Synthesis of Molybdenum Imido Alkylidene Complexes That Contain 3,3′-Dialkyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diolates (Alkyl = *t*-Bu, Adamantyl). Catalysts for Enantioselective Olefin Metathesis Reactions

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Two 3,3′-dialkyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diols (where alkyl = *t*-Bu, adamantyl) were prepared in two steps and resolved as the menthol phosphate derivative. Addition of the dipotassium salt of each biphenolate to various Mo(N-Aryl)(CHR)$(OTf)_2$(DME) complexes produced racemic and enantiopure compounds of the type Mo(N-aryl)(CHR)(biphenolate). X-ray crystallographic studies of *syn*-Mo(N-2,6-*i*-$Pr_2C_6H_3$)($CHCMe_2Ph$)[(*S*)-Biphen] and *syn*-Mo(N-2-$CF_3C_6H_4$)($CHCMe_3$)[(*S*)-Biad](pyridine) proved the absolute stereochemistry of the biphenolate ligands. Neophylidene and neopentylidene complexes were found to have predominantly the *syn* conformation in solution. The [syn]/[anti] equilibrium constant for Mo(N-Aryl)(CHR)[Biphen] complexes increased in magnitude with decreasing size of the arylimido ligand, and decreased upon reducing the steric bulk of the alkylidene substituent. The rates of exchange of *syn* and *anti* isomers, as determined by single-parameter line shape analysis and by spin saturation transfer, were found to be on the order of ~1 s^{-1} at 22 °C.

Introduction

Metal-catalyzed olefin metathesis,[1] and most recently molybdenum- and ruthenium-catalyzed ring-closing metathesis,[2−7] has emerged as a powerful method in organic synthesis. Although only a *cis* versus *trans* stereochemistry can be established at a carbon−carbon double bond in a metathesis reaction, there are many circumstances in which an enantiomerically pure catalyst might be employed in order to establish chirality at a remote carbon center as a consequence of a metathesis reaction in a kinetic resolution or desymmetrization mode. We became interested in that possibility as a consequence of exploring ring-opening metathesis polymerization (ROMP) of norbornenes and disubstituted norbornadienes catalyzed by molybdenum complexes of the type Mo(N-aryl)(CHR)(diolate).[8−11] We found that when the diolate was a racemic biphenolate or binaphtholate, the tacticity of the resulting poly(norbornene) or poly(norbornadiene) could be controlled to a significant degree, as could the configuration about the carbon−carbon double bond. Therefore, we began to explore the possibility of preparing a stable, enantiomerically pure initiator for an asymmetric metathesis reaction. We prepared a catalyst that contained an enantiomerically pure 3,3′-dimethylphenylsilyl-substituted binaphtholate ligand, but preliminary evidence suggested that the catalyst slowly decomposed during the course of a ROMP metathesis reaction. In an effort to prevent decomposition, we turned to the synthesis of ligands in which the substituent in the 3- and 3′-positions is carbon-based and relatively bulky.

One of the potentially resolvable biphenols that we examined in our ROMP studies was 3,3′,5,5′-tetra-*tert*-butyl-6,6′-dimethyl-1,1′-biphenyl-2,2′-diol,[12] which can be prepared readily on a large scale in 50% yield by oxidative coupling of 2,4-di-*tert*-butyl-5-methylphenol.[10] However, we were unable to resolve this relatively soluble species. Therefore, we turned to ligands derived from readily available and inexpensive (and less soluble)

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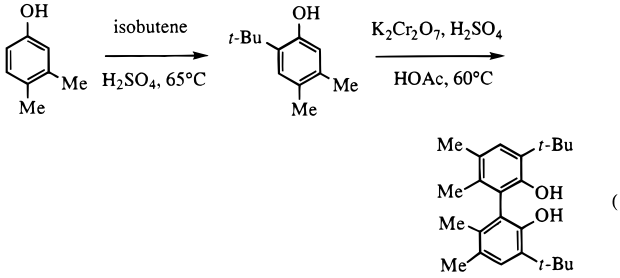
3,4-dimethylphenol, namely 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diol (H_2[Biphen]) and 3,3′-bis(1-adamantyl)-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diol ([H_2[Biad]). The results of these efforts are reported here. In the last two years enantiomerically pure complexes of the type Mo(CHR)(NAr)(Biphen) have been employed in a variety of relatively successful asymmetric metathesis reactions,[13−17] and one version, Mo(N-2,6-i-$Pr_2C_6H_3$)($CHCMe_2Ph$)(Biphen), is available commercially from Strem Chemicals, Inc. in both enantiomerically pure forms. All indications at this stage suggest that the nature of the imido group is also an important determinant of activity and that a variety of catalysts eventually should be available for testing in order to achieve the optimum combination of catalyst and substrate.

Results

Synthesis and Resolution of H_2[Biphen] and H_2[Biad]. Racemic 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diol[12] (H_2[Biphen]) can be prepared from 3,4-dimethylphenol in two steps. Treatment of 3,4-dimethylphenol at 65 °C under 2 atm of isobutene in the presence of a catalytic amount of sulfuric acid[18] followed by oxidative coupling with potassium dichromate gave H_2[Biphen] in 50% overall yield (eq 1). 3,3′-Bis(1-adamantyl)-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diol ([H_2[Biad]) was prepared in a similar fashion in ~70% overall yield from 2-(1-adamantyl)-4,5-dimethylphenol[19,20] in ~50% yield overall (eq 2).



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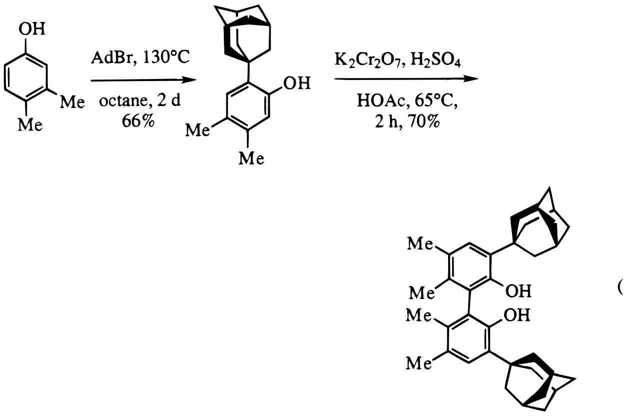

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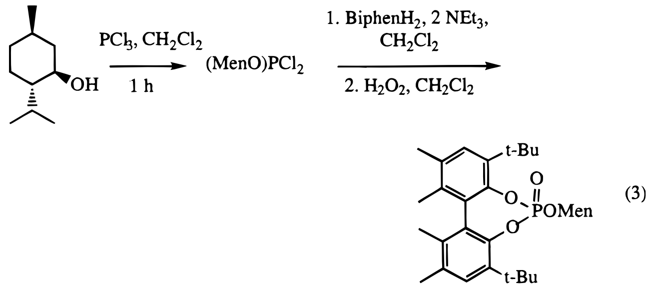
(−)-Menthoxy dichlorophosphite[10,21] (MenOPCl_2) was prepared by addition of (−)-menthol to a dichloromethane solution of excess PCl_3 followed by vacuum distillation to separate MenOPCl_2 from PCl_3. Addition of a mixture of H_2[Biphen] and triethylamine to a dichloromethane solution of MenOPCl_2 followed by treatment with 30% hydrogen peroxide afforded a diastereomeric mixture of phosphates, BiphenP(O)(OMen) (eq 3). The (*S*)-BiphenP(O)(OMen) 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)(OMen) in >99% de (eq 4). The acetic acid was removed by vacuum distillation from the fraction enriched in (*R*)-BiphenP(O)(OMen), and the residue was recrystallized from refluxing methanol. Diastereomerically pure (*R*)-BiphenP(O)(OMen) was obtained after two crystallizations (eq 5). The phosphate that remained in the methanol solution was approximately racemic. Treatment of (*S*)-BiphenP(O)(OMen) with excess Red-Al in toluene produced enantiomerically pure (*S*)-H_2[Biphen]. (*R*)-H_2[Biphen] was obtained similarly by reduction of (*R*)-BiphenP(O)(OMen). Approximately 20 g each of (*S*)-H_2[Biphen] and (*R*)-H_2[Biphen] typically can be obtained from 100 g of racemic H_2[Biphen]. The approximately 60 g of racemic H_2[Biphen] is then recycled through the resolution process. The absolute configuration of (*S*)-H_2[Biphen] was established via an X-ray structure of a molybdenum compound to be discussed later. This method of resolving H_2[Biphen] is more convenient than that published in the preliminary communication on this subject.[13]



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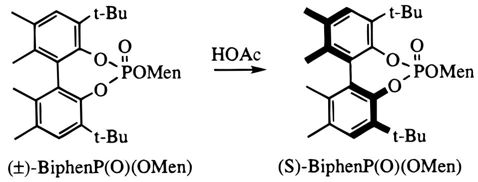

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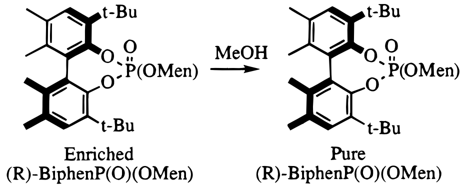

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Table 1. Reaction Details, Yields (from the Corresponding Bis(triflates)), and NMR Data for Biphen and Biad Complexes[a]

complex	cryst solvent	yield (%)	δ(*syn*)	J_{CH}(*syn*)	δ(*anti*)	J_{CH}(*anti*)	K_{eq}
$Mo(NArPr_2)(CHCMe_2Ph)$[Biphen]	ether	72	10.98	123	12.77	146	17
$Mo(NArPr_2)(CHCMe_2Ph)$[(*S*)-Biphen]	ether	78					
$Mo(NArPr_2)(CHEt)$[Biphen][b]			10.68		12.15		3.1
$Mo(NArPr_2)(CHMe)$[Biphen][b]			10.64		13.37		2.0
$Mo(NArEt_2)(CHCMe_2Ph)$[Biphen]	ether	60	11.04	121	12.94		110
$Mo(NArEt_2)(CHCMe_2Ph)$[(*S*)-Biphen]	ether/i-Pr_2O	27					
$Mo(NArMe_2)(CHCMe_2Ph)$[Biphen]	ether	77	11.01	121	13.03		244
$Mo(NArMe_2)(CHCMe_2Ph)$[(*S*)-Biphen]	ether	30					
$Mo(NArCF_3)(CHCMe_2Ph)$[Biphen][c]	x	96	10.91	124			large
$Mo(NArCF_3)(CHCMe_3)$[Biphen] [c]	pentane	38	10.61	120			large
$Mo(NArCF_3)(CHCMe_3)$[(*S*)-Biphen][c]	x	95					
$Mo(NArCF_3)[CHC_6H_4(OMe)]$[Biphen][d]	ether	74			12.85	151	small
$Mo(NArCF_3)[CHC_6H_4(OMe)]$[(*S*)-Biphen][d]	ether	12					
$Mo(NArBu_2Me)(CHCMe_3)$[(*S*)-Biphen]	pentane	36	10.63	126	12.86		51
$Mo(NArPr_2)(CHCMe_2Ph)$[Biad]	pentane	54	10.94	120	12.88		12
$Mo(NArPr_2)(CHCMe_2Ph)$[(*S*)-Biad]	pentane	34					
$Mo(NArEt_2)(CHCMe_2Ph)$[(*S*)-Biad]	pentane	30	11.03	121	12.91		100
$Mo(NArMe_2)(CHCMe_2Ph)$[Biad]	ether	35	11.04	122			large
$Mo(NArMe_2)(CHCMe_2Ph)$[(*S*)-Biad]	i-Pr_2O	44					
$Mo(NArCF_3)(CHCMe_3)$[Biad][c]	pentane	41	10.64	120			large
$Mo(NArCF_3)(CHCMe_3)$[(*S*)-Biad][c]	pentane	43					

[a] The reaction solvent was THF, unless otherwise noted. NMR data were obtained on ~15 mg of complex in C_6D_6 at 20 °C, unless otherwise noted. In the crystallization solvent category "x" means that the complex could not be crystallized and was isolated by simply removing the solvent in vacuo. K_{eq} was measured at ~22 °C. [b] These species were prepared on an NMR scale in toluene-d_8; see text. [c] The reaction solvent was toluene. [d] The reaction solvent was diethyl ether.

The phosphate resolution developed for H_2[Biphen] also allows (*S*)-H_2[Biad] to be isolated in moderate yield, but so far (*R*)-H_2[Biad] has not been isolated in pure form. Deprotonation of H_2[Biad] with excess benzylpotassium followed by addition of $MenOPCl_2$ generates the diastereomeric mixture of phosphites (^{31}P NMR resonances at 143.6 and 138.8 ppm). Oxidation of BiadP(OMen) with 30% hydrogen peroxide yielded a mixture of diastereomeric phosphates with ^{31}P NMR resonances at −3.29 and −5.57 ppm in benzene. (*S*)-BiadP(O)(OMen) (^{31}P NMR δ −3.29 ppm, 98% de) could be obtained by Soxhlet extraction of BiadP(O)(OMen) with refluxing acetone. The phosphate remaining in the acetone was enriched in (*R*)-BiadP(O)(OMen) (~90% de), but we were not able to increase the diastereomeric excess of (*R*)-BiadP(O)(OMen) above 90%. Reduction of (*S*)-BiadP(O)(OMen) with Red-Al yielded (*S*)-H_2[Biad], the absolute configuration of which was established in an X-ray study of a molybdenum compound to be described later.

Synthesis of Molybdenum Imido Alkylidene Complexes. A list of all compounds prepared here can be found in Table 1. $Mo(NArPr_2)(CHEt)$[Biphen] and $Mo(NArPr_2)(CHMe)$[Biphen] were prepared and observed in situ as part of an NMR study to be described later.

The most facile synthesis of precursors to molybdenum imido alkylidene complexes that contain a given arylimido group consists of the series of steps shown in eq 6. The only difference between this sequence and that

$$\mathrm{Na_2MoO_4} \xrightarrow{(a)} \mathrm{Mo(NAr)_2Cl_2(DME)} \xrightarrow{(b)} \mathrm{Mo(NAr)_2(CH_2R)_2} \xrightarrow{(c)} \mathrm{Mo(NAr)(CHR)(OTf)_2(DME)} \quad (6)$$

Legend: (a) 2 $ArNH_2$, 4 NEt_3, 10 TMSCl, DME,
60−65 °C, 4−12 h; (b) 2 RCH_2MgCl, ether,
12−24 h; (c) 3 HOTf, DME, −25 °C, 4−16 h

which has been published[22−24] is the use of sodium molybdate instead of ammonium dimolybdate in the first step. The advantage is that significantly less trimethylchlorosilane is required (8 vs 17 equiv). Known species were prepared that contain N-2,6-*i*-$Pr_2C_6H_3$ ($NArPr_2$), N-2,6-$Me_2C_6H_3$ ($NArMe_2$), or N-2-$CF_3C_6H_4$ ($NArCF_3$) imido groups. The only new imido ligands reported here are N-2,6-$Et_2C_6H_3$ ($NArEt_2$) and N-2,4-*t*-Bu_2-6-MeC_6H_3 ($NArBu_2Me$). The synthesis of $Mo(NArEt_2)(CHCMe_2Ph)(OTf)_2(DME)$ (DME = 1,2-dimethoxyethane) was carried out without difficulty in a manner analogous to that published for related species. However, the reaction of 2,4-di-*tert*-butyl-6-methylaniline with sodium molybdate, triethylamine, and chlorotrimethylsilane generated what we propose to be $[HNEt_3][Mo(NArBu_2Me)_2Cl_3]$ in 35% isolated yield, although it could not be purified by recrystallization. The lutidinium salt $[lutidineH][Mo(NArBu_2Me)_2Cl_3]$ was prepared in a 81% crystallized yield in a similar manner and was analyzed successfully. Presumably the increased steric bulk of the arylimido ligand prevents DME coordination to give $Mo(NArBu_2Me)_2Cl_2(DME)$, but there is still sufficient room to bind one chloride to yield $[Mo(NArBu_2Me)_2Cl_3]^-$. Addition of 3 equiv of neopentylmagnesium chloride to $[HBase][Mo(NArBu_2Me)Cl_3]$ (Base = NEt_3, 2,6-lutidine) in diethyl ether generated $Mo(NArBu_2Me)_2(CH_2$-*t*-$Bu)_2$ as a viscous red oil which crystallized upon cooling. The ^1H NMR spectrum of $Mo(NArBu_2Me)_2(CH_2$-*t*-$Bu)_2$ at room temperature did not reveal resolved methylene protons. However, at −40 °C in toluene-d_8 the diastereotopic methylene protons H_a and H_b could be resolved as an AB pattern at 3.10 and 1.54 ppm with J_{HH} = 14 Hz. These data suggest that the molecule has C_2 symmetry as a consequence of a preferred

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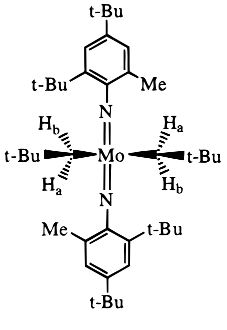
orientation of the aryl groups:



(pseudotetrahedral core)

At 60 °C a broad singlet was observed for the neopentyl methylene resonances as a consequence of relatively rapid rotation of the aryl rings about the $C_{ipso}-N$ bond.

A slight excess of potassium hydride or a stoichiometric quantity of benzylpotassium was employed to doubly deprotonate H_2[Biphen] in THF. We believe that benzylpotassium yields more reproducible results than does potassium hydride. Then either a solution of Mo(N-Aryl)(CHR)(OTf)$_2$(DME) is added *to* a THF solution of BiphenK_2 or vice versa. The latter procedure appears to produce purer products. The desired complex generally was separated from KOTf by extraction into benzene or pentane. Isolated yields of recrystallized products generally were in the 40−50% range, although in several cases the yield was much higher. Yields also tended to be higher in larger scale syntheses, especially of the more soluble species. Not all yields were optimized. In all formulas of compounds discussed here the ligand should be assumed to be racemic if no specific enantiomer is noted.

Complexes in which the arylimido group contained only one *o*-CF_3 substituent could not be prepared in good yield using potassium hydride for deprotonation of H_2[Biphen]; the benzene extract of the reaction mixture contained significant amounts of H_2[Biphen] in addition to the desired product. However, a pure product was obtained when H_2[Biphen] was deprotonated with 2 equiv of benzylpotassium. Base-free Mo(NArCF_3)(CHCMe$_3$)[Biphen] could be prepared in 38% yield when toluene was employed, but Mo(NArCF_3)(CHCMe$_3$)[(*S*)-Biphen] could not be crystallized. (If THF is employed as the reaction solvent and diethyl ether as the solvent of crystallization, THF and diethyl ether are found in the sample, most likely as a consequence of their binding to the sterically more accessible metal; see later.) Addition of a slight excess of 2-methoxystyrene to Mo(NArCF_3)(CHCMe$_2$Ph)[Biphen] generated a benzylidene complex, Mo(NArCF_3)(CH-*o*-MeOC_6H_4)[Biphen], which precipitated from the reaction mixture in 74% yield. At first glance formation of this type of complex would appear to be a good approach to less soluble and more crystalline pseudo-six-coordinate alkylidene complexes. Unfortunately, if too much stilbene is generated via homometathesis of the styrene, the desired product is difficult to separate from the stilbene by crystallization.

Racemic and optically pure complexes that contain the Biad ligand were prepared by methods analogous to those employed to prepare the Biphen complexes. These included Mo(NArPr$_2$)(CHCMe$_2$Ph)[Biad], Mo(NArMe$_2$)(CHCMe$_2$Ph)[Biad], and Mo(N-Aryl)(CHCMe$_2$Ph)[(*S*)-Biad] (N-Aryl = NArPr$_2$, NArEt$_2$, NArMe$_2$). Toluene was employed as the reaction solvent in order to prepare solvent-free Mo(NArCF_3)(CHCMe$_3$)[Biad] and Mo(NArCF_3)(CHCMe$_3$)[(*S*)-Biad].

One of the problems with the isolation of enantiomerically pure Biphen or Biad complexes is their generally higher solubility relative to their racemic analogues, which are often already relatively soluble. As can be seen in Table 1, isolated yields of enantiomerically pure complexes in general are lower than those of the racemic complexes, even though crude yields, according to proton NMR, are often relatively high. Complexes that contain the NArBu$_2$Me ligand were especially soluble. In fact, spectroscopically pure Mo(NArBu$_2$Me)(CHCMe$_3$)[(*S*)-Biphen] was prepared on three occasions, but in only one case could it be isolated from pentane by crystallization. Crystals of Mo(NArCF_3)(CHCMe$_2$Ph)[Biphen] can be obtained from pentane, but Mo(NArCF_3)(CHCMe$_3$)[(*S*)-Biphen] so far has not yet been purified by crystallization.

One confusing aspect of the synthesis of Mo(NArCF_3) complexes has come to light that has yet to be completely elucidated. On the basis of the presence of a downfield resonance in the ^{13}C NMR spectrum that is not split by a proton, it is proposed that variable amounts of (e.g.) Mo(NHArCF_3)(CCMe$_3$)[(*S*)-Biphen] are formed under some conditions. (See the NMR section for a more detailed discussion.) Although trialkoxoalkylidyne complexes of Mo and W[25] are not known to react readily with olefins, contamination of the imido alkylidene complex by the amido alkylidyne complex in principle could lead to spurious and irreproducible enantioselectivities.

X-ray Crystallographic Studies of Mo(NArPr$_2$)(CHCMe$_2$Ph)[(*S*)-Biphen] and Mo(NArCF_3)(CHCMe$_3$)[(*S*)-Biad](pyridine). X-ray crystallographic studies were carried out on single crystals of Mo(NArPr$_2$)(CHCMe$_2$Ph)[(*S*)-Biphen] (**1**) and Mo(NArCF_3)(CHCMe$_3$)[(*S*)-Biad](py) (**2**). The latter was prepared straightforwardly by addition of pyridine to Mo(NArCF_3)(CHCMe$_3$)[(*S*)-Biad]; crystals of Mo(NArCF_3)(CHCMe$_3$)[(*S*)-Biad] suitable for an X-ray study could not be obtained. Crystallographic data, collection parameters, and refinement parameters for both complexes are given in Table 2, while selected bond lengths, angles, and dihedral angles are given in Table 3. The *S* configurations of the Biphen and Biad ligands were established during the solution process using the usual criteria.

The molecular structure of *syn*-Mo(NArPr$_2$)(CHCMe$_2$Ph)[(*S*)-Biphen] along with the atom-labeling scheme is shown in Figure 1. (The *syn* isomer of Mo(NArPr$_2$)(CHCMe$_2$Ph)[(*S*)-Biphen] is the major isomer in solution; see below.) This structure is related to that of several other molybdenum and tungsten imido alkylidene bis(alkoxide) and biphenolate complexes.[9,10,26] The (*S*)-Biphen bite angle O(1)−Mo−O(2) (127.0°) and dihedral angle between the two aryl rings of the Biphen backbone (C(31)/C(32)/C(42)/C(41) = 102.2°) are essentially identical with the corresponding values in *syn*-

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Table 2. Crystallographic Data, Collection Parameters, and Refinement Parameters for $Mo(NArPr_2)(CHCMe_2Ph)[(S)\text{-Biphen}]$ (1) and $Mo(NArCF_3)(CHCMe_3)[(S)\text{-Biad}](py)$ (2)[a]

	1	2
empirical formula	$C_{46}H_{61}MoNO_2$	$C_{53}H_{63}F_3MoN_2O_2$
fw	755.90	912.99
cryst dimens (mm)	0.20 × 0.20 × 0.20	0.15 × 0.15 × 0.30
cryst syst	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 (deg)	90	90
β (deg)	103.8060(10)	90
γ (deg)	90	90
V (Å^3), Z	2091.58(12), 2	11191(4), 8
D_{calcd} (Mg/m^3)	1.200	1.084
θ range (deg)	1.41–23.24	1.34–20.00
scan type	ω	ω
temp (K)	173(2)	170(2)
no. of rflns collected	8659	33 558
no. of indep rflns	5360 (R_{int} = 0.0547)	10 427 (R_{int} = 0.1033)
no. of params	452	543
R1 ($I > 2\sigma(I)$, all data)	0.0587, 0.0634	0.1119, 0.1312
wR2 ($I > 2\sigma(I)$, all data)	0.1445, 0.1555	0.2789, 0.2991
GOF	1.191	1.199

[a] Data were collected on a Siemens SMART/CCD diffractometer using Mo Kα (0.710 73 Å) radiation, and the structure was solved using a full-matrix least-squares refinement on F^2. No absorption correction was applied.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for the Non-Hydrogen Atoms in 1 and 2

1		2A and 2B	2A	2B
		Bond Lengths		
Mo–O(1)	1.999(5)	Mo–O(1)	2.020(11)	2.022(10)
Mo–O(2)	2.006(5)	Mo–O(2)	1.986(10)	1.962(13)
Mo–C(1)	1.885(10)	Mo–C(40)	1.90(2)	1.87(2)
Mo–N	1.738(6)	Mo–N(1)	1.70(2)	1.73(2)
N–C(11)	1.407(9)	Mo–N(2)	2.276(12)	2.270(13)
C(1)–C(2)	1.489(13)	C(40)–C(41)	1.51(2)	1.49(3)
O(1)–C(31)	1.385(9)	O(1)–C(16)	1.35(2)	1.36(2)
O(2)–C(41)	1.366(9)	O(2)–C(22)	1.36(2)	1.35(2)
		Bond Angles		
N–Mo–O(1)	110.2(2)	N(1)–Mo–O(1)	101.2(6)	101.5(6)
N–Mo–O(2)	107.9(3)	N(1)–Mo–O(2)	136.7(7)	133.7(6)
N–Mo–C(1)	105.2(3)	N(1)–Mo–C(40)	107.1(8)	113.3(9)
O(1)–Mo–O(2)	127.0(2)	O(1)–Mo–O(2)	88.8(4)	90.3(5)
O(1)–Mo–C(1)	96.9(3)	Mo–N(1)–C(38)	167.3(14)	148.2(12)
O(2)–Mo–C(1)	107.0(3)	Mo–C(40)–C(41)	148.0(13)	148(2)
Mo–N–C(11)	169.0(6)	N(2)–Mo–O(1)	165.1(4)	167.0(5)
Mo–C(1)–C(2)	143.8(7)	O(1)–Mo–C(40)	95.3(6)	91.0(7)
Mo–O(1)–C(31)	97.1(4)	N(1)–Mo–N(2)	85.6(6)	83.4(6)
Mo–O(2)–C(41)	96.8(4)	N(2)–Mo–O(2)	77.4(4)	77.9(5)
		N(2)–Mo–C(40)	95.3(6)	98.2(7)
		Dihedral Angles		
C(31)/C(32)/ C(42)/C(41)	102.2	C(16A)/C(15A)/ C(17A)/C(22A)	72.3	

$Mo(NArMe_2)(CHCMe_2Ph)[t\text{-}Bu_4Me_2\text{Biphen}]$ ([t-Bu_4Me_2-Biphen] = 6,6′-dimethyl-3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diolate; 123.5 and 102.5°, respectively).[10] Other distances and angles in *syn*-$Mo(NArPr_2)(CHCMe_2Ph)[(S)\text{-Biphen}]$ are virtually identical with what they are in *syn*-$Mo(NArMe_2)(CHCMe_2Ph)[t\text{-}Bu_4Me_2\text{Biphen}]$.

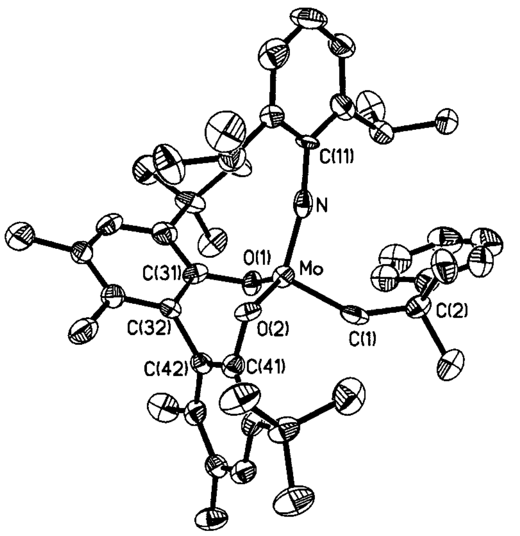

Figure 1. ORTEP drawing of the structure of *syn*-Mo(N-2,6-i-$Pr_2C_6H_3$)($CHCMe_2Ph$)[(S)-Biphen] (**1**).

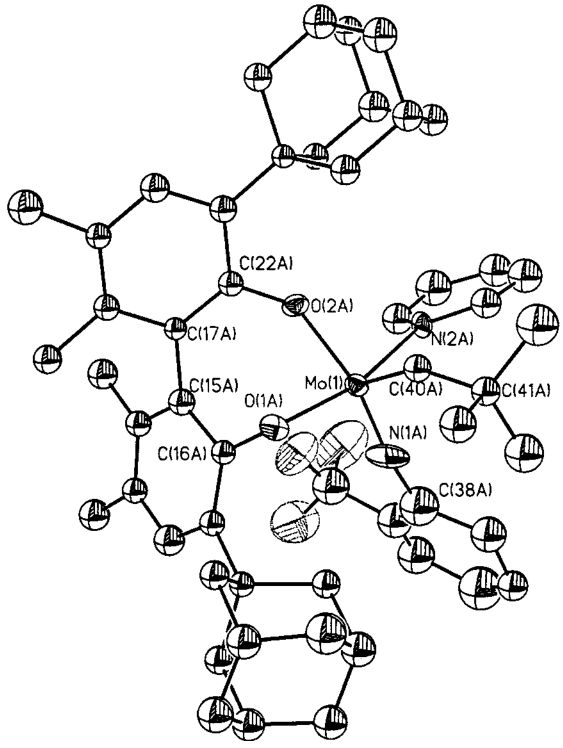

Figure 2. ORTEP drawing of the structure of *syn*-Mo(N-2-$CF_3C_6H_4$)($CHCMe_3$)[(S)-Biad](pyridine) (**2A**).

Yellow blocks of $Mo(NArCF_3)(CHCMe_3)[(S)\text{-Biad}](py)$ (Figure 2) were grown from a mixture of ether and pyridine. The unit cell contains two independent molecules, one in which the CF_3 group points away from the alkylidene (**2A**; Figure 2), and one in which the CF_3 group points toward the alkylidene (**2B**). The major difference between the two molecules is that the imido group is considerably more bent in **2B**, as a consequence of steric repulsion between the trifluoromethyl group and the alkylidene ligand. We will discuss only **2A** here. The pyridine is found to have added to the C(40A)/N(1A)/O(2A) face to give one of the two possible diastereomers of the *syn* isomer; the resulting N(2A)–Mo(1)–O(1A) angle is 165.1(4)°. This species is analogous to the mirror image of the diastereomer of *syn*-$Mo(NArPr_2)(CHCMe_2Ph)[(R)\text{-BINO(TRIP)}_2](py)$ (where (R)-BINO(TRIP)_2 is the dianion of (R)-3,3′-bis(2,4,6-triisopropylphenyl)-2,2′-dihydroxy-1,1′-dinaphthyl).[17] The Biad "bite angle" (O(1A)–Mo–O(2A) = 88.8(4)°), $Mo{=}C_\alpha{-}C_\beta$ angle (Mo(1)–C(40A)–C(41A) = 148.0(13)°), Mo=N–C

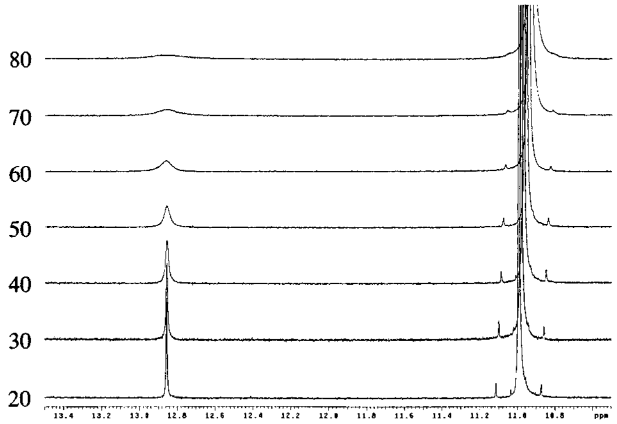

Figure 3. Variable-temperature ^{1}H NMR spectra of Mo(NArPr$_2$)(CHCMe$_2$Ph)(Biphen) in toluene-d_8.

angle (Mo(1)−N(1A)−C(38A) = 167.3(14)°), and dihedral angle between the aryl rings (C(16A)/C(15A)/C(17A)/C(22A) = 72.3°) are all similar to the corresponding angles in *syn*-Mo(NArPr$_2$)(CHCMe$_2$Ph)[(*R*)-BINO(TRIP)$_2$](py) (86.5(3), 149.5(10), 158.6(8), and 60.0°, respectively). An X-ray structure of a third adduct of this type, *anti*-Mo(NArMe$_2$)(CHCMe$_2$Ph)[BINO(Ph)$_2$](THF),[10] reveals similar analogous angles, except for the Mo=C$_\alpha$−C$_\beta$ angle of 128.1(6)°, which is characteristically smaller[26] as a consequence of the *anti* conformation of the alkylidene ligand. A smaller ligand "bite angle" and smaller dihedral angle between the aryl rings in five-coordinate adducts versus four-coordinate *syn*-Mo(NArPr$_2$)(CHCMe$_2$Ph)[(*S*)-Biphen] and *syn*-Mo(NArMe$_2$)(CHCMe$_2$Ph)[*t*-Bu$_4$Me$_2$Biphen][10] are a direct consequence of the manner in which the biaryloxide ligand is bound (axial/equatorial) in pseudo-trigonal-bipyramidal adducts. The arylimido ring is approximately coplanar with C(40A) and C(41A) of the neopentylidene ligand, and the CF$_3$ group points away from the *syn* neopentylidene ligand. The arylimido ligand in Mo(NArCF$_3$)(CHCMe$_3$)[(*S*)-Biad](py) is approximately linear, despite the monosubstituted nature of the aryl ring. Like other arylimido rings in related adducts, the aryl ring lies approximately in the equatorial plane of the trigonal bipyramid.

Proton NMR Studies. The ^{1}H NMR spectrum of Mo(NArPr$_2$)(CHCMe$_2$Ph)[Biphen] in toluene-d_8, which is typical for a solvent-free complex in this study, revealed alkylidene H$_\alpha$ resonances for the two possible isomers (Table 1; Figure 3). The sharp H$_\alpha$ resonance at 10.98 ppm (at 22 °C) can be ascribed to the *syn* isomer on the basis of the J_{CH} value of 123 Hz. (In this work coupling constants typically were determined in a high signal-to-noise (~1000 transients) spectrum by observing the ^{13}C satellites (1.1% total area); in several cases they were confirmed in a proton-coupled ^{13}C NMR spectrum.) A second (weak) resonance at 12.77 ppm (in C$_6$D$_6$) could be ascribed to H$_\alpha$ for the *anti* isomer on the basis of a J_{CH} value of 146 Hz. At 20.7 °C (in toluene-d_8) the ratio of these resonances ([*syn*]/[*anti*] = K_{eq}) was found to be 17.0. The value for K_{eq} varied from 29.5 at −10.9 °C to 11.6 at 68.2 °C (Table 4). A plot of ln K_{eq} versus 1/T gave values of $\Delta H° = -2.0(0.3)$ kcal/mol and $\Delta S° = -1.0(0.7)$ eu, with $\Delta G°_{298} = -1.7(0.3)$ kcal/mol. Other species reported here behaved similarly, as did Mo(NArPr$_2$)(CHCMe$_2$Ph)(DIPP)$_2$ (DIPP = O-2,6-*i*-Pr$_2$C$_6$H$_3$), a compound that has been studied previously.[27]

Table 4. ^{1}H NMR Line Widths, Equilibrium Constants, and Rate Constants k_{as} and k_{sa}, for *syn* and *anti* Isomers of Mo(NAr)(CHCMe$_2$Ph)[Biphen] in Toluene-d_8 between −10.9 and 68.2 °C

temp (°C)	ω_{syn} (Hz)	ω_{anti} (Hz)	k_{as} (s^{-1})	k_{sa} (s^{-1})	K_{eq}
68.2	7.639	46.529	145.18	12.52	11.6
59.4	4.103	32.298	100.47	8.21	12.2
50.2	2.610	13.034	39.95	3.08	13.0
40.7	1.870	9.243	28.04	2.02	13.9
31.7	1.548	5.108	15.05	0.95	15.9
20.7	1.172	3.060	8.61	0.50	17.0
10.5	1.365	2.389	6.50	0.32	20.3
−0.3	1.615	2.314	6.27	0.26	24.2
−10.9	1.338	1.974	5.20	0.18	29.5

The proton NMR spectrum of Mo(NArPr$_2$)(CHCMe$_2$Ph)[Biphen] in the alkylidene region is temperature dependent (Figure 3). At room temperature resonances for the two alkylidene isomer are sharp. The ^{13}C satellites on the H$_\alpha$ resonance for the *syn* isomer can be seen clearly up to ~70 °C, and the *syn* H$_\alpha$ resonance (more than the *anti*) shifts slightly upfield at higher temperatures. The ^{13}C satellites cannot be seen for the *anti* H$_\alpha$ resonance as a consequence of its relatively low intensity. The *anti* H$_\alpha$ resonance begins to broaden by 40 °C, and by 80 °C it has almost disappeared into the baseline, without shifting significantly. This behavior is fully reversible, independent of concentration, and fully consistent with interconversion of *syn* and *anti* isomers at a rate of the order of the NMR time scale. The rates of interconversion for several complexes were measured and are discussed later. The *syn* and *anti* alkylidene resonances do not change appreciably when the sample is cooled below 20 °C.

The variable-temperature proton NMR spectrum of Mo(NArPr$_2$)(CHCMe$_2$Ph)[Biphen] in THF-d_8 is shown in Figure 4. At −80 °C four alkylidene resonances are observed at 13.97, 13.92, 12.81, and 12.39 ppm in a ratio of 54.9:11.8:4.5:1. We assign the resonances at 13.97 and 13.92 ppm to the two diastereomeric THF adducts of the *anti* isomer and the relatively weak resonances at 12.81 and 12.39 ppm to the two diastereomeric THF adducts of the *syn* isomer. Note that each set is 1−2 ppm downfield of the *anti* and *syn* resonances for the "base-free" species in toluene-d_8 (Figure 3). The two diastereomers of the *syn* THF adduct begin to interconvert rapidly on the NMR time scale at ca. −50 °C as a consequence of THF dissociating rapidly from each *syn* THF adduct. At higher temperatures the average *syn* resonance moves upfield toward the resonance for the "base-free" *syn* alkylidene resonance near 11 ppm as the equilibrium between *syn* THF adducts and base-free *syn* species shifts toward the base-free species. Also, the equilibrium between *anti* and *syn* alkylidene isomers shifts toward the *syn* isomer between −40 and 40 °C. At 20 °C the *syn* alkylidene is largely base-free, according to the position of the *syn* alkylidene resonance near 11 ppm. In contrast, the *anti* THF adducts equilibrate less readily (−40 to −30 °C), but the average does not shift appreciably toward the position of the "base-free" *anti* resonance near 13 ppm in toluene-d_8. According to these data we can say that the *anti* alkylidene complex binds THF much more strongly than the *syn* alkylidene complex and that the ratio of the *anti* THF adduct and

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[27] Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; O'Regan, M. B.; Schofield, M. H. *Organometallics* **1991**, *10*, 1832.

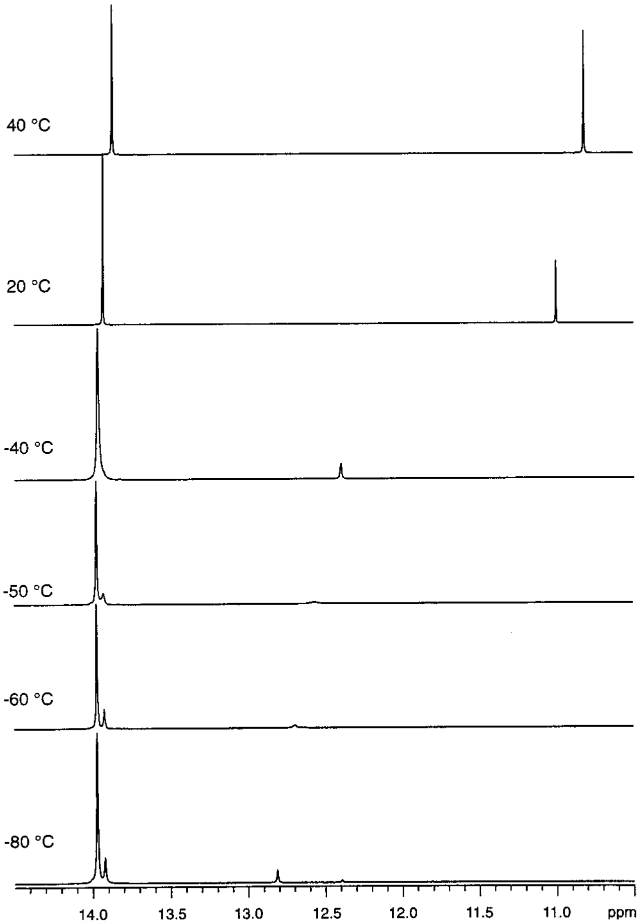

Figure 4. Variable-temperature ^{1}H NMR spectra of Mo($NArPr_2$)($CHCMe_2Ph$)[Biphen] in THF-d_8.

the *syn,* largely base-free, species near room temperature is approximately 3:1. Note that at the highest temperature in Figure 4, the interconversion of *anti* and *syn* isomers is still relatively slow on the NMR time scale. (It is believed that only base-free *syn* and *anti* isomers can interconvert readily and that their interconversion therefore is retarded in the presence of a base that can bind to the metal.[26]) The behavior of Mo($NArPr_2$)($CHCMe_2Ph$)[Biphen] in THF-d_8 is relevant to asymmetric metathesis of substrates that contain an ether functionality,[13−17] although the details are still obscure at this stage.

Addition of *trans*-3-hexene to Mo($NArPr_2$)($CHCMe_2$-Ph)[Biphen] at 22 °C generated a mixture of *syn*- and *anti*-Mo($NArPr_2$)($CHCMe_2Ph$)[Biphen], *syn*- and *anti*-Mo($NArPr_2$)(CHEt)[Biphen], *cis*- and *trans*-$PhMe_2CCH{=}CHEt$, and *cis*- and *trans*-3-hexene. Approximately a 20-fold excess of *trans*-3-hexene was required in order to generate a mixture that contained ∼5% Mo($NArPr_2$)(CHEt)[Biphen]. It was not possible to isolate Mo($NArPr_2$)(CHEt)[Biphen], because its concentration was too low to allow it to be crystallized selectively from the mixture, and because removal of the volatile components of such a mixture resulted in re-formation of exclusively *syn*- and *anti*-Mo($NArPr_2$)($CHCMe_2Ph$)[Biphen] through the back-reaction of *syn*- and *anti*-Mo($NArPr_2$)(CHEt)[Biphen] with $PhMe_2CCH{=}CHEt$. However, it is interesting to note that the ratio of *syn*-Mo($NArPr_2$)(CHEt)[Biphen] to *anti*-Mo($NArPr_2$)(CHEt)[Biphen] is 3.1 at 22 °C (Table 1), which suggests that a smaller substituent on the alkylidene allows a larger amount of the *anti* isomer to be formed. Similar experiments involving *cis*-2-butene and Mo($NArPr_2$)($CHCMe_2$-Ph)[Biphen] are consistent with this proposal, K_{eq} for *syn*-Mo($NArPr_2$)(CHMe)[Biphen] and *anti*-Mo($NArPr_2$)(CHMe)[Biphen] being 2.0 (Table 1). The equilibrium constant (K = [Mo(CHMe)][$PhMe_2CH{=}CHMe$]/[Mo($CHCMe_2Ph$)][$MeCH{=}CHMe$]) was measured in this case and found to be 9.1×10^{-4} at 20 °C.

Decreasing the size of the substituents in the ortho positions of the disubstituted imido ligand led to formation of more *syn* isomer, i.e, $K_{eq} = 110$ for Mo($NArEt_2$)($CHCMe_2Ph$)[Biphen] and 244 for Mo($NArMe_2$)($CHCMe_2$-Ph)[Biphen] (Table 1). The K_{eq} value for Mo($NArBu_2$-Me)($CHCMe_2Ph$)[Biphen] was 51, which suggests that the steric influence of the $NArBu_2Me$ group is roughly between that of the $NArPr_2$ and $NArEt_2$ groups. (One might expect some “weighted average” steric influence in view of the presence of a methyl group in one ortho position and a *tert*-butyl group in the other, depending on the percentage of different rotamers that result from restricted rotation about the N−C_{ipso} bond.) The value of K_{eq} for Mo($NArCF_3$)($CHCMe_2Ph$)[Biphen] could not be measured readily, although it was clear that the magnitude was large (>300). Apparently the $NArCF_3$ group is operationally the smallest of the imido groups, at least as measured in terms of the *syn*/*anti* equilibrium. Only the *anti* isomer is observed in the case of Mo($NArCF_3$)[$CHC_6H_4(OMe)$][Biphen] (H_α at 12.85 ppm, J_{CH} = 151 Hz), as expected as a consequence of coordination of the *o*-methoxy group to the metal. The ability of donors to stabilize the *anti* isomer has been known for some time in the literature.[29]

NMR spectra of the Biad complexes that contain the $NArPr_2$ and $NArEt_2$ imido groups are similar to those for the Biphen complexes, and the values for K_{eq} are roughly the same. However, essentially only the *syn* H_α resonance is observable in the spectrum of Mo($NArCF_3$)($CHCMe_2Ph$)[Biad] and Mo($NArMe_2$)($CHCMe_3$)[Biad].

Relatively facile interconversion of *syn* and *anti* isomers of molybdenum imido alkylidene complexes has been reported in the literature for two aryloxide complexes, Mo($NArPr_2$)($CHCMe_2Ph$)($DIPP$)$_2$ and Mo($NArPr_2$)($CHCMe_2Ph$)(O-2-*t*-BuC_6H_4)$_2$.[27] The reported activation parameters for their interconversion, determined by line shape analysis, are listed in Table 5. A redetermination of the overall rate constant for interconversion of isomers of Mo($NArPr_2$)($CHCMe_2Ph$)(DIPP)$_2$ at −42 °C using line shape analysis gave $k = 3.81 \times 10^{-4}$ s^{-1}, which is faster than the literature value ($k = 1.35 \times 10^{-4}$ s^{-1})[27,28] by a factor of ∼3. The rate constant at −42 °C was determined using spin saturation transfer and found to be 2.61×10^{-5} s^{-1}, which is slower than the literature value by a factor of ∼4. (The discrepancy between line shape analysis and the spin saturation transfer experiments, in part, may be due to the assumption that T_1 was the same for both isomers; see Experimental Section for a further discussion.)

The activation parameters for interconversion of *syn* and *anti* isomers of Mo($NArPr_2$)($CHCMe_2Ph$)[Biphen]

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[28] Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 11831.

[29] Fox, H. H.; Lee, J.-K.; Park, L. Y.; Schrock, R. R. *Organometallics* **1993**, *12*, 759.

Table 5. Activation Parameters by Line Shape Analysis (lsa) and Spin Saturation Transfer (sst)

complex[a]	technique	$\Delta G^{\ddagger}_{298}$[b]	$\Delta H^{\ddagger}$ [b]	$\Delta S^{\ddagger}$ [c]
$Mo(NArPr_2)(CHCMe_2Ph)[Biphen]$	lsa	16.0(2.3)	12.5(1.2)	−11.6(3.7)
$Mo(NArPr_2)(CHCMe_2Ph)[Biphen]$	sst	16.2(1.6)	15.1(0.8)	−4.0(2.8)
$Mo(NArPr_2)(CHCMe_2Ph)[Biad]$	sst	16.7(3.6)	14.4(1.8)	−7.4(6.2)
$Mo(NArPr_2)(CHCMe_2Ph)(DIPP)_2$	lsa	17.2(1.5)	16.2(0.8)	−3.4(2.4)
$Mo(NArPr_2)(CHCMe_2Ph)(DIPP)_2$	sst	17.6(1.4)	20.1(0.7)	8.3(2.3)
$Mo(NArPr_2)(CHCMe_2Ph)(DIPP)_2$[d]	lsa	17.5(1)	17.8(1.0)	1.0(2.7)
$Mo(NArPr_2)(CHCMe_2Ph)(O\text{-}2\text{-}t\text{-}BuC_6H_4)_2$[d]	lsa	18.3(1)	22.8(2.1)	15(6)

[a] Amount of complex ∼15 mg in toluene-d_8. [b] Units in kcal/mol. [c] Units in eu. [d] Values from ref 27.

were determined by both line shape analysis (lsa) and spin saturation transfer (sst) (Table 5). (In lsa experiments only rate constants that were obtained at room temperature or above yielded a linear Eyring plot.) The values from the two methods largely agree and are similar to those found for $Mo(NArPr_2)(CHCMe_2Ph)(DIPP)_2$. The activation parameters for interconversion of *syn* and *anti* isomers of $Mo(NArPr_2)(CHCMe_2Ph)$[Biad] were found to be consistent with the other values shown in Table 5. The most important conclusion to be drawn from these data is that relatively rapid interconversion of isomers does not appear to depend on whether the aryloxide in question is bidentate or monodentate. It is also important to note that the rates of interconversion for aryloxide species near room temperature are 4−5 orders of magnitude faster than the rate of conversion of the *syn* isomer of $Mo(NArPr_2)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ to the *anti* isomer (where K_{eq} is ∼2500) and approximately the same as the estimated rate of conversion of the *syn* isomer of $Mo(NArPr_2)(CHCMe_2Ph)[OCMe_3]_2$ to the *anti* isomer.[28]

If the stoichiometry is carefully controlled, the synthesis of $Mo(NArCF_3)$ complexes yields samples that are essentially pure *syn*, according to proton NMR studies, the notable exception being $Mo(NArCF_3)(CH\text{-}o\text{-}MeOC_6H_4)$[Biphen]. It also can be shown readily that *syn* complexes which contain the $N\text{-}2\text{-}CF_3C_6H_4$ ligand bind THF more readily than *syn* complexes which contain $N\text{-}2,6\text{-}R_2C_6H_3$ ligands, presumably as a consequence of the overall less crowded coordination sphere. However, occasionally samples that contain a resonance near 11.7 ppm are produced. For example, the sample shown in Figure 5 contains about 5% of this "impurity." These spectra at first glance appear to be characteristic of mixtures of *syn* and *anti* isomers. However, the resonance near 11.7 ppm broadens and *shifts upfield* upon raising the temperature, unlike a typical base-free *anti* resonance. Furthermore, the 11.7 ppm resonance varies in intensity from sample to sample. Finally, a singlet resonance is observed at 315.7 ppm in the carbon NMR spectrum in an amount that correlates with the intensity of the 11.7 ppm resonance in the proton NMR, a region that is characteristic of alkylidyne α-carbon atoms in high-oxidation-state Mo and W complexes.[25] Therefore, we propose that the resonance near 11.7 ppm is actually the NH proton in $Mo(NHArCF_3)(CCMe_2Ph)$[Biphen], which is formed as an impurity during the synthesis of $Mo(NArCF_3)(CHCMe_2Ph)$[Biphen]. However, once $Mo(NHArCF_3)(CCMe_2Ph)$[Biphen] and $Mo(NArCF_3)(CHCMe_2Ph)$[Biphen] are formed, they cannot be interconverted cleanly in a base-catalyzed (NEt_3 or K_2Biphen) reaction. Other compounds discussed here did not contain significant amounts of an analogous amido alkylidyne complex, although small amounts of impurities that have one or more resonances in the alkylidene region of the proton NMR spectrum are often observed in crude samples. A possible mechanism of forming the amido alkylidyne complex is presented in the Discussion.

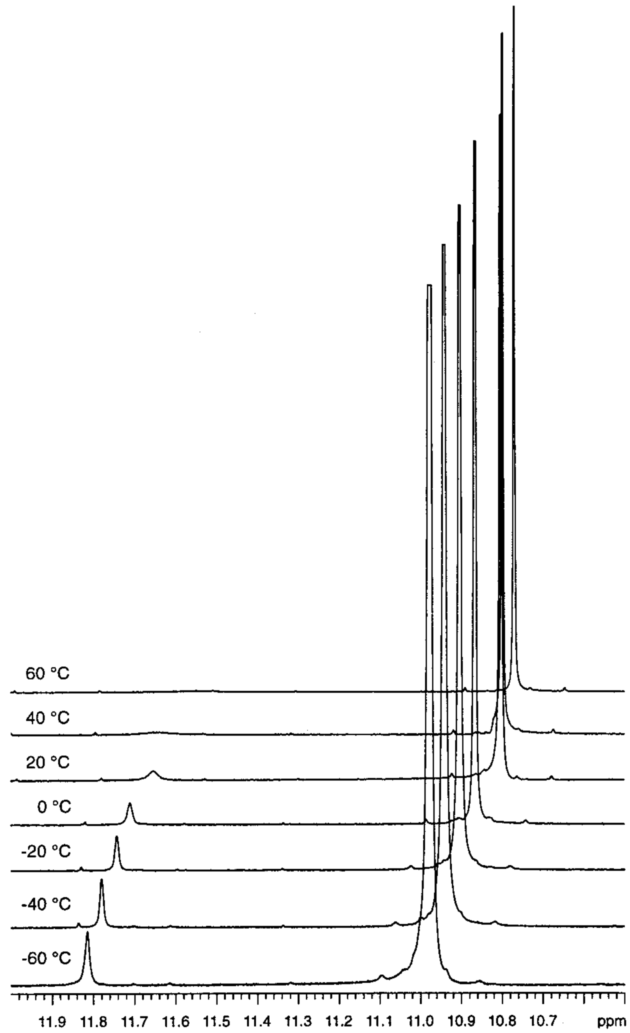


Figure 5. Variable-temperature ^1H NMR spectra of $Mo(NArCF_3)(CHCMe_2Ph)$[Biphen] in toluene-d_8.

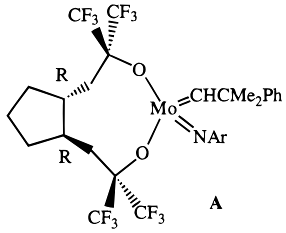
Discussion

In general, complexes of the type $Mo(NR)(CHR')(OR'')_2$ cannot be isolated unless R is a (bulky) substituted aryl group, R′ is CMe_3 or CMe_2Ph, and R″ is a bulky group such as CMe_3, $CMe(CF_3)_2$, a 2,6-disubstituted aryl group, etc. The presence of four bulky groups discourages bimolecular decomposition of an alkylidene complex of this type.[26] Complexes that contain a smaller R′ group, e.g., an ethylidene complex, can be observed in solution but cannot be isolated. This type of alkylidene complex is a 14-electron species if donation of an electron pair from the imido ligand is included and donation of π electron density from the oxygen atoms is ignored. Five-coordinate, 16-electron adducts are comparatively stable toward bimolecular decomposition, but the base must be lost to generate the 14-electron four-coordinate species in order for the alkylidene to react with an olefin. The complexes prepared here fall into the category of sterically hindered Mo(NR)(CHR′)(OR″)$_2$ species as a consequence of *tert*-butyl or adamantyl groups being present in the 3- and 3′-positions of the biphenolate ligand. Bulky groups in the 3- and 3′-positions are highly desirable in order to transmit chiral information efficiently to an incoming olefin, which is believed to bind to the metal first on a CNO face of the pseudo tetrahedron, and also in order to discourage coordination of a base such as THF, which would behave as a competitive inhibitor in reactions involving olefins. Several of the Biphen complexes reported here in fact are highly efficient for enantioselective ring-closing, ring-opening/ring-closing, and ring-opening/cross-metathesis reactions.[13-17] A comparison of the rates and efficiencies of enantiomerically pure Biphen and Biad complexes for asymmetric metathesis of a variety of substrates will be presented in due course elsewhere.

One of the important issues in reactions involving Mo(NR)(CHR′)(OR″)$_2$ complexes is the relative reactivity of *syn* and *anti* isomers and their rate of interconversion. We have found that *syn* and *anti* isomers interconvert readily in biphenolate complexes, as they do in monodentate phenoxide complexes. We believe this is a more desirable circumstance than one in which *syn* to *anti* conversion is slow: e.g., in Mo(NArPr$_2$)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ ($\sim 10^{-5}$ s^{-1} at room temperature).[30] The relative reactivities of *syn* and *anti* isomers of course depend on the nature of the imido ligand and the substrate in question. However, if *syn* and *anti* isomers interconvert readily, as found here, then the relative reactivities become difficult to determine experimentally. Although it was estimated that the relatively inaccessible *anti* form of Mo(NArPr$_2$)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ was several orders of magnitude more reactive than the *syn* form toward one specific substrate (2,3-bis(trifluoromethyl)norbornadiene), we cannot *assume* that to be the case in biphenolate complexes, even though evidence suggests that the *anti* isomer in general binds a base more strongly than the *syn* isomer. Therefore, at this stage we are uncertain whether the difference in reactivities of *syn* and *anti* isomers of the Biphen and Biad complexes is large or not.

The situation becomes even more complex when one considers that even weakly basic functionalities within a substrate involved in a metathesis reaction (e.g., ethers) could bind to the metal and inhibit reaction of an olefin with one of the two isomers present. Perhaps a more interesting possibility is that a donor and an olefin that are present in the substrate could both bind to the 14-electron alkylidene complex (if π donation from the alkoxide to the metal is not a consideration) and thereby *accelerate* the reaction between an alkylidene ligand and an incoming substrate. Attempts to answer some of these intriguing questions are in the offing.

It is worth pointing out some differences between the biphenolate complexes reported here and a complex (**A**) that contains a chiral chelating alkoxide which forms a pseudo-nine-membered ring with the molybdenum (NAr = N-2,6-i-Pr$_2$C$_6$H$_3$).[31-33] This complex appears to be much less successful in enantioselective ring-closing metathesis reactions than the complexes reported here. Perhaps the most obvious difference is the large, relatively nonrigid nature of the diolate ring and the relatively remote chiral centers δ with respect to the metal center. This particular chiral ligand perhaps was chosen in order to mimic the high metathesis activity of Mo(NArPr$_2$)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$. Although the rate of interconversion of *syn* and *anti* isomers in **A** was not determined, it seems likely to be as slow, as it is in Mo(NArPr$_2$)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ itself. If the more reactive *anti* isomer is also more enantioselective, then enantioselectivity would suffer if it could not be accessed readily.



A

One of the characteristics of the compounds reported here that contain a 2,6-disubstituted arylimido ligand is that they bind THF more weakly than imido neophylidene analogues that contain the dianion of 3,3′-bis(2,4,6-triisopropylphenyl)-2,2′-dihydroxy-1,1′-dinaphthyl[17] ([BINOTrip$_2$]$^{2-}$). In both systems, however, THF binds more strongly to the *anti* isomer than to the *syn* isomer, according to NMR studies. Dissociation of THF from the *anti* isomer is relatively fast at 60 °C in [BINOTrip$_2$]$^{2-}$ species. Recent results concerning imido neophylidene initiators that contain the dianion of 3,3′,6,6′-tetra-*tert*-butyl-2,2′-dihydroxy-1,1′-dinaphthyl suggest that they too will not readily bind THF.[34] Therefore, it is the *tert*-butyl groups in particular in either biphenolate or binaphtholate ligands that lead to somewhat weaker binding of THF, probably largely for steric reasons. A stronger base such as pyridine will bind even to a Biad complex, as reported here, and complexes that contain the smaller N-*o*-CF$_3$C$_6$H$_4$ ligand will also bind THF more strongly than complexes that contain N-2,6-R$_2$C$_6$H$_3$ ligands.

One of the potential complications of synthesis of imido alkylidene complexes of the type reported here, especially complexes that contain imido ligands that are not substituted in the 2- and 6-positions, is formation of an amido alkylidyne complex. It is interesting to note that the first imido alkylidene complexes were prepared from neopentylidyne amido complexes by a base-catalyzed migration of a proton from the amido ligand to the alkylidyne carbon.[26] Proton transfer does not take place readily once alkoxides have been attached to the

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metal, but only in dihalide or bis(triflate) complexes where it is arguably more acidic. At the present time we propose that the amido alkylidyne impurity that forms in N-2-$CF_3C_6H_4$ complexes is formed at an early stage in the synthesis before the triflates are completely substituted by the biphenolate and that it is a phenolate base that moves the proton. We hope to gather more information about proton transfer reactions of this type in future studies and determine whether amido alkylidyne complexes are, in fact, relatively inert toward olefins, as brief observations of related amido alkylidyne complexes in the past have suggested.

Many of the enantiomerically pure catalysts described here cannot be prepared readily in a high yield, in part because of low yields upon crystallization. The yields of enantiomerically pure Biad complexes reported here, for example, currently are unacceptable. However, another disadvantage in the long run is that the ligand must be resolved. Therefore, it would be useful if more efficient methods of resolving Biphen and (especially) Biad ligands could be found. In the meantime, in general we will continue to search for new diolate/imido ligand combinations that will allow enantiomerically pure catalysts to be isolated relatively easily. The long-term goal will be to prepare and compare a number of catalysts for efficient enantioselectivity, which on the basis of ongoing studies we already know can vary dramatically with the substrate. Ultimately we hope to test a variety of catalysts, substrates, and reaction types using high throughput screening techniques. Efforts aimed in these directions are currently under way.

Experimental Section

General Procedures. Unless otherwise noted, all experiments were performed in the absence of oxygen and moisture in a dinitrogen-filled glovebox or using standard Schlenk procedures. Diethyl ether, THF, and pentane were degassed with dinitrogen and passed through two 1 gal columns of activated alumina.[35] Toluene and benzene were distilled from sodium benzophenone ketyl. Methylene chloride was distilled from calcium hydride. NMR spectra were acquired at 75.4 or 125.8 MHz for ^{13}C and 300 or 500 MHz for ^1H. ^1H NMR spectra were referenced using residual protons in the deuterated solvents (7.16 ppm for C_6D_5H, 2.09 ppm for toluene-d_8 (CD_2H)). $^{13}C\{^1H\}$ NMR spectra were referenced assuming δ 128.4 ppm in 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 calibrated with external ethylene glycol ($T > 20$ °C) or methanol ($T < 20$ °C) and the *tempcal* macro in the Varian software. Benzylpotassium,[36] 2-methoxystyrene,[37] 2,4-di-*tert*-butyl-6-methylaniline,[38] t-$BuCH_2MgCl$,[39] $PhMe_2CCH_2MgCl$,[39] and known molybdenum bis(triflates)[22−24,40,41] were prepared according to literature procedures. Potassium hydride was purchased from Aldrich as a 35% dispersion in mineral oil; it was washed repeatedly with pentane and dried in vacuo. Isopropyl ether (Aldrich) was distilled from sodium and stored over 4 Å molecular sieves for 1 day prior to use. H_2[Biphen][12] and 2-*tert*-butyl-4,5-dimethylphenol[18] were prepared by modified literature procedures (see below). 2-(1-Adamantyl)-4,5-dimethylphenol was prepared by the literature procedure.[20] All other reagents were used as received from Lancaster Synthesis, Inc., or Aldrich Chemical Co., Inc. C_6D_6 and toluene-d_8 (Cambridge Isotope Laboratories) were degassed with dinitrogen and dried over 4 Å molecular sieves for approximately 1 day prior to use. Elemental analyses were performed in our laboratories on a Perkin-Elmer 2400 CHN analyzer or by 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 (H_2[Biphen]). (This method is a variation of that reported in the literature.[12]) Potassium dichromate (54 g, 0.184 mol) in sulfuric acid (100 mL) and water (300 mL) was slowly added over a period of 10 min to an acetic acid (550 mL) solution of 3,4-dimethyl-2-*tert*-butylphenol (137 g, 0.544 mol) at 60 °C. The color changed from orange to green, and a tan precipitate formed. The reaction mixture was then heated for 1 h at 60 °C, and cooled to room temperature. The reaction mixture was filtered, and the brown solid was washed with water (2 × 250 mL) and methanol (3 × 200 mL). The off-white solid was dried in vacuo to give H_2[Biphen] (54.4 g, 50%): ^1H NMR ($CDCl_3$) δ 7.12 (s, 2, Ar), 4.79 (s, 2, OH), 2.24 (s, 6, Me), 1.80 (s, 6, Me), 1.38 (s, 18, t-Bu); $^{13}C\{^1H\}$ NMR δ 151.24, 134.60, 134.13, 127.73, 128.79, 121.64, 35.15, 30.19. 20.46, 16.35.

(Menthoxy)PCl_2 (MenOPCl_2).[10] 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 min. The mixture was stirred at room temperature for 1 h under a nitrogen atmosphere before removing the volatile components by vacuum transfer (room temperature, 100 mTorr). Purification by short-path vacuum distillation yielded MenOPCl_2 (bp 62 °C/150 mTorr): $^{31}P\{^1H\}$ NMR (THF) δ 177.4.

BiphenP(OMen). Triethylamine (30 mg, 0.3 mmol) and H_2[Biphen] (35 mg, 0.1 mmol) were dissolved in THF (3 mL). MenOPCl_2 (26 mg, 0.1 mmol) was added, and the reaction mixture stood at room temperature for 18 h. The precipitate was removed by filtration and dissolved in THF for NMR examination: $^{31}P\{^1H\}$ NMR (THF) δ 143.7 ((*R*)-BiphenP(OMen)), 138.0 ((*S*)-BiphenP(OMen)).

Resolution of (*R*)- and (*S*)-H_2[Biphen] via BiphenP(O)(OMen). A solution of (−)-menthol (44 g, 282 mmol) in CH_2Cl_2 (100 mL) was added to a 0 °C solution of phosphorus trichloride (1.5 equiv, 58 g, 423 mmol) in CH_2Cl_2 (200 mL) over a period of 30 min. The ice bath was removed, and after 1 h at room temperature, the volatile components 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 equiv, 118 mL, 847 mmol) and H_2[Biphen] (100 g, 282 mmol) was added over 30 min. After 2 h 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 2 h, and the layers were allowed to separate. 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 give a white solid, which was dried in vacuo to afford BiphenP(O)(OMen) (124 g, 85%): $^{31}P\{^1H\}$ NMR δ −3.37 ((*S*)-BiphenP(O)(OMen)), −4.89 ((*R*)-BiphenP(O)(OMen)).

The diastereomeric mixture of phosphates was dissolved in a minimum amount of refluxing acetic acid (∼450 mL). After 16 h white crystals were collected by filtration and washed with cold acetic acid (2 × 50 mL). The solid was then dried in vacuo to give (*S*)-BiphenP(O)(OMen) (42 g, 97−99% de). This

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material was recrystallized from refluxing acetic acid to afford (*S*)-BiphenP(O)(OMen) (37.8 g, >99% de, corresponding to 61% of the *S* diastereomer).

The liquor from the first crystallization was concentrated in vacuo to give a solid enriched with (*R*)-BiphenP(O)(OMen). This solid was recrystallized from refluxing MeOH (300 mL). When the solution was cooled 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)(OMen) in two crops (26.8 g, >99% de, 43% *R* diastereomer).

The MeOH solution was concentrated to give approximately racemic BiphenP(O)(OMen), which was reused in subsequent resolution processes.

Resolved (*S*)-BiphenP(O)(OMen) (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 to the phosphate solution. The reaction mixture was stirred at room temperature for 16 h and then carefully quenched with water (75 mL) and bleach (75 mL). The slurry was filtered through Celite, and the pad was washed with toluene (250 mL). The layers were allowed to separate. 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*)-H_2[Biphen] was collected by filtration and dried in vacuo; yield 17.5 g (70%, >99% ee). The optical purity of (*S*)-H_2[Biphen] was tested by ^{31}P NMR of the (*S*)-BiphenP-(OMen) derivative. The reduction of (*R*)-BiphenP(O)(OMen) to (*R*)-H_2[Biphen] followed an identical procedure.

2-(1-Adamantyl)-4,5-dimethylphenol. This compound was prepared by a literature procedure:[19,20,42] mp 135−138 °C; ^{1}H NMR ($CDCl_3$) δ 6.96 (s, 1), 6.47 (s, 1), 4.50 (s, 1), 2.19 (s, 3), 2.17 (s, 3), 2.10 (s, 6), 2.05 (br s, 3), 1.78 (s, 6).

3,3′-Bis(1-adamantyl)-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diol (H_2[Biad]). A solution of potassium dichromate (6.50 g, 22.1 mmol) in sulfuric acid (12 mL) and water (48 mL) was added dropwise over 30 min to an acetic acid (64 mL) slurry of 2-(1-adamantyl)-4,5-dimethylphenol (16.0 g, 63.0 mmol) at 65 °C. The reaction mixture was stirred for 2 h at 65 °C. The green suspension was then cooled to room temperature and filtered. The precipitate was washed with water (250 mL) and triturated with methanol (3 × 150 mL). The resulting white solid was dried in vacuo to afford the title compound (±)-BiadH_2 (11.1 g, 70% yield, mp >300 °C): ^{1}H NMR ($CDCl_3$) δ 7.07 (s, 2), 4.80 (s, 2), 2.25 (s, 6), 2.13 (br s, 12), 2.06 (br s, 6), 1.82 (s, 6), 1.76 (br s, 12); ^{13}C NMR ($CDCl_3$) δ 150.6, 134.0, 133.8, 128.7, 128.3, 121.1, 40.7, 37.4, 36.9, 29.4, 20.4, 16.3; IR (neat) 2911, 2886, 2848, 1602, 1451, 1174, 1111 cm^{-1}. Anal. Calcd for $C_{36}H_{46}O_2$: C, 84.66; H, 9.08. Found. C, 84.78; H, 9.18.

BiadP(OMen). To a slurry of H_2[Biad] (25 mg, 0.049 mmol) in THF (1 mL) was added potassium hydride (5 mg, 0.12 mmol). Upon addition of MenOPCl$_2$ (13 mg, 0.051 mmol) in THF (0.5 mL) to the blue solution, the reaction mixture became yellow and a white precipitate formed. The mixture was filtered through a Kimwipe plug into an NMR tube for examination: ^{31}P{^{1}H} NMR (THF) δ 143.6 ((*R*)-BiadP(OMen)), 138.8 ((*S*)-BiadP(OMen)).

Preparation of Racemic Phosphates. (±)-3,3′-Bis(1-adamantyl)-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diol ((±)-H_2-[Biad]; 1.00 g, 1.96 mmol) was suspended in THF (16 mL) at ambient temperature under an argon atmosphere. Benzylpotassium in THF (2 M) was added dropwise until an orange color persisted. The orange solution was stirred, and MenOPCl$_2$ (0.51 g, 1.98 mmol) in THF (1.0 mL) was added over 5 min. The reaction mixture was stirred for 10 min, and water (0.2 mL) was added dropwise. The volatile components were removed by rotary evaporation to yield a pale yellow solid. The crude phosphite was dissolved in CH_2Cl_2 (13 mL), and hydrogen peroxide (30%, 2.0 mL, 17.6 mmol) was added. The biphasic mixture was stirred vigorously for 1 h. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (1 × 5 mL). The combined organic layers were rinsed with water (1 × 20 mL) and brine (1 × 20 mL). The organic layer was dried with magnesium sulfate. The mixture was filtered, and the solvent was removed from the filtrate under reduced pressure to produce an orange-yellow solid. The crude material was purified by silica gel column chromatography (4:1 pentane/diethyl ether, $R_f = 0.44$): ^{1}H NMR ($CDCl_3$) δ 4.37, 4.26; ^{31}P NMR (C_6H_6) δ −3.29, −5.57; ^{31}P NMR ($CDCl_3$) δ −4.97, −6.30.

Preparation of Diastereomerically Pure Phosphate. The crude mixture of (±)-BiadP(O)(OMen) diastereomers (1.37 g, 1.93 mmol) was placed in a Soxhlet extraction apparatus under an argon atmosphere. Acetone (20 mL) was added, and the reaction mixture was heated to reflux. After 18 h all the material had disappeared from the thimble. The reaction mixture was cooled to room temperature, and the white precipitate was collected by filtration. The product was diastereomerically pure (*S*)-BiadP(O)(OMen), as determined by ^{31}P NMR ($CDCl_3$) −4.97 (0.41 g, 30% over three steps). The remaining acetone solution was then concentrated to give enriched (*R*)-BiadP(O)(OMen) (mp 239−242 °C; $[\alpha]^{20}_D = -52.5°$ ($c = 1.34$, CH_2Cl_2)): ^{1}H NMR ($CDCl_3$) δ 7.18 (s, 1), 7.16 (s, 1), 4.37 (dq, $J = 6.6$, 2.7 Hz, 1 H), 2.32−2.24 (m, 3), 2.28 (s, 3), 2.26 (s, 3), 2.19 (s, 9), 2.22−2.06 (m, 12), 1.95−1.90 (m, 1), 1.84−1.74 (m, 17), 1.70−1.60 (m, 2), 1.37−1.28 (m, 2), 1.07−0.92 (m, 2), 0.88 (d, 3, $J = 4.3$ Hz), 0.85 (d, 3, $J = 4.3$ Hz), 0.82 (d, $J = 2.1$ Hz, 3); IR (neat) 2904, 2848, 1451, 1293, 1218, 998 cm^{-1}. Anal. Calcd for $C_{46}H_{63}O_4P$: C, 77.71; H, 8.93; P, 4.36. Found. C, 77.46; H, 8.80; P, 4.15.

(*S*)-3,3′-Bis(1-adamantyl)-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diol ((*S*)-H_2[Biad]). Diastereomerically pure (*S*)-BiadP(O)(OMen) (2.50 g, 3.52 mmol) was dissolved in toluene (4 mL) at −23 °C under an argon atmosphere. Red-Al (4.20 mL, 14.0 mmol, 65 wt % in toluene) was added dropwise via syringe. The reaction mixture was warmed to ambient temperature while it was stirred over a period of 1.5 h. Water (50 mL) and bleach (50 mL) were added slowly, and the reaction mixture was stirred for 30 min. The mixture was filtered through Celite, and the solid was rinsed with toluene (100 mL). The layers were separated, and the organic layer was rinsed with H_2O (1 × 100 mL) and brine (1 × 100 mL). The organic layer was dried with magnesium sulfate, and the mixture was filtered. The solvent was removed from the filtrate to give a white solid. The material was rinsed with hexanes (3 × 20 mL) in order to remove any residual menthol. Optically pure (*S*)-BiadH_2 was dried in vacuo (1.46 g, 81%). $[\alpha]^{20}_D = -32.1°$ ($c = 3.3$, THF). Spectral data were identical with data for the racemic compound.

Mo(N-2,6-$Et_2C_6H_3$)$_2$$Cl_2$(DME). Sodium molybdate (5 g, 24.3 mmol) was suspended in DME (200 mL). Triethylamine (4 equiv, 9.8 g, 97.2 mmol) and 2,6-diethylaniline (2 equiv, 7.24 g, 48.6 mmol) were added sequentially with rapid stirring over 5 min. Chlorotrimethylsilane (8 equiv, 21 g, 194 mmol) was then introduced. The reaction vessel was sealed and heated to 60 °C for 5 h. The solution became brick red, and copious amounts of salt precipitated. The suspension was filtered through Celite, and the pad was washed with dimethoxyethane until only a pale orange color persisted in the pad. The volume was reduced to ~75 mL in vacuo, and the solution was stored overnight at −25 °C. Analytically pure dark red blocks were recovered from the DME solution (3.71 g). A second crop (1.6 g) was collected from diethyl ether (30 mL); total yield 5.3 g (40%): ^{1}H NMR δ 6.90 (d, 4, $J_{HH} = 7.2$ Hz, *m*-Ar), 6.81 (t, 2, $J_{HH} = 7.2$ Hz, *p*-Ar), 3.40 (s, 6, OCH_3), 3.23 (q, 8, $J_{HH} = 7.8$ Hz, C$H_2$$CH_3$), 3.32 (s, 4, OCH_2), 1.27 (t, 12, $J_{HH} = 7.8$ Hz,

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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; N, 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 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 h. 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%): ^1H NMR δ 8.30 (br s, 1, $HNEt_3$), 7.46 (d, 2, J_{HH} = 1.8 Hz, Ar), 7.12 (d, 2, J_{HH} = 1.8 Hz, Ar), 3.06 (s, 6, Me), 2.65 (d q, 6, CH_2Me), 1.92 (s, 18, *t*-Bu), 1.20 (s, 18, *t*-Bu), 0.83 (t, 9, 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.

[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 with sodium molybdate (11.29 g, 54.8 mmol), 2,6-lutidine (35.2 g, 329 mmol), 2,4-di-*tert*-butyl-6-methylaniline hydrochloride (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 h. 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. The bright red solid was collected by filtration, washed with pentane (100 mL), and dried in vacuo; yield 33.3 g (81%): ^1H NMR δ 14.55 (br s, 1, Hlut), 7.48 (d, 2, J_{HH} = 2.1 Hz, Ar), 7.13 (d, 2, J_{HH} = 2.7 Hz, Ar), 6.86 (t, 1, J_{HH} = 8.1 Hz, *p*-lut), 6.30 (d, 2, J_{HH} = 7.8 Hz, *m*-lut), 3.08 (s, 6, Me), 2.46 (s, 6, Me), 1.934 (s, 18, *t*-Bu), 1.22 (s, 18, *t*-Bu); $^{13}C\{^1H\}$ 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 $C_{37}H_{56}Cl_3MoN_3$: C, 59.64; H, 7.57; N, 5.64. Found: 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)$_2$. Mo(N-2,6-Et$_2$C$_6$H$_3$)$_2$Cl$_2$(DME) (5.02 g, 9.11 mmol) was dissolved in ether (100 mL), and the solution was cooled to −25 °C. Neophylmagnesium chloride (18.9 mL, 0.99 M in ether, 18.68 mmol) was added over a period of 5 min with rapid stirring. The solution color turned from red to orange, and a precipitate formed. The reaction mixture was stirred at room temperature for 2 h and filtered through Celite, and the pad was washed with ether until it was pale yellow. The red solution was concentrated to 10 mL. Orange blocks formed on standing at room temperature for 1 h. The solution was then cooled to −25 °C for 3 h. The supernatant was decanted, and the crystals of Mo(N-2,6-Et$_2$C$_6$H$_3$)$_2$(CH$_2$CMe$_2$Ph)$_2$ were dried in vacuo; yield 4.47 g (75%): ^1H NMR δ 7.41 (d, 4, *m*-Ar), 7.18 (t, 2, J_{HH} = 2 Hz, *p*-Ph), 7.05 (t, 2, *p*-Ar), 6.95−6.85 (m, 8, *o*-,*m*-Ph), 2.66 (q, 8, CH_2CH_3), 1.81 (s, 4, $MoCH_2R$), 1.46 (s, 12, $C(CH_3)_2Ph$), 1.07 (t, 12, 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-MeC$_6$H$_2$)$_2$(CH$_2$CMe$_3$)$_2$. A slurry of [HNEt$_3$][Mo(N-2,4-*t*-Bu-6-MeC$_6$H$_2$)$_2$Cl$_3$] (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 min, and the reaction mixture was stirred at room temperature for 16 h. 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 δ 7.46 (br d, 2, NAr), 7.01 (br d, 2, NAr), 2.16 (s, 6, Me), 1.82 (s, 18, *t*-Bu), 1.24 (s, 18, *t*-Bu), 1.19 (s, 18, *t*-Bu); ^1H NMR (C_7D_8, −40 °C) δ 7.44 (br s, 2, Ar), 6.96 (br s, 2, Ar), 3.10 (br d, 2, J_{HH} = 14.4 Hz, CH_aH_b*t*-Bu), 2.07 (s, 6, Me), 1.79 (s, 18, *t*-Bu), 1.54 (br d, 2, J_{HH} = 13.5 Hz, CH_aH_b-*t*-Bu), 1.21 (s, 18, *t*-Bu), 1.14 (s, 18, *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 $C_{40}H_{68}MoN_2$: C, 71.39; H, 10.19; N, 4.16. Found: C, 71.46; H, 10.28; N, 4.07.

Mo(N-2-CF$_3$C$_6$H$_4$)$_2$(CH$_2$CMe$_3$)$_2$. Neopentylmagnesium chloride (52 mL, 2.27 M in ether, 117.7 mmol) was added over 30 min to a cooled ether (500 mL) solution of Mo(N-2-CF$_3$C$_6$H$_4$)$_2$Cl$_2$(DME) (33.68 g, 58.6 mmol). The reaction mixture was stirred at room temperature for 12 h 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, 89%): ^1H NMR δ 7.31 (d, 2, Ar), 7.18 (d, 2, Ar), 6.79 (t, 2, Ar), 6.55 (t, 2, Ar), 2.33 (s, 4, CH_2-*t*-Bu), 1.16 (s, 18, *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 $C_{24}H_{30}F_6MoN_2$: C, 51.80; H, 5.43; N, 5.03. Found: C, 51.65; H, 5.53; N, 4.92.

Mo(N-2,6-Et$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OTf)$_2$(DME). Triflic acid (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$_2$C$_6$H$_3$)$_2$(CH$_2$CMe$_2$Ph)$_2$ (4.264 g, 6.5 mmol). The solution was stirred at room temperature for 18 h. The volatile components were removed in vacuo, and the yellow residue was extracted with cold toluene (∼175 mL). The mixture was then filtered through Celite. The toluene was removed from the filtrate in vacuo, and the solid was washed with ether (50 mL) to yield a pale yellow powder (1.5 g) which was pure by ^1H NMR. The ether filtrate was then concentrated to 7 mL to give additional yellow powder (700 mg, total yield 44%): ^1H NMR δ 14.28 (s, 1, Mo(CHR)), 7.62 (d, 2, J_{HH} = 8.4 Hz, *o*-Ph), 6.98 (t, 1, J_{HH} = 7.6 Hz, *p*-Ph), 6.80−6.66 (m, 5, Ar), 3.83 (s, 3, OCH_3), 3.24 (br t, 2, J_{HH} = 5.1 Hz, OCH_2), 2.95−2.67 (m, 4, diastereotopic CH_2CH_3), 2.82 (br t, 2, J_{HH} = 5.1 Hz, OCH_2), 2.67 (s, 3, OCH_3), 1.77 (s, 6, CMe_2Ph), 1.22 (t, 6, CH_2CH_3); $^{13}C\{^1H\}$ 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-MeC$_6$H$_2$)(CHCMe$_3$)(OTf)$_2$(DME). 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-MeC$_6$H$_2$)$_2$(CH$_2$-*t*-Bu)$_2$ (7.84 g, 11.67 mmol) in DME (125 mL). The reaction mixture was stirred for 16 h at room temperature and then concentrated in vacuo to a light brown solid. The product was extracted with benzene (100 mL), and the extract was filtered through Celite. The pad was washed with additional benzene until colorless. The filtrate was concentrated in vacuo to a tan foam. Ether (30 mL) was added. A yellow powder was collected by filtration, washed with ether until the solid was bright yellow, and dried in vacuo (5.4 g, 60%): ^1H NMR δ 14.16 (s, 1, CH-*t*-Bu), 7.38 (d, 1, J = 1.8 Hz, Ar), 7.06 (d, 1, J = 1.8 Hz, Ar), 3.97 (s, 3, OCH_3), 3.60 (br t, 1, OCH_2), 2.98 (br t, 2, OCH_2), 1.74 (br s, 7, overlapped ArMe, OCH_3, and one OCH_2), 1.60 (s, 9, *t*-Bu), 1.43 (s, 9, *t*-Bu), 1.14 (s, 9, *t*-Bu); $^{13}C\{^1H\}$ NMR 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 $C_{26}H_{43}F_6MoNO_8S_2$: C, 40.47; H, 5.62; N, 1.82. Found: C, 40.68; H, 5.75; N, 1.76.

Mo(N-2-CF$_3$C$_6$H$_4$)(CHCMe$_3$)(OTf)$_2$(DME). Triflic acid (15.9 g, 105.9 mmol) was dissolved in cold DME (50 mL) and added to a cold (−25 °C) solution of Mo(N-2-CF$_3$C$_6$H$_4$)$_2$(CH$_2$CMe$_3$)$_2$ (19.63 g, 35.3 mmol) in DME (200 mL). The reaction mixture was stirred at room temperature for 16 h and concentrated in vacuo to yield a brown solid. Toluene (50 mL) was added, and the solution was concentrated again in vacuo to remove residual DME. The brown residue was extracted with toluene (250 mL) and benzene (200 mL), and the extracts were filtered through Celite. The filtrate 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 isomers) major δ 14.02 (s, 1, C*H*-*t*-Bu), 8.38 (d, 1, Ar), 7.04 (d, 1, Ar), 6.82 (t, 1, Ar), 6.52 (t, 1, Ar), 3.65 (br s, 3, OC*H*$_3$), 3.22 (br s, 2, OC*H*$_2$), 2.82 (br s, 5, OC*H*$_3$ and OC*H*$_2$), 1.44 (s, 9, *t*-Bu), minor δ 15.03 (s, 1, C*H*-*t*-Bu), 8.38 (d, 1, Ar), 7.04 (d, 1, Ar), 6.82 (t, 1, Ar), 6.52 (t, 1, Ar), 3.59 (s, 3, OC*H*$_3$), 3.42 (br t, 1, OC*H*$_2$), 3.15 (s, 4, OC*H*$_3$ and one OC*H*$_2$), 2.64 (br t, 1, OC*H*$_2$), 1.21 (s, 9, *t*-Bu); ^{13}C{^{1}H} NMR 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 $C_{18}H_{24}F_9MoNO_8S_2$: C, 30.30; H, 3.39; N, 1.96. Found: C, 30.36; H, 3.37; N, 2.00.

Mo(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)[Biphen]. Potassium hydride (440 mg, 11 mmol) was added in portions to a stirred THF (40 mL) solution of H$_2$[Biphen] (1.77 g, 5 mmol). After 3 h, solid Mo(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OTf)$_2$(DME) (3.96 g, 5 mmol) was added. The red solution was stirred for 2 h and then concentrated in vacuo. The residue was extracted with benzene (10 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 was taken up in diethyl ether (18 mL) and transferred to a 20 mL vial. When the vial stood for 12 h uncapped in a well-purged glovebox, the volume decreased to ~5 mL. The red solution was decanted and the red blocks were washed with cold ether and dried in vacuo (2.71 g, 72%): ^{1}H NMR *syn* δ 10.98 (s, 1, J_{CH} = 123 Hz, MoCH), 7.42 (m, 3, Biphen and *o*-Ph), 7.16 (m, 3, Biphen and *m*-Ph), 7.05 (br t, J_{HH} = 7.6 Hz, 1, *p*-Ph), 6.92 (s, 3, Ar), 3.70 (sept, J_{HH} = 7.0 Hz, 2, C*H*Me$_2$), 2.13 (s, 3, Biphen), 2.05 (s, 3, Biphen), 1.85 (s, 3, Biphen), 1.74 (s, 3, Biphen), 1.66 (s, 3, C(C*H*$_3$)(MePh)), 1.59 (s, 9, *t*-Bu), 1.54 (s, 9, *t*-Bu), 1.14 (d, J_{HH} = 7.0 Hz, 6, CH(C*H*$_3$)(Me), 1.13 (s, 3, C(C*H*$_3$)(MePh), 0.90 (d, J_{HH} = 7.0 Hz, 6, CH(C*H*$_3$)(Me)), *anti* δ 12.77 (s, J_{CH} = 146 Hz, 1, MoCH); ^{13}C{^{1}H} NMR δ 277.1 (d, J_{CH} = 123 Hz, *C*HR), 155.4, 154.5, 154.3, 151.3, 146.8, 140.0, 138.0, 136.5, 135.7, 132.0, 131.1, 130.9, 130.7, 130.6, 129.6, 128.7, 127.9, 127.3, 126.3, 123.8 (aryl), 53.7 (*C*Me$_2$Ph), 36.0, 35.7 (*C*Me$_3$), 33.2, 33.0 (C(*C*H$_3$)(MePh), 30.9, 30.4 (C(*C*H$_3$)$_3$), 29.2 (*C*HMe$_2$), 24.6 (CH(*C*H$_3$)$_2$), 20.8, 20.7, 17.2, 16.7 (aryl-CH$_3$). 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-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)[(*S*)-Biphen]. Potassium hydride (1.2 g, 30 mmol) was added in portions to a THF (100 mL) solution of (*S*)-H$_2$[Biphen] (3.54 g, 10 mmol). After the solution was stirred for 18 h at room temperature, solid Mo(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OTf)$_2$(DME) (0.99 equiv, 7.83 g, 9.9 mmol) was added to the reaction mixture. The solution was stirred for 3 h, and the solvent was removed 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 from the filtrate in vacuo, and the residue was dissolved in ether (30 mL). The volume was reduced to ~10 mL in vacuo and allowed to stand at 20 °C for 2 h. Mo(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)[(*S*)-Biphen] was collected as red microcrystals in four crops and dried in vacuo; yield 5.81 g (78%).

Mo(N-2,6-Et$_2$C$_6$H$_3$)(CHCMe$_2$Ph)[Biphen]. Potassium hydride (3 equiv, 190 mg, 4.8 mmol) was added in portions to a stirred THF (10 mL) solution of H$_2$[Biphen] (561 mg, 1.58 mmol). After 18 h solid Mo(N-2,6-Et$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OTf)$_2$(DME) (1.21 g, 1.6 mmol) was added. After 3 h, the solution was concentrated to dryness in vacuo. The red solid was extracted with benzene (10 mL), and the suspension was filtered through Celite. The benzene was removed from the filtrate in vacuo, and the residue was crystallized from ether (5 mL). Red crystals of the product formed upon standing the solution in an open vial for 1 h at room temperature (550 mg). Reducing the volume of the liquor afforded additional precipitate (180 mg); yield 730 mg combined (60%): ^{1}H NMR *syn* δ 11.04 (s, 1, J_{CH} = 121 Hz, C*H*R), 7.45 (s, 1, Biphen), 7.39 (br s, 2, *o*-Ph), 7.36 (s, 1, Biphen), 7.16 (t, 2, J_{HH} = 6.7 Hz, *m*-Ph), 7.00 (t, 1, J_{HH} = 6.7 Hz, *p*-Ph), 6.83 (br s, 3, Ar), 2.80 (q, 4, J_{HH} = 7.4 Hz, C*H*$_2$CH$_3$), 2.14 (s, 3, Biphen), 2.03 (s, 3, Biphen), 1.78 (s, 3, Biphen), 1.76 (s, 3, Biphen), 1.68 (s, 3, C(C*H*$_3$)(MePh), 1.60 (s, 9, Biphen), 1.54 (s, 9, Biphen), 1.20 (s, 3, C(C*H*$_3$)(MePh), 1.06 (t, 6, J_{HH} = 7.4 Hz, CH$_2$C*H*$_3$); *anti* δ 12.94 (s, 1, C*H*R); ^{13}C{^{1}H} 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 $C_{44}H_{57}MoNO_2$: C, 72.61; H, 7.89; N, 1.92. Found: C, 72.50; H, 7.80; N, 2.13.

Mo(N-2,6-Et$_2$C$_6$H$_3$)(CHCMe$_2$Ph)[(*S*)-Biphen]. Potassium hydride (3.1 equiv, 250 mg, 6.2 mmol) was added in portions to a stirred THF (30 mL) solution of (*S*)-H$_2$[Biphen] (708 mg, 2 mmol). After 12 h, solid Mo(N-2,6-Et$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OTf)$_2$(DME) (1 equiv, 1.526 g, 2 mmol) was added. The solution was stirred for 4 h, and the volatile components were then removed in vacuo. The solid was extracted with benzene (20 mL) and the suspension was filtered through Celite. The benzene was then removed in vacuo and the residue dissolved in ether/isopropyl ether (1:1, 4 mL). The solution was cooled to −30 °C. Two crops of the dark orange product were collected by filtration; yield 390 mg (27%).

Mo(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)[Biphen]. Potassium hydride (240 mg, 6 mmol) was added to a THF (50 mL) solution of H$_2$[Biphen] (708 mg, 2 mmol). After 18 h, solid Mo(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OTf)$_2$(DME) (1.446 g, 2 mmol) was added. After 3 h the solvents were removed in vacuo and the residue was extracted with benzene (40 mL). The suspension was filtered through Celite, and the benzene was removed from the filtrate in vacuo. The residue was triturated with ether (10 mL) and the resulting orange powder was collected by filtration, washed with ether (5 mL), and dried in vacuo: yield 1.06 g (77%); ^{1}H NMR *syn* δ 11.01 (s, 1, J_{CH} = 121 Hz, C*H*R), 7.39 (s, 1, Biphen), 7.25 (d, 2, *o*-Ph), 7.11 (s, 1, Biphen), 7.05 (t, 2, *m*-Ph), 6.88 (t, 1, *p*-Ph), 6.63 (s, 3, Ar), 2.22 (s, 6, ArC*H*$_3$), 2.10 (s, 3, Biphen), 1.97 (s, 3, Biphen), 1.72 (s, 3, Biphen), 1.61 (s, 3, Biphen), 1.56 (s, 3, C(C*H*$_3$)(MePh), 1.53 (s, 9, *t*-Bu), 1.50 (s, 9, *t*-Bu), 1.20 (s, 3, C(C*H*$_3$)(MePh); *anti* δ 13.03 (s, 1, C*H*R); ^{13}C{^{1}H} NMR δ 278.94 (d, J_{CH} = 121 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, 54.16, 36.00, 35.76, 32.83, 31.93, 30.92, 30.56, 20.84, 20.73, 19.80, 17.34, 16.82. Anal. Calcd for $C_{42}H_{53}MoNO_2$: C, 72.08; H, 7.63; N, 2.00. Found C, 72.21; H, 7.58; N, 1.94.

Mo(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)[(*S*)-Biphen]. Potassium hydride (3 equiv, 360 mg, 9 mmol) was added in portions to a stirred solution of (*S*)-H$_2$[Biphen] (1.062 g, 3 mmol) in THF (100 mL). After 18 h, solid Mo(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OTf)$_2$(DME) (0.94 equiv, 2.235 g, 2.83 mmol) was added. After 3 h, the solvents were removed in vacuo and the residue was extracted with benzene. The suspension was filtered through Celite, and the benzene was removed from the filtrate in vacuo. The residue was dissolved in ether (6 mL). Red crystals formed at room temperature over 1 h and were collected by filtration; yield 600 mg (30%).

Mo(N-2-CF$_3$C$_6$H$_4$)(CHCMe$_2$Ph)[Biphen]. Solid benzylpotassium (2 equiv, 260 mg, 2.0 mmol) was added in portions to a solution of H$_2$[Biphen] (355 mg, 1.0 mmol) in toluene (15 mL). After 2 h, solid Mo(N-2-CF$_3$C$_6$H$_4$)(CHCMe$_2$Ph)(OTf)$_2$(DME) (780 mg, 1.0 mmol) was added to the reaction mixture and the resulting red solution was stirred for 1 h. The volatile components 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 $Mo(NArCF_3)(CHCMe_2Ph)$[Biphen] as a red powder: yield 708 mg (96%); ^1H NMR δ 10.91 (s, 1, $J_{CH} = 123$ Hz, *syn* C*H*R), 7.44 (m, 3, Biphen and *o*-Ph), 7.19 (d, 1, $J_{HH} = 7.6$ Hz, *p*-Ph), 7.15 (s, 1, Biphen), 7.12 (d, 1, $J_{HH} = 7.9$ Hz, $3\text{-}C_6H_4CF_3$), 7.00 (m, 2, *m*-Ph), 6.80 (d, 1, $J_{HH} = 7.2$ Hz, $6\text{-}C_6H_4CF_3$), 6.76 (“t”, 1, $J_{HH} = 7.7$ Hz, $5\text{-}C_6H_4CF_3$), 6.47 (“t”, 1, $J_{HH} = 7.4$ Hz, $4\text{-}C_6H_4CF_3$), 2.10 (s, 3, Biphen), 2.01 (s, 3, Biphen), 1.70 (s, 6, Biphen and C*Me*MePh), 1.69 (s, 3, Biphen), 1.64 (s, 9, *t*-Bu), 1.54 (s, 9, *t*-Bu), 1.16 (s, 3, C*Me*MePh); $^{13}C\{^1H\}$ NMR δ 279.27, 153.79, 153.41, 152.84, 151.53, 139.36, 139.19, 135.89, 135.56, 131.60, 131.57, 131.14, 130.86, 130.47, 130.29, 129.76, 129.48, 128.42, 127.13, 125.64 (q, $J_{CF} = 30.0$ Hz), 125.64 (q, $J_{CF} = 274$ Hz), 126.05, 126.00, 125.64 (q, $J_{CF} = 5.1$ Hz), 54.77, 35.78, 35.37, 32.61, 31.63, 30.29, 30.14, 20.48, 20.37, 16.87, 16.51. 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.

If several equivalents of THF is added to the pentane solution of $Mo(N\text{-}2\text{-}CF_3C_6H_4)(CHCMe_2Ph)$[Biphen], then the isolated product contains 1 equiv of THF bound to the metal.

$Mo(N\text{-}2\text{-}CF_3C_6H_4)(CHCMe_3)$[Biphen]. Solid benzylpotassium (2.0 equiv, 260 mg, 2.0 mmol) was added in portions to a toluene (20 mL) solution of H_2[Biphen] (354 mg, 1.0 mmol) at room temperature. After 5 h, the reaction mixture was cooled to −25 °C and solid $Mo(N\text{-}2\text{-}CF_3C_6H_4)(CHCMe_3)(OTf)_2(DME)$ (714 mg, 1 mmol) was added. After 45 min the solvents were removed in vacuo and the residue was extracted with pentane (40 mL). The suspension was filtered through Celite, and the filtrate volume was reduced to 4 mL. The solution was cooled to −25 °C overnight. The red precipitate of $Mo(NArCF_3)(CHCMe_3)$[Biphen] was collected by filtration, washed with cold pentane (1 mL), and dried in vacuo: yield 260 mg (38%); ^1H NMR *syn* δ 10.61 (s, 1, C*H*-*t*-Bu), 7.59 (d, 1, $J_{HH} = 8.1$ Hz, Ar), 7.48 (s, 1, Biphen), 7.16 (s, 1, Biphen), 7.12 (d, 1, $J_{HH} = 6.9$ Hz, Ar), 6.91 (t, 1, $J_{HH} = 7.5$ Hz, Ar), 6.52 (t, 1, $J_{HH} = 7.5$ Hz, Ar), 2.15 (s, 3, Biphen), 2.01 (s, 3, Biphen), 1.73 (s, 3, Biphen), 1.67 (s, 9, *t*-Bu), 1.64 (s, 3, Biphen), 1.59 (s, 9, *t*-Bu), 1.14 (s, 9, *t*-Bu); $^{13}C\{^1H\}$ 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, $J_{CF} = 274$ 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: C, 63.84; H, 6.80; N, 2.22.

$Mo(N\text{-}2\text{-}CF_3C_6H_4)(CHCMe_3)$[(*S*)-Biphen]. Benzylpotassium (325 mg, 2.50 mmol) was added to a toluene (40 mL) solution of (*S*)-H_2[Biphen] (442 mg, 1.25 mmol). After 1 h, the reaction mixture was cooled to −25 °C and solid $Mo(N\text{-}2\text{-}CF_3C_6H_3)(CHCMe_3)(OTf)_2(DME)$ (892 mg, 1.25 mmol) was added. After an additional 1 h at room temperature the volatile components were removed in vacuo and the red solid was dissolved in pentane. The mixture was filtered through Celite, and the pentane was removed from the filtrate in vacuo. The resulting foam was crushed to give spectroscopically pure $Mo(N\text{-}2\text{-}CF_3C_6H_3)(CHCMe_3)$[(*S*)-Biphen] as a red powder; yield 804 mg (95%). Recrystallization conditions for $Mo(N\text{-}2\text{-}CF_3C_6H_3)(CHCMe_3)$[(*S*)-Biphen] were not perfected.

$Mo(N\text{-}2\text{-}CF_3C_6H_4)(CH\text{-}2\text{-}MeOC_6H_4)$[Biphen]. 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 $Mo(N\text{-}2\text{-}CF_3C_6H_4)(CHCMe_2Ph)$[Biphen](THF) (1.217 g, 1.5 mmol), and the reaction mixture was stirred for 10 min. The solvents were removed in vacuo, and the residue was triturated with ether (5 mL) and collected by filtration. The red powder was washed with ether and dried in vacuo: yield 800 mg (74%); ^1H NMR *anti* δ 12.85 (s, 1, $J_{CH} = 151$ Hz, C*H*Ar), 7.29 (d, 1, $J_{HH} = 7.5$ Hz, Ar), 7.28 (s, 1, Biphen), 7.20 (s, 1, Biphen), 7.11 (br d, 1, $J_{HH} = 8.0$ Hz, Ar), 6.93 (br t, 1, $J_{HH} = 7.5$ Hz, Ar), 6.88 (br t, 1, $J_{HH} = 7.5$ Hz, Ar), 6.61 (br t, 1, $J_{HH} = 7.5$ Hz, Ar), 6.51 (br t, 1, $J_{HH} = 7.5$ Hz, Ar), 6.42 (br d, 1, $J_{HH} = 8.5$ Hz, Ar), 3.26 (s, 3, OCH_3), 2.20 (s, 6, 2 Me), 1.91 (s, 3, Me), 1.65 (s, 3, Me), 1.48 (s, 9, *t*-Bu), 1.39 (s, 9, *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: C, 64.25; H, 6.15; N, 1.74.

$Mo(N\text{-}2\text{-}CF_3C_6H_4)(CH\text{-}2\text{-}MeOC_6H_4)$[(*S*)-Biphen]. Benzylpotassium (520 mg, 4 mmol) was added in portions to a stirred THF (40 mL) solution of (*S*)-H_2[Biphen] (708 mg, 2 mmol). After 20 min, solid $Mo(N\text{-}2\text{-}CF_3C_6H_3)(CHCMe_2Ph)(OTf)_2(DME)$ (1.550 g, 2 mmol) was added, and the red solution was stirred for an additional 1 h. The volatile components were removed in vacuo, and the solid was extracted with benzene (20 mL). The suspension was filtered through Celite. 2-Methoxystyrene (326 mg, 2.4 mmol) was added, and the solution was stirred for 15 min. The volatile components were removed in vacuo, and the dark red residue was dissolved in ether (15 mL). The mixture was filtered through Celite, and the filtrate was concentrated to 5 mL in vacuo and stored at −25 °C overnight. Colorless plates of a mixture of *cis*- and *trans*-2,2′-dimethoxystilbene[43] were collected by filtration (60 mg). The mother liquor was then concentrated to 3 mL. A brick red powder precipitated after 2 h at room temperature. The product was collected by filtration, washed with pentane, and dried in vacuo; yield 174 mg (12%).

$Mo(N\text{-}2,4\text{-}t\text{-}Bu_2\text{-}6\text{-}MeC_6H_2)(CHCMe_3)$[(*S*)-Biphen]. Benzylpotassium (286 mg, 2.2 mmol) was added in portions to a stirred THF (25 mL) solution of (*S*)-H_2[Biphen] (354 mg, 1 mmol) until a pale orange color persisted. After 10 min, solid $Mo(N\text{-}2,4\text{-}t\text{-}Bu\text{-}6\text{-}MePh)(CHCMe_3)(OTf)_2(DME)$ (772 mg, 1 mmol) was added. After 30 min, the volatile components were removed in vacuo. The residue was dissolved in benzene (30 mL), and the suspension was filtered through Celite. The benzene was removed from the filtrate in vacuo, and the red residue was dissolved in pentane (2 mL). When the solution was transferred to a vial with a pipet, small orange crystals formed. The crystals were collected by filtration, washed with cold pentane (1 mL), and dried in vacuo; yield 266 mg (36%). The crystallization conditions could not be reproduced, and the source of the inconsistencies could not be identified: ^1H NMR *syn* δ 10.63 (s, 1, $J_{CH} = 126$ Hz, C*H*R), 7.48 (s, 1, Biphen), 7.32 (d, 1, $J_{HH} = 1.8$ Hz, Ar), 7.22 (d, 1, $J_{HH} = 1.8$ Hz, Ar), 7.16 (s, 1, Biphen), 2.95 (s, 3, $ArCH_3$), 2.18 (s, 3, Biphen), 2.00 (s, 3, Biphen), 1.81 (s, 3, Biphen), 1.60 (s, 3, Biphen), 1.64 (s, 9, *t*-Bu), 1.55 (s, 9, *t*-Bu), 1.53 (s, 9, *t*-Bu), 1.18 (s, 9, *t*-Bu), 1.13 (s, 9, *t*-Bu); *anti* δ 12.86 (s, 1, 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, 35.91, 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, 8.90; N, 1.90. Found: C, 71.83; H, 8.16; N, 1.84.

$Mo(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(CHCMe_2Ph)$[Biad]. Benzylpotassium (269 mg, 2.07 mmol) was added in portions to a THF (30 mL) solution of H_2[Biad] (510 mg, 1 mmol) until a pale orange color persisted. After 10 min solid $Mo(NArPr_2)(CHCMe_2Ph)(OTf)_2(DME)$ (791 mg, 1 mmol) was added. After 1 h, the volatile components were removed in vacuo, and the residue was taken up in benzene (15 mL). The suspension was filtered through Celite, and the benzene was removed from the filtrate in vacuo. The resulting orange powder was triturated with pentane (15 mL), and orange $Mo(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(CHCMe_2Ph)$[Biad] was collected by filtration, washed with cold pentane, and dried in vacuo; yield 495 mg (54%): ^1H NMR *syn* δ

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[43] Pascal, P.; Normand, L. *Bull. Soc. Chim. Fr.* **1911**, *9*, 1059.

10.94 (s, 1, J_{CH} = 120 Hz, C*H*R), 7.47 (d, 2, J_{HH} = 7.5 Hz, *o*-Ph), 7.34 (s, 1, Biad), 7.25 (t, 2, J_{HH} = 8 Hz, *m*-Ph), 7.11 (s, 1, Biad), 7.06 (t, 1, J_{HH} = 7.5 Hz, *p*-Ph), 6.91 (s, 3, *m*,*p*-Ar), 3.65 (sept, 2, J_{HH} = 7.0 Hz, C*H*Me_2), 2.37 (AB q, 6, Ad-CH_2), 2.28 (AB q, 6, Ad-CH_2), 2.21 (s, 3, Biad), 2.14 (br d, 6, Ad-C*H*), 2.13 (s, 3, Biad), 1.90 (s, 3, CH(CH_3)(MePh)), 2.1−1.82 (m, 12, Ad), 1.78 (s, 3, Biad), 1.74 (s, 3, Biad), 1.16 (d, 6, J_{HH} = 7.0 Hz, CH(CH_3)(Me)), 1.15 (s, 3, C(CH_3)(Me)Ph)), 0.94 (d, 6, J_{HH} = 7.0 Hz, CH(CH_3)(Me)), *anti* δ 12.88 (s, 1, C*H*R), 7.75 (d, 2, J_{HH} = 7.5 Hz, *o*-Ph), 7.29 (t, 2, J_{HH} = 8.0 Hz, *m*-Ph), 7.12 (s, 1, Biad), 3.48 (sept, 2, C*H*Me_2), 1.42 (d, 6, CH(CH_3)(Me)), 1.03 (d, 6, CH(CH_3)(Me)); $^{13}C\{^1H\}$ 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-*i*-$Pr_2C_6H_3$)($CHCMe_2Ph$)[(*S*)-Biad]. Solid benzylpotassium (2.04 equiv, 53 mg, 0.41 mmol) was added in portions to a solution of (*S*)-H_2[Biad] (102 mg, 0.2 mmol) in THF (6 mL). After 10 min, Mo(N-2,6-*i*-$Pr_2C_6H_3$)($CHCMe_2Ph$)($OTf)_2$(DME) (158 mg, 0.2 mmol) in THF (2 mL) was added. After 1 h, the volatile components were removed in vacuo. The residue was dissolved in toluene (2 mL), and the solution was concentrated again in vacuo in order to remove residual THF. The solid was then extracted with pentane (10 mL). The suspension was filtered through Celite, and the filtrate's volume was reduced to ∼1 mL. A golden precipitate formed when the solution stood for 1 h at room temperature, which was collected by filtration and dried in vacuo; yield 62 mg (34%).

Mo(N-2,6-$Et_2C_6H_3$)($CHCMe_2Ph$)[(*S*)-Biad]. Benzylpotassium (2.08 equiv, 146 mg, 1.12 mmol) was added in portions to a stirred solution of (*S*)-H_2[Biad] (275 mg, 0.54 mmol) in THF (30 mL). After 30 min solid Mo(N-2,6-$Et_2C_6H_3$)($CHCMe_2Ph$)($OTf)_2$(DME) (412 mg, 0.54 mmol) was added. After 1 h, the volatile components were removed in vacuo and the residue was dissolved in pentane (5 mL). The red slurry was filtered through Celite. Orange microcrystals formed in the filtrate. Two crops were collected by filtration and dried in vacuo: yield 145 mg (30%); ^1H NMR *syn* δ 11.03 (s, 1, J_{CH} = 121 Hz, C*H*R), 7.37 (d, 2, J_{HH} = 7.0 Hz, *o*-Ph), 7.37 (s, 1, Biad), 7.19 (t, 2, J_{HH} = 8.0 Hz, *m*-Ph), 7.08 (s, 1, Biad), 7.02 (t, 1, J_{HH} = 7.5 Hz, *p*-Ph), 6.86−6.79 (m, 3, m, *p*-Ar), 2.93 (ABX_3 sextet, 2, CH_aH_bMe), 2.74 (ABX_3 sextet, 2, CH_aH_bMe), 2.37 (AB q, 6, Ad-CH_2), 2.28 (AB q, 6, Ad-CH_2), 2.21 (s, 3, Biad), 2.16 (br s, 3, Ad-C*H*), 2.11 (br s, 3, Ad-C*H*), 2.10 (s, 3, Biad), 1.93−1.80 (2 overlapping AB q, 12, 2 Ad-CH_2), 1.97 (s, 3, Me), 1.769 (s, 3, Biad), 1.73 (s, 3, C(CH_3)(MePh)), 1.20 (s, 3, C(CH_3)(MePh)), 1.01 (t, 6, *J* = 7.5 Hz, $CH_aH_bCH_3$); *anti* δ 12.91 (s, 1, C*H*R), 3.35 (ABX_3 m, 4, CH_aH_bMe), 0.95 (t, 6, CH_2CH_3); $^{13}C\{^1H\}$ 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-$Me_2C_6H_3$)($CHCMe_2Ph$)[Biad]. Benzylpotassium (286 mg, 2.2 mmol) was added in portions to a solution of H_2[Biad] (510 mg, 1 mmol) in THF (25 mL). After 1 h, solid Mo(N-2,6-$Me_2C_6H_3$)($CHCMe_2Ph$)($OTf)_2$(DME) (735 mg, 1 mmol) was added and the resulting dark red solution was stirred for 75 min. The reaction mixture was then concentrated in vacuo to yield a red film. The product was extracted into benzene (10 mL), and the suspension was filtered through Celite. The benzene was removed from the filtrate in vacuo, and the residue was dissolved in ether (4 mL). Orange crystals began to form at room temperature. After 20 min, the solution was cooled to −25 °C to promote additional crystallization. Two crops were collected by filtration and dried in vacuo: yield 297 mg (33%); ^1H NMR δ 11.04 (s, 1, J_{CH} = 122 Hz, C*H*R), 7.37 (s, 1, Biad), 7.31 (d, 2, *o*-Ph), 7.13 (t, 2, *m*-Ph), 7.10 (s, 1, Biad), 6.98 (t, 1, *p*-Ph), 6.69 (s, 3, Ar), 2.34 (br AB pattern, 12 H, Ad-CH_2), 2.31 (s, 6, Ar(C$H_3)_2$), 2.22 (s, 3, Biad), 2.14 (br s, 6, Ad-C*H*), 2.08 (s, 3, Biad), 1.86 (br AB pattern, 12, Ad-CH_2), 1.80 (s, 3, Biad), 1.71 (s, 3, Biad), 1.65 (s, 3, C(CH_3)(MePh)), 1.24 (s, 3, C(CH_3)(MePh)); $^{13}C\{^1H\}$ 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, 37.99, 32.94, 32.26, 30.10, 21.10, 20.96, 19.92, 17.43, 17.01.

Mo(N-2,6-$Me_2C_6H_3$)($CHCMe_2Ph$)[(S)-Biad]. Benzylpotassium (146 mg, 1.12 mmol) was added in portions to a stirred solution of (*S*)-H_2[Biad] (255 mg, 0.5 mmol) in THF (30 mL). After 30 min, solid Mo(N-2,6-$Me_2C_6H_3$)($CHCMe_2Ph$)($OTf)_2$(DME) (368 mg, 0.5 mmol) was added. After 1 h, the volatile components were removed in vacuo and benzene (10 mL) was added to the residue. The slurry was filtered through Celite, and the solvents were removed from the filtrate 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; yield 190 mg (44%).

Mo(N-2-$CF_3C_6H_4$)($CHCMe_3$)[Biad]. Benzylpotassium (52 mg, 0.4 mmol) was added in portions to a solution of H_2[Biad] (102 mg, 0.2 mmol) in toluene (6 mL). After 2 h solid Mo(N-2-$CF_3C_6H_4$)($CHCMe_3$)($OTf)_2$(DME) (142 mg, 0.2 mmol) was added. After an additional 45 min, all solvents were removed in vacuo. The dark red residue was extracted with pentane (5 mL), and the suspension was filtered through Celite. The filtrate was concentrated to 2 mL, at which point red microcrystals began to form. The solution was stored at −25 °C overnight. The red-orange microcrystals were collected by decanting the liquor and drying in vacuo: yield 68 mg (41%); ^1H NMR δ 10.64 (s, 1, J_{CH} = 120, C*H*-*t*-Bu), 7.62 (d, 1, J_{HH} = 7.8 Hz, Ar), 7.42 (s, 1, Biad), 7.11 (d, 1, J_{HH} = 7.5 Hz, Ar), 7.06 (s, 1, Biad), 6.92 (t, 1, J_{HH} = 7.8 Hz, Ar), 6.53 (t, 1, J_{HH} = 7.8 Hz, Ar), 2.45 (br q, 6, Ad-CH_2), 2.31 (br s, 6, Ad-CH_2), 2.22 (s, 3, Biad), 2.17 (br q, 6, Ad-C*H*), 2.06 (s, 3, Biad), 2.02−1.82 (multiple signals, 12, Ad), 1.76 (s, 3, Biad), 1.68 (s, 3, Biad), 1.16 (s, 9, *t*-Bu); $^{13}C\{^1H\}$ 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-$CF_3C_6H_4$)($CHCMe_3$)[(*S*)-Biad]. Solid benzylpotassium (130 mg, 1.0 mmol) was added in portions to a stirred solution of (*S*)-H_2[Biad] (254 mg, 0.5 mmol) in toluene (40 mL). After 1 h solid Mo(N-2-$CF_3C_6H_4$)($CHCMe_3$)($OTf)_2$(DME) (356 mg, 0.5 mmol) was added. After 1.5 h, the solvents were removed in vacuo and the residue was dissolved in pentane (75 mL). The suspension was filtered through Celite, and the volume of the filtrate was 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; yield 180 mg (43%).

Observation of Mo($NArPr_2$)(CHMe)[Biphen]. *cis*-2-Butene (∼20 mg) was added to a toluene-d_8 (0.7 mL) solution of Mo($NArPr_2$)($CHCMe_2Ph$)[Biphen] (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 ^1H NMR spectrum revealed a mixture of Mo($NArPr_2$)($CHCMe_2Ph$)[Biphen] (rel 16), Mo($NArPr_2$)(CHMe)[Biphen] (1.0), and *cis*-/*trans*-2-butene (rel 68): δ 13.37 (q, 1, J_{HH} = 8.5 Hz, *anti* C*H*Me), 10.64 (q, 1, J_{HH} = 6.5, *syn* C*H*Me); $K_{syn/anti}$ = 2.0.

Observation of Mo(NArPr$_2$)(CHEt)[Biphen]. A sealed NMR sample was prepared as described immediately above that contained [Biphen](NArPr$_2$)Mo(CHCMe$_2$Ph) (38 mg, 0.05 mmol), hexamethylbenzene (1−2 mg), toluene-d_8 (0.7 mL), and 3-hexene (42 mg, 0.5 mmol). After 2 days a ^{1}H NMR spectrum showed that it contained a mixture of Mo(NArPr$_2$)(CHCMe$_2$-Ph)[Biphen] and Mo(NArPr$_2$)(CHEt)[Biphen] in a 17.4:1 ratio and that $K_{syn/anti} = 3.1$: δ 12.15 (dd, 1, $J_{\mathrm{HH}} = 11.9$, 7.0 Hz, *anti* C*H*Et), 10.68 (dd, 1, $J_{\mathrm{HH}} = 6.8$, 6.4 Hz, *syn* C*H*Et).

Activation Parameters by Spin-Saturation Transfer. T_1 measurements were obtained for *syn* and *anti* isomers of Mo(NArPr$_2$)(CHCMe$_2$Ph)[Biphen] at −10 °C, where the rate of isomer interconversion is ~0.02 s^{-1}. At this temperature $T_1(syn) = 1.00$ s and $T_1(anti) = 0.72$ s. It was assumed in calculations below that $R_1(syn) = R_1(anti)$.

Rotational exchange between *syn* and *anti* isomers broaden NMR resonances to a degree that depends on the relative chemical shifts, the rate constants for exchange (k_{as} and k_{sa}), the transverse relaxation times (T_2), and the populations of the different sites.[44] The line broadening of the *anti* resonance (ω_{anti}) is a function of the transverse relaxation time, i.e., $\omega_{anti} = (\pi[T_2(\mathrm{anti})])^{-1}$. The observed relaxation time $(T_2(\mathrm{obs}))^{-1}$ is a sum of the natural line broadening $(T_2(\mathrm{nat}))^{-1}$, broadening due to the spectrometer $(T_2(\mathrm{spect}))^{-1}$, and broadening due to exchange ($T_2(\mathrm{exch})^{-1}$) (eq 7).

$$\frac{1}{T_2(\mathrm{obs})} = \frac{1}{T_2(\mathrm{nat})} + \frac{1}{T_2(\mathrm{spect})} + \frac{1}{T_2(\mathrm{exch})} \qquad (7)$$

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

Equations 8 and 9[45,46] were employed in this study. The

$$\ln\{(a_\infty + b_\infty) - (a_t + b_t)\} = -R_1 t + C \qquad (8)$$

$$\ln\left(a_t - \frac{a_\infty}{b_\infty} b_t\right) = \left[-R_1 - k_{\mathbf{ab}}\left(1 + \frac{a_\infty}{b_\infty}\right)\right] t + C \qquad (9)$$

study of the interconversion of *syn* (isomer **a**) and *anti* (isomer **b**) forms of *cis*-Pd(THT)$_2$(C$_6$BrF$_4$)$_2$[46] is analogous to the interconversion of *syn* and *anti* isomers studied here. The resonance for one isomer was selectively inverted and spectra were recorded, varying the delay time, *t* (in s), between inversion and data acquisition. The equilibrium concentrations of atropisomers **a** and **b** were a_∞ and b_∞, and the integration areas for **a** and **b** at delay time, *t*, were a_t and b_t. The relaxation time ($R_1 = T_1$) for the nuclei under investigation was obtained using eq 8. The rate constant $k_{\mathbf{ab}}$ was obtained by inserting the value for R_1 into eq 9. The derivation of these equations assumed that the relaxation times (R_1) for **a** and **b** were the same.

Applying eqs 8 and 9 to alkylidene rotation generated eqs 10 and 11, substituting *anti* for **a** and *syn* for **b**. A T_1 measurement was attempted at room temperature for [Biphen]-(NArPr$_2$)Mo(CHCMe$_2$Ph), which yielded $T_1(\mathrm{syn}) = 1.2$ s and $T_1(\mathrm{anti}) = 1$ s. The delay time was varied ($t = 0$, 0.05, 0.1, ..., 0.5, 0.6, 0.7, 0.8, 0.9, 1, 2, 12 s), and the integrated areas for syn_t and $anti_t$ were collected. The values for $t = 12$ s were assigned to be syn_∞ and $anti_\infty$, as both isomers had sufficient time to completely relax to the ground state ($t \approx 10T_1$). A linear regression of eqs 10 and 11 gave k_{as} for [Biphen](NArPr$_2$)Mo-(CHCMe$_2$Ph). 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 isomer exchange.

$$\ln\{(anti_\infty + syn_\infty) - (anti_t + syn_t)\} = -R_1 t + C \qquad (10)$$

$$\ln\left(anti_t - \frac{anti_\infty}{syn_\infty} syn_t\right) = \left[-R_1 - k_{\mathrm{as}}\left(1 + \frac{anti_\infty}{syn_\infty}\right)\right] t + C \qquad (11)$$

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Supporting Information Available: Labeled ORTEP drawings, crystallographic data, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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