Synthesis of Molybdenum Imido Alkylidene Complexes Containing N,N′-Disubstituted 2,2′-Bisamido-1,1′-binaphthyl Ligands

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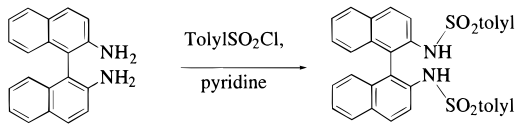
Addition of the dipotassium salt of 2,2′-bis-*p*-tolylsulfonamido-1,1′-binaphthyl (K_2[BINA-($NTs)_2$]) to Mo(NAr)($CHCMe_2Ph$)($OTf)_2$(dme) (Ar = 2,6-*i*-$Pr_2C_6H_3$; OTf = OSO_2CF_3), Mo(N-2-$CF_3C_6H_4$)($CHCMe_2Ph$)($OTf)_2$(dme), and Mo(N-2-$CF_3C_6H_4$)(CH-*t*-Bu)($OTf)_2$(dme) gave Mo-(NAr)($CHCMe_2Ph$)[BINA($NTs)_2$] (**1a**), Mo(N-2-$CF_3C_6H_4$)($CHCMe_2Ph$)[BINA($NTs)_2$] (**1b**), and Mo(N-2-$CF_3C_6H_4$)(CH-*t*-Bu)[BINA($NTs)_2$] (**1c**), respectively. The X-ray crystal structure of **1c** showed that one sulfonyl oxygen is coordinated to the molybdenum. Related complexes, Mo(NAr)($CHCMe_2Ph$)[BINA(N−i-Pr)$_2$] (**2**) and Mo(NAr)($CHCMe_2Ph$)[BINA($NTMS)_2$] (**3**), were prepared similarly. The pseudotetrahedral nature of **2** was confirmed in an X-ray study. None of these complexes reacts readily with ethylene, styrene, benzaldehyde, or diallyl ether.

Introduction

Molybdenum imido alkylidene complexes[1−3] have been employed as catalysts in processes such as ring-opening metathesis polymerization (ROMP),[4] acyclic diene metathesis polymerization (ADMET),[5−8] and ring-closing metathesis (RCM).[3,9−13] Recently we have prepared new molybdenum imido alkylidene complexes that catalyze the asymmetric ring-closing metathesis (ARCM) of olefins.[14−17] These complexes contain either an optically pure biphenoxide[14,15] or binaphtholate,[16] which effectively control the enantioselectivity of the ring-closing step in the catalytic process. Ligands of this type initially were used in order to control the tacticity of polymers prepared by ROMP.[18] While we have been inspired to explore variations of bisaryloxide ligands for ARCM reactions, we also have been interested in optically pure, readily accessible alternatives to bisaryloxides. We report here our results for molybdenum imido alkylidene complexes that contain N,N′-disubstituted 2,2′-diamido-1,1′-binaphthyl ligands.[19−21]

Results

The first derivative of 2,2′-diamino-1,1′-binaphthyl to be prepared was a bis-*p*-tolylsulfonamide derivative, H_2-[BINA($NTs)_2$] (eq 1). It can be isolated in essentially quantitative yield and recrystallized readily from dichloromethane.



(1)

H_2[BINA($NTs)_2$]

A THF solution of benzyl potassium was added to H_2-[BINA($NTs)_2$] in THF until a slight red tinge persisted in the solution. Addition of Mo(NAr)($CHCMe_2Ph$)($OTf)_2$-(dme) to the solution of K_2[BINA($NTs)_2$] caused the reaction mixture to turn dark brownish-red immediately. Canary yellow Mo(NAr)($CHCMe_2Ph$)[BINA($NTs)_2$]

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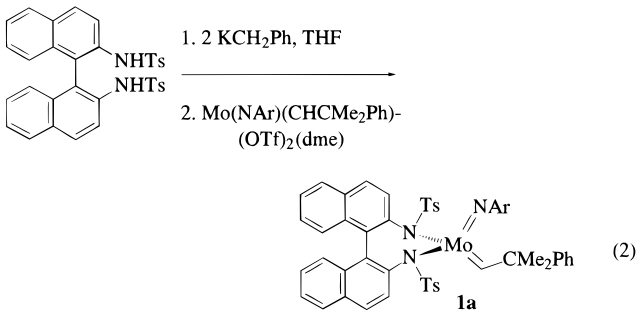
(**1a**) could be isolated in 68% yield (eq 2). By ^{1}H NMR



(2)

spectroscopy, both the syn (H_α at 14.49 ppm, J_{CH} = 122.7 Hz) and anti (H_α at 15.35 ppm, J_{CH} = 147.0 Hz) isomers[1,3] were observed in a ratio of 6:1. Variable-temperature ^{1}H NMR studies of **1a** showed that there was no measurable change in the ratio of syn to anti between 20 and 80 °C and that the compound did not decompose readily at 80 °C. The syn resonance did shift upfield by 0.2 ppm upon raising the temperature to 80 °C. While it is possible that the energy difference between syn and anti isomers is temperature independent between 20 and 80 °C, that would be the first example to our knowledge.[1] Therefore, we propose that there is no exchange between syn and anti on the chemical time scale of several minutes at 80 °C. As we shall see below, a sulfonyl oxygen in one of the tosyl groups is coordinated to the metal. Since alkylidene rotation has been observed to be possible only when a base dissociates from a five-coordinate adduct of this general type,[22] alkylidene rotation must be effectively blocked by intramolecular sulfonyl coordination. Since anti isomers have been shown to be stabilized by bases[22] and compounds of this general type that are *four*-coordinate are virtually exclusively syn (vide infra), we believe that the presence of ~15% of the anti isomer of **1a** can be attributed to intramolecular coordination of the sulfonyl oxygen.

A compound analogous to **1a** containing an N-2-$CF_3C_6H_4$ group was prepared in a similar fashion from Mo(N-2-$CF_3C_6H_4$)($CHCMe_2Ph$)$(OTf)_2$(dme). Mo(N-2-$CF_3C_6H_4$)($CHCMe_2Ph$)[BINA$(NTs)_2$] (**1b**) was isolated in 70% yield as a yellow powder from a mixture of ether and pentane at −30 °C. The ^{1}H NMR spectrum of **1b** showed it to be primarily (50:1) the syn isomer (H_α at 14.24 ppm, J_{CH} = 125.4 Hz), with H_α for the anti isomer being observed at 15.42 ppm. A neopentylidene species, Mo(N-2-$CF_3C_6H_4$)(CH-*t*-Bu)[BINA$(NTs)_2$] (**1c**), could be prepared in 66% yield in an analogous fashion. The ^{1}H NMR spectrum showed that **1c** exists as a 100:1 mixture of syn (H_α at 14.14 ppm, J_{CH} = 125.6 Hz) and anti isomers (H_α at 15.18 ppm). The greater percentage of the syn isomer in the Mo(N-2-$CF_3C_6H_4$) complexes we believe can be attributed to the reduced steric interaction between the alkylidene substituent and the smaller imido ligand (relative to a 2,6-disubstituted imido ligand) in the syn isomer.

A single crystal of **1c** suitable for X-ray crystallographic analysis was grown from a mixture of THF, ether, and pentane at room temperature. (See Tables 1 and 2 and Figure 1.) Compound **1c** is a distorted five-coordinate species in which the alkylidene is in the expected syn conformation. The Mo=C bond length and Mo−C(1)−C(2) bond angle are typical of syn imido alkylidene complexes, as are the Mo=N bond length and

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Table 1. Crystal Data and Structure Refinement for Mo(N-2-$CF_3C_6H_4$)(CH-*t*-Bu)[BINA$(NTs)_2$] (1c) and Mo(N-2,6-i-$Pr_2C_6H_3$)($CHCMe_2Ph$)-[BINA(N-i-Pr)$_2$] (2)[a]

	1c	2
empirical formula	$C_{46}H_{40}F_3MoN_3O_4S_2$	$C_{48}H_{55}MoN_3$
fw	915.87	769.89
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a (Å)	11.5657(6)	11.2917(5)
b (Å)	15.0079(8)	13.9058(6)
c (Å)	24.9382(13)	15.0708(6)
α (deg)	90	62.54°
β (deg)	92.6240(10)	89.923(1)
γ (deg)	90	77.667(1)
volume (Å^3)	4324.2(4)	2038.4(2)
Z	4	2
density (calcd; Mg/m^3)	1.407	1.254
abs coeff (mm^{-1})	0.459	0.358
F(000)	1880	812
cryst size (mm)	0.2 × 0.2 × 0.2	0.5 × 0.5 × 0.4
θ range for data collection	1.58 to 20.00	3.06 to 46.48
limiting indices	$-12 \le h \le 12$ $-15 \le k \le 16$ $-13 \le l \le 27$	$-12 \le h \le 9$ $-15 \le k \le 11$ $-16 \le l \le 16$
no. of reflns collected	12 509	8434
no. of ind reflns	4027 (R_{int} = 0.0541)	5732 (R_{int} = 0.0338)
abs corr	none	from *ψ*-scans
no. of data/restraints/params	4001/0/533	5718/0/469
goodness-of-fit on F^2	1.339	1.068
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0638, wR2 = 0.1324	R1 = 0.0346, wR2 = 0.0886
R indices (all data)	R1 = 0.0746, wR2 = 0.1516	R1 = 0.0368, wR2 = 0.0922
extinction coeff	0.0016(2)	0.0000(8)
largest diff peak and hole (e Å^{-3})	0.382 and −0.453	0.800 and −0.542

[a] All data were collected at 183(2) K using Mo Kα radiation (0.71073 Å) and refined by full-matrix least-squares on F^2.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Mo(N-2-$CF_3C_6H_4$)(CH-*t*-Bu)[BINA$(NTs)_2$] (1c) and Mo(N-2,6-i-$Pr_2C_6H_3$)($CHCMe_2Ph$)-[BINA(N-i-Pr)$_2$] (2)

1c		2	
Mo−C(1)	1.861(8)	Mo−C(1)	1.904(3)
Mo−N(1)	1.737(7)	Mo−N(1)	1.747(2)
Mo−N(2)	2.158(6)	Mo−N(2)	2.004(2)
Mo−N(3)	2.076(6)	Mo−N(3)	1.981(2)
C(1)−Mo−N(1)	101.3(3)	C(1)−Mo−N(1)	104.96(11)
C(1)−Mo−N(2)	112.3(3)	C(1)−Mo−N(2)	103.92(11)
C(1)−Mo−N(3)	100.4(3)	C(1)−Mo−N(3)	110.46(11)
N(1)−Mo−N(2)	144.8(3)	N(1)−Mo−N(2)	117.04(10)
N(1)−Mo−N(3)	102.4(3)	N(1)−Mo−N(3)	113.01(10)
N(2)−Mo−N(3)	82.2(2)	N(2)−Mo−N(3)	107.00(9)
C(1)−Mo−O(22)	102.9(3)		
N(1)−Mo−O(22)	99.2(2)		
N(2)−Mo−O(22)	63.9(2)		
N(3)−Mo−O(22)	144.2(2)		
Mo−N(1)−C(51)	171.3(5)	Mo−N(1)−C(11)	172.2(2)
Mo−C(1)−C(2)	143.6(7)	Mo−C(1)−C(2)	144.0(2)
Mo−N(3)−S(2)	127.5(3)	Mo−N(3)−C(46)	136.4(2)
Mo−N(3)−C(11)	105.8(4)	Mo−N(3)−C(42)	106.4(2)
Mo−N(2)−S(1)	98.5(3)	Mo−N(2)−C(43)	132.8(2)
Mo−N(2)−C(21)	134.8(5)	Mo−N(2)−C(23)	112.2(2)
Mo−O(22)	2.206(5)		
S(1)−O(22)	1.491(5)		
S(1)−O(21)	1.431(5)		

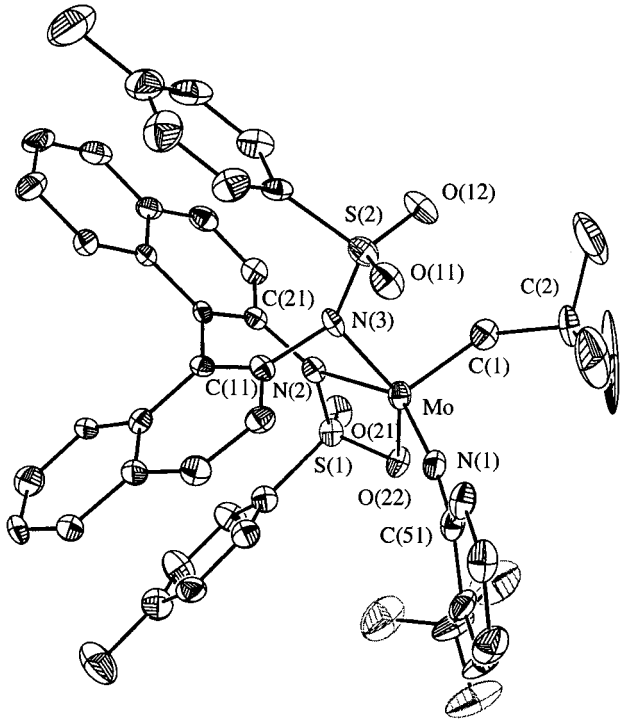
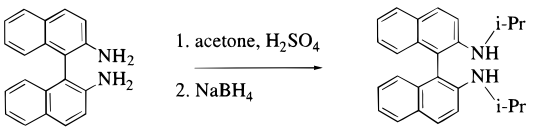


Figure 1. ORTEP drawing of the structure of Mo(N-2-$CF_3C_6H_4$)(CH-*t*-Bu)[BINA($NTs)_2$] (**1c**).

Mo−N(1)−C(51) bond angle.[1] The angle between the two naphthyl rings is 64.9°. The Mo−N_{amido} bond lengths are not unusual, although one (Mo−N(2)) is ∼0.08 Å longer than the other. The sum of the angles at N(3) is 352.7°, and that at N(2) is 359.8°. The main finding is that one of the sulfonyl oxygens (O(22)) is coordinated to the molybdenum center, judging from the Mo−O(22) bond distance of 2.206(5) Å. The S(1)−O(22) bond length therefore is slightly longer than the S(1)−O(21) bond length.

We turned to the synthesis of derivatives analogous to **1** in which the substituent on nitrogen is not likely to coordinate to the metal. We first chose H_2[BINA(N−i-Pr)$_2$], since it can be prepared readily following a literature procedure,[21] as shown in eq 3. Deprotonation



(3)

H_2[BINA(N-i-Pr)$_2$]

of H_2[BINA(N-i-Pr)$_2$] with methyllithium followed by addition of a solution of Mo(NAr)($CHCMe_2Ph$)$(OTf)_2$(dme) gave Mo(NAr)($CHCMe_2Ph$)[BINA(N-i-Pr)$_2$] (**2**) as ruby red blocks in 60% yield. Attempted deprotonation of H_2[BINA(N-i-Pr)$_2$] with benzyl potassium was not successful; the reaction mixture turned bright red after addition of a small fraction of the necessary benzyl potassium. The ^{1}H NMR spectrum of **2** suggests that it exists solely as the syn isomer (H_α at 10.46 ppm, J_{CH} = 117.0 Hz).

An X-ray study of a single crystal of **2** (see Tables 1 and 2 and Figure 2) revealed it to be a pseudo-tetrahedral syn species with no unusual bond lengths or angles. Each amido nitrogen is essentially planar,

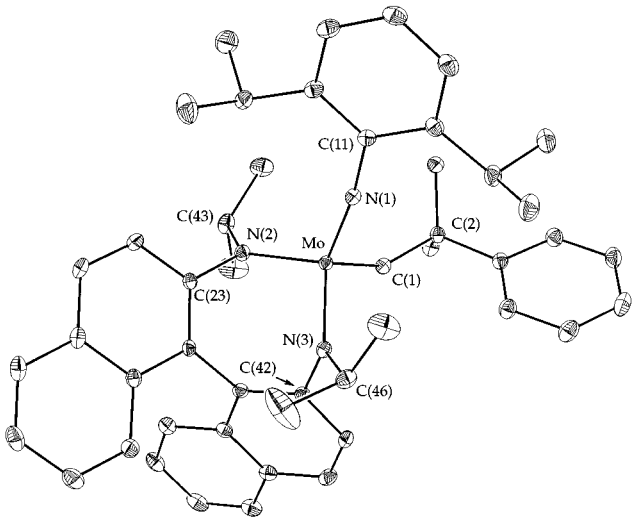
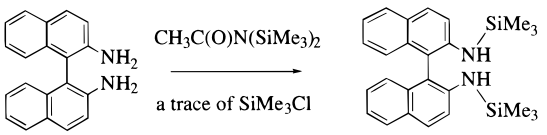


Figure 2. ORTEP drawing of the structure of Mo(N-2,6-i-$Pr_2C_6H_3$)($CHCMe_2Ph$)[BINA(N-i-Pr)$_2$] (**2**).

judging from the sum of the angles at each. The angle between the two naphthyl rings is 69.0° (cf. 64.9° in **1c**). Although there are some small differences in bond lengths and angles in **1c** versus **2**, in our opinion they are not significant enough to warrant discussion. What is striking, however, is the virtually mutually perpendicular orientation of the N(2) and N(3) amido ligand planes. Therefore, the p orbitals on N(2) and N(3) that are employed to form the Mo−N π bonds also must be roughly perpendicular to one another. The Mo−N(2) and Mo−N(3) distances are virtually identical and relatively short, which suggests that N(2) and N(3) are both strongly π bound to the metal.

A third type of substituted 2,2′-diamino-1,1′-binaphthyl, H_2[BINA($NTMS)_2$], was easily synthesized according to known procedures,[23] as shown in eq 4. Deprotonation of H_2[BINA($NTMS)_2$] with methyllithium followed by addition of a solution of Mo(NAr)($CHCMe_2Ph$)$(OTf)_2$(dme) gave Mo(NAr)($CHCMe_2Ph$)[BINA($NTMS)_2$] (**3**) as ruby red blocks in 52% yield. Proton NMR spectra suggest that **3** exists only as the syn isomer (H_α at 10.50 ppm, J_{CH} = 117.2 Hz).



(4)

H_2[BINA($NTMS)_2$]

Compounds **1a**, **1b**, **1c**, **2**, and **3** all showed a startling lack of reactivity toward olefins, and even benzaldehyde, which usually reacts readily in a Wittig-like fashion with bisalkoxide derivatives of molybdenum imido alkylidene complexes.[1] There was no change in the proton NMR spectrum of compound **1a** in C_6D_6 after 3 h at 22 °C in the presence of diallyl ether (0.1 M **1a**, 2 M diallyl ether), after 13 h in the presence of benzaldehyde (0.4 M **1a**, 0.4 M benzaldehyde), after 19 h in the presence of styrene (0.1 M **1a**, 0.2 M styrene), or after 2 h under 40 psi of ethylene at 80 °C. A similar lack of reactivity

(23) Drost, C.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1996**, *17*, 3595.

was observed for **1b** (with diallyl ether, ethylene, or benzaldehyde at 60 °C for 2 h), **1c** (with ethylene, benzaldehyde at 80 °C for 3 h, or styrene), **2** (with benzaldehyde, styrene, or diallyl ether), and **3** (with diallyl ether, benzaldehyde, or styrene). Compound **2** did appear to decompose to a small extent to give free ligand in the presence of diallyl ether or ethylene, but less than 5% dihydrofuran, the expected product of a ring-closing metathesis reaction, was formed.

Discussion

Chelating diamido ligands have become popular as ligands for synthesizing group 4 olefin polymerization catalysts.[24,25] Although amido ligands are good σ and π donors, they allow a cationic group 4 metal to retain a significant degree of electrophilic character and appear to create circumstances that are conducive to living polymerizations of ordinary olefins.[24a,b,t,25a−c] However, the only diamido ligand that has been employed to stabilize group 6 imido alkylidene complexes appears to be the bis(trimethylsilyl)*o*-phenylenediamido ligand for both tungsten[26−28] and more recently molybdenum.[29] For example, heating a toluene solution of W(NPh)(CH_2-*t*-Bu)$_2$[*o*-$(Me_3SiN)_2C_6H_4$] to 70 °C in the presence of an excess of PMe_3 for 24 h resulted in formation of neopentane and W(NPh)(CH-*t*-Bu)[*o*-$(Me_3SiN)_2C_6H_4$](PMe_3).[26] This complex appears to be reactive toward olefins only when PMe_3 dissociates from the metal, as has been found for other imido alkylidene complexes of tungsten and molybdenum.[1] Interestingly, the amido nitrogens of the [*o*-$(Me_3SiN)_2C_6H_4]^{2-}$ ligand are not planar, consistent with a poor π-bonding ability, although a weak interaction of the phenylene ring with the metal might be partially responsible for the observed ligand conformation. In any case, the authors argue that the metal is electron deficient, namely, a 14-electron species counting only π donation from the imido ligand to the metal.

We were surprised to find that complexes **1a**, **1b**, and **1c** did not react at all with ethylene, styrene, or benzaldehyde, even though we suspected that a sulfonyl oxygen would coordinate to the metal on the basis of structures of titanium complexes that contain bis(sulfonamido) ligands.[30−32] However, we were not prepared for the low reactivity of pseudotetrahedral **2** and **3**. Although steric hindrance near the metal is severe in **2** and **3**, we propose that electronic factors are largely to blame. Unlike tungsten complexes that contain the [*o*-$(Me_3SiN)_2C_6H_4]^{2-}$ ligand, complexes of type **1** and **2**, and we assume also **3**, contain amido nitrogens that are planar. While planarity alone does not guarantee that π bonding is efficient, the relatively short Mo−N bonds in **1c** and **2** suggest that to be the case. By inspection it can be seen that a tetrahedral σ-bonding framework can be constructed from primarily s and p orbitals, leaving five π bonds to be formed employing the five d orbitals. If we take the *z* axis to be coincident with the Mo−N(1) axis and the *x* axis to lie parallel to the Mo−N(2) bond, the pseudotriple Mo−N(1) bond can be formed using d_{xz} and d_{yz} orbitals. The $d_{x^2-y^2}$ and d_{xy} orbitals are then employed to form π bonds to the symmetric and asymmetric combination of p orbitals on C(1) and N(3). (The π bonds that are formed employing the $d_{x^2-y^2}$ and d_{xy} orbitals of course are not equal, with that formed using the $d_{x^2-y^2}$ orbital dominating, and the contributions from p orbitals on C(1) and N(3) to the symmetric and asymmetric combinations also are not equal.) The main point is that the only remaining orbital, the d_{z^2} orbital, can be used to form a π bond between Mo and N(2), a fact that accounts for the orientation of the p orbital on N(2) roughly parallel to the Mo−N(1) axis. In short, if a total of five π bonds are present, **2** is an 18-electron species with no low-energy LUMO to which an incoming olefin can bind. Coordination of the sulfonyl oxygen in **1c** to the metal could be said to lead to a lower degree of π bonding, or none at all, to N(2); therefore in **1c** there is only one π bond to an amido nitrogen (N(3)), but still an 18-electron count. One could argue that the 1,1′-binaphthyl backbone of the 2,2′-diamino-1,1′-binaphthyl ligand naturally reinforces the relative orientation of the p orbitals on N(3) and N(2) and therefore allows the amido nitrogens to play their more normal role as π-bonding ligands, especially in a pseudo-tetrahedral environment, in contrast to the constrained *o*-phenylene backbone of the [*o*-$(Me_3SiN)_2C_6H_4]^{2-}$ ligand.

The low reactivity of **1**, **2**, and **3** contrasts with the high reactivity of molybdenum imido alkylidene complexes that contain bulky alkoxide ligands, especially relatively electron-withdrawing fluoro-*tert*-butoxide

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ligands or phenoxide ligands. Even alkoxides in which the substituent is relatively bulky are much less sterically encumbered near the metal than are the [BINA-$(NR)_2]^{2-}$ ligands. An alkoxide oxygen is also likely to be a poorer σ and π donor than an amido nitrogen, thereby leaving the metal more electron deficient, with the LUMO at a lower, more accessible energy. It is interesting to note that the imido/dialkoxide combination seems to be a favorable one for metathesis activity for Mo and W. The imido/diamido combination, at least in the form we have explored, is not. Therefore it is interesting to speculate whether an oxo/diamido combination would lead to a more reactive metathesis catalyst than one having a imido/diamido combination. Unfortunately, the synthesis of precursors to oxo alkylidene complexes is not as facile as the synthesis of precursors to imido alkylidene complexes,[33,34] and oxo alkylidene complexes are more likely to decompose bimolecularly than arylimido alkylidene complexes as a consequence of a relatively low degree of steric protection against a bimolecular reaction. Therefore the question cannot be answered at this time.

Experimental Section

General Details. All experiments were conducted under nitrogen in a Vacuum Atmospheres drybox or using standard Schlenk techniques. THF, toluene, diethyl ether, and pentane were sparged with nitrogen and passed through alumina columns.[35] Benzene was distilled from sodium benzophenone ketyl. 2,2′-Diamino-1,1′-binaphthyl,[20] benzyl potassium,[36] H_2-[BINA(N-i-Pr)$_2$],[21] H_2[BINA(NTMS)$_2$],[23] Mo(NAr)(CHCMe$_2$Ph)-(OTf)$_2$(dme),[37] Mo(N-2-$CF_3C_6H_4$)(CHCMe$_2$Ph)(OTf)$_2$(dme),[38] and Mo(N-2-$CF_3C_6H_4$)(CH-*t*-Bu)(OTf)$_2$(dme)[38] were prepared according to literature procedures. C_6D_6 and $CDCl_3$ were sparged with nitrogen and stored over 4 Å molecular sieves. ^{1}H and ^{13}C NMR data are listed in parts per million downfield from tetramethylsilane and were referenced using the residual protio solvent peak. Spectra were taken in C_6D_6 at 22 °C unless otherwise noted. ^{19}F NMR data were referenced externally using $CFCl_3$ in $CHCl_3$ as a standard. Routine NMR coupling constants are not reported. Elemental analyses were performed by H. Kolbe Laboratories, Mülheim an der Ruhr, Germany. X-ray data were collected on a Siemens SMART/CCD diffractometer with λ(Mo Kα) = 0.71073 Å and solved using a full-matrix least-squares refinement on F^2. No absorption correction was applied for **1c**. For **2**, a semiempirical absorption correction from ψ-scans was applied. (See Table 1 and Supporting Information.)

H_2[BINA(NTs)$_2$]. *p*-Toluenesulfonyl chloride (13.10 g, 68.71 mmol) was added to a solution of 2,2′-diamino-1,1′-binaphthyl (5.00 g, 17.50 mmol) in pyridine (200 mL). The mixture was stirred overnight at room temperature. Methanol was added to the red solution, and a white precipitate formed. This precipitate was isolated by filtration, dried in vacuo, and recrystallized from dichloromethane to give H_2[BINA(NTs)$_2$] quantitatively as a white solid (10.37 g): ^{1}H NMR (300 MHz) δ 8.37 (d, 2, Ar*H*), 7.58 (d, 2, Ar*H*), 7.48 (d, 4, Ar*H*), 7.41 (d, 2, Ar*H*), 6.97 (t, 2, Ar*H*), 6.64 (d, 4, Ar*H*), 6.59 (t, 2, Ar*H*), 6.51 (d, 2, Ar*H*), 6.10 (s, 2, N*H*), 1.92 (s, 6, PhCH_3); ^{13}C NMR ($CDCl_3$, 125.8 MHz) δ 144.35, 135.42, 134.01, 132.00, 130.79, 130.62, 129.71, 128.17, 127.57, 127.00, 125.29, 124.19, 117.99, 117.32, 21.43; MS calcd for $C_{34}H_{28}N_2S_2O_4$ 592.149051; found 592.1480.

Mo(NAr)(CHCMe$_2$Ph)[BINA(NTs)$_2$] (1a). Benzyl potassium (120 mg, 0.92 mmol) was dissolved in THF (1 mL) and added to a suspension of H_2[BINA(NTs)$_2$] (218 mg, 0.37 mmol) in THF (3 mL) until the solution retained a pale orange tint. A solution of Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(dme) (291 mg, 0.37 mmol) in THF (2 mL) was then added. The reaction turned blood red immediately. After 15 h, the solvent was removed in vacuo and the resulting solid was extracted with benzene. This solution was filtered through Celite, the benzene was removed in vacuo, and the resulting solid was dissolved in a minimal amount of ether. Pentane was added to the ether solution until the solution was barely cloudy, and the mixture was then stored at −30 °C to give **1a** as a canary yellow powder (248 mg, 67.7%): ^{1}H NMR (500 MHz) δ (major isomer) 14.49 (s, 1, Mo=C*H*, J_{CH} = 122.7 Hz), 8.31 (d, 1, Ar*H*), 7.65 (d, 2, Ar*H*), 7.40 (m, 3, Ar*H*), 7.25 (m, 3, Ar*H*), 7.05 (m, 9, Ar*H*), 6.83 (m, 2, Ar*H*), 6.48 (m, 4, Ar*H*), 6.08 (br m, 2, Ar*H*), 5.90 (d, 2, Ar*H*), 4.33 (sept, 2, C*H*Me$_2$), 2.33 (s, 3, ArCH_3), 2.09 (s, 3, ArCH_3), 1.57 (d, 6, CH(CH_3)$_2$), 1.52 (d, 6, CH(CH_3)$_2$), 1.19 (s, 3, CHC(CH_3)$_2$Ph), 1.17 (s, 3, CHC(CH_3)$_2$Ph); ^{13}C NMR (125.8 MHz) δ (mixture of isomers) 329.55, 310.98, 154.24, 152.80, 150.64, 149.80, 148.48, 147.84, 144.47, 144.28, 141.27, 140.63, 140.13, 138.93, 138.78, 137.57, 137.27, 135.91, 135.69, 134.59, 134.43, 134.23, 134.00, 133.25, 133.19, 133.06, 132.39, 132.26, 132.06, 131.71, 131.44, 130.03, 129.86, 129.52, 129.40, 129.20, 129.11, 128.92, 128.54, 128.20, 127.93, 127.89, 127.77, 127.43, 127.27, 126.98, 126.92, 126.48, 126.37, 126.22, 126.15, 126.04, 124.76, 124.68, 124.27, 123.58, 122.41, 121.93, 68.22, 57.08, 55.30, 33.73, 30.68, 29.84, 29.31, 28.95, 28.54, 26.24, 25.84, 25.05, 24.95, 24.65, 21.61, 21.38. Anal. Calcd for $MoC_{56}H_{55}N_3O_4S_2$: C, 67.66; H, 5.58; N, 4.23. Found: C, 67.38; H, 5.62; N, 4.28.

Mo(N-2-$CF_3C_6H_4$)(CHCMe$_2$Ph)[BINA(NTs)$_2$] (1b). This compound was prepared in a manner analogous to the synthesis of **1a** from benzyl potassium (219 mg, 1.68 mmol), H_2-[BINA(NTs)$_2$] (399 mg, 0.67 mmol), and Mo(N-2-$CF_3C_6H_4$)-(CHCMe$_2$Ph)(OTf)$_2$(dme) (500 mg, 0.67 mmol); yield 460 mg (69.9%): ^{1}H NMR (500 MHz) δ (major isomer) 14.24 (s, 1, Mo=C*H*, J_{CH} =125.4 Hz), 8.35 (d, 1, Ar*H*), 8.24 (d, 1, Ar*H*), 8.20 (br s, 1, Ar*H*), 7.70 (d, 2, Ar*H*), 7.49 (d, 1, Ar*H*), 7.45 (d, 1, Ar*H*), 7.38 (d, 1, Ar*H*), 7.33 (d, 1, Ar*H*), 7.27 (d, 2, Ar*H*), 7.20 (t, 2, Ar*H*), 7.12 (d, 1, Ar*H*), 7.09 (t, 1, Ar*H*), 6.97 (br t, 3, Ar*H*), 6.90 (t, 2, Ar*H*), 6.67 (t, 1, Ar*H*), 6.43 (t, 1, Ar*H*), 6.33 (br d, 2, Ar*H*), 6.26 (d, 1, Ar*H*), 5.98 (d, 2, Ar*H*), 5.93 (br s, 2, Ar*H*), 2.25 (s, 3, ArCH_3), 1.92 (s, 3, ArCH_3), 1.60 (s, 3, CHC-(CH_3)$_2$Ph), 1.52 (s, 3, CHC(CH_3)$_2$Ph); ^{13}C NMR (125.8 MHz) δ 311.80, 153.02, 149.17, 144.31, 141.42, 139.40, 138.67, 137.00, 134.76, 134.55, 134.23, 133.06, 132.46, 131.76, 131.48, 130.35, 129.60, 129.55, 129.32, 129.01, 128.81, 128.68, 128.49, 128.30, 128.10, 127.93, 127.87, 127.56, 126.91, 126.85, 126.32, 126.23, 126.19, 126.14, 125.91, 124.82, 66.26, 58.18, 33.23, 28.95, 21.50, 21.26, 15.96; ^{19}F NMR (282 MHz) δ −61.75 (s). Anal. Calcd for $MoC_{51}H_{42}F_3N_3O_4S_2$: C, 62.64; H, 4.33; N, 4.30. Found: C, 62.66; H, 4.33; N, 4.21.

Mo(N-2-$CF_3C_6H_4$)(CH-*t*-Bu)[BINA(NTs)$_2$] (1c). This compound was prepared in a manner analogous to the synthesis of **1a** from benzyl potassium (219 mg, 1.68 mmol), H_2[BINA-(NTs)$_2$] (400 mg, 0.67 mmol), and Mo(N-2-$CF_3C_6H_4$)(CH-*t*-Bu)-(OTf)$_2$(dme) (481 mg, 0.67 mmol); yield 404 mg (65.3%): ^{1}H NMR (500 MHz) δ (major isomer) 14.13 (s, 1, Mo=C*H*, J_{CH} = 125.6 Hz), 8.40 (q, 3, Ar*H*), 7.54 (d, 1, Ar*H*), 7.46 (d, 1, Ar*H*), 7.39 (d, 1, Ar*H*), 7.33 (d, 1, Ar*H*), 7.31 (d, 2, Ar*H*), 7.12 (t, 2,

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Ar*H*), 7.03 (br d, 2, Ar*H*), 6.90 (m, 2, Ar*H*), 6.64 (t, 1, Ar*H*), 6.42 (m, 1, Ar*H*), 6.35 (br m, 2, Ar*H*), 6.25 (d, 1, Ar*H*), 5.99 (d, 2, Ar*H*), 5.94 (br d, 2, Ar*H*), 1.58 (s, 3, ArCH_3), 1.56 (s, 9, C(CH_3)$_3$), 1.51 (s, 3, ArCH_3); ^{13}C NMR (125.8 MHz) δ 315.08, 153.37, 144.20, 141.37, 139.91, 138.60, 137.15, 134.79, 134.32, 133.08, 133.02, 132.27, 131.74, 131.37, 130.18, 129.60, 129.30, 128.78, 128.67, 128.09, 128.04, 127.86, 126.71, 126.31, 126.28, 126.09, 125.80, 125.29, 124.75, 122.91, 68.16, 51.71, 31.37, 26.15, 21.46, 21.22; ^{19}F NMR (282 MHz) δ −61.96 (s). Anal. Calcd for $MoC_{46}H_{40}N_3S_2O_4F_3$: C, 60.32; H, 4.40; N, 4.59. Found: C, 60.22; H, 4.52; N, 4.51.

Mo(NAr)(CHCMe$_2$Ph)[BINA(N-i-Pr)$_2$] (2). Methyllithium (1.57M in ether, 0.80 mL, 1.25 mmol) was added dropwise to a solution of H_2[BINA(N-i-Pr)$_2$] (210 mg, 0.57 mmol) in THF (4 mL). After no further CH_4 evolution was observed (∼10 min), a solution of Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(dme) (450 mg, 0.57 mmol) in THF (2 mL) was added. After 18 h **2** was isolated as described for **1a**; yield 264 mg (60.3%): ^{1}H NMR (500 MHz) δ 10.46 (s, 1, Mo=C*H*, J_{CH} = 117.0 Hz), 7.81 (d, 1, Ar*H*), 7.79 (d, 1, Ar*H*), 7.74 (d, 1, Ar*H*), 7.68 (d, 1, Ar*H*), 7.63 (d, 1, Ar*H*), 7.60 (d, 1, Ar*H*), 7.54 (d, 2, Ar*H*), 7.27 (d, 2, Ar*H*), 7.25 (d, 2, Ar*H*), 7.13 (d, 1, Ar*H*), 7.11−7.04 (m, 4, Ar*H*), 6.94−6.90 (m, 3, Ar*H*), 4.22 (br sept, 2, C*H*Me$_2$ imido), 3.99 (br sept, 1, NC*H*Me$_2$), 3.92 (br sept, 1, NC*H*Me$_2$), 1.97 (s, 3, CHC(CH_3)$_2$-Ph), 1.41 (s, 3, CHC(CH_3)$_2$Ph), 1.21 (br m, 12, CH(CH_3)$_2$ imido), 1.06 (br d, 3, NCH(CH_3)$_2$), 1.02 (br d, 3, NCH(CH_3)$_2$), 0.95 (br d, 3, NCH(CH_3)$_2$), 0.72 (br d, 3, NCH(CH_3)$_2$); ^{13}C NMR (125.8 MHz) δ 268.83, 153.56, 151.59, 151.40, 146.00, 144.94, 134.60, 134.53, 133.49, 131.67, 131.38, 131.26, 130.33, 130.21, 129.86, 128.76, 128.68, 128.49, 128.29, 127.17, 127.01, 126.79, 126.41, 126.18, 125.50, 125.13, 123.81, 61.99, 61.55, 53.07, 33.55, 32.15, 28.39, 28.14, 26.73, 25.87, 25.09, 24.81, 23.63. Anal. Calcd for $MoC_{48}H_{55}N_3$: C, 74.88; H, 7.20; N, 5.46. Found: C, 75.08; H, 7.18; N, 5.34.

Mo(NAr)(CHCMe$_2$Ph)[BINA(NTMS)$_2$] (3). This compound was prepared in a manner analogous to that described for **2** from methyllithium (1.60 M in ether, 0.52 mL, 0.84 mmol), H_2[BINA(NTMS)$_2$] (164 mg, 0.38 mmol), and Mo(NAr)-(CHCMe$_2$Ph)(OTf)$_2$(dme) (302 mg, 0.38 mmol); yield 164 mg (51.7%): ^{1}H NMR (500 MHz) δ 10.50 (s, 1, Mo=C*H*, J_{CH} = 117.2 Hz), 7.70 (d, 2, Ar*H*), 7.65 (d, 2, Ar*H*), 7.64 (d, 1, Ar*H*), 7.61 (d, 1, Ar*H*), 7.55 (d, 2, Ar*H*), 7.35 (d, 1, Ar*H*), 7.30 (m, 3, Ar*H*), 7.15−7.00 (m, 6, Ar*H*), 6.95 (t, 2, Ar*H*), 4.19 (sept, 2, C*H*(CH$_3$)$_2$), 1.94 (s, 3, C(CH_3)$_2$Ph), 1.29 (d, 6, CH(CH_3)$_2$), 1.28 (s, 3, C(CH_3)$_2$Ph), 1.19 (d, 6, CH(CH_3)$_2$), −0.06 (s, 9, Si(CH_3)$_3$), −0.13 (s, 9, Si(CH_3)$_3$); ^{13}C NMR (125.8 MHz) δ 269.62, 153.65, 151.30, 149.74, 145.50, 145.41, 135.16, 134.88, 133.89, 132.28, 132.03, 131.63, 131.48, 131.06, 129.65, 129.61, 129.09, 129.01, 128.78, 128.62, 127.61, 127.47, 127.25, 127.03, 126.69, 126.37, 125.75, 125.22, 124.17, 54.15, 33.82, 31.50, 28.15, 25.56, 25.37, 3.01, 2.67. Anal. Calcd for $MoC_{48}H_{59}N_3Si_2$: C, 69.29; H, 7.15; N, 5.05. Found: C, 68.81; H, 7.07; N, 4.83.

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Supporting Information Available: A labeled ORTEP drawing, crystal and structural refinement data, atomic coordinates, final thermal parameters, and bond lengths and angles for Mo(N-2-CF$_3$C$_6$H$_4$)(CH-*t*-Bu)[BINA(NTs)$_2$] (**1c**) and Mo(NAr)(CHCMe$_2$Ph)[BINA(N-i-Pr)$_2$] (**2**) are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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