Molybdenum Imido Alkylidene Complexes Containing Biphen Ligands that Have Silyl Groups Attached through the 6 and 6′ Methyl Group Carbon Atoms

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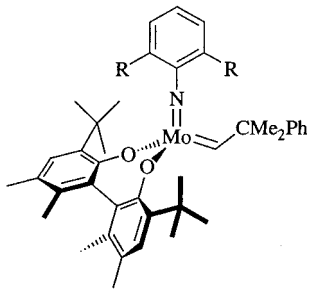
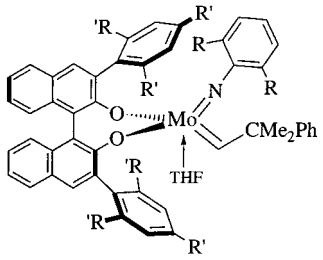
Two new biphenolate ligands were prepared starting from 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-2,2′-dimethoxy-1,1′-biphenyl via deprotonation of the 6 and 6′ methyl group with KO-*t*-Bu/*n*-BuLi, reaction with dichlorodimethylsilane or chlorotrimethylsilane, and deprotection with boron tribromide. Molybdenum imido alkylidene complexes were prepared by treating Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME) with the dipotassium salt of each biphenolate. X-ray crystallographic studies of *syn*-Mo(NAr)(CHCMe$_2$Ph)[(*rac*)-Me$_2$SiBiphen] and *syn*-Mo(NAr)(CHCMe$_2$Ph)[(*rac*)-TMS$_2$Biphen] revealed a significantly different geometry of the biphenolate ligands compared to previously structurally characterized four-coordinate biphenolate molybdenum imido alkylidene complexes. The enantiopure complexes were shown to catalyze asymmetric olefin metathesis with an enantioselectivity comparable to that of Mo(NAr)(CHCMe$_2$Ph)[(*S*)-Biphen].

Introduction

Olefin metathesis[1] is now an important carbon−carbon bond forming reaction in organic chemistry, especially in the form of ring-closing metathesis.[2,3] Interest in olefin metathesis in the past decade has been fueled as a consequence of the development of well-defined Mo[3f,g] and Ru[4] catalysts and their availability, either commercially or through reliable syntheses. A relatively recent development has been the synthesis of enantiomerically pure biphenolate (**1**) and binaphtholate (**2**) catalysts for efficient asymmetric metathesis reactions.[5] Examples include kinetic resolutions, desymmetrizations, ring-opening metathesis/cross metatheses, and ring-opening/ring-closing metathesis reactions.[5] These catalysts are enantiomerically pure variations of racemic catalysts that were employed for controlling the *cis*/*trans* structure and tacticity of polymers prepared by ring-opening metathesis polymerization.[6,7] Enantiomerically pure Mo catalysts that do not contain a biphenolate or binaphtholate ligand have been prepared, but they do not show efficiencies comparable to **1** and **2**.[8]



1a R = *i*-Pr
1b R = Me



2a R = *i*-Pr; R′= *i*-Pr
2b R = Me; R′= *i*-Pr

In the long run it would be desirable to attach catalysts for asymmetric metathesis to an insoluble

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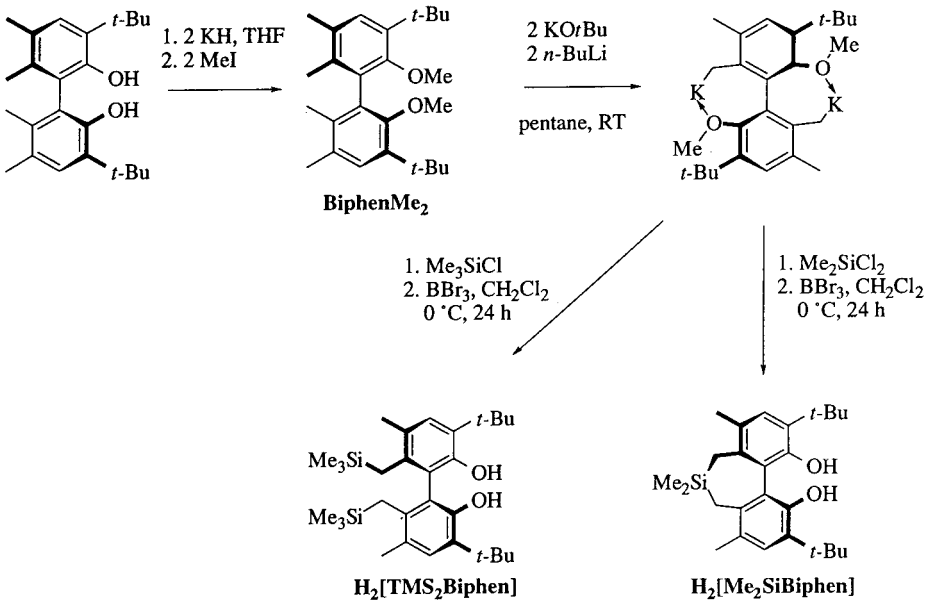
Scheme 1



support in order (i) to permit ready separation of catalyst from product and (ii) to slow bimolecular decomposition of alkylidene intermediates. Ideally one would like to attach *any* soluble catalyst to a support employing a universal coupling reaction, most desirably through the relatively remote and sterically inconsequential para position of the imido ligand. Unfortunately, we have not yet been able to conceive of a practical method of accomplishing this feat. Therefore we have turned to goals that are more immediately achievable, namely, derivatization of the biphenol or binaphthol in a way that would allow it to be attached to or incorporated into a support such as cross-linked polystyrene. The molybdenum then could be attached in the final step by addition of Mo(NAr)(CHCMe$_2$Ph)-(OTf)$_2$(dme) (NAr = N-2,6-*i*-Pr$_2$C$_6$H$_3$).[9]

In this paper we reveal one method of derivatizing the biphenolate ligand found in catalysts **1**. These catalysts also have been tested for selected asymmetric reactions and the results compared with reactions employing **1a**. Although a second method of derivatization was developed simultaneously and ultimately was the one chosen for taking the project into the next phase of supported catalyst development,[10] the method described here has potential as a means of attaching the biphenol to a support, not only in order to prepare supported metathesis catalysts but also in order to prepare asymmetric catalysts for other types of reactions. Catalysts that contain the new biphenolate ligands also are potentially useful additions to the class of enantiomerically pure homogeneous catalysts of this type that have been described in the literature so far.[5]

Results and Discussion

Modification of the Biphen Ligand. H$_2$[Biphen] (H$_2$[Biphen] = 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-2,2′-dihydroxy-1,1′-biphenyl) is readily available on a multigram scale, and resolution of both enantiomers has been reported.[5f] H$_2$[Biphen] first was protected in the form of a methyl ether (BiphenMe$_2$; Scheme 1; the S form of the ligand is shown in Scheme 1; the racemic form was employed initially). We expected that the "super base", *n*-BuLi/KO-*t*-Bu,[11] would deprotonate the methyl groups of BiphenMe$_2$ in the 5 and 5′ positions on the basis of reports in the literature on protected phenols and the apparently greater steric accessibility of the methyl groups in the 5 and 5′ positions. However, in pentane the methyl groups in the 6 and 6′ positions are deprotonated selectively. We propose that this result is the consequence of binding of the methoxy oxygen in the neighboring aromatic ring to lithium and/or potassium during the reaction and thereby directing the deprotonation. The dipotassium salt, which is shown in Scheme 1 in the proposed "methoxy-stabilized" form, precipitates as an orange-red powder from pentane and may be isolated by filtration. Addition of D$_2$O to the dipotassium salt yields the parent biphenol that contains ~85% CH$_2$D in the 6 and 6′ positions, which suggests that the deprotonation reaction is at least 85% complete. Reaction of BiphenMe$_2$ with only 1 equiv of *n*-BuLi/KO-*t*-Bu resulted in the formation of only 50% of the dipotassium salt, the remaining BiphenMe$_2$ being left in solution. Apparently the second deprotonation is faster than the first, perhaps because the rings are held in a favorable orientation as a consequence of the first deprotonation.

Treatment of the dipotassium salt with dichlorodimethylsilane or chlorotrimethylsilane followed by deprotection with boron tribromide in dichloromethane and chromatography gave the pure racemic ligands H$_2$[Me$_2$-SiBiphen] and H$_2$[TMS$_2$Biphen] in 30−40% overall yield

(6) Totland, K. M.; Boyd, T. J.; Lavoie, G. G.; Davis, W. M.; Schrock, R. R. *Macromolecules* **1996**, *29*, 6114.
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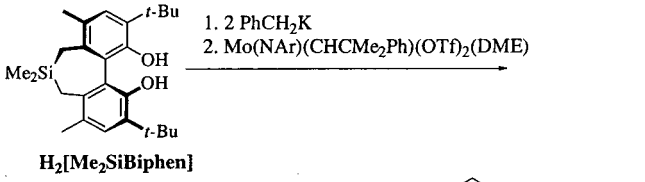
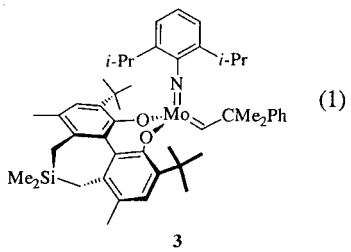
starting from BiphenMe$_2$. The enantiomerically pure (S) ligands were prepared analogously from (*S*)-H$_2$[Biphen]. Enantiomeric purity was verified by ^{31}P NMR spectroscopy of the menthyl phosphite derivative containing each biphenolate.[5f]

Synthesis and Characterization of Complexes. The molybdenum complexes **3** and **4** (eqs 1 and 2) were prepared by a standard procedure involving deprotonation of the ligand with benzyl potassium followed by addition of Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME).[9] The racemic complexes may be recrystallized from cold ether. The optically pure complexes show significantly increased solubility in hydrocarbon solvents and a decreased tendency to crystallize; (*S*)-**4** was crystallized from pentane at −20 °C in 45% yield, whereas (*S*)-**3** could not be crystallized from pentane and therefore was employed without further purification.

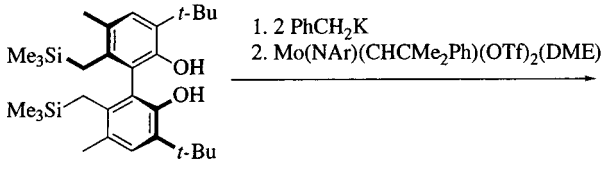


H$_2$[Me$_2$SiBiphen]

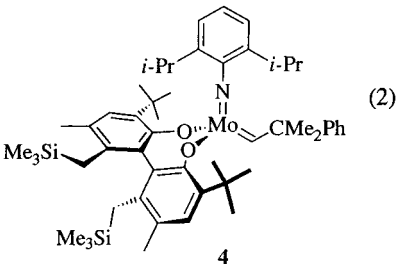


(1)

3



H$_2$[TMS$_2$Biphen]



(2)

4

The ^{1}H NMR spectrum of **3** in toluene-d_8 at 20 °C shows a major alkylidene resonance for the *syn* isomer at 11.31 ppm ($^1J_{CH}$ = 121 Hz) and a minor resonance for the *anti* isomer at 13.51 ppm; the *syn*/*anti* ratio ($K_{s/a}$) was 21.6, which is close to the value of 17.0 found for **1a**. The rate constant for conversion of the *anti* isomer of **3** to the *syn* isomer of **3** (k_{as}), determined by spin saturation methods analogous to those published for **1a**,[5f] was found to be 0.160 ± 0.004 s^{-1} at 20 °C, which is a 20-fold decrease compared to 3.7 ± 0.1 s^{-1} in **1a**. The activation parameters ($\Delta H^{\ddagger}$ = 17.7 ± 0.6 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −1.6 ± 2.0 eu) were obtained from an Eyring plot. The slight increase in activation enthalpy, compared to the value of 15.1 ± 0.6 kcal mol^{-1} found for **1a**, is the main reason for the decreased rate of *syn*/*anti* interconversion, although the *syn*/*anti* ratio remains approximately the same.

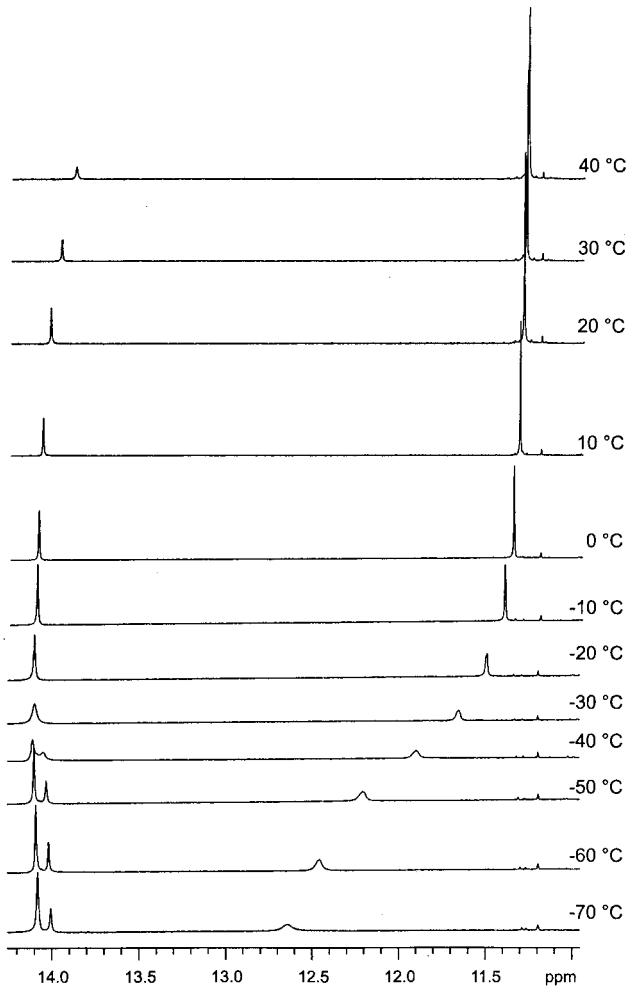


Figure 1. Temperature dependence of the ^{1}H NMR spectrum of **3** in the presence of 3.4 equiv of THF in toluene-d_8.

In the presence of THF the ^{1}H NMR spectrum of **3** at 20 °C shows one *syn* resonance at 11.29 ppm, which corresponds to the largely THF-free species, and one *anti* resonance at 14.02 ppm, which corresponds to what is largely a THF adduct (Figure 1). The *anti* isomer binds THF more tightly as a consequence of its increased Lewis acidity.[5f] The slight upfield shift in the *anti* resonance between 0 and 40 °C *may* indicate that a significant amount of THF-free *anti* form is present in rapid equilibrium with the THF adduct at the higher temperatures. The *syn*/*anti* ratio shifts from 3.5 at 20 °C to 0.45 at −30 °C (Figure 1). A plot of ln $K_{s/a}$ vs 1/T led to a value for the reaction enthalpy (ΔH_r) of 6.9 ± 0.2 kcal mol^{-1} and a large positive reaction entropy (ΔS_r = 25.9 ± 0.8 eu), which is consistent with loss of THF from the *anti* isomer during the isomerization reaction. The large downfield shift of the *syn* resonance between −10 and −70 °C suggests that a significant amount of the sample consists of a THF adduct at the lower temperatures, which is in rapid equilibrium with the THF-free species. At −40 °C the *anti* resonance splits into two as a consequence of a slowing of THF dissociation from the two diastereotopic CNO faces of the complex. At −70 °C the ratio of the two *anti* THF adducts is 2.7:1. The observation of only one (broad)

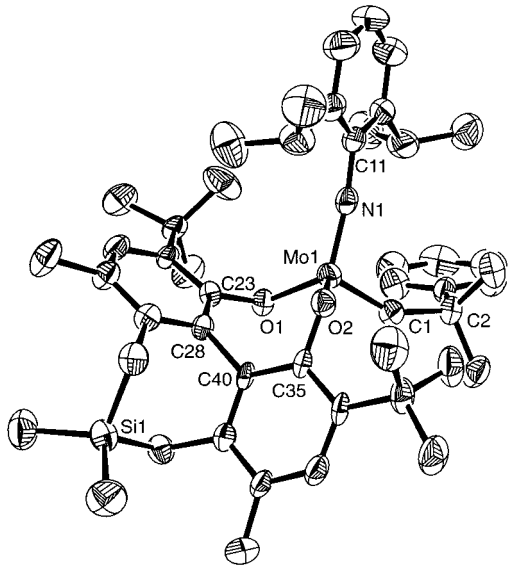


Figure 2. ORTEP diagram of the molecular structure of (*rac*)-**3**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for the sake of clarity.

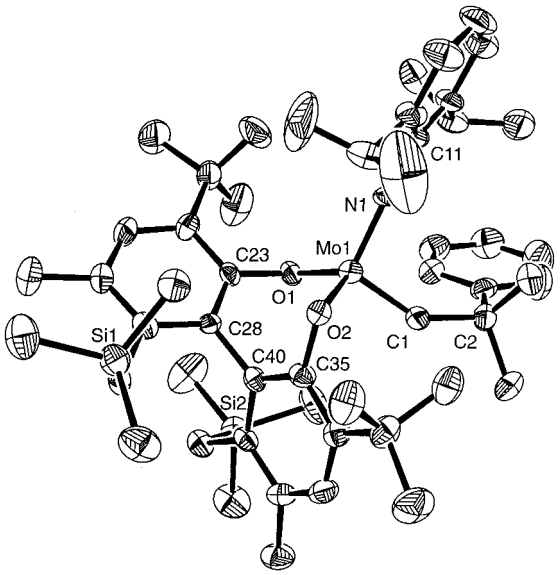


Figure 3. ORTEP diagram of the molecular structure of (*rac*)-**4**. Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for the sake of clarity.

resonance for the *syn* THF adduct at −70 °C may be attributed either to selective formation of only one diastereomer or to a fast exchange between the two diastereomers via THF dissociation even at −70 °C. The behavior found here strongly resembles that found for **1a**.[5f]

The NMR behavior of **4** was found to be analogous to that of **3**, although **4** was not investigated in detail. At 22 °C the value of $K_{s/a}$ was found to be ∼150; we believe the *anti* rotamer to be more disfavored for **4** as a consequence of unfavorable steric interactions of the neophylidene ligand with one of the trimethylsilylmethyl groups, according to an X-ray study (see below).

Molecular Structures of Mo(NAr)(CHCMe$_2$Ph)[(*rac*)-Me$_2$SiBiphen] and Mo(NAr)(CHCMe$_2$Ph)[(*rac*)-TMS$_2$Biphen]. Clear brick-red crystals of (*rac*)-**3** and (*rac*)-**4** suitable for X-ray diffraction were obtained by slowly cooling concentrated ether solutions of each to −20 °C. ORTEP drawings of the structures of **3** and **4** are shown in Figures 2 and 3. Crystallographic data can be found in Table 1. Complexes **3** and **4** are solvent-free *syn* isomers; that is, the alkylidene substituent points toward the imido ligand. The overall geometry is similar to that found in (*S*)-**1a**,[5f] Mo(NAr′)(CHCMe$_2$Ph)(*t*-Bu$_4$Me$_2$Biphen) (NAr′ = N-2,6-Me$_2$C$_6$H$_3$; *t*-Bu$_4$Me$_2$Biphen = 6,6′-dimethyl-3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diolate),[6] Mo(NAr)(CHCMe$_2$Ph)(Bitet) (Bitet = 5,5′,6,6′,7,7′,8,8′-octahydro-3,3′-di-*tert*-butyl-1,1′-dinaphthyl-2,2′-diolate),[5i] and other four-coordinate molybdenum imido alkylidene complexes.[12] However, there are significant differences in detail between **3** and **4** and two of the other three structures. These five structures are compared in Table 2.

The most striking feature of **3** is a significantly decreased dihedral angle between the two aromatic rings; the C35−C40−C28−C23 dihedral angle is 78.7(5)°, compared with 102.2° in (*S*)-**1a**, 102.5° in Mo(NAr′)(CHCMe$_2$Ph)(*t*-Bu$_4$Me$_2$Biphen), and 88.6(15)° in Mo(NAr)(CHCMe$_2$Ph)(Bitet). The dihedral angle in **4** (84.3(7)°) is slightly larger than that in **3**, but still significantly smaller than the dihedral angles in (*S*)-**1a** and Mo(NAr′)(CHCMe$_2$Ph)(*t*-Bu$_4$Me$_2$Biphen). Similarly, the bite angles of the biphenolate ligands in **3** and **4** (O(1)−Mo(1)−O(2) = 111.73(11)° in **3** and 115.46(16)° in **4**) are significantly smaller than the 127.0(2)° observed in (*S*)-**1a**. The Mo−O−C$_{ipso}$ angles in **3** (108.5(2)°, 109.4(2)°) and **4** (101.5(3)°, 108.8(3)°) are slightly larger than those in (*S*)-**1a** (97.1(4)°, 96.8(4)°), which could lead to slightly more π-donation from the oxygen

Table 1. Experimental Data of the Crystal Structure Determination of Mo(NAr)(CHCMe$_2$Ph)[(*rac*)-Me$_2$SiBiphen] ((*rac*)-3) and Mo(NAr)(CHCMe$_2$Ph)[(*rac*)-TMS$_2$Biphen] ((*rac*)-4)

	(*rac*)-**3**	(*rac*)-**4**
empirical formula	$C_{48}H_{65}MoNO_2Si$	$C_{52}H_{77}MoNO_2Si_2$
fw	812.04	900.27
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	11.353(6)	11.245(2)
b, Å	12.937(12)	44.656(8)
c, Å	17.105(12)	11.245(2)
α, deg	87.23(6)	90
β, deg	71.28(4)	115.385(3)
γ, deg	67.36(6)	90
V, Å^3	2188(3)	5102.0(17)
Z	2	4
ρ_{calcd}, g cm^{-3}	1.233	1.172
μ(Mo Kα), mm^{-1}	0.364	0.341
F(000)	864	1928
wavelength	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
T, K	293(2)	293(2)
θ range	2 to 24	2 to 22.5
index ranges	*h*, −8 to 12; *k*, −6 to 14; *l*, −14 to 18	*h*, −11 to 12; *k*, −48 to 43; *l*, −12 to 11
no. of rflns measd	4216	19 310
no. of indep rflns	4171 (R_{int} = 0.0503)	6643 (R_{int} = 0.1152)
GOF	0.993	1.017
R	0.0326	0.0639
wR_2 ($I > 2\sigma(I)$)	0.0855	0.0963
largest *e*-max, *e*-min, e·Å^{-3}	0.366, −0.391	0.352, −0.382

(12) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1.

Table 2. Comparison of Bond Lengths (Å) and Angles (deg) in Biphenolate Imido Alkylidene Complexes

	(*rac*)-**3**	(*rac*)-**4**	(*S*)-**1a**[a]	Mo(*t*-Bu$_4$Me$_2$Biphen)[b]	Mo(Bitet)[c]
Mo1−O1	1.941(3)	1.957(3)	1.999(5)	1.990(6)	1.949(8)
Mo1−O2	1.948(3)	1.958(4)	2.006(5)	2.003(6)	1.980(9)
Mo1−C1	1.878(4)	1.863(5)	1.885(10)	1.868(9)	1.919(13)
Mo1−N1	1.729(3)	1.721(5)	1.738(6)	1.731(8)	1.761(11)
O1−Mo1−O2	111.73(11)	115.46(16)	127.0(2)	123.6(2)	119.9(5)
Mo1−C1−C2	151.1(3)	147.0(5)	143.8(7)	144.5(7)	146.4(11)
Mo1−O1−C23	108.5(2)	108.8(3)	97.1(4)	96.5(5)	102.8(7)
Mo1−O2−C35	109.4(2)	101.5(3)	96.8(4)	103.5(5)	102.0(8)
Mo1−N1−C11	172.6(3)	171.9(4)	169.0	173.6(8)	169.9(11)
N1−Mo1−O1	118.85(15)	115.01(19)	110.2(2)	108.5(3)	105.9(5)
N1−Mo1−O2	107.38(14)	111.14(19)	107.9(3)	114.3(3)	115.0(5)
N1−Mo1−C1	106.25(15)	102.4(2)	105.2(3)	100.3	106.0(6)
O1−Mo1−C1	101.45(15)	100.62(19)	96.8	106.9	109.5(4)
O2−Mo1−C1	110.83(16)	110.8(2)	107.0	100.0	99.6(5)
C35−C40−C28−C23	78.7(5)	84.3(7)	102.2	102.5	88.6(15)

[a] See ref 5f. [b] Mo(*t*-Bu$_4$Me$_2$Biphen) = *syn*-Mo(NAr′)(CHCMe$_2$Ph)(6,6′-dimethyl-3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diolate); see ref 6. [c] Mo(Bitet) = *syn*-Mo(NAr)(CHCMe$_2$Ph)(5,5′,6,6′,7,7′,8,8′-octahydro-3,3′-di-*tert*-butyl-1,1′-dinaphthyl-2,2′-diolate); see ref 5i.

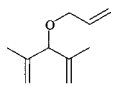
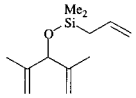
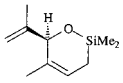
atoms in **3** and **4** compared with (*S*)-**1a**. The Mo−O bond lengths in **3** and **4** (1.941−1.958 Å) are shorter than in **1a** (1.999 and 2.006 Å), consistent with more π-donation from the oxygen atoms in **3** and **4**. The Mo−C$_\alpha$−C$_\beta$− angles of 151.1(3)° in **3** and 147.0(5)° in **4** are in the normal range for *syn* alkylidenes,[12] although they are the largest among the five compounds in Table 2.

We were surprised to find that the biphenolate ligands in **3** and **4** are both "flatter" (by ∼20° in the C(35)−C(40)−C(28)−C(23) dihedral angle) than the biphenolate ligands in (*S*)-**1a**. A flatter ligand in **3** was expected in view of effectively tying two methyl groups together with a SiMe$_2$ bridge. The flatter ring in **4** was a surprise. We suggest that the flatter ring in **4** is a consequence of increased steric interaction (relative to the biphenoxide ligand in **1a**) between the TMS group that contains Si(2) and the alkylidene and between the TMS group that contains Si(1) and an amido isopropyl group. Since the TMS groups that contain Si(1) and Si(2) turn away from each other, there is little or no additional steric interaction between them in **4** compared to **1a**. The similarity between the structures of **3** and **4** and that of Mo(NAr)(CHCMe$_2$Ph)(Bitet) is also now understandable; the "flatter" biphenolate ring in Mo(NAr)(CHCMe$_2$Ph)(Bitet) was also rationalized in terms of additional steric interaction between the hydrogenated binaphtholate rings and the other bulky groups in the molecule.[5i]

It should be kept in mind that both *syn* and *anti* isomers are accessible during the course of a typical reaction and that it is not yet known which, if either, is the more reactive and/or enantioselective in an asymmetric metathesis reaction. Therefore differences between the solid-state structures of *syn* alkylidenes may not be useful for rationalizing differences in behavior in an asymmetric metathesis reaction, as we show in the next section.

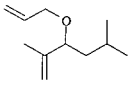
Asymmetric Ring-Closing Metathesis. How complexes **3** and **4** perform in several typical catalytic asymmetric metathesis reactions are shown in Tables 3−5. Catalytic desymmetrization of substrate **5** in C_6D_6 at room temperature using (*S*)-**3** and (*S*)-**4** gave the ring-closed product with slightly higher enantioselectivity than observed for (*S*)-**1a** and in high yield (Table 3, entry 1). As is the case with (*S*)-**1a** as a catalyst,[5c] (*S*)-**3** and (*S*)-**4** are less successful (in terms of % ee) in desymmetrization reactions that give six-membered rings (Table 3, entry 2), and some homocoupled product of the starting material is observed. The % ee employing (*S*)-**3** and (*S*)-**4** decreases with increasing temperature, which contrasts with results obtained using Mo(NAr)(CHCMe$_2$Ph)(Bitet),[5i] where a 96% ee is observed at 80 °C. In the kinetic resolution of the 1,6-diene, **7** (Table 4), both new catalysts are more selective at room temperature than (*S*)-**1a**. Whereas (*S*)-**4** is only slightly more selective than (*S*)-**1a**, the k_{rel} values for **7** obtained with (*S*)-**3** exceed the value of 23 obtained with (*S*)-**1a**

Table 3. Catalytic Desymmetrization of Trienes 5 and 6 by (*S*)-3 and (*S*)-4[a]

entry	substrate	product	cat. (5 mol%)	*T* (°C); time (h)	conv. (%);[b] dimer (%)[b]	product ee%[c]
1	 **5**		(*S*)-**1a**[d]	22; 6	94; --	93
			(*S*)-**3**	22; 1	89; --	97
			(*S*)-**4**	22; 1.5	88; --	97
2	 **6**		(*S*)-**1a**[e]	22; 24	50; 32	65
			(*S*)-**3**	22; 26	46; 22	60
				60; 24	52; 21	42
			(*S*)-**4**	22; 26	63; 6	27
				70; 24	56; 19	22
			(*R*)-Mo(Bitet)[f]	80; 3	69; 11	96

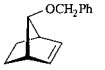
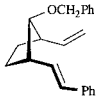
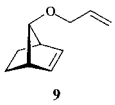
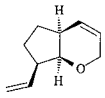
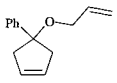
[a] Conditions: 5 mol % cat., C_6D_6. [b] Conversion determined by ^{1}H NMR analysis of the crude reaction mixture. The "dimer" is the homocoupled product formed from the substrate via loss of ethylene. Essentially no dimer was formed from **5**. [c] Determined by chiral GLC. [d] See ref 5b. [e] See ref 5c. [f] (*R*)-Mo(Bitet) = Mo(NAr)(CHCMe$_2$Ph)[(*R*)-(5,5′,6,6′,7,7′,8,8′-octahydro-3,3′-di-*tert*-butyl-1,1′-dinaphthyl-2,2′-diolate)]; see ref 5i.

Table 4. Kinetic Resolution of an Allylic Ether

substrate	product	cat.	*T* (°C); time (min)	conv. (%)[b]	unre. subst. ee%[c]	k_{rel}[d]
 **7**		(*S*)-**1a**	22; 15	79	99	7
			-25; 600	56	95	23[e]
		(*S*)-**3**	22; 35	56	97	30
		(*S*)-**4**	22; 20	45	61	13

[a] Conditions: 5 mol % cat., C_6D_6 or toluene-d_8. [b] Conversion determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Determined by chiral GLC. [d] Calculated from the % ee of the unreacted starting material; see: Kagan, H. B.; Fiaud, J. C. *Top. Stereochem.* **1988**, *18*, 249. [e] See ref 5b.

Table 5. Tandem Catalytic Asymmetric Ring-Opening Metathesis/Cross Metathesis[a] and Tandem Catalytic Asymmetric Ring-Opening Metathesis/Ring-Closing Metathesis[b]

entry	substrate	product	cat.	time (min); conv. (%)[c]	product ee%
1[a]	 **8**		(*S*)-**1a**	30; 100	99[d]
			(*S*)-**3**	30; 100	99[d]
			(*S*)-**4**	60; 100	99[d]
2[b]	 **9**		(*S*)-**1a**	30; 100	69[e]
			(*S*)-**3**	15; 100	58[e]
			(*S*)-**4**	20; 100	73[e]
3[b]	 **10**		(*S*)-**1a**	30;100	21[e]
			(*S*)-**3**	75; 100	32[e]
			(*S*)-**4**	120; 100	42[e]

[a] Conditions: 5 mol % catalyst, 2 equiv of styrene, 22 °C, C_6D_6. [b] Conditions: 5 mol % catalyst, 22 °C, C_6D_6. [c] Conversion determined by ^{1}H NMR analysis of the crude reaction mixture. [d] Determined by chiral HPLC. [e] Determined by chiral GLC.

at −20 °C in toluene. Asymmetric ring-opening metathesis/cross metathesis (Table 5, entry 1) proceeds to high conversion with high enantioselectivity and with >98% *trans* selectivity with (*S*)-**3** and (*S*)-**4**, comparable to results obtained with (*S*)-**1a**. Although asymmetric ring-opening metathesis/ring-closing metatheses (Table 5, entries 2 and 3) give the desired products in high conversion, the enantioselectivites are not high, which is similar to enantioselectivities obtained with (*S*)-**1a**.

We were surprised to find that (*S*)-**3** and (*S*)-**4** behave so similarly and that their behavior is not *much* different from that of (*S*)-**1a**, at least with the substrates employed so far. Many asymmetric metathesis reactions that we have examined so far are relatively sensitive to the nature of the catalyst.[5h] Therefore we had anticipated that joining the 6 and 6′ methyl groups together would constitute a significant change and would lead to dramatically different results in asymmetric reactions. So far that does not appear to be the case. An explanation of the differences that are observed, especially the difference between the performance of (*S*)-**4** and (*R*)-Mo(Bitet) in ring-closing **6** at higher temperatures, has not been forthcoming.

Conclusions

We have shown that the methyl groups in the 6 and 6′ positions in 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-2,2′-dimethoxy-1,1′-biphenyl can be deprotonated by *n*-BuLi/KO-*t*-Bu and that silyl groups can be attached to give either "linked" or "unlinked" new biphenols. These new biphenols can be employed to yield molybdenum imido alkylidene complexes whose behavior in solution does not differ significantly from the behavior of **1a**, in terms of enantioselectivity, in most asymmetric metathesis reactions that were explored. However, since the number of substrates examined was small and some differences between various catalysts were observed, we do not yet know whether this will be true in general. Although we have chosen to pursue derivatization of 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-2,2′-dimethoxy-1,1′-biphenyl through the 5 and 5′ positions as a means of preparing a supported catalyst,[10] the method described here still has potential, not only in order to prepare supported metathesis catalysts but to prepare asymmetric catalysts for other types of reactions.

Experimental Section

General Procedures. ^{1}H NMR (300, 400, or 500 MHz) and ^{13}C NMR (75, 100, 125 MHz) spectra were recorded on Varian or Bruker spectrometers. Chemical shifts in ^{1}H NMR spectra are reported in ppm from tetramethylsilane with the undeuterated portion of the solvent as internal standard ($CDCl_3$ δ 7.24, C_6D_6 δ 7.15). Chemical shifts in ^{13}C NMR spectra are reported in ppm from tetramethylsilane with the solvent as internal standard ($CDCl_3$ δ 77.0, C_6D_6 δ 128.0). ^{31}P NMR spectra were recorded at 121.5 MHz and were referenced versus an external standard of PPh_3 in C_6D_6 (δ −4.80 ppm). Enantiomer ratios were determined by chiral GLC analysis (Alltech Associates Chiraldex GTA column (30 m × 0.25 mm) or BETADEX 120 column (30 m × 0.25 mm)) or chiral HPLC analysis (Chiral Technologies Chiralcel OJ) in comparison to authentic racemic materials. High-resolution mass spectrometry was performed at MIT. Elemental analyses were performed by H. Kolbe, Mikroanalytisches Laboratorium (Mühlheim an der Ruhr, Germany).

All reactions were conducted in oven-dried (135 °C) and flame-dried glassware under an inert atmosphere of dry dinitrogen employing standard Schlenk and glovebox techniques. Benzene, THF, and DME were distilled from sodium/benzophenone ketyl. *n*-Pentane was stirred over concentrated H_2SO_4 for 5 days, washed with water, dried over $CaCl_2$, degassed, and then passed through two l-gallon columns of activated alumina. CH_2Cl_2 was distilled from CaH_2. Toluene and Et_2O were degassed and then passed through two l-gallon columns of activated alumina.[13]

Benzyl potassium,[14] $PhCMe_2CH_2MgCl$,[15] Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME),[9] and (*rac*)-H_2[Biphen][16]were prepared according to literature procedures. (*rac*)-H_2[Biphen] was resolved via its diasteromeric phosphates.[5f] Potassium hydride was purchased from Aldrich as a 35% dispersion in mineral oil, washed repeatedly with pentane, and dried in vacuo. All other reagents were used as received. Catalytic asymmetric metathesis reactions were carried out under conditions as reported in the literature.[5]

(*rac*)-3,3′-Di-*tert*-butyl-5,5′,6,6′-tetramethyl-2,2′-dimethoxy-1,1′-biphenyl ((*rac*)-BiphenMe$_2$). A −20 °C solution of (*rac*)-H_2[Biphen] (10.00 g, 28.2 mmol) in THF (150 mL) was treated with small portions of solid KH (2.40 g, 59.9 mmol). The suspension was allowed to warm to room temperature and was stirred for 3 h. Methyl iodide (8.60 g, 60.6 mmol) was then added, and the mixture stirred for 16 h. The solvent was removed in vacuo, and the remaining white solid was extracted with toluene (3 × 30 mL). The solution was filtered to remove KI, and the filtrate was concentrated in vacuo to give (*rac*)-BiphenMe$_2$ (10.73 g, 99% yield) as a colorless oil, which slowly crystallized: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (s, 2, aryl-H), 3.10 (s, 6, OCH_3), 2.25, 1.89 (s, 6, aryl-CH_3), 1.37 (s, 18, C(CH_3)$_3$); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 155.7, 139.5, 134.6, 132.5, 130.5, 127.2 (aryl), 59.3 (OCH$_3$), 34.6 (*C*(CH$_3$)$_3$), 30.8 (C(*C*H$_3$)$_3$), 20.5, 16.6 (aryl-*C*H$_3$); HRMS calcd for $C_{26}H_{38}O_2$ 382.2872, found 382.2866.

(*S*)-3,3′-Di-*tert*-butyl-5,5′,6,6′-tetramethyl-2,2′-dimethoxy-1,1′-biphenyl ((*S*)-BiphenMe$_2$). A solution of (*S*)-H_2[Biphen]

(13) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
(14) Lochmann, L.; Trekoval, J. *J. Organomet. Chem.* **1987**, *326*, 1.
(15) Schrock, R. R.; Sancho, J.; Pedersen, S. F. *Inorg. Synth.* **1989**, *26*, 44.
(16) Albert, H. E. *J. Am. Chem. Soc.* **1954**, *76*, 4983.

(7.08 g, 20.0 mmol) in THF (60 mL) was treated with small portions of solid KH (1.70 g, 42.4 mmol), and the resulting mixture was stirred for 4 h. Methyl iodide (6.70 g, 47.2 mmol) was then added and the mixture stirred for 16 h. The solvent was removed in vacuo, and the remaining oily solid was extracted with toluene (2 × 20 mL). The solution was filtered to remove KI, and the filtrate was concentrated in vacuo to give (*S*)-BiphenMe$_2$ (6.62 g, 87% yield) as a white crystalline solid.

(*rac*)-Me$_2$SiBiphenMe$_2$. A solution of *n*-BuLi (18 mL, 1.5 M in hexanes, 27 mmol) was added to a suspension of (*rac*)-BiphenMe$_2$ (5.07 g, 13.3 mmol) and potassium *tert*-butoxide (3.00 g, 26.7 mmol) in pentane (100 mL) at room temperature. The suspension turned orange-red, and a red solid started to precipitate. After 9 h the suspension was filtered and the solid washed with pentane (50 mL). The solid was dissolved in THF (100 mL) at −20 °C, and dichlorodimethylsilane (7.10 g, 55 mmol) was added. The milky suspension was stirred for 18 h at room temperature. The solvent and excess silane were then removed in vacuo, and the residual solid was extracted with toluene (50 + 2 × 30 mL). The mixture was filtered in order to remove KCl, and the filtrate was concentrated in vacuo to give (*rac*)-Me$_2$SiBiphenMe$_2$ (5.56 g, 95%) as an off-white foam, which was used without further purification for the deprotection step: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (s, 2, aryl), 2.94 (s, 6, OCH_3), 2.24 (s, 6, aryl-CH_3), 1.97, 1.55 (d, $^2J_{HH}$ = 13.4, 2, aryl-CH_2), 1.37 (s, 18, C(CH_3)$_3$), 0.07 (s, 6, Si(CH_3)$_2$); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 156.3, 138.0, 136.0, 130.0, 127.4, 127.0 (aryl), 58.9 (OCH_3), 34.6 (*C*(CH$_3$)$_3$), 30.7 (C(*C*H$_3$)$_3$), 20.7 (aryl-*C*H$_3$), 18.2 (aryl-CH_2), −3.2 (Si(CH$_3$)$_2$); HRMS calcd for $C_{28}H_{42}O_2Si$ 438.2954, found 438.2964.

(*rac*)-H$_2$[Me$_2$SiBiphen]. A solution of (*rac*)-Me$_2$SiBiphenMe$_2$ (5.56 g, 12.7 mmol) in CH_2Cl_2 (100 mL) was treated with a solution of boron tribromide (26 mL, 1 M in CH_2Cl_2, 26 mmol) at −30 °C. The dark brown solution was allowed to warm to room temperature and stirred for 24 h. The reaction was quenched by addition of water (40 mL), and the organic layer was separated and dried over $MgSO_4$. The solvent was removed in vacuo, and the residual oil was subjected to column chromatography with hexane as eluent to give pure colorless microcrystals of (*rac*)-H$_2$[Me$_2$SiBiphen] (2.24 g, 43% yield) from the first fraction (R_f = 0.2): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (s, 2, aryl), 5.00 (s, 2, aryl-OH), 2.20 (s, 6, aryl-CH_3), 1.94, 1.44 (d, $^2J_{HH}$ = 13.4, 2, aryl-CH_2), 1.38 (s, 18, C(CH_3)$_3$), 0.01 (s, 6, Si(CH_3)$_2$); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 149.2, 136.7, 132.2, 128.8, 125.5, 119.1 (aryl), 34.5 (*C*(CH$_3$)$_3$), 29.7 (C(*C*H$_3$)$_3$), 20.3 (aryl-*C*H$_3$), 18.7 (aryl-CH_2), −3.3 (Si(CH$_3$)$_2$); HRMS calcd for $C_{26}H_{38}O_2Si$ 410.2641, found 410.2651. Anal. Calcd for $C_{26}H_{38}O_2Si$: C 76.04, H 9.33. Found: C 75.88, H 9.39.

(*rac*)-Me$_2$SiBiphenP(OMen). To a solution of (*rac*)-H$_2$[Me$_2$SiBiphen] (50 mg, 122 μmol) and triethylamine (50 mg, 0.49 mmol) in CH_2Cl_2 (2.5 mL) was added a solution of (−)-menthyldichlorophosphite (40 mg, 156 μmol) in CH_2Cl_2 (2.5 mL) at room temperature. The solution was stirred for 3 h and then evaporated to dryness. The remaining solid was taken up in $CDCl_3$ (0.6 mL) and filtered into a NMR tube: ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 144.1 ((*R*)-Me$_2$SiBiphenP(OMen)), 138.6 ((*S*)-Me$_2$SiBiphenP(OMen)).

(*S*)-H$_2$[Me$_2$SiBiphen]. A solution of *n*-BuLi (11 mL, 1.5 M in hexanes, 16.5 mmol) was added to a suspension of (*S*)-BiphenMe$_2$ (3.01 g, 7.9 mmol) and potassium *tert*-butoxide (1.87 g, 16.7 mmol) in pentane (50 mL) at room temperature. The suspension turned orange-red, and a red solid started to precipitate. After 19 h the suspension was filtered, the solid was dissolved in THF (50 mL) at −78 °C, and dichlorodimethylsilane (2.0 mL, 2.13 g, 16.5 mmol) was added dropwise. The solution was allowed to warm to room temperature and stirred for 3 h. The solvent and excess silane were removed in vacuo. The remaining solid was extracted with toluene (3 × 10 mL). The extract was filtered in order to remove KCl and the filtrate concentrated in vacuo. The yellow oil was dissolved in CH_2Cl_2 (50 mL) and treated with a solution of boron tribromide (8 mL, 1 M in CH_2Cl_2, 8 mmol) at 0 °C. The dark brown solution was allowed to warm to room temperature and stirred for 24 h. The reaction was quenched by addition of water (10 mL), and the organic layer was separated and dried over $MgSO_4$. The solvent was removed in vacuo, and the residual oil was subjected to column chromatography with hexanes as eluent to give a colorless oil of (*S*)-H$_2$[Me$_2$SiBiphen] (0.99 g, 31% yield) from the first fraction, which crystallized slowly upon standing at −25 °C.

(*rac*)-3,3′-Di-*tert*-butyl-2,2′-dimethoxy-5,5′-dimethyl-6,6′-bis-trimethylsilanylmethyl-1,1′-biphenyl ((*rac*)-TMS$_2$-BiphenMe$_2$). To a suspension of (*rac*)-BiphenMe$_2$ (765 mg, 2.00 mmol) and potassium *tert*-butoxide (463 mg, 4.13 mmol) in pentane (13 mL) was added a solution of *n*-BuLi (2.7 mL, 1.5 M in hexane, 4.1 mmol) at room temperature. The suspension turned orange-red and a red solid started to precipitate. After 20 h, the suspension was filtered and the solid washed with pentane (6 mL). The solid was dissolved in THF (15 mL) at −20 °C, and chlorotrimethylsilane (1.00 g, 9.20 mmol) was added. The milky suspension was stirred for 15 min at room temperature. The solvent and excess silane were removed in vacuo, and the residual solid was extracted with toluene (3 × 10 mL). The extract was filtered in order to remove KCl, and the filtrate was concentrated in vacuo to give (*rac*)-TMS$_2$BiphenMe$_2$ (1.01 g, 96%) as a yellow oil, which was used without further purification for the deprotection step: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (s, 2, aryl), 3.24 (s, 6, OCH_3), 2.17 (s, 6, aryl-CH_3), 1.74, 1.68 (d, $^2J_{HH}$ = 13.7, 2, aryl-CH_2), 1.35 (s, 18, C(CH_3)$_3$), −0.12 (s, 18, Si(CH$_3$)$_3$); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 154.9, 138.6, 137.9, 132.1, 129.7, 127.7 (aryl), 59.3 (OCH_3), 34.5 (*C*(CH$_3$)$_3$), 31.2 (C(*C*H$_3$)$_3$), 22.0 (aryl-CH_2), 21.9 (aryl-*C*H$_3$), 0.3 (Si(CH$_3$)$_3$); HRMS calcd for $C_{32}H_{54}O_2Si_2$ 526.3662, found 526.3651.

(*rac*)-3,3′-Di-*tert*-butyl-5,5′-dimethyl-6,6′-bistrimethylsilanylmethyl-1,1′-biphenyl-2,2′-diol ((*rac*)-H$_2$[TMS$_2$Biphen]). A solution of (*rac*)-TMS$_2$BiphenMe$_2$ (3.97 g, 7.53 mmol) in CH_2Cl_2 (50 mL) was treated with a solution of boron tribromide (17 mL, 1 M in CH_2Cl_2, 17 mmol) at 0 °C. The dark brown solution was allowed to warm to room temperature and stirred for 14 h. The reaction was quenched by addition of water (20 mL), and the organic layer was separated and dried over $MgSO_4$. The solvent was removed in vacuo, and the residual oil was subjected to column chromatography with hexane as the eluent to give pure colorless microcrystals of (*rac*)-H$_2$[TMS$_2$Biphen] (1.37 g, 36% yield) from the first fraction (R_f = 0.61): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (s, 2, aryl), 4.80 (s, 2, aryl-OH), 2.16 (s, 6, aryl-CH_3), 1.88, 1.73 (d, $^2J_{HH}$ = 13.7, 2, aryl-CH_2), 1.35 (s, 18, C(CH_3)$_3$), −0.23 (s, 18, Si(CH$_3$)$_3$); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 149.8, 138.2, 131.5, 129.0, 127.1, 119.4 (aryl), 34.5 (*C*(CH$_3$)$_3$), 29.8 (C(*C*H$_3$)$_3$), 21.3 (aryl-CH_2), 21.2 (aryl-*C*H$_3$), −0.1 (Si(CH$_3$)$_3$); HRMS calcd for $C_{30}H_{50}O_2Si_2$ 498.3349, found 498.3342. Anal. Calcd for $C_{30}H_{50}O_2Si_2$: C 72.23, H 10.10. Found: C 72.29, H 10.16.

(*rac*)-TMS$_2$BiphenP(OMen). To a solution of (*rac*)-H$_2$[TMS$_2$Biphen] (50 mg, 100 μmol) and triethylamine (50 mg, 0.49 mmol) in CH_2Cl_2 (1 mL) was added a solution of (−)-menthyldichlorophosphite (50 mg, 194 μmol) in CH_2Cl_2 (1 mL) at room temperature. The solution was stirred for 4 h and then evaporated to dryness. The remaining solid was taken up in $CDCl_3$ (0.5 mL) and filtered into a NMR tube: ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 142.5 ((*R*)-TMS$_2$BiphenP(OMen)), 136.5 ((*S*)-TMS$_2$BiphenP(OMen)).

(*S*)-3,3′-Di-*tert*-butyl-5,5′-dimethyl-6,6′-bistrimethylsilanylmethyl-1,1′-biphenyl-2,2′-diol ((*S*)-H$_2$[TMS$_2$Biphen]). To a suspension of (*S*)-BiphenMe$_2$ (3.31 g, 8.65 mmol) and potassium *tert*-butoxide (2.00 g, 17.8 mmol) in pentane (50 mL) was added a solution of *n*-BuLi (12 mL, 1.5 M in hexane, 18.0 mmol) at room temperature. The suspension turned orange-red, and a red solid started to precipitate. After 19 h the suspension was filtered. The solid was dissolved in THF (50

mL), and chlorotrimethylsilane (4.5 mL, 3.85 g, 35.4 mmol) was added at −78 °C. The suspension was allowed to warm to room temperature and stirred for 4 h. The solvent and excess silane were removed in vacuo, the residual solid was extracted with toluene (3 × 10 mL) and filtered to remove KCl, and the filtrate was concentrated in vacuo. The remaining yellow oil was dissolved in CH_2Cl_2 (50 mL) and treated with a solution of boron tribromide (13 mL, 1 M in CH_2Cl_2, 13 mmol) at 0 °C. The dark brown solution was allowed to warm to room temperature and stirred for 24 h. The reaction was quenched by addition of water (10 mL), and the organic layer was separated and dried over $MgSO_4$. The solvent was removed in vacuo, and the residual oil was subjected to column chromatography with hexane as eluent to give pure colorless crystals of (*S*)-H_2[TMS_2Biphen] (1.47 g, 34% yield) from the first fraction.

Mo(NAr)(CHCMe$_2$Ph)[(*rac*)-Me$_2$SiBiphen] ((*rac*)-3). To a solution of (*rac*)-H_2[Me_2SiBiphen] (436 mg, 1.06 mmol) in THF (8 mL) was added solid benzyl potassium (320 mg, 2.45 mmol) in small portions. After 30 min the solution was cooled to −20 °C and was added dropwise to a cold solution of Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME) (840 mg, 1.06 mmol) in THF (5 mL). The red-brown solution was stirred for 3 h at room temperature. The solvent was removed in vacuo, and the remaining brown solid was extracted with benzene (6 mL). The solution was filtered to remove potassium triflate and the filtrate concentrated in vacuo. Recrystallization from Et_2O at −20 °C gave brick-red crystals (580 mg, 67% yield): ^{1}H NMR (500 MHz, C_6D_6) δ 13.56 (s, *anti* CHR), 11.28 (s, $^1J_{CH}$ = 121, 1, *syn* CHR), 7.44 (s, 1, Biphen), 7.25 (d, $^3J_{HH}$ = 8.5, 2, *o*-Ph), 7.24 (s, 1, Biphen), 7.12 (m, 2, *m*-Ph), 7.00 (m, 1, p-Ph), 6.92 (m, 3, Ar), 3.75 (sept, $^3J_{HH}$ = 6.7, 2, C*H*(CH$_3$)$_2$), 2.22, 2.07 (s, 3, aryl-CH$_3$), 1.91 (d, $^2J_{HH}$ = 13.1, 1, aryl-CH$_2$), 1.84 (s, 3, CHC(C*H*$_3$)$_2$Ph), 1.80, 1.67 (d, $^2J_{HH}$ = 13.1, 1, aryl-CH$_2$), 1.52, 1.51 (s, 9, C(CH$_3$)$_3$), 1.38 (d, $^2J_{HH}$ = 13.1, 1, aryl-CH$_2$), 1.16 (s, 3, CHC(C*H*$_3$)$_2$Ph), 1.15, 0.92 (d, $^3J_{HH}$ = 6.7, 6, CH(C*H*$_3$)$_2$), −0.15, −0.19 (s, 3, Si(CH$_3$)$_2$); ^{13}C{^{1}H} NMR (125 MHz, C_6D_6) δ 283.5 (MoCH), 155.8, 155.6, 154.7, 150.7, 145.8, 138.2, 137.7, 136.9, 135.9 (aryl), 131.0, 129.6 (Biphen, aryl-CH), 129.5 (aryl), 128.3 (*m*-Ph), 127.7 (aryl), 127.5 (*p*-Ar), 127.2 (aryl), 126.7 (*o*-Ph), 126.0 (*p*-Ph), 123.4 (*m*-Ar), 53.8 (CH*C*Me$_2$Ph), 35.8, 35.5 (*C*(CH$_3$)$_3$), 32.4, 32.3 (CHC(*C*H$_3$)$_2$Ph), 30.9, 30.6 (C(*C*H$_3$)$_3$), 29.1 (*C*H(CH$_3$)$_2$), 24.3, 24.2 (CH(*C*H$_3$)$_2$), 21.2, 21.1 (aryl-*C*H$_3$), 20.0, 19.7 (aryl-CH$_2$), −3.3, −3.5 (Si(CH$_3$)$_2$). Anal. Calcd for $C_{48}H_{65}MoNO_2Si$: C 70.99, H 8.07, N 1.72. Found: C 70.97, H 7.94, N 1.64.

Mo(NAr)(CHCMe$_2$Ph)[(*S*)-Me$_2$SiBiphen] ((*S*)-3). To a solution of (*S*)-H_2[Me_2SiBiphen] (305 mg, 0.74 mmol) in THF (5 mL) was added solid benzyl potassium (197 mg, 1.51 mmol) in small portions. After 20 min the solution was cooled to −20 °C and was added dropwise to a cold solution of Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME) (585 mg, 0.74 mmol) in THF (5 mL). The red-brown solution was stirred for 14 h at room temperature. The solvent was removed in vacuo, and the remaining brown solid was extracted with benzene (5 mL). The solution was filtered to remove potassium triflate and the filtrate concentrated in vacuo to give a red-brown solid (520 mg, 87% yield).

Mo(NAr)(CHCMe$_2$Ph)[(*rac*)-TMS$_2$Biphen] ((*rac*)-4). To a solution of (*rac*)-H_2[TMS_2Biphen] (747 mg, 1.50 mmol) in THF (7 mL) was added solid benzyl potassium (395 mg, 3.03 mmol) in small portions. After 20 min the solution was cooled to −20 °C and was added dropwise to a cold solution of Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME) (1.20 g, 1.52 mmol) in THF (7 mL). The solution was kept at −20 °C for 14 h, after which it was allowed to warm to room temperature and was stirred for an additional 2 h. The solvent was removed in vacuo, and the remaining brown solid was extracted with benzene (3 × 2 mL). The solution was filtered to remove potassium triflate and the filtrate concentrated in vacuo. Recrystallization from pentane at −20 °C gave brick-red crystals (940 mg, 70% yield): ^{1}H NMR (500 MHz, C_6D_6) δ 13.45 (s, *anti* CHR), 10.99 (s, $^1J_{CH}$ = 122, 1, *syn* CHR), 7.45 (s, 1, Biphen), 7.41 (d, $^3J_{HH}$ = 8.5, 2, *o*-Ph) 7.24 (s, 1, Biphen), 7.22 (t, $^3J_{HH}$ = 7.9, 2, *m*-Ph), 7.05 (m, 1, *p*-Ph), 6.98 (m, 3, Ar), 3.83 (sept, $^3J_{HH}$ = 6.7, 2, C*H*(CH$_3$)$_2$), 2.21, 2.17 (s, 3, aryl-CH$_3$), 2.10 (d, $^2J_{HH}$ = 13.4, 1, aryl-CH$_2$), 1.95 (d, $^2J_{HH}$ = 13.7, 1, aryl-CH$_2$), 1.94 (d, $^2J_{HH}$ = 13.4, 1, aryl-CH$_2$), 1.92 (s, 3, CHC(C*H*$_3$)$_2$Ph), 1.66 (d, $^2J_{HH}$ = 14, 1, aryl-CH$_2$), 1.56, 1.52 (s, 9, C(CH$_3$)$_3$), 1.23 (d, $^3J_{HH}$ = 6.7, 6, CH(C*H*$_3$)$_2$), 1.17 (s, 3, CHC(C*H*$_3$)$_2$Ph), 1.02, (d, $^3J_{HH}$ = 7.0, 6, CH(C*H*$_3$)$_2$), 0.06, −0.06 (s, 9, Si(CH$_3$)$_3$); ^{13}C{^{1}H} NMR (125 MHz, C_6D_6) δ 281.0 (MoCH), 156.3, 155.6, 154.4, 151.2, 146.5, 146.3, 141.2, 139.5, 138.2, 135.2, 132.2, 130.2, 129.7, 129.3, 128.7, 128.3, 127.7, 126.9, 126.0, 123.4 (aryl), 53.5 (CH*C*Me$_2$Ph), 35.6, 35.5 (*C*(CH$_3$)$_3$), 32.9, 32.1 (CHC(*C*H$_3$)$_2$Ph), 31.3, 30.7 (C(*C*H$_3$)$_3$), 30.0, 29.0 (*C*H(CH$_3$)$_2$), 24.3, 24.2 (CH(*C*H$_3$)$_2$), 22.4, 22.0 (aryl-CH$_2$), 21.9, 21.6 (aryl-*C*H$_3$), 0.6, 0.3 (Si(CH$_3$)$_3$). Anal. Calcd for $C_{52}H_{77}MoNO_2Si_2$: C 69.37, H 8.62, N 1.56. Found: C 69.26, H 8.54, N 1.48.

Mo(NAr)(CHCMe$_2$Ph)[(*S*)-TMS$_2$Biphen] ((*S*)-4). To a solution of (*S*)-H_2[TMS_2Biphen] (768 mg, 1.54 mmol) in THF (10 mL) was added solid benzyl potassium (415 mg, 3.19 mmol) in small portions at −20 °C. The solution was allowed to warm to room temperature and was stirred for 1 h. The solution was cooled again to −20 °C and was added dropwise to a cold solution of Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME) (1.22 g, 1.54 mmol) in THF (5 mL). The solution was allowed to warm to room temperature and was stirred for 3 h. The solvent was removed in vacuo, and the remaining red-brown oily solid was extracted with benzene (3 × 2 mL). The solution was filtered to remove potassium triflate and the filtrate concentrated in vacuo. Recrystallization from pentane at −20 °C gave brick-red crystals (620 mg, 45% yield).

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Supporting Information Available: Experimental details and fully labeled ORTEP drawings, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **3** and **4** are available free of charge via the Internet at http://pubs.acs.org.

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