1) |
| F(1A) | -5945(11) | -8030(5) | -3004(5) | 106(4) |
| F(2A) | -5674(16) | -7873(7) | -2358(6) | 150(5) |
| F(3A) | -6151(13) | -7397(6) | -2752(7) | 136(5) |
| O(1A) | -5453(8) | -8631(3) | -4093(3) | 35(3) |
| O(2A) | -5707(8) | -9246(3) | -3380(3) | 35(3) |
| N(1A) | -4221(15) | -8249(5) | -3389(5) | 65(5) |
| N(2A) | -4074(10) | -9038(5) | -2878(4) | 33(4) |
| C(1A) | -5644(11) | -7656(5) | -4426(4) | 31(3) |
| C(2A) | -5675(13) | -7903(6) | -4862(5) | 40(4) |
| C(3A) | -4496(12) | -7670(6) | -4270(5) | 40(4) |
| C(4A) | -5908(13) | -7139(6) | -4510(5) | 41(5) |
| C(5A) | -4094(14) | -6915(6) | -4677(6) | 57(6) |
| C(6A) | -3747(15) | -7424(6) | -4625(6) | 59(6) |
| C(7A) | -3922(16) | -7709(7) | -5040(7) | 77(7) |
| C(8A) | -4951(13) | -7659(6) | -5212(6) | 53(5) |
| C(9A) | -5309(15) | -7164(6) | -5259(6) | 60(6) |
| C(10A) | -5173(14) | -6899(6) | -4847(6) | 52(5) |
| C(11A) | -6379(13) | -7907(6) | -4100(5) | 34(4) |
| C(12A) | -7215(15) | -7659(7) | -3918(6) | 52(5) |
| C(13A) | -8000(13) | -7882(6) | -3678(5) | 36(4) |
| C(14A) | -7984(12) | -8356(6) | -3624(5) | 37(4) |
| C(15A) | -7140(13) | -8612(6) | -3783(6) | 38(3) |
| C(16A) | -6302(13) | -8375(6) | -3995(5) | 30(3) |
| C(17A) | -7196(12) | -9141(5) | -3825(5) | 26(4) |
| C(18A) | -8003(13) | -9330(6) | -4099(5) | 35(4) |
| C(19A) | -8103(12) | -9814(6) | -4110(5) | 33(4) |
| C(20A) | -7449(13) | -10105(7) | -3880(5) | 43(3) |
| C(21A) | -6638(12) | -9934(6) | -3620(5) | 37(3) |
| C(22A) | -6526(13) | -9425(5) | -3608(5) | 33(3) |
| C(23A) | -5936(12) | -10262(5) | -3360(5) | 28(4) |

| | | | | |
|---|---|---|---|---|
| C(24A) | -5806(13) | -10162(6) | -2881(5) | 37(4) |
| C(25A) | -4833(13) | -10259(6) | -3578(6) | 44(5) |
| C(26A) | -6295(14) | -10785(6) | -3408(6) | 40(5) |
| C(27A) | -5482(15) | -10993(6) | -2665(5) | 44(5) |
| C(28A) | -5077(15) | -10482(7) | -2637(7) | 52(5) |
| C(29A) | -4023(15) | -10471(7) | -2860(6) | 52(5) |
| C(30A) | -4091(15) | -10592(6) | -3334(6) | 47(5) |
| C(31A) | -4507(15) | -11108(6) | -3369(6) | 58(5) |
| C(32A) | -5562(15) | -11128(7) | -3155(6) | 58(5) |
| C(33A) | -4410(19) | -7568(8) | -2879(7) | 74(6) |
| C(34A) | -4216(20) | -7201(9) | -2602(8) | 86(7) |
| C(35A) | -3109(24) | -7047(11) | -2677(11) | 115(10) |
| C(36A) | -2476(16) | -7211(7) | -2914(6) | 53(5) |
| C(37A) | -2784(18) | -7655(8) | -3107(7) | 71(5) |
| C(38A) | -3860(21) | -7813(9) | -3142(9) | 89(6) |
| C(39A) | -5525(22) | -7733(10) | -2800(9) | 85(5) |
| C(40A) | -3501(13) | -9067(6) | -3867(5) | 38(5) |
| C(41A) | -2409(13) | -9023(6) | -4035(6) | 40(5) |
| C(42A) | -1795(19) | -9454(8) | -3908(8) | 82(7) |
| C(43A) | -2479(16) | -8982(7) | -4567(7) | 61(6) |
| C(44A) | -1913(18) | -8581(8) | -3879(7) | 73(7) |
| C(45A) | -3140(16) | -9215(7) | -2795(6) | 51(5) |
| C(46A) | -2774(18) | -9317(7) | -2390(7) | 67(6) |
| C(47A) | -3424(17) | -9231(7) | -2039(7) | 66(6) |
| C(48A) | -4381(20) | -9074(8) | -2103(8) | 80(7) |
| C(49A) | -4673(17) | -8955(6) | -2544(7) | 57(5) |
| C(50A) | -8873(15) | -7570(7) | -3482(7) | 57(6) |
| C(51A) | -8827(15) | -8589(7) | -3358(6) | 54(5) |
| C(52A) | -8646(14) | -9031(6) | -4387(6) | 42(5) |
| C(53A) | -8898(15) | -10048(7) | -4417(6) | 59(6) |
| Mo(2) | 653(1) | -5124(1) | -3748(1) | 39(1) |
| F(1B) | -1666(12) | -6833(5) | -3934(5) | 106(4) |
| F(2B) | -578(15) | -6354(7) | -4178(6) | 150(5) |
| F(3B) | -490(13) | -6586(5) | -3513(7) | 136(5) |
| O(1B) | 1027(8) | -4894(4) | -3138(3) | 41(3) |
| O(2B) | 650(9) | -4474(4) | -3965(3) | 50(3) |

| | | | | |
|---|---|---|---|---|
| N(1B) | -309(13) | -5525(5) | -3632(4) | 55(4) |
| N(2B) | 89(10) | -5214(5) | -4450(4) | 39(4) |
| C(1B) | -117(12) | -5335(5) | -2364(5) | 31(3) |
| C(2B) | -929(19) | -5707(8) | -2420(8) | 137(12) |
| C(3B) | 882(22) | -5565(10) | -2542(9) | 185(17) |
| C(4B) | 6(23) | -5230(8) | -1884(8) | 149(13) |
| C(5B) | 1291(19) | -5858(10) | -1794(8) | 133(12) |
| C(6B) | 1140(17) | -6051(8) | -2251(7) | 95(9) |
| C(7B) | 183(18) | -6329(8) | -2324(8) | 105(9) |
| C(8B) | -702(18) | -6162(8) | -2092(8) | 110(9) |
| C(9B) | -567(18) | -5971(8) | -1656(7) | 91(8) |
| C(10B) | 321(19) | -5673(8) | -1591(7) | 118(10) |
| C(11B) | -381(12) | -4877(6) | -2620(5) | 34(4) |
| C(12B) | -1267(14) | -4645(6) | -2507(6) | 46(5) |
| C(13B) | -1593(16) | -4237(7) | -2687(7) | 57(6) |
| C(14B) | -978(14) | -3998(6) | -2991(6) | 46(5) |
| C(15B) | -45(13) | -4228(6) | -3108(6) | 38(3) |
| C(16B) | 203(13) | -4669(5) | -2958(5) | 30(3) |
| C(17B) | 806(14) | -3951(6) | -3358(6) | 43(5) |
| C(18B) | 1265(15) | -3561(7) | -3160(6) | 47(5) |
| C(19B) | 1970(16) | -3302(7) | -3374(7) | 62(6) |
| C(20B) | 2231(14) | -3429(6) | -3826(6) | 43(3) |
| C(21B) | 1799(13) | -3816(6) | -4032(5) | 37(3) |
| C(22B) | 1099(12) | -4084(6) | -3797(5) | 33(3) |
| C(23B) | 2097(14) | -3912(6) | -4507(6) | 42(5) |
| C(24B) | 1058(15) | -3882(7) | -4792(6) | 57(6) |
| C(25B) | 2595(17) | -4410(7) | -4566(7) | 59(6) |
| C(26B) | 2821(16) | -3566(7) | -4703(6) | 58(6) |
| C(27B) | 1326(18) | -4003(7) | -5289(7) | 64(6) |
| C(28B) | 1769(17) | -4469(7) | -5338(7) | 64(6) |
| C(29B) | 2798(16) | -4509(7) | -5068(6) | 55(6) |
| C(30B) | 3552(18) | -4150(8) | -5238(8) | 73(7) |
| C(31B) | 3081(18) | -3659(8) | -5208(8) | 75(7) |
| C(32B) | 2055(18) | -3652(8) | -5457(8) | 75(7) |
| C(33B) | -1832(15) | -6071(7) | -3678(6) | 54(5) |
| C(34B) | -2844(15) | -6150(8) | -3618(6) | 60(6) |

| | | | | |
|---|---|---|---|---|
| C(35B) | -3466(22) | -5791(9) | -3495(9) | 97(8) |
| C(36B) | -1397(14) | -5626(6) | -3604(6) | 47(5) |
| C(37B) | -2064(17) | -5250(8) | -3460(7) | 71(5) |
| C(38B) | -3124(20) | -5329(9) | -3412(8) | 89(6) |
| C(39B) | -1172(22) | -6443(10) | -3818(9) | 85(5) |
| C(40B) | 1955(17) | -5399(8) | -3813(7) | 67(6) |
| C(41B) | 2616(13) | -5825(6) | -3772(6) | 41(5) |
| C(42B) | 1975(22) | -6262(10) | -3692(10) | 111(9) |
| C(43B) | 3253(17) | -5871(8) | -4191(7) | 66(6) |
| C(44B) | 3273(23) | -5753(10) | -3376(9) | 111(10) |
| C(45B) | 386(14) | -5584(6) | -4708(5) | 37(4) |
| C(46B) | -100(15) | -5657(6) | -5109(6) | 47(5) |
| C(47B) | -793(16) | -5378(7) | -5243(7) | 55(5) |
| C(48B) | -1100(16) | -4995(7) | -5016(7) | 61(6) |
| C(49B) | -636(14) | -4941(6) | -4594(6) | 44(5) |
| C(50B) | -2685(16) | -4020(7) | -2565(7) | 66(6) |
| C(51B) | -1284(17) | -3531(7) | -3201(7) | 63(6) |
| C(52B) | 1006(17) | -3411(7) | -2686(6) | 63(6) |
| C(53B) | 2543(21) | -2883(9) | -3164(9) | 99(9) |

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