Diphenylamido Precursors to Bisalkoxide Molybdenum Olefin Metathesis Catalysts

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We have found that Mo(NAr)(CHR′)$(NPh_2)_2$ (R′ = t-Bu or CMe_2Ph) and Mo(NAr′)$(CHCMe_2Ph)(NPh_2)_2$ (Ar = 2,6-i-$Pr_2C_6H_3$; Ar′ = 2,6-$Me_2C_6H_3$) can be prepared through addition of 2 equiv of $LiNPh_2$ to Mo(NR″)(CHR′)$(OTf)_2$(dme) species (R″ = Ar or Ar′, dme = 1,2-dimethoxyethane), although yields are low. A high-yield route consists of addition of $LiNPh_2$ to bishexafluro-*tert*-butoxide species. An X-ray structure of Mo(NAr)$(CHCMe_2Ph)(NPh_2)_2$ reveals that the two diphenylamido groups are oriented in a manner that allows an 18-electron count to be achieved. The diphenylamido complexes react readily with t-BuOH and $(CF_3)_2MeCOH$, but not readily with the sterically demanding biphenol H_2[Biphen] (Biphen^{2-} = 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diolate). The diphenylamido complexes do react with various 3,3′-disubstituted binaphthols to yield binaphtholate catalysts that can be prepared in situ and employed for a simple asymmetric ring-closing metathesis reaction. In several cases conversions and enantioselectivities were comparable to reactions in which isolated catalysts were employed.

Introduction

We have been searching for methods of synthesizing Mo(NR)(CHR′)$(OR'')_2$ species (or related species that contain enantiomerically pure biphenolate or binaphtholate ligands[1]) in situ. The main reason is that an increasing number of applications (e.g., asymmetric olefin metathesis[1]) require an evaluation of many catalysts having different combinations of imido and alkoxide ligands for a given chemical transformation and therefore the synthesis, isolation, and storage of many catalysts. It also would be desirable to synthesize well-defined supported catalysts (e.g., on partially dehydroxylated silica[2]). We have reported the synthesis of catalysts in situ in a manner that is essentially the same as that employed to prepare and isolate each catalyst, i.e., addition of the potassium salt of a biphenolate or a binaphtholate to a Mo(NR)(CHR′)$(OTf)_2$(dme) species in THF.[3] However, the most attractive goal would be to prepare a Mo(NR)(CHR′)X_2 precursor that could be transformed readily into Mo(NR)(CHR′)$(OR'')_2$ (or a related biphenolate or binaphtholate species) simply through addition of the monoalcohol or diol to the Mo(NR)(CHR′)X_2 precursor. This method would require that the HX product of this reaction not interfere to any significant degree with subsequent reactions that involve Mo(NR)(CHR′)$(OR'')_2$ and also not react with any organic species in the reaction. A wide variety of Mo(NR)(CHR′)$(OR'')_2$ catalysts then could be generated in situ and evaluated relatively rapidly. We first focused on species in which X = CH_2CMe_3, but we found that Mo(NAr)(CH-t-Bu)$(CH_2$-t-Bu$)_2$ and related species react with only 1 equiv of alcohols to yield complexes of the type Mo(NAr)(CH-t-Bu)$(CH_2$-t-Bu)(OR), or precursors to them, Mo(NAr)$(CH_2$-t-Bu$)_3$(OR) species,[4] even on silica surfaces.[5] Although Mo(NAr)(CH-t-Bu)$(CH_2$-t-Bu)(OR) and related species are surprisingly active catalysts and are of fundamental interest in their own right, we had to reevaluate our approach to bisalkoxide precursors.

Amido groups have been employed extensively in transition metal chemistry, especially early metal chemistry, and it is well known that they often can be protonated readily.[6] Some high oxidation state Mo chemistry reported by Cummins is especially noteworthy. He and his group have prepared trisalkoxide complexes of the type Mo(X)$(OAd)_3$ through addition of 3 equiv of adamantanol to Mo(X)[N(i-Pr)(3,5-$C_6H_3Me_2$)]$_3$ species (X = CCH_2SiMe_3,[7] N,[8] P[9]). Moore has extended this approach in order to prepare alkylidyne catalysts of molybdenum for the metathesis of alkynes.[10] Therefore we turned to the possibility of preparing bisamido catalyst precursors, Mo(NR)(CHR′)$(amido)_2$.

The only known M(NR)(CHR′)$(amido)_2$ (M = Mo or W) species is W(NAr)(CHEt)$(NPh_2)_2$, which was prepared in 73% yield as golden-orange crystals upon treating W(CHEt)(NAr)$[OCMe(CF_3)_2]_2$(3-hexene)$_{0.8}$ with 2 equiv of $LiNPh_2$.[11] (W(CHEt)-

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(1) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4592.
(2) Copéret, C.; Chabanas, M.; Saint-Arroman, R. P.; Basset, J.-M. *Angew. Chem., Int. Ed.* **2003**, *42*, 156.
(3) Teng, X.; Cefalo, D. R.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 10779.
(4) Sinha, A.; Lopez, L. P. H.; Schrock, R. R.; Hock, A. S.; Müller, P. *Organometallics* **2006**, *25*, 1412.
(5) Blanc, F.; Baudouin, A.; Copéret, C.; Thivolle-Cazat, J.; Basset, J.-M.; Lesage, A.; Emsley, L.; Sinha, A.; R., S. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 1216.
(6) Gade, L. H.; Mountford, P. *Coord. Chem. Rev.* **2001**, *216−217*, 65.
(7) Tsai, Y. C.; Diaconescu, P. L.; Cummins, C. C. *Organometallics* **2000**, *19*, 5260.
(8) Cherry, J.-P. F.; Stephens, F. H.; Johnson, M. J. A.; Diaconescu, P. L.; Cummins, C. C. *Inorg. Chem.* **2001**, *40*, 6860.
(9) Stephens, F. H.; Figueroa, J. S.; Diaconescu, P. L.; Cummins, C. C. *J. Am. Chem. Soc.* **2003**, *125*, 9264.
(10) (a) Zhang, W.; Kraft, S.; Moore, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 329. (b) Weissman, H.; Plunkett K. N.; Moore J. S. *Angew. Chem., Int. Ed.* **2006**, *45*, 585. (c) Zhang, W.; Kraft, S.; Moore, J. S. *Chem. Commun.* **2003**, 832.
(11) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L. Y.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Krüger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262.

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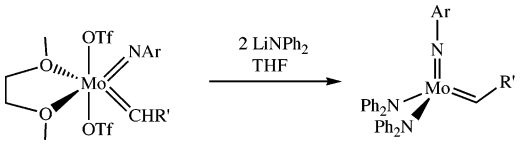
$(NAr)[OCMe(CF_3)_2]_2(3\text{-hexene})_{0.8}$ is believed to be a mixture of a propylidene complex and a triethylmetallacyclobutane complex.) Complexes that contain chelating (diamido) ligands are known, e.g., molybdenum complexes that contain a *N,N′*-disubstituted-2,2′-bisamido-1,1′-binaphthyl ligand.[12] Boncella has isolated $M(NPh)(CH\text{-}t\text{-}Bu)[o\text{-}(Me_3SiN)_2C_6H_4](PMe_3)$ (M = Mo, W) species as the products of the reactions between $M(NPh)(CH_2\text{-}t\text{-}Bu)_2[o\text{-}(Me_3SiN)_2C_6H_4]$ (M = Mo, W) and 5 equiv of PMe_3, and other chemistry of both Mo and W compounds that contain the $[o\text{-}(Me_3SiN)_2C_6H_4]^{2-}$ diamido ligand has been published.[13,14] In view of the existence of $W(NAr)(CHEt)(NPh_2)_2$ we therefore first sought to prepare $Mo(NAr)(CH\text{-}t\text{-}Bu)(NPh_2)_2$ and to employ it as a precursor for the in situ synthesis of asymmetric metathesis catalysts. This paper reports the results of these and related studies.

Results

Synthesis of Bisdiphenylamido Species. Addition of a cold suspension of 2 equiv of $LiNPh_2$ in THF or toluene to a stirred suspension of $Mo(NAr)(CHR')(OTf)_2(dme)$ (R′ = t-Bu, CMe_2Ph) in THF at −25 to −30 °C produced $Mo(NAr)(CH\text{-}t\text{-}Bu)(NPh_2)_2$ as a red solid, but the isolated yield was only 12%. The yield in the case of $Mo(NAr)(CHCMe_2Ph)(NPh_2)_2$ was 35%. In both cases much manipulation was required to isolate a solid product. Alkylidene proton resonances for $Mo(NAr)(CH\text{-}t\text{-}Bu)(NPh_2)_2$ and $Mo(NAr)(CHCMe_2Ph)(NPh_2)_2$ in benzene-d_6 are found at 10.96 and 11.18 ppm, respectively, and alkylidene carbon resonances were found at 294.8 and 292.6 ppm, respectively. The J_{CH} values (117 and 119 Hz, respectively) are consistent with a *syn* orientation of the alkylidene.[15,16] In the case of $Mo(NAr)(CHCMe_2Ph)(NPh_2)_2$, a second minor alkylidene proton resonance is observed at 11.78 ppm (~5% of the total). We ascribe this resonance to the *anti* isomer, although we have not proven that to be the case through a determination of the value for J_{CH}.



(1)

R' = t-Bu, CMe_2Ph

Single crystals of $Mo(NAr)(CHCMe_2Ph)(NPh_2)_2$ suitable for X-ray crystallographic studies were obtained by layering a concentrated solution of the complex in dichloromethane with a minimum amount of pentane and storing the sample at −30 °C. In the solid state $Mo(NAr)(CHCMe_2Ph)(NPh_2)_2$ has a pseudotetrahedral geometry about the metal with the alkylidene ligand in the *syn* orientation, as expected (Figure 1). The Mo−C(37) double bond distance (1.877(3) Å) and the Mo−C(37)−C(38) bond angle (146.2(3)°) are typical of those found in a *syn* complex of this general type.[15,16] The $Mo-N_{amide}$ bond lengths

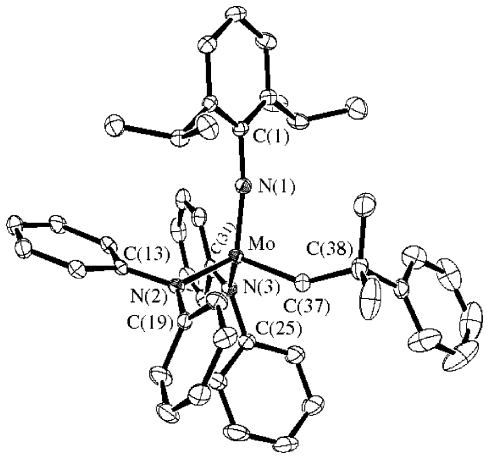
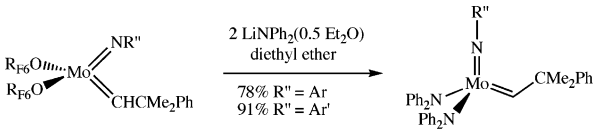


Figure 1. Thermal ellipsoid drawing (50%) of $Mo(NAr)(CHCMe_2Ph)(NPh_2)_2$. (Hydrogen atoms are removed for clarity.)

(2.009(3) and 2.007(3) Å) are similar to those found in a complex that contains a chelating diamido ligand, $Mo(NAr)(CHCMe_2Ph)[BINA(N\text{-}i\text{-}Pr)_2]$ ($Mo-N_{amide}$ = 1.993 Å; $[BINA(N\text{-}i\text{-}Pr)_2]^{2-}$ = *N,N′*-diisopropyl-2,2′-bisamido-1,1′-binaphthyl).[12] The amido nitrogen atoms are essentially planar, as expected, and the two amido planes are virtually perpendicular to one another, as in $Mo(NAr)(CHCMe_2Ph)[BINA(N\text{-}i\text{-}Pr)_2]$. Therefore the lone pairs from both amido nitrogens can be donated to the metal, and the total electron count at the metal can be said to be 18.

The main problem with the route shown in eq 1 appears to be deprotonation of the alkylidene to yield a mixture of alkylidyne and other species, and diphenylamine. This type of side reaction has been documented in some cases,[17] but not for reactions that involve amides. Since diphenylamine is extremely difficult to separate from the desired products, we believe that it is the presence of diphenylamine, rather than an inherently low yield, that limits how much pure product can be isolated, a statement that is supported by NMR analysis of crude reaction mixtures. In view of the reported synthesis of $W(NAr)(CHEt)(NPh_2)_2$[11] (vide supra) we therefore explored bishexafluoro-*tert*-butoxides as starting materials.

$Mo(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ can be obtained as yellow crystals in ~85% yield in the reaction between $Mo(NAr)(CHCMe_2Ph)(OTf)_2(dme)$ and 2 equiv of $LiOCMe(CF_3)_2$ in diethyl ether.[18] (Hexafluoro-*tert*-butoxide is a relatively weak base that does not deprotonate the alkylidene.) Treating a prechilled solution (−30 °C) of $Mo(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ in diethyl ether with 2 equiv of $LiNPh_2(0.5\ Et_2O)$ afforded $Mo(NAr)(CHCMe_2Ph)(NPh_2)_2$ as bright orange crystals in 78% isolated yield (eq 2). $Mo(NAr')(CHCMe_2Ph)(NPh_2)_2$ can



(2)

R" = Ar, Ar'; $OR_{F6} = OCMe(CF_3)_2$

be prepared similarly as red-orange crystals in 91% yield starting from $Mo(NAr')(CHCMe_2Ph)[OCMe(CF_3)_2]_2$. The complexes prepared in this manner are identical to the samples obtained directly from the bistriflate species. Despite the extra step

(12) Jamieson, J. Y.; Schrock, R. R.; Davis, W. M.; Bonitatebus, P. J.; Zhu, S. S.; Hoveyda, A. H. *Organometallics* **2000**, *19*, 92.
(13) Ortiz, C. G.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1999**, *18*, 4253.
(14) (a) VanderLende, D. D.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1994**, *13*, 3378. (b) Vaughan, W. M.; Abboud, K. A.; Boncella, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 11015. (c) Wang, S.-Y. S.; VanderLende, D. D.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1998**, *17*, 2628. (d) Vaughan, W. M.; Abboud, K. A.; Boncella, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 11015.
(15) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1.
(16) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145.
(17) Schrock, R. R.; Jamieson, J. Y.; Araujo, J. P.; Bonitatebus, P. J., Jr.; Sinha, A.; Lopez, L. P. H. *J. Organomet. Chem.* **2003**, *684*, 56.
(18) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

Table 1. Crystal Data and Structure Refinement for Mo(NAr)(CHCMe$_2$Ph)(NPh$_2$)$_2$

empirical formula	$C_{46}H_{49}N_3Mo$
fw	739.82
temperature	100(2) K
wavelength	0.71073 Å
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	$a = 9.279(3)$ Å, $\alpha = 79.848(6)$ Å
	$b = 20.158(7)$ Å, $\beta = 89.997(6)$ Å
	$c = 20.739(8)$ Å, $\gamma = 83.507(6)$ Å
volume	3793(2)Å^3
Z	4
density (calcd)	1.296 Mg/m^3
absorp coeff	0.382 mm^{-1}
F(000)	1552
cryst size	0.20 × 0.15 × 0.05 mm^3
θ range for data collection	1.00 to 28.49°
index ranges	$-12 \le h = 12$, $-26 \le k = 27$, $0 \le l = 27$
no. of reflns collected	23 610
no. of indep reflns	23 612 [nonmerohedral twin]
completeness to $\theta = 28.49°$	97.2%
absorp corr	semiempirical from equivalents
max. and min. transmn	0.9812 and 0.9276
refinement method	full-matrix least-squares on F^2
data/restraints/params	23 612/0/914
goodness-of-fit on F^2	1.020
final R indices [$I > 2\sigma(I)$]	R1 = 0.0486, wR2 = 0.1032
R indices (all data)	R1 = 0.0726, wR2 = 0.1119
largest diff peak and hole	0.946 and −0.517 e Å^{-3}

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Mo(NAr)(CHCMe$_2$Ph)(NPh$_2$)$_2$

Mo−N(1)	1.739(3)	Mo−C(37)	1.877(3)
Mo−N(3)	2.007(3)	Mo−N(2)	2.009(3)
N(1)−C(1)	1.406(4)	N(1)−Mo−C(37)	103.98(13)
N(1)−Mo−N(2)	114.03(11)	N(1)−Mo−N(3)	116.34(11)
N(2)−Mo−N(3)	110.32(10)	N(2)−Mo−C(37)	104.07(12)
N(3)−Mo−C(37)	106.86(12)	Mo−C(37)−C(38)	146.2(3)
Mo−N(1)−C(1)	169.0(2)	C(13)−N(2)−C(19)	115.2(2)
C(13)−N(2)−Mo	118.61(19)	C(19)−N(2)−Mo	125.61(19)
C(31)−N(3)−C(25)	117.6(3)	C(31)−N(3)−Mo	132.3(2)
C(25)−N(3)−Mo	110.1(2)		

(synthesis of hexafluoro-*tert*-butoxides), this is the preferred method of producing pure product in high yield relatively quickly. It is known that the acidity of an alkylidene proton is reduced dramatically in alkoxide (even hexafluoro-*tert*-butoxide) complexes compared to what it is in (e.g.) a triflate or a chloride complex,[15] so deprotonation of the alkylidene is no longer problematic relative to substitution of the alkoxide.

Synthesis of Mo[N(R^1)(3,5-C$_6$H$_3$Me$_2$)]$_2$ Complexes. Mo(NAr)(CH-t-Bu)[N(R^1)(3,5-C$_6$H$_3$Me$_2$)]$_2$ (R^1 = t-Bu, i-Pr) can be synthesized by treating a prechilled solution (−30 °C) of Mo(NAr)(CH-t-Bu)(OTf)$_2$(dme) in diethyl ether or toluene with 2 equiv of the corresponding LiN(R^1)(3,5-C$_6$H$_3$Me$_2$)(ether) salt. We believe that the yields again are compromised as a consequence of deprotonation of alkylidenes and consequent contamination of the product with the relatively high boiling parent amine. For example, Mo(NAr)(CH-t-Bu)[N(t-Bu)(3,5-C$_6$H$_3$Me$_2$)]$_2$ can be prepared and isolated in pure form as an orange-red crystalline solid in 34% yield. Proton and carbon NMR data (Table 3) are those expected for *syn* isomers. No alkylidene resonance for the *anti* isomer of Mo(NAr)(CH-t-Bu)[N(t-Bu)(3,5-C$_6$H$_3$Me$_2$)]$_2$ could be found at 22 °C. The 3,5-Me$_2$C$_6$H$_3$ ring was found to be freely rotating on the NMR time scale. On the other hand, solid Mo(NAr)(CH-t-Bu)[N(i-Pr)(3,5-C$_6$H$_3$Me$_2$)]$_2$ could not be isolated free of HN(i-Pr)(3,5-C$_6$H$_3$Me$_2$) despite repeated attempts at triturating the oily material with cold pentane or lyophilizing it in benzene. No improvement in the yield and purity of the desired product was observed when

Table 3. NMR Data for Bisamido Complexes in Benzene-d_6 at 22 °C

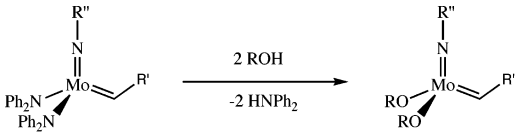
compound	δH_α	δC_α	J_{CH}
Mo(NAr)(CH-t-Bu)[N(t-Bu)(3,5-C$_6$H$_3$Me$_2$)]$_2$	10.71	293.0	120
Mo(NAr)(CH-t-Bu)[N(i-Pr)(3,5-C$_6$H$_3$Me$_2$)]$_2$	11.10	285.5	119
Mo(NAr)(CH-t-Bu)(NPh$_2$)$_2$	10.96	294.8	117
Mo(NAr)(CHCMe$_2$Ph)(NPh$_2$)$_2$	11.18	292.6	119
Mo(NAr′)(CHCMe$_2$Ph)(NPh$_2$)$_2$	11.08	292.5	122

the different solvents (toluene, THF) and/or lower temperatures (−78 °C) were employed.

Attempted syntheses of bisdimethylamido complexes from either Mo(NAr) or Mo(NAr′) triflates failed. Complex oily mixtures were obtained from which the pure products could not be isolated. Bright orange Mo(NAr)(CHCMe$_2$Ph)(NMe$_2$)$_2$ could be obtained in a reaction between 2 equiv of LiNMe$_2$ and Mo(NAr)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$, but only in 16% yield (δH_α = 10.69 ppm, δC_α = 270.1 ppm). Since this synthesis is not viable in the long run, this compound was not fully characterized.

Reactions of Mo(NR′′)(CHR′)(NR$_2$)$_2$ Complexes. None of the bisamido complexes reacted readily with simple olefins such as ethylene and diallyl ether, or with benzaldehyde (e.g., several equivalents at room temperature over a period of 10 h), behavior that is similar to that found for [BINA(NR)$_2$]$^{2-}$ complexes.[12] Although steric factors are significant, the primary reason we believe is an 18-electron count at the metal center (vide infra).

Both Mo(NAr)(CH-t-Bu)(NPh$_2$)$_2$ and Mo(NAr′)(CHCMe$_2$Ph)(NPh$_2$)$_2$ react readily with t-BuOH and (CF$_3$)$_2$MeCOH. Upon addition of the alcohol to 30 mM benzene solutions of the bisamide complexes, the bisalkoxide species, Mo(NAr)(CH-t-Bu)(OR)$_2$ and Mo(NAr′)(CHCMe$_2$Ph)(OR)$_2$ (OR = O-t-Bu, OCMe(CF$_3$)$_2$), are obtained within 10 min along with the expected amount of the free amine Ph$_2$NH (eq 3). There was



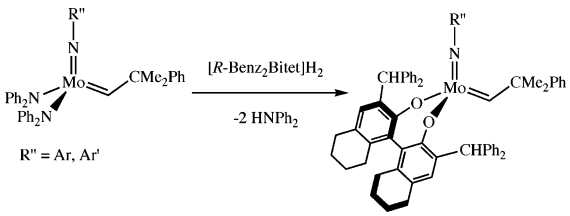
(3)

R" = Ar, R' = t-Bu
R" = Ar', R' = CMe$_2$Ph

ROH = t-BuOH, Me(CF$_3$)$_2$COH

no indication that diphenylamine bound to the metal to give an adduct in either case; that is, the chemical shift of the alkylidene proton is identical to that published for the base-free compounds. There is no evidence of any irreversible protonation of either the imido or the alkylidene ligand.

Mo(NAr)(CHCMe$_2$Ph)(NPh$_2$)$_2$ and Mo(NAr′)(CHCMe$_2$Ph)(NPh$_2$)$_2$ (27 mM in benzene-d_6) also react with 1 equiv of H$_2$[*R*-Benz$_2$Bitet] to give the known Benz$_2$Bitet complexes (eq 4). The two reactions proceed ∼90% to completion in 15 h at room

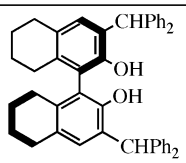
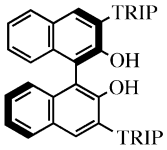
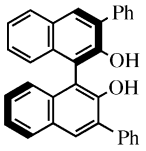
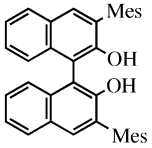
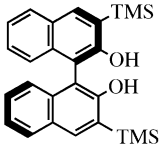


(4)

R" = Ar, Ar'

temperature, with the reaction involving Mo(NAr′)(CHCMe$_2$Ph)(NPh$_2$)$_2$ proceeding about twice as fast as that involving Mo(NAr)(CHCMe$_2$Ph)(NPh$_2$)$_2$ and the conversion being slightly higher, presumably as a consequence of the lower steric demands of the 2,6-dimethylphenylimido ligand.

Table 4. Generation of Binaphtholate Catalysts in Situ and Conversions (ee) for Asymmetric Ring-Closing Metathesis (eq 5)

			time (h), temp (°C)	% amide conv (% catalyst)	% substrate conv (% ee)
H_2[*R*-Benz$_2$Bitet]		R" = Ar	8.0, 50	100(81)	77(94)[a]
		R" = Ar'	1.0, 70	100(100)	99(97)
H_2[*R*-TRIP$_2$BINO]		R" = Ar	48.0, 60	100(100)	82(95)
		R" = Ar'	48.0, 60	100(100)	99(96)
H_2[*R*-Ph$_2$BINO]		R" = Ar	0.5, 50	100(100)	90(68)[b]
		R" = Ar'	1.0, 70	100(100)	95(87)
H_2[*rac*-Mes$_2$BINO]		R" = Ar	14.0, 70	100(100)	75[c]
		R" = Ar'	14.0, 70	91(86)	93
H_2[*R*-TMS$_2$BINO]		R" = Ar	8.0, 50	82(56)	92(72)
		R" = Ar'	36.0, 70	90(90)	99(56)

[a] With isolated catalyst[22] 95% conversion, 93% ee. [b] With isolated catalyst[20] 90% conversion, 75% ee. [c] With isolated enantiomerically pure catalyst[20] 92% conversion, 86% ee.

Reactions between Mo(NR″)(CHCMe$_2$Ph)(NPh$_2$)$_2$ (NR″ = NAr, NAr′) and the sterically demanding biphenol H_2[Biphen] (Biphen^{2-} = 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diolate) were slow and incomplete and in some cases produced byproducts. For example, no reaction was observed when H_2[Biphen] was added to a benzene-d_6 (0.1 M) solution of Mo(NAr)(CHCMe$_2$Ph)(NPh$_2$)$_2$ over a period of 2 days at room temperature. Heating the solution at 50 °C for 1 day shows 44% conversion to the desired Mo(NAr)(CHCMe$_2$Ph)[Biphen] species, but also four new alkylidene resonances appeared in the 11.40−11.80 ppm region (a total 20% of the mixture). The nature of the complex or complexes responsible for the new alkylidene resonances is (are) not known. When Mo(NAr)(CHCMe$_2$Ph)(NPh$_2$)$_2$ was added to a benzene solution of H_2[Biphen], the *extra* alkylidene peaks amount to less than 8% of the reaction mixture. However, complete conversion again was not observed. The reaction between H_2[Biphen] and Mo(NAr′)(CHCMe$_2$Ph)(NPh$_2$)$_2$ was also slow, with only 64% conversion to Mo(NAr′)(CHCMe$_2$Ph)[Biphen] observed in 7 days at 50 °C at concentrations of ~0.1 M.

The binaphthols H_2[*R*-TRIP$_2$BINO],[19] H_2[*R*-Ph$_2$BINO],[20] H_2[*rac*-Mes$_2$BINO],[20] and H_2[*R*-TMS$_2$BINO][21] react more readily with Mo(NR″)(CHCMe$_2$Ph)(NPh$_2$)$_2$ (NR″ = NAr, NAr′) species than does H_2[Biphen] (Table 4), but still not immediately. The reactions shown in Table 4 were carried out by adding the bisdiphenylamido complex to the diol in 2 drops of benzene-d_6 (0.3 M). After heating the reaction mixtures for the stipulated time, more solvent was added and the percent conversion and percent product were determined by ^{1}H NMR spectroscopy versus an internal standard. Good to excellent conversions were found for virtually all the reactions, although the product mixture in some cases was found to contain small amounts (5−10%) of unidentified new alkylidenes along with the desired diolate product. The impurities amounted to ~25% when the diol employed was H_2[*R*-TMS$_2$BINO], the dianion of which has not been studied extensively in the context of Mo(NR″)(CHCMe$_2$Ph)(diolate*) chemistry.

Reactions between alcohols and Mo(NAr)(CHR′)[N(R^1)(3,5-C$_6$H$_3$Me$_2$)]$_2$ complexes proceeded only very slowly (according to NMR studies) or not at all compared to similar reactions with Mo(NAr)(CHR′)(NPh$_2$)$_2$ species, probably largely for steric reasons. Mo(NAr)(CH-t-Bu)[N(t-Bu)(3,5-C$_6$H$_3$Me$_2$)]$_2$ reacted at room temperature with (CF$_3$)$_2$MeCOH in benzene-d_6 (28 mM) to give the bisalkoxide within 10 min. However, the analogous reaction proceeded very slowly (~12−15 h) when t-BuOH was employed. Reactions involving Mo(NAr)(CH-t-Bu)[N(i-Pr)(3,5-C$_6$H$_3$Me$_2$)]$_2$ with both (CF$_3$)$_2$MeCOH and t-BuOH were complete in 10 min under conditions noted above. All Mo(NAr)(CHR′)[N(R^1)(3,5-C$_6$H$_3$Me$_2$)]$_2$ complexes showed virtually a

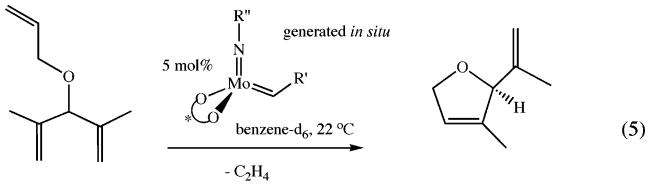
(19) Zhu, S. S.; Cefalo, D. R.; La, D. S.; Jamieson, J. Y.; Davis, W. M.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 8251.

(20) Tsang, W. C. P.; Schrock, R. R.; Hoveyda, A. H. *Organometallics* **2001**, *20*, 5658.

(21) Totland, K. M.; Boyd, T. J.; Lavoie, G. G.; Davis, W. M.; Schrock, R. R. *Macromolecules* **1996**, *29*, 6114.

complete lack of reactivity toward the enantiomerically pure diols shown in Table 4.

Conversions and enantioselectivities in a simple asymmetric ring-closing metathesis reaction (eq 5) are also listed in Table 4. Conversions of the substrate range from 56% to 97% with the highest ee being 97%. For the first[22] and third[20] entries the



(5)

ring-closing also has been carried out with isolated catalyst. The results for the in situ generated catalyst and for the isolated catalyst are comparable. In particular the %ee's are essentially the same. The in situ catalyst appears to be somewhat slower (first and fourth entries) versus the isolated catalysts, although detailed studies have not been carried out. It should be noted that the first three in situ catalysts that contain a 2,6-dimethylphenyl imido ligand are slightly superior in terms of %ee than catalysts that contain the 2,6-diisopropylphenyl imido ligand; the 2,6-diisopropylphenyl imido derivatives were the only isolated catalysts that were examined.

Conclusions

We have demonstrated that bisamido complexes can be prepared starting from bistriflate complexes, although yields are low and the products are difficult to isolate. In some cases yields can be improved through the use of Mo(NR″)(CHR′)[OCMe(CF$_3$)$_2$]$_2$ complexes as starting materials. Reactions in which bisdiphenylamido complexes are prepared from hexafluoro-*tert*-butoxide species are high yielding and clean and, for this reason, are preferred over reactions that start with bistriflates. On the basis of preliminary studies, NAr and NAr′ complexes containing NPh$_2$ ligands react with a variety of enantiomerically pure binaphthols to give the desired chiral catalysts in situ, the exception being H$_2$[Biphen], which is the most sterically demanding. In these reactions diphenylamine apparently does not bind to the metal, nor does it hinder asymmetric reactions (to the degree that we have explored for one substrate) in terms of either substrate conversion or %ee. Therefore this approach to in situ catalyst generation and use is an attractive one, especially if a nitrogen-based anionic ligand can be found that produces a catalyst precursor in high yield and if that catalyst precursor were to react with even the most sterically demanding biphenols or binaphthols. In this manner we hope to be able to reduce the problem of catalyst evaluation to the synthesis and storage of a few Mo(NR″)(CHR′)X$_2$ precursors.

Experimental Section

General Procedures. All operations were performed under a nitrogen atmosphere in the absence of oxygen and moisture in a Vacuum Atmospheres glovebox or using standard Schlenk procedures. All glassware, including NMR tubes, were flame- and/or oven-dried prior to use. Ether, pentane, toluene, and benzene were degassed with dinitrogen and passed through activated alumina columns. Dimethoxyethane was distilled from a dark purple solution of sodium benzophenone ketyl and degassed three time by freeze−pump−thaw techniques. Dichloromethane was distilled from CaH$_2$ under N$_2$. All dried and deoxygenated solvents were stored over 4 Å molecular sieves in a nitrogen-filled glovebox. ^{1}H, ^{13}C, and ^{19}F NMR spectra were acquired at room temperature (unless otherwise noted) using Varian Mercury (^{1}H 300 MHz, ^{13}C 75 MHz, ^{19}F 282 MHz) or Varian Inova (^{1}H 500 MHz, ^{13}C 125 MHz) spectrometers and referenced to the residual protio solvent resonances or external C$_6$F$_6$ (−163.0 ppm). Elemental analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany. Mo(NR″)(CHR′)(OTf)$_2$(dme) complexes**,** LiN(i-Pr)(3,5-C$_6$H$_3$Me$_2$), and LiN(t-Bu)(3,5-C$_6$H$_3$Me$_2$) were prepared as described in the literature.[18,23−25] LiNPh$_2$ was prepared by reacting HNPh$_2$ with n-BuLi (1.6 M in hexane) in toluene. LiNPh$_2$(0.5 ether) was obtained by crystallizing LiNPh$_2$ from diethyl ether. LiNMe$_2$ was prepared by reacting HNMe$_2$ with n-BuLi (1.6 M in hexane) in toluene. All other chemicals were procured from commercial sources and used as received.

Mo(NAr)(CH-t-Bu)(NPh$_2$)$_2$. A solution of Mo(NAr)(CH-t-Bu)(OTf)$_2$(dme) (6.00 g, 8.22 mmol) in 80 mL of THF at −30 °C was treated with a prechilled solution of LiNPh$_2$ (2.88 g, 16.44 mmol) in 20 mL of THF. The color changed from yellow to red immediately. The reaction mixture was stirred for 1 h and allowed to warm to room temperature. The volatiles were removed in vacuo, and the residue was extracted with pentane. The extracts were filtered through Celite, and the solvents again were removed in vacuo to give an oil that was triturated with minimal pentane. Filtration yielded an orange-red powder in 12% yield (669 mg). The remaining pentane-soluble red oil was found to consist mostly of the desired complex according to proton NMR: ^{1}H NMR (C$_6$D$_6$) δ 10.96 (s, 1, C*H*CMe$_3$, J_{CH} = 117 Hz), 7.12−6.83 (overlapping peaks, 23, Ar*H*, NP*h*$_2$), 3.90 (sept, 2, C*H*Me$_2$), 1.81 (d, 12, CH*Me*$_2$), 0.98 (s, 9, CHC*Me*$_3$); ^{13}C NMR (C$_6$D$_6$) δ 294.8. Anal. Calcd for C$_{41}$H$_{47}$MoN$_3$: C, 72.66; H, 6.99; N, 6.20. Found: C, 72.52; H, 7.08; N, 6.11.

Mo(NAr)(CHCMe$_2$Ph)(NPh$_2$)$_2$. Method A: Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(dme) (500 mg, 0.63 mmol) was dissolved in 8 mL of THF, and the solution was cooled to −30 °C. A prechilled solution of LiNPh$_2$ (221 mg, 1.26 mmol) in 2 mL of THF was added to the above solution in a dropwise fashion to immediately afford a red solution. After 1 h the volatiles were removed in vacuo to give a red foam, which was extracted with pentane. The extract was filtered through Celite, and the filtrate was concentrated to dryness to yield a red oil. The oil was triturated with cold pentane several times to give 163 mg of an orange-red powder (35% yield).

Method B: A yellow solution of Mo(NAr)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (505 mg, 0.66 mmol) in 50 mL of ether was cooled to −30 °C. Gradual addition of 2 equiv of LiNPh$_2$(Et$_2$O)$_{0.5}$ (280 mg, 1.32 mmol) to the above reaction resulted in a change in color from yellow to orange to red as the reaction mixture was allowed to warm to room temperature. The reaction mixture was stirred for 1 h. The solvents were partially removed, and the concentrated solution was layered with 5 mL of pentane; a bright orange product crystallized out. The orange crystals were washed with 5 mL of cold pentane (−30 °C) to afford the desired complex in 78% yield (380 mg) in two crops: ^{1}H NMR (C$_6$D$_6$) δ 11.78 (s, 0.04, *anti* C*H*CMe$_2$Ph), 11.18 (s, 1, *syn* C*H*CMe$_2$Ph, J_{CH} = 119 Hz), 7.10−6.79 (overlapping peaks, 28, Ar*H*, NP*h*$_2$), 3.86 (sept, 2, C*H*Me$_2$), 1.45 (s, 6, CHC*Me*$_2$Ph), 1.61 (d, 12, CH*Me*$_2$); ^{13}C NMR (C$_6$D$_6$) δ 292.6, 155.5, 154.1, 148.5, 146.3, 129.9, 128.9, 127.8, 126.5, 126.4,

(22) Schrock, R. R.; Jamieson, J. Y.; Dolman, S. J.; Miller, S. A.; Bonitatebus, P. J., Jr.; Hoveyda, A. H. *Organometallics* **2002**, *21*, 409.

(23) Oskam, J. H.; Fox, H. H.; Yap, K. B.; McConville, D. H.; O'Dell, R.; Lichtenstein, B. J.; Schrock, R. R. *J. Organomet. Chem.* **1993**, *459*, 185.

(24) Tsai, Y. C.; Stephens, F. H.; Meyer, K.; Mendiratta, A.; Gheorghiu, M. D.; Cummins, C. C. *Organometallics* **2003**, *22*, 2902.

(25) Micovic, I. V.; Ivanovic, M. D.; Piatak, D. M.; Bojic, V. J. *Synthesis* **1991**, 1043.

124.6, 123.9, 123.6, 55.7, 31.0, 28.6, 24.7. Anal. Calcd for $C_{46}H_{49}MoN_3$: C, 74.68; H, 6.68; N, 5.68. Found: C, 74.57; H, 6.62; N, 5.69.

Mo(NAr′)(CHCMe$_2$Ph)(NPh$_2$)$_2$. Mo(NAr′)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (539 mg, 0.76 mmol) in 55 mL of ether was chilled to −30 °C. Gradual addition of 2 equiv of LiNPh$_2$(Et$_2$O)$_{0.5}$ (322 mg, 1.52 mmol) to the above reaction resulted in a change in color from yellow to orange to red-orange as the reaction mixture was allowed to warm to room temperature. The reaction mixture was stirred for 1 h, and the solvents were partially removed in vacuo. The concentrated solution was layered with 5 mL of pentane. A bright red-orange solid crystallized out and was washed with 3 mL of cold (−30 °C) pentane; yield 475 mg (91%): ^{1}H NMR (C_6D_6) δ 11.08 (s, 1, C*H*CMe$_2$Ph, J_{CH} = 122 Hz), 7.10−6.81 (overlapping peaks, 28, Ar*H*, N*Ph*$_2$), 2.33 (s, 6, CHC*Me*$_2$Ph), 1.37 (s, 6, Ar′*Me*$_2$); ^{13}C NMR (C_6D_6) δ 292.5, 157.2, 155.2, 148.4, 135.4, 129.9, 128.8, 126.8, 126.5, 126.4, 124.5, 123.6, 55.3, 30.5, 19.6. Anal. Calcd for $C_{42}H_{41}MoN_3$: C, 73.78; H, 6.04; N, 6.15. Found: C, 73.59; H, 6.12; N, 6.02.

Mo(NAr)(CH-t-Bu)[N(t-Bu)(3,5-C$_6$H$_3$Me$_2$)]$_2$. LiN(t-Bu)(3,5-C$_6$H$_3$Me$_2$)(ether) (330 mg, 1.28 mmol) was added to a suspension of Mo(NAr)(CH-t-Bu)(OTf)$_2$(dme) (468 mg, 0.64 mmol) in 30 mL of ether at −30 °C. The red solution was stirred at ambient temperature for 1.5 h. The volatiles were removed in vacuo, and the residue was extracted into pentane. The pentane was removed in vacuo to give a red oil. Extensive trituration with cold pentane gave a waxy, red solid. The waxy solid was dissolved in a minimum amount of pentane, and the solution was stored at −30 °C overnight to give 152 mg (34%) of the product as orange-red crystals: ^{1}H NMR (C_6D_6) δ 10.71 (s, 1, C*H*CMe$_3$, J_{CH} = 120 Hz), 7.17 (br s, 2, Ar*H*), 7.09 (br s, 5, Ar*H*), 6.68 (br s, 2, Ar*H*), 4.58 (sept, 2, C*H*Me$_2$), 2.22 (s, 12, C$_6$H$_3$*Me*$_2$), 1.38 (d, 12, CH*Me*$_2$), 1.34 (s, 18, NC*Me*$_3$), 0.98 (s, 9, CHC*Me*$_3$); ^{13}C NMR (C_6D_6) δ 293.0, 157.2, 153.9, 144.9, 137.9, 129.7, 126.6, 126.2, 124.3, 59.5, 48.7, 32.3, 31.5, 27.6, 24.6, 21.7. Anal. Calcd for $C_{41}H_{63}N_3Mo$: C, 70.97; H, 9.15; N, 6.06. Found: C, 71.06; H, 9.06; N, 5.97.

Mo(NAr)(CH-t-Bu)[N(i-Pr)(3,5-C$_6$H$_3$Me$_2$)]$_2$. An ether solution of LiN(i-Pr)(3,5-C$_6$H$_3$Me$_2$)(ether) (343 mg, 1.41 mmol) was added to a suspension of Mo(NAr)(CH-t-Bu)(OTf)$_2$(dme) (6.00 g, 8.22 mmol) in 40 mL of ether at −30 °C. The deep red reaction mixture stood at room temperature for 1 h, and all solvents were removed under reduced pressure. The residue was extracted with pentane, and the extract was filtered through Celite to yield a red liquid, which was concentrated in vacuo to yield a red oil that contained 70% Mo(NAr)(CH-t-Bu)[N(i-Pr)(3,5-C$_6$H$_3$Me$_2$)]$_2$ and 30% HN(i-Pr)(3,5-C$_6$H$_3$Me$_2$) that could not be removed on a high-vacuum line or by heating the oil under reduced pressure: ^{1}H NMR (C_6D_6) δ 11.10 (s, 1, C*H*CMe$_3$, J_{CH} = 119 Hz), 7.07 (br s, 3, Ar*H*), 6.85 (br s, 4, Ar*H*), 6.56 (br s, 2, Ar*H*), 4.25 (sept, 2, C*H*Me$_2$), 4.01 (sept, 2, C*H*Me$_2$), 2.14 (s, 12, C$_6$H$_3$*Me*$_2$), 1.26 (d, 12, CH*Me*$_2$), 1.23 (d, 12, CH*Me*$_2$), 1.19 (s, 9, CHC*Me*$_3$); ^{13}C NMR (C_6D_6): δ 285.2, 154.9, 145.0, 138.5, 126.4, 125.0, 123.7, 123.2, 58.6, 48.4, 32.2, 28.2, 25.4, 25.0, 24.9, 21.9.

Representative Method for Generating Mo(NR″)(CHCMe$_2$Ph)(diolate*) and Using It As a Catalyst for Ring-Closing. The bisamido precursor (10−20 mg) was added to a solution of the enantiomerically pure diol in 0.5 mL drops of benzene-d_6 in a J-Young tube. The reaction mixture was heated at 60 °C until the starting materials were consumed. The progress of the reaction was monitored by ^{1}H NMR spectroscopy versus an internal standard.

To the Mo(NR″)(CHCMe$_2$Ph)(diolate*) species generated as described above was added 20 equiv of the substrate. The conversion was followed by ^{1}H NMR spectroscopy, and the enantiomeric excess was determined with a GC equipped with a Chiraldex column.

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Supporting Information Available: Crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement parameters for Mo(NAr)(CHCMe$_2$Ph)(NPh$_2$)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org. Data for the structure (04220) are also available to the public at http://www.reciprocalnet.org/.

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