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Ligand variation in alkylidene complexes of the type $Mo(CHR)(NR')(OR'')_2$ *

John H. Oskam, Harold H. Fox, Kimo B. Yap, David H. McConville, Richard O'Dell, Bradley J. Lichtenstein and Richard R. Schrock

Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, MA 02139 (USA)

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Abstract

A variety of complexes of the type $Mo(NR)_2Cl_2L_2$ (R = 4-Br-2,6-^{i}Pr$_2$-C_6H_2, 4-CN-2,6-^{i}Pr$_2$-C_6H_2, 3,5-Me_2-C_6H_3, 2-^{i}Pr-C_6H_4, 2-CF_3-C_6H_4, 2-Ph-C_6H_4, and 1-adamantyl; L = 1/2 DME or pyridine) have been synthesized by treating $[NH_4]_2[Mo_2O_7]$ with four equivalents of RNH_2 in the presence of Me_3SiCl and Et_3N. They are readily alkylated by Grignard reagents to give complexes of the type $Mo(NR)_2(CH_2R')_2$ (R = 4-Br-2,6-^{i}Pr$_2$-C_6H_2, 4-CN-2,6-^{i}Pr$_2$-C_6H_2, 2,6-Me_2-C_6H_3, 3,5-Me_2-C_6H_3, 2-^{t}Bu-C_6H_4, 2-^{i}Pr-C_6H_4, 2-CF_3-C_6H_4, 2-Ph-C_6H_4, 1-adamantyl, R' = ^{t}Bu or $PhMe_2C$) from which alkylidene complexes of the type $Mo(NR)(CHR')(OTf)_2(DME)$ are formed upon addition of triflic acid. Addition of various alkoxides to the triflate complexes yields four-coordinate complexes of the type $Mo(NR)(CHR')(OR'')_2$ (combinations include R = 2,6-^{i}Pr$_2$-C_6H_3, 4-Br-2,6-^{i}Pr$_2$-C_6H_2, 4-CN-2,6-^{i}Pr$_2$-C_6H_2, 2,6-Me_2-C_6H_3, 3,5-Me_2-C_6H_3, 2-^{t}Bu-C_6H_4, 2-^{i}Pr-C_6H_4, 2-CF_3-C_6H_4, 2-Ph-C_6H_4, and 1-adamantyl; OR'' = $OCMe_3$, $OCEt_3$, O-1-adamantyl, $OCHMe_2$, $OCMe_2(CF_3)$, $OCMe(CF_3)_2$, $OC(CF_3)_3$, and $OC(CF_3)_2CF_2CF_2CF_3$).

1. Introduction

Complexes of the types $M(N\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)(CHR)(OR'')_2$ (M = Mo [1–3], W [4,5]), $W(N\text{-}2,6\text{-}Me_2\text{-}C_6H_3)(CHR)(OR'')_2$ [5], and $Re(CR)(CHR)(OR'')_2$ [6,7] (R = CMe_3 or CMe_2Ph and R'' = CMe_3, $CMe_2(CF_3)$, $CMe(CF_3)_2$), have been shown to be effective catalysts for the metathesis of ordinary olefins (Mo [1,3], W [4,5,8], Re [6,9]) and for the ring-opening metathesis polymerization of a variety of bicyclic monomers [10–14]. Variations of the tungsten catalysts (including base adducts) have been synthesized and employed in ROMP reactions [15,16] and the tungsten and molybdenum catalysts have been used in several related catalytic reactions [17–19] including the catalytic ring-closing of dienes [20,21]. In the long term, molybdenum complexes will probably be the catalysts of choice for most reactions since molybdenum is the cheapest metal of the three, molybdenum catalysts are currently the easiest to synthesize, and molybdenum catalysts appear to tolerate functionalities to a greater degree than analogous tungsten catalysts. To date most studies have employed molybdenum catalysts that contain the 2,6-diisopropylphenylimido ligand and primarily OR'' = $OCMe_3$ or $OCMe(CF_3)_2$. Such species are readily available from the "universal precursor," $Mo(N\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)(CHR)(OSO_2CF_3)_2(DME)$ (R = CMe_3 or CMe_2Ph) [1], which can be prepared in three high yield steps from $[NH_4]_2[Mo_2O_7]$. It is clear that the activity of the catalyst depends dramatically upon the electron-withdrawing ability of the alkoxides, upon whether coordinating ligands (including coordinating solvents) are present, and upon whether the alkylidene is in the *syn* or the *anti* configuration [22]. It also has been shown recently that polymers with dramatically different microstructures can be obtained if one employs catalysts that contain different monodentate alkoxides (OR'') [23] or C_2 symmetric alkoxides [24].

Among the questions that have not yet been addressed are to what extent can the electronic and steric properties of the *imido* ligand be varied and how do such variants behave with respect to metathesis of ordinary olefins or ring-opening metathesis of cyclic

Correspondence to: Prof. Dr. R.R. Schrock.

* Dedicated to Prof. Dr. E.O. Fischer on the occasion of his 75th birthday.

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olefins? The imido ligand almost certainly is *not* simply a "spectator" ligand [25], since from both a steric and an electronic perspective it stands a good chance of being able to alter, perhaps dramatically, the reactivity of the metal center. Therefore it is important to continue to explore the synthesis and reactivity of variations of the basic catalyst system. In this paper we explore the synthesis of complexes that contain several different imido groups, and report several new alkoxide derivatives of 2,6-diisopropylphenylimido catalysts.

2. Results and discussion

Recently we reported that $[NH_4]_2[Mo_2O_7]$ is the preferred starting material for the synthesis of complexes of the type $Mo(NR)_2Cl_2(DME)$ and demonstrated that the method works well for complexes in which R = ^{t}Bu, Ph, C_6F_5, 2,6-^{i}Pr$_2$-C_6H_3, 2,6-Me_2-C_6H_3, or 2-^{t}Bu-C_6H_4 [2]. This synthetic procedure has now been extended to a number of new imido complexes of the type $Mo(NR)_2Cl_2L_2$ (**1**; eqn. (1); Table 1). A potentially important modification of this procedure is the use of a solvent other than 1,2-dimethoxyethane (DME). Complexes that are only slightly soluble in DME, such as $Mo(N\text{-}2\text{-}Ph\text{-}C_6H_4)_2Cl_2(py)_2$ (**1e**) and $Mo(N\text{-}1\text{-}adamantyl)_2Cl_2(DME)$ (**1f**) were easily prepared in good yield in benzene or toluene in the presence of an excess of stabilizing ligand (pyridine or DME). $Mo(N\text{-}4\text{-}CN\text{-}2,6\text{-}^iPr_2\text{-}C_6H_2)_2Cl_2(DME)$ (**1b**) could not be synthesized directly in DME, perhaps because of the diminished basicity of the aniline, but could be prepared readily in acetonitrile. In that case the DME adduct was prepared by dissolving the crude product in DME and removing all salts by filtration.

$$(NH_4)_2Mo_2O_7 \xrightarrow[4\ RNH_2]{\text{excess } NEt_3,\ Me_3SiCl \text{ and } L} 2\ Mo(NR)_2Cl_2L_2 \quad (1)$$

(**1**)

L = 1/2 DME or pyridine (py)

R = 4-Br-2,6-^{i}Pr$_2$-C_6H_2; 4-CN-2,6-^{i}Pr$_2$-C_6H_2; 3,5-Me_2-C_6H_3; 2-^{i}Pr-C_6H_4; 2-CF_3-C_6H_4; 2-^{t}Bu-C_6H_4; 1-adamantyl

The next step in the catalyst synthesis consists of alkylating **1** with a neopentyl or neophyl Grignard reagent to give **2** (eqn. (2); Table 2). Neophyl is the preferred alkyl at present because it is relatively inexpensive and because neophyl complexes are sometimes more crystalline and easier to isolate than neopentyl

$$1 + 2\ R'CH_2MgCl \xrightarrow[\text{ether}]{\text{THF or}} Mo(NR)_2(CH_2R')_2 + 2\ MgCl_2 + 2\ L \quad (2)$$

(**2**)

L = 1/2 DME or py

R′ = ^{t}Bu or $PhMe_2C$

complexes. The yields are typically high. In an attempt to prepare imido complexes with less steric protection than the 2,6-disubstituted or 2-substituted phenyl derivatives, we have attempted the alkylation of $Mo(NPh)_2Cl_2(DME)$ [2] under a variety of conditions, but upon isolation, an insoluble material is formed. We have succeeded in preparing a 3,5-dimethylphenylimido derivative (**2e**), which can be carried through the subsequent steps in the synthesis of 4-coordinate imido alkylidene complexes.

TABLE 1. Reaction conditions and yields for the synthesis of compounds of type **1**

Compound	Solvent	Time (h)	Temp. (°C)	Yield (%)
$Mo(N\text{-}4\text{-}Br\text{-}2,6\text{-}^iPr_2\text{-}C_6H_2)_2Cl_2(DME)$ (**1a**)	DME	68	45	99
$Mo(N\text{-}4\text{-}CN\text{-}2,6\text{-}^iPr_2\text{-}C_6H_2)_2Cl_2(DME)$ (**1b**)	CH_3CN	120	25	71
$Mo(N\text{-}3,5\text{-}Me_2\text{-}C_6H_3)_2Cl_2(DME)$ (**1c**)	75% toluene/25% DME	36	25	88
$Mo(N\text{-}2\text{-}^iPr_2\text{-}C_6H_4)_2Cl_2(DME)$ (**1d**)	DME	12	52	97
$Mo(N\text{-}2\text{-}CF_3\text{-}C_6H_4)_2Cl_2(DME)$ (**1e**)	DME	12	65	74
$Mo(N\text{-}2\text{-}Ph\text{-}C_6H_4)_2Cl_2(py)_2$ (**1f**)	95% benzene/5% pyridine	12	60	80
$Mo(N\text{-}1\text{-}adamantyl)_2Cl_2(DME)$ (**1g**)	85% toluene/15% DME	12	70	70

TABLE 2. Reaction conditions and yields of complexes of type 2

Compound	Solvent	Yield (%)
Mo(N-4-CN-2,6-$^{i}Pr_2$-C_6H_2)$_2$(CH_2CMe_3)$_2$ (**2a**)	thf	45
Mo(N-4-Br-2,6-$^{i}Pr_2$-C_6H_2)$_2$(CH_2CMe_2Ph)$_2$ (**2b**)	thf	44
Mo(N-2,6-Me_2-C_6H_3)$_2$(CH_2CMe_2Ph)$_2$ (**2c**)	ether	82
Mo(N-2,6-Me_2-C_6H_3)$_2$(CH_2CMe_3)$_2$ (**2d**)	ether	68
Mo(N-3,5-Me_2-C_6H_3)$_2$(CH_2CMe_2Ph)$_2$ (**2e**)	thf	66
Mo(N-2-^{i}Pr-C_6H_4)$_2$(CH_2CMe_2Ph)$_2$ (**2f**)	ether	66
Mo(N-2-CF_3-C_6H_4)$_2$(CH_2CMe_2Ph)$_2$ (**2g**)	thf	99
Mo(N-2-^{t}Bu-C_6H_4)$_2$(CH_2CMe_2Ph)$_2$ (**2h**)	thf	98
Mo(N-2-^{t}Bu-C_6H_4)$_2$(CH_2CMe_3)$_2$ (**2i**)	ether	87
Mo(N-2-Ph-C_6H_4)$_2$(CH_2CMe_2)$_2$ (**2j**)	ether	71
Mo(N-1-adamantyl)$_2$(CH_2CMe_2Ph)$_2$ (**2k**)	ether	82

The third step in the synthesis of the "universal precursor" (**3**, eqn. (3), Table 3; $OTf = O_3SCF_3$) involves the addition of triflic acid to **2**. This step can be problematic, although problems usually can be traced to the use of impure triflic acid or dimethoxyethane.

$$\mathbf{2} + 3\ TfOH \xrightarrow{DME} \underset{(\mathbf{3})}{Mo(NR)(CHR')(OTf)_2(DME)} + [RNH_3][OTf] + R'CH_3 \quad (3)$$

α-Hydrogen abstraction proceeds cleanly in all cases except in the attempted synthesis of Mo(N-4-CN-2,6-$^{i}Pr_2$-C_6H_2)-(CHR')$(OTf)_2$(DME). In this case α-hydrogen abstraction proceeds very slowly in DME and the products are unstable. In acetonitrile α-hydrogen abstraction is fast, but the product is stable only in acetonitrile and therefore cannot be isolated. It should be noted that other alkyl ligands can undergo α-hydrogen abstraction. For example, we have found that α-hydrogen abstraction in Mo(N-2,6-$^{i}Pr_2$-C_6H_3)$_2$(CH_2Ph)$_2$ proceeds cleanly to yield the corresponding benzylidene complex [3].

In general, two isomers of complexes of type **3** are found in solution. The major isomer is a symmetric species that contains a *syn* alkylidene ligand as shown in Fig. 1(a); an example of a complex with this structure has been characterized crystallographically [1]. The minor isomer has no plane of symmetry. Since the alkylidene and imido ligands are most likely *cis* to one another, the triflate ligands must be *cis*. Spectroscopic

TABLE 3

Yields and selected NMR data for complexes of type 3

Compound		Yield (%)	δH_α (ppm) [a]	δC_α (ppm) [a]	$^{1}J_{CH}$ (Hz)
Mo(N-4-Br-2,6-$^{i}Pr_2$-C_6H_2)(CHCMe$_2$Ph)$(OTf)_2$(DME) (**3a**)		70	14.31	328.5	122
Mo(N-2,6-Me_2-C_6H_3)(CHCMe$_3$)$(OTf)_2$(DME) (**3b**)	(major, 85%) (minor)	82	14.07 [b] 14.80 [b]	330.2 [b]	118
Mo(N-2,6-Me_2-C_6H_3)(CHCMe$_2$Ph)$(OTf)_2$(DME) (**3c**)		70	14.23	326.2	122
Mo(N-3,5-Me_2-C_6H_3)(CHCMe$_2$Ph)$(OTf)_2$(DME) (**3d**)	(major, 97%) (minor)	74	13.80 14.96	323.6	126
Mo(N-2-^{i}Pr-C_6H_4)(CHCMe$_2$Ph)$(OTf)_2$(DME) (**3e**)	(major, 94%) (minor)	74	14.14 15.08	326.1	
Mo(N-2-CF_3-C_6H_4)(CHCMe$_2$Ph)$(OTf)_2$(DME) (**3f**)	(major, 80%) (minor)	60	14.05 15.17	325.9 334.4	
Mo(N-2-^{t}Bu-C_6H_4)(CHCMe$_2$Ph)$(OTf)_2$(DME) (**3g**)	(major, 63%) (minor)	71	14.10 [b] 14.82 [b]	325.2 [b] 332.3 [b]	
Mo(N-2-^{t}Bu-C_6H_4)(CHCMe$_3$)$(OTf)_2$(DME) (**3h**)	(major, 85%) (minor)	67	13.99 [b] 14.76 [b]	328.8 [b]	
Mo(N-2-Ph-C_6H_4)(CHCMe$_3$)$(OTf)_2$(DME) (**3i**)	(major, 55%) (minor)	72	13.99 [c] 14.66 [c]	328.9 [c] 337.8 [c]	
Mo(N-1-adamantyl)(CHCMe$_2$Ph)$(OTf)_2$(DME) (**3j**)	(major, 67%) (minor)	67	14.72 [b] 13.87 [b]	327.4 [b] 318.9 [b]	128 121

[a] In C_6D_6 unless otherwise noted. [b] In CD_2Cl_2. [c] In $CDCl_3$.

data (^{1}H, ^{13}C and ^{19}F NMR) indicate that the methylene groups in the DME ligand are inequivalent, the triflate ligands are inequivalent, and in complexes containing the neophylidene ligand, the neophylidene methyl groups are inequivalent. Therefore, we conclude that the geometry is one of the two structures

TABLE 4. Yields and selected NMR data (C_6D_6 unless noted) for complexes of type **4**

Compound	Yield (%)	$\delta(^1H_\alpha)$ ppm	$\delta(^{13}C_\alpha)$ ppm	$^1J_{CH}$ (Hz)
Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCEt$_3$)$_2$ **(4a)**	oil	11.17	261.8	119
Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(O-1-adamantyl)$_2$ **(4b)**	75	11.33	262.2	119
Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)[OCMe$_2$(CMe$_3$)]$_2$ **(4c)**	65	11.29	236.4	119
Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCHMe$_2$)$_2$ **(4d)**	73	11.24		
Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe$_3$)$_2$ **(4e)** [1]		11.34		119
Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)[OCMe$_2$(CF$_3$)]$_2$ **(4f)**	53	11.68	273.9	120
Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ **(4g)** [3]		12.12	284.9	120
Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)[OC(CF$_3$)$_3$]$_2$)$_2$ **(4h)**	78	12.87 [a]	298.6	122
Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)[OC(CF$_3$)$_2$CF$_2$CF$_2$CF$_3$]$_2$ **(4i)**	68	12.92	299.6	122
Mo(N-4-Br-2,6-^{i}Pr$_2$-C$_6$H$_2$)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ **(4j)**	60	12.01 [a]	284.9	121
Mo(N-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe$_3$)$_2$ **(4k)**	27 [b]	11.31	266.3	115
Mo(N-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)[OCMe(CF$_3$)]$_2$ **(4l)**	68 [c]	11.72	274.6	
Mo(N-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_3$)(O-2,6-^{i}Pr$_2$-C$_6$H$_3$)$_2$ **(4m)**	26	11.43	277.9	116
Mo(N-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)[OCMe$_2$(CF$_3$)$_2$]$_2$ **(4n)**	30	12.18	289.5	
Mo(N-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)[OC(CF$_3$)$_2$CF$_2$CF$_2$CF$_3$]$_2$ **(4o)**	60	12.86	299.2	123
Mo(N-3,5-Me$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ **(4p)**	oil	11.91		
Mo(N-2-^{i}Pr$_2$-C$_6$H$_4$)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ **(4q)**	78	11.96	283.4	121
Mo(N-2-CF$_3$-C$_6$H$_4$)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ **(4r)**	74	11.93	284.7	
Mo(N-2-^{t}Bu-C$_6$H$_4$)(CHCMe$_2$Ph)(OCMe$_3$)$_2$ **(4s)**	oil	11.05		
Mo(N-2-^{t}Bu-C$_6$H$_4$)(CHCMe$_3$)(OCMe$_3$)$_2$ **(4t)**	oil	10.98	262.7	113
Mo(N-2-^{t}Bu-C$_6$H$_4$)(CHCMe$_2$Ph)(O-1-adamantyl)$_2$ **(4u)**	40	11.06	259.4	
Mo(N-2-^{t}Bu-C$_6$H$_4$)(CHCMe$_3$)(O-2,6-^{i}Pr$_2$-C$_6$H$_3$)$_2$ **(4v)**	oil	11.52		
Mo(N-2-^{t}Bu-C$_6$H$_4$)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ **(4w)**	77	11.79	281.5	
Mo(N-2-^{t}Bu-C$_6$H$_4$)(CHCMe$_3$)[OCMe(CF$_3$)$_2$]$_2$ **(4x)**	73	11.71	284.3	118
Mo(N-2-Ph-C$_6$H$_4$)(CHCMe$_3$)[OCMe(CF$_3$)$_2$]$_2$ **(4y)**	63	11.81 [c]	287.0 [c]	117 [c]
Mo(N-1-adamantyl)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ **(4z)**	65	11.84 [d] 13.10 [e]	278.3 [f]	120 [f]

[a] Value is reported in toluene-d_8. [b] The high solubility of **4k** limits the yield of isolated crystalline product. [c] Value reported in $CDCl_3$. [d] Major (90%, *syn*). [e] Minor (10%, *anti*). [f] Value is reported in CD_2Cl_2.

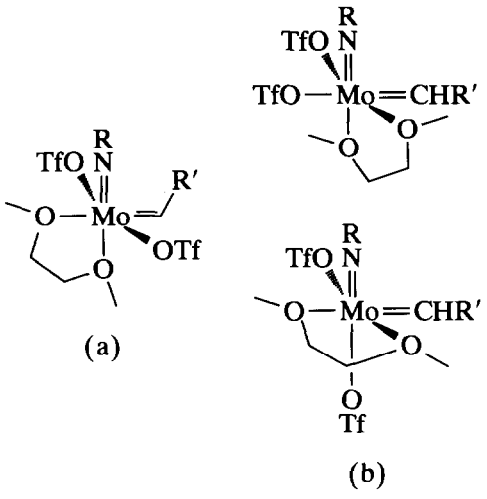

Fig. 1. (a) Major isomer of **3** and (b) the two possible core structures of the minor isomer of **3**.

depicted in Fig. 1(b). We are less certain about whether the minor isomer contains a *syn* or an *anti* alkylidene rotamer. In four- and and five-coordinate alkylidene complexes, the magnitude of J_{CH} can be used to assign the *syn/anti* orientation of the alkylidene relative to the imide [26]. However, in six-coordinate species such as $Mo(CH_2)(N\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)[OCMe(CF_3)_2]_2$(bipyridine), J_{CH} is the same for each of the methylene protons [3]. In polar solvents such as dichloromethane, the amount of the minor isomer increases relative to the major isomer, as one might expect on the basis of the likely higher dipole moment for the minor isomer.

The final step in the catalyst synthesis involves addition of an alkoxide to **3** (eqn. (4)).

$$3 + 2\ MOR'' \xrightarrow[-30°C]{-DME} \underset{(4)}{Mo(NR)(CHR')(OR'')_2} + M(OTf) \quad (4)$$

M = Li, K

OR'' = $OCMe_3$, $OCEt_3$, O-1-adamantyl, $OCMe_2CF_3$, $OCMe(CF_3)_2$, $OC(CF_3)_3$, $OC(CF_3)_2CF_2CF_2CF_3$ or $O(2,6\text{-}^iPr_2\text{-}C_6H_3)$

Complexes that have been synthesized along with pertinent NMR data are listed in Table 4. The conditions for addition of the alkoxide vary little from those previously reported except that in some cases the reaction proceeds in higher yield in tetrahydrofuran than in diethyl ether. A crucial requirement for the success of this reaction is that **3** be completely free from any ammonium salt that was formed during its synthesis. It is interesting to note that imido ligands that are considerably less sterically demanding than 2,6-diisopropylphenylimido still provide enough steric protection to stabilize four-coordinate neopentylidene or neophylidene complexes. (The stability of analogs that contain relatively small alkylidene ligands is likely to be significantly lower.) For example, even complexes that contain 2-substituted phenylimido ligands can be synthesized in good yields. In some cases, the products could only be obtained as oils (**4a**, **4s**, **4t**, and **4v**), most notably complexes containing $OCMe_3$ and $OCEt_3$ ligands. However, analogous adamantoxy complexes are crystalline (compare **4s** with **4u**). Complexes that contain *tert*-butyl imido ligands have been synthesized by other means but are oils [27]. In contrast, the adamantylimido complex (**4z**) is a crystalline species. Adamantylimido complexes are expected to offer the greatest potential contrast with phenylimido derivatives as a result of the electron-donating ability of the adamantyl group relative to the phenyl group and the roughly spherical shape of the adamantyl group.

As has been noted previously in complexes of this type, the alkylidene proton and carbon chemical shifts correlate with the electron-withdrawing ability of the alkoxide ligand [1]. This is most obvious in complexes that contain the 2,6-diisopropylphenylimido ligand (**4a–4i**; Table 4). (It is unlikely that **4i** is actually more electron-withdrawing than **4h** since a less electronegative carbon in **4h** is replaced by a fluorine in **4i**.) It should also be noted that *ca.* 10% of the *anti* rotamer can be observed at room temperature in the case of **4z**. All other initiators exist as predominantly the *syn* rotamer at room temperature.

Some of the variations reported here, as well as others that should be readily preparable by these procedures, could help shed light on the mechanism of acyclic or cylic olefin metathesis. Some of the factors that may be important are the magnitude of the *anti/syn* equilibrium and their rates of interconversion, the relative reactivity of *anti* and *syn* rotamers, in addition to the possibility of more than one mode of attack of an olefin on the metal [22]. Future papers will be aimed toward the exploration of these issues in detail.

3. Experimental details

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques unless otherwise specified. Pentane was washed with sulfuric/nitric acid (95/5 v/v), sodium bicarbonate, and water, stored over calcium chloride, and distilled from sodium benzophenone ketyl under nitrogen. Reagent grade diethyl ether, tetrahydrofuran, toluene, benzene, and 1,2-dimethoxy-

ethane were distilled from sodium benzophenone ketyl under nitrogen. Reagent grade dichloromethane and acetonitrile were distilled from calcium hydride under nitrogen. Reagent grade N,N-dimethylformamide was dried over molecular sieves (4 Å). Benzene-d_6, toluene-d_8 and CD_2Cl_2 were sparged with argon and stored over molecular sieves (4 Å). CD_3CN was vacuum distilled from CaH_2. $CDCl_3$ was passed through a column of Al_2O_3 and stored over molecular sieves (4 Å). NMR data are listed in parts per million downfield from tetramethylsilane for proton and carbon and downfield from $CFCl_3$ for fluorine. Coupling constants are listed in hertz. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN analyzer. All chemicals were reagent grade and were purified by known methods [28]. Trifluoromethanesulfonic acid (triflic acid) is best used from a freshly opened ampoule. Potassium alkoxide salts were prepared by treating the alcohol with KH or KCH_2Ph [29], and lithium alkoxide salts by treating the alcohol with ^{n}BuLi. $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)(OSO_2CF_3)_2(DME)$ [1], $HOC(CF_3)_2CF_2CF_2CF_3$ [30], $KOC(CF_3)_3$ [31], $Mo(N\text{-}2,6\text{-}Me_2C_6H_3)_2Cl_2(DME)$ [2] and $Mo(N\text{-}2\text{-}^tBu\text{-}C_6H_4)Cl_2(DME)$ [2] were prepared by literature methods. The syntheses of bisimido complexes (**1**) reported here are adapted from the procedure used to prepare $Mo(N\text{-}2,6\text{-}^iPr_2\text{-}C_6H_3)_2Cl_2(DME)$ [2]; conditions are listed in Table 1. The alkylation procedure used to prepare complexes **2** is analogous to that reported elsewhere [1]; solvents and yields are listed in Table 2. Complexes **3** were prepared using synthetic procedures derived from that reported earlier [1] on a 5–10 mmol scale; yields and NMR data for the alkylidene ligand are listed in Table 3. The syntheses of dialkoxide complexes **4** followed the procedure reported elsewhere [1] and were executed on a 1–3 mmol scale. Yields and alkylidene NMR data for complexes **4** are listed in Table 4. Only significant differences in procedures are noted below.

3.1. *4-Br-2,6-$^iPr_2$-$C_6H_2NH_2$*

Bromine (35.4 g, 0.222 mol) was added via a dropping funnel to a stirred slurry of $2,6\text{-}^iPr_2\text{-}C_6H_3NH_3Cl$ (47.4 g, 0.222 mol) in 1 L of glacial acetic acid. After addition was complete the reaction mixture was stirred for 1 h. The precipitated salt was washed with fresh acetic acid, air dried, and recrystallized from benzene. The free base was prepared by adding aqueous NaOH and ether to the solid salt. The ether phase was dried over $MgSO_4$, filtered, and the ether removed *in vacuo* to yield the colorless liquid product (35.0 g, 61%). ^{1}H NMR (CD_2Cl_2): δ 7.10 (s, 2, H_m), 3.76 (br, 2, NH_2), 2.88 (sept, 2, CHMe$_2$), 1.24 (d, 12, CH*Me*$_2$).

3.2. *4-CN-2,6-$^iPr_2$-$C_6H_2NH_2$*

$4\text{-Br-}2,6\text{-}^iPr_2\text{-}C_6H_2NH_2$ (35.0 g, 0.14 mol) and CuCN (15 g, 0.17 mol) were combined with 25 ml of N,N-dimethylformamide in a 100 ml flask fitted with a reflux condenser. The mixture was refluxed for 12 h. Soon after heating began the reaction mixture turned deep purple to nearly black. The hot mixture was poured directly into 100 ml of aqueous NaCN (27.4 g, 0.56 mol) and the flask was washed with a small quantity of benzene. The mixture was shaken vigorously for five minutes and then transferred to a separatory funnel where the aqueous phase was separated and washed twice with benzene. The organic layers were combined and washed vigorously twice with NaCN solution, and then washed twice again with water. The organic layer was dried over $MgSO_4$ and filtered. The solvents were removed *in vacuo* to yield essentially pure (according to proton NMR) black product. The product was purified by slow sublimation under high vacuum at 90°C. ^{1}H NMR (CD_2Cl_2): δ 7.29 (s, 2, H_m), 4.29 (br, 2, NH_2), 2.87 (sept, 2, CHMe$_2$), 1.26 (d, 12, CH*Me*$_2$). ^{13}C NMR (CD_2Cl_2): δ 145.4, 132.6, 127.6 (C Ar), 121.3 (CN), 100.2 (C_p), 28.2 (CHMe$_2$), 22.1 (CH*Me*$_2$). IR (Nujol) 3510, 3410 (NH), 2170 (CN) cm^{-1}. Anal. Found: C, 77.13; H, 9.17; N, 13.57. $C_{18}H_{18}N_2$ calcd.: C, 77.18; H, 8.97; N, 13.85%. M.p. (corr.) 92.8–93.7°C.

3.3. *Mo(N-4-Br-2,6-$^iPr_2$-C_6H_2)$_2Cl_2$(DME) (1a)*

^{1}H NMR (C_6D_6): δ 7.30 (s, 4, H_m), 4.08 (sept, 4, CHMe$_2$), 3.37 (s, 6, OMe), 3.10 (s, 4, OCH_2), 1.06 (d, 24, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 152.2, 147.1, 126.8, 121.7 (C Ar), 70.9 (OMe), 62.6 (OCH_2), 28.1 (CHMe$_2$), 24.6 (CH*Me*$_2$). Anal. Found: C, 44.35; H, 5.90; N, 3.43. $MoC_{28}H_{42}Br_2Cl_2N_2O_2$ calcd.: C, 43.94; H, 5.53; N, 3.66%.

3.4. *Mo(N-4-CN-2,6-$^iPr_2$-C_6H_2)$_2Cl_2$(DME) (1b)*

Triethylamine (2.26 g, 22.3 mmol), chlorotrimethylsilane (4.86 g, 44.9 mmol), and $4\text{-CN-}2,6\text{-}^iPr_2\text{-}C_6H_2NH_2$ (2.262 g, 11.18 mmol) were added to a stirred slurry of ammonium dimolybdate (0.964 g, 2.83 mmol) in 50 ml of acetonitrile at room temperature. Addition of TMSCl produced a yellow solution, while addition of the aniline produced a red solution. The mixture was stirred for 5 days at 25–30°C. Solvent was removed *in vacuo* and the solids were extracted with a minimum amount of DME. The salts were filtered off and washed with DME until the washings were colorless. Removal of solvent from the filtrate yielded the crude product in quantitative yield. The product was recrystallized from a mixture of DME and ether at −30°C to yield a brick red powder (2.55 g, 71%). ^{1}H NMR (CD_3CN): δ 7.42 (s, 4, H_m), 3.85 (sept, 4, CHMe$_2$), 3.49 (br, 4, OCH_2), 3.31 (br, 6, OMe), 1.01 (d, 24, CH*Me*$_2$). ^{13}C NMR

(C_6D_6, a drop of DME was added to solubilize the complex): δ 155.2 (C_{ipso}), 145.8 (C_o), 127.5 (C_m), 119.0 (CN), 110.9 (C_p), 71.9 (OCH_2), 58.8 (OMe), 28.0 ($CHMe_2$), 24.3 ($CHMe_2$).

3.5. Mo(N-3,5-Me_2-C_6H_3)$_2Cl_2$(DME) (1c)

Triethylamine (11.90 g, 117.4 mmol), chlorotrimethylsilane (28.86 g, 266.6 mmol), and 3,5-Me_2-$C_6H_3NH_2$ (7.13 g, 58.8 mmol) were added to a stirred slurry of ammonium dimolybdate (5.00 g, 14.7 mmol) in a mixture of 30 ml of DME and 90 ml of toluene at room temperature for 36 h. The mixture was filtered through Celite to remove the salts formed during the reaction. The volatiles were removed to afford 12.85 g of product (88%). ^{1}H NMR (C_6D_6): δ 7.10 (s, 4, H Ar), 6.46 (s, 2, H Ar), 3.52 (br s, 6, OMe), 3.36 (s, 4, OCH_2), 1.91 (s, 12, Me). ^{13}C NMR (C_6D_6): δ 157.3, 138.1, 129.3, 121.7 (C Ar), 71.4 (OMe), 62.5 (br, OCH_2), 21.0 (Me).

3.6. Mo(N-2-^{i}Pr-C_6H_4)$_2Cl_2$(DME) (1d)

^{1}H NMR (C_6D_6): δ 7.68 (d, 2, H_o), 7.03 (d, 2, H_m), 6.84 (dd, 2, H_m or H_p), 6.77 (dd, 2, H_m or H_p), 3.89 (sept, 2, $CHMe_2$), 3.44 (s, 6, OMe), 3.19 (s, 4, OCH_2), 1.25 (d, 12, $CHMe_2$). ^{13}C NMR (C_6D_6): δ 155.5, 141.5, 127.2, 126.4, 125.5, 125.3 (C Ar), 71.1 (OCH_2), 62.8 (OMe), 28.9 ($CHMe_2$), 24.0 ($CHMe_2$). Anal. Found: C, 50.12; H, 6.19; N, 5.36. $MoC_{22}H_{32}Cl_2N_2O_2$ calcd.: C, 50.49; H, 6.16; N, 5.35%.

3.7. Mo(N-2-CF_3-C_6H_4)$_2Cl_2$(DME) (1e)

^{1}H NMR (C_6D_6): δ 7.80 (d, 2, H Ar), 7.16 (d, 2, H Ar), 6.75 (dd, 2, H Ar), 6.40 (dd, 2, H Ar), 3.47 (s, 6, OMe), 3.13 (s, 4, OCH_2). ^{13}C NMR (C_6D_6): δ 153.2, 132.4, 126.0, 122.0, 125.5 (C Ar), 123.9 (CF_3), 119.4 (C_o), 71.2 (OCH_2), 63.2 (OMe). ^{19}F NMR (C_6D_6): δ −60.6 (CF_3).

3.8. Mo(N-2-Ph-C_6H_4)$_2Cl_2$(py)$_2$ (1f)

Triethylamine (2.58 g, 25.5 mmol), chlorotrimethylsilane (5.89 g, 54.2 mmol), pyridine (5.04 g, 63.8 mmol) and 2-Ph-$C_6H_4NH_2$ (2.16 g, 12.8 mmol) were added to a stirred slurry of ammonium dimolybdate (1.08 g, 3.19 mmol) in 50 ml of benzene at room temperature. The mixture was stirred for 12 h at 60°C, cooled to room temperature, and filtered through Celite. The salts were washed with benzene until the washings were colorless. The solvent was removed from the filtrate *in vacuo*. The red-purple product was recrystallized from a mixture of dichloromethane and pentane at −30°C (3.36 g, 80%). ^{1}H NMR ($CDCl_3$): δ 8.36 (d, 4, H Ar), 7.66 (d, 2, H Ar), 7.56 (d, 4, H Ar), 7.48 (t, 2, H Ar), 7.34 (d, 2, H Ar), 7.27–7.05 (m, 10, H Ar), 6.87 (m, 4, H Ar). ^{13}C NMR ($CDCl_3$): δ 154.4, 151.4, 138.7, 137.2, 134.0, 130.4, 129.0, 128.9, 127.9, 127.6, 127.0, 126.9, 123.2 (C Ar). Anal. Found: C, 61.96; H, 4.30; N, 8.10. $MoC_{34}H_{28}N_4Cl_2$ calcd.: C, 61.92; H, 4.28; N, 8.50%.

3.9. Mo(N-1-adamantyl)$_2Cl_2$(DME) (1g)

Ammonium dimolybdate (5.0 g, 14.7 mmol) was suspended in a mixture of 150 ml of toluene and 20 ml of DME. Triethylamine (16.9 g, 159 mmol), chlorotrimethylsilane (25.8 g, 238 mmol), and 1-aminoadamantane (8.0 g, 52.9 mmol) were added sequentially and the mixture was heated to 70°C for 12 h. The salts were filtered off and the solvents were removed from the filtrate *in vacuo*. The yellow-orange product was recrystallized from toluene (11.3 g, 76%). ^{1}H NMR (CD_2Cl_2): δ 3.80 (s, 4, OCH_2), 3.75 (s, 6, OMe), 2.12 (m, 6, CH), 2.05 (m, 12, CH_2), 1.66 (m, 12, CH_2). ^{13}C NMR (C_6D_6): δ 73.8 (NC), 71.3 (OMe), 63.2 (OCH_2), 43.5 (CH_2), 36.5 (CH_2), 30.0 (CH).

3.10. Mo(N-4-CN-2,6-^{i}Pr_2-C_6H_2)$_2$(CH_2CMe_3)$_2$ (2a)

^{1}H NMR (toluene-d_8): δ 7.10 (s, 4, H_m), 3.36 (sept, 4, $CHMe_2$), 2.20 (s, 4, CH_2), 1.12 (s, 18, CMe_3), 0.84 (d, 24, $CHMe_2$). Anal. Found: C, 67.75; H, 8.41; N, 8.86. $MoC_{36}H_{54}N_4$ calcd.: C, 67.69; H, 8.52; N, 8.77%.

3.11. Mo(N-4-Br-2,6-^{i}Pr_2-C_6H_2)$_2$(CH_2CMe_2Ph)$_2$ (2b)

^{1}H NMR (C_6D_6): δ 7.36 (d, 4, H Ar), 7.25 (s, 4, H Ar), 7.19 (dd, 4, H Ar), 7.06 (t, 2, H Ar), 3.41 (sept, 4, $CHMe_2$), 1.60 (s, 4, CH_2), 1.40 (s, 12, CMe_2Ph), 0.91 (d, 24, $CHMe_2$). ^{13}C NMR (C_6D_6): δ 152.0, 150.1, 144.9, 128.6, 126.7, 126.6, 126.5, 119.9 (C Ar), 79.9 (CH_2), 39.9 (CMe_2Ph), 32.4 (CMe_2Ph), 28.5 ($CHMe_2$), 23.5 ($CHMe_2$). Anal. Found: C, 60.77; H, 6.80; N, 3.06. $MoC_{44}H_{58}Br_2N_2$ calcd.: C, 60.70; H, 6.71; N, 3.22%.

3.12. Mo(N-2,6-Me_2-C_6H_3)$_2$(CH_2CMe_2Ph)$_2$ (2c)

^{1}H NMR (C_6D_6): δ 7.39 (d, 4, H Ar), 7.15 (dd, 4, H Ar), 7.05 (t, 2, H Ar), 6.87 (d, 4, H_m NAr), 6.67 (t, 2, H Ar), 2.13 (s, 12, Me), 1.74 (s, 4, CH_2), 1.43 (s, 12, CMe_2Ph). ^{13}C NMR (C_6D_6): δ 156.5, 150.6, 132.4, 128.6, 127.9, 126.6, 126.3, 124.9 (C Ar), 77.4 (CH_2), 39.7 (CMe_2Ph), 32.3 (CMe_2Ph), 18.9 (Me). Anal. Found: C, 71.74; H, 7.31; N, 4.38. $MoC_{36}H_{44}N_2$ calcd.: C, 71.98; H, 7.38; N, 4.66%.

3.13. Mo(N-2,6-Me_2-C_6H_3)$_2$(CH_2CMe_3)$_2$ (2d)

^{1}H NMR (C_6D_6): δ 6.87 (d, 4, H Ar), 6.77 (t, 2, H Ar), 2.25 (s, 12, Me), 2.20 (s, 4, CH_2), 1.18 (s, 18, CMe_3). ^{13}C NMR (C_6D_6): δ 156.6, 132.4, 128.4, 125.1 (C Ar), 79.7 (CH_2), 33.9 (CMe_3), 33.8 (CMe_3), 19.1 (Me). Anal. Found: C, 65.64; H, 8.62; N, 6.01. $MoC_{26}H_{40}N_2$ calcd.: C, 65.53; H, 8.46; N, 5.88%.

3.14. Mo(N-3,5-Me_2-C_6H_3)$_2$(CH_2CMe_2Ph)$_2$ (2e)

^{1}H NMR (C_6D_6): δ 7.41 (d, 4, H Ar), 7.16 (dd, 4, H Ar), 7.05 (t, 2, H Ar), 6.59 (s, 4, H Ar), 6.50 (s, 2, H Ar), 2.21 (s, 4, CH_2), 2.03 (s, 12, Me), 1.57 (s, 12, Me). ^{13}C NMR (C_6D_6): δ 158.1, 152.0, 137.7, 128.5, 127.3, 126.3, 125.7, 122.3 (C Ar), 81.2 (t, CH_2), 42.0 (s, *C*Me_2Ph), 33.4 (q, C*Me*$_2$Ph), 21.1 (q, Me).

3.15. Mo(N-2-^{i}Pr-C_6H_4)$_2$(CH_2CMe_2Ph)$_2$ (2f)

^{1}H NMR (C_6D_6): δ 7.38 (d, 4, H Ar), 7.17 (dd, 4, H Ar), 7.09–7.04 (m, 6, H Ar), 6.88–6.80 (m, 4, H Ar), 3.70 (sept, 2, C*H*Me_2), 1.85 (s, 4, CH_2), 1.47 (s, 12, C*Me*$_2$Ph), 1.20 (d, 12, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 154.8, 151.1, 141.0, 128.6, 126.4, 126.3, 126.2, 126.2, 125.9, 125.4 (C Ar), 78.5 (CH_2), 40.8 (*C*Me_2Ph), 32.8 (C*Me*$_2$Ph), 28.5 (*C*HMe_2), 23.5 (CH*Me*$_2$).

3.16. Mo(N-2-CF_3-C_6H_4)$_2$(CH_2CMe_2Ph)$_2$ (2g)

^{1}H NMR (C_6D_6): δ 7.36 (d, 4, H Ar), 7.27 (d, 2, H Ar), 7.11 (dd, 4, H Ar), 6.98 (t, 2, H Ar), 6.77 (d, 2, H Ar), 6.69 (dd, 2, H Ar), 6.50 (dd, 2, H Ar), 2.00 (s, 4, C*H*$_2$), 1.43 (s, 12, C*Me*$_2$Ph). ^{13}C NMR (C_6D_6): δ 153.3, 150.3, 132.2, 128.7, 128.1, 126.2, 126.1, 124.5, 125.7 (C Ar), 124.5 (q, CF_3), 120.5 (C Ar), 82.4 (CH_2), 40.9 (*C*Me_2Ph), 32.3 (C*Me*$_2$Ph). ^{19}F (C_6D_6): δ −60.7 (CF_3). Anal. Found: C, 60.36; H, 5.40; N, 4.01. $MoC_{34}H_{34}F_6N_2$ calcd.: C, 60.00; H, 5.04; N, 4.12%.

3.17. Mo(N-2-^{t}Bu-C_6H_4)$_2$(CH_2CMe_2Ph)$_2$ (2h)

^{1}H NMR (C_6D_6): δ 7.40 (d, 4, H Ar), 7.18 (d, 2, H Ar), 7.17 (dd, 4, H Ar), 7.10 (d, 2, H Ar), 7.03 (t, 2, H Ar), 6.76 (dd, 2, H Ar), 6.71 (dd, 2, H NAr), 1.90 (s, 4, CH_2), 1.60 (s, 18, C*Me*$_3$), 1.51 (s, 12, C*Me*$_2$Ph). ^{13}C NMR (C_6D_6): δ 154.4, 151.3, 139.8, 130.8, 128.7, 126.8, 126.2, 126.2, 126.0, 125.6 (C Ar), 81.0 (CH_2), 41.0 (*C*Me_2Ph), 35.7 (*C*Me_3), 32.8 (C*Me*$_2$Ph), 30.5 (C*Me*$_3$).

3.18. Mo(N-2-^{t}Bu-C_6H_4)$_2$(CH_2CMe_3)$_2$ (2i)

^{1}H NMR (C_6D_6): δ 7.33 (d, 2, H Ar), 7.21 (d, 2, H Ar), 6.79 (dd, 2, H Ar), 6.72 (dd, 2, H Ar), 2.11 (s, 4, CH_2), 1.95 (s, 18, C*Me*$_3$), 1.67 (s, 18, C*Me*$_3$). ^{13}C NMR (C_6D_6): δ 154.5, 139.7, 131.1, 126.9, 126.2, 125.8 (C Ar), 82.8 (CH_2), 36.3 (*C*Me_3), 35.3 (*C*Me_3), 33.9 (C*Me*$_3$), 30.8 (C*Me*$_3$).

3.19. Mo(N-2-Ph-C_6H_4)$_2$(CH_2CMe_3)$_2$ (2j)

^{1}H NMR (C_6D_6): δ 7.65 (m, 4, H Ar), 7.41 (m, 2, H Ar), 7.27–7.09 (m, 6, H Ar), 6.96–6.83 (m, 6, H Ar), 1.73 (s, 4, CH_2), 0.96 (s, 18, C*Me*$_3$). ^{13}C NMR ($CDCl_3$): δ 153.9, 139.9, 133.8, 129.9, 129.7, 127.8, 127.6, 127.0, 126.8, 124.9 (C Ar), 83.1 (CH_2), 34.7 (*C*Me_3), 33.1 (C*Me*$_3$). Anal. Found: C, 71.44: H, 7.09; N, 4.57. $MoC_{34}H_{40}N_2$ calcd.: C, 71.31; H, 7.04; N, 4.89%.

3.20. Mo(N-1-adamantyl)$_2$(CH_2CMe_2Ph)$_2$ (2k)

^{1}H NMR (C_6D_6): δ 7.40 (d, 4, H Ar), 7.30 (dd, 4, H Ar), 7.14 (t, 2, H Ar), 2.09 (br, 6, CH), 1.88 (br d, 12, CH_2), 1.67 (br t, 12, CH_2), 1.59 (s, 4, CH_2), 1.44 (s, 12, C*Me*$_2$Ph). ^{13}C NMR (C_6D_6): δ 153.0, 128.3, 126.2, 125.5 (C Ar), 72.3 (CH_2), 68.7 (NC), 46.0 (CH_2), 39.8 (*C*Me_2Ph), 36.7 (CH_2), 33.4 (C*Me*$_2$Ph), 30.5 (CH). Anal. Found: C, 71.74; H, 7.31; N, 4.38. $MoC_{36}H_{44}N_2$ calcd.: C, 71.98; H, 7.38; N, 4.66%.

3.21. Synthesis of bistriflate complexes

In order to obtain high yields it is important that reagents and solvents be absolutely pure. In a typical procedure, chilled triflic acid is added to chilled DME prior to adding it to a solution of **2**. The reaction proceeds well if the triflic acid/DME solution is colorless, pale yellow, or even slightly brown. If, however, the color is black or purple the reaction does not proceed in high yield and pure product is difficult to separate from side products. In some cases the workup procedure has also been modified from that previously reported. The crude solid product is typically brown. The dark-colored impurities may be removed by washing the crude product with cold diethyl ether. It is important that the ether be chilled since in many cases **3** is slightly soluble in ether. Alternatively, the washing step may be performed after initial removal of salt.

3.22. Mo(N-4-Br-2,6-^{i}Pr_2-C_6H_2)(CHCMe_2Ph)(OSO_2-CF_3)$_2$(DME) (3a)

The dark crude product was extracted with toluene and the anilinium triflate was filtered off. The product was purified by crystallization from toluene followed by washing with cold toluene. ^{1}H NMR δ (C_6D_6): 14.31 (s, 1, CH), 7.52 (d, 2, H Ar), 7.22 (s, 2, H Ar), 7.09 (dd, 2, H Ar), 6.87 (t, 1, H Ar), 3.75 (s, 3, OMe), 3.65 (sept, 2, C*H*Me_2), 3.22 (m, 2, OCH_2), 2.85 (m, 2, OCH_2), 2.78 (m, 3, OMe), 1.82 (s, 6, C*Me*$_2$Ph), 1.21 (d, 6, CH*Me*$_2$), 1.05 (d, 6, CH*Me*$_2$). ^{13}C (C_6D_6): δ 328.5 (d, J_{CH} = 122, CH), 154.0, 150.4, 148.3, 128.6, 127.6, 126.7, 126.6, 125.5 (C Ar), 119.9 (q, CF_3), 72.8 (OCH_2), 70.1 (OCH_2), 65.8 (OMe), 62.0 (OMe), 58.9 (*C*Me_2Ph), 31.0 (C*Me*$_2$Ph), 28.4 (*C*HMe_2), 25.2 (CH*Me*$_2$), 22.3 (CH*Me*$_2$). ^{19}F (C_6D_6): δ −77.0 (CF_3).

3.23. Mo(N-2,6-Me_2-C_6H_3)(CHCMe_3)(OSO_2CF_3)$_2$-(DME) (3b)

The solvents were removed *in vacuo* and the remaining solids loaded into a Soxhlet extractor and extracted overnight with benzene. The benzene was removed *in vacuo* and the solids recrystallized from DME. ^{1}H NMR (CD_2Cl_2): δ (major isomer, 85%) 14.07 (s, 1, CH), 7.16 (t, 1, H Ar), 7.08 (d, 2, H Ar), 4.29 (s, 3, OMe), 4.08 (br m, 2, OCH_2), 3.85 (br m, 2,

OCH_2), 3.50 (s, 3, OMe), 2.48 (s, 6, Me), 1.26 (s, 9, CMe_3); (minor isomer, 15%, partially assigned) 14.80 (CH), 4.17 (s, 3, OMe), 4.00 (m, 1, OCH_2), 3.67 (s, 3, OMe), 3.59 (m, 1, OCH_2), 3.32 (m, 1, OCH_2), 2.52 (s, 6, Me), 1.24 (s, 9, CMe_3). ^{13}C NMR (CD_2Cl_2): δ (major isomer only) 330.2 (d, $J_{CH} = 118$, CH), 141.0, 132.4, 129.9, 128.9 (C Ar), 119.6 (q, CF_3), 74.1 (OCH_2), 70.9 (OCH_2), 66.1 (OMe), 62.6 (OMe), 52.5 (CMe_3), 30.5 (CMe_3), 19.6 (Me). Anal. Found: C, 34.00; H, 4.18; N, 2.24. $MoC_{19}H_{29}O_8NF_6S_2$ calcd.: C, 33.88; H, 4.34; N, 2.08%.

3.24. *Mo(N-2,6-Me_2-C_6H_3)(CHCMe_2Ph)(OSO_2CF_3)$_2$(DME) (3c)*

The light yellow crude product was extracted with benzene and the insoluble anilinium salt was removed by filtration. The benzene was removed and the solid was recrystallized from ether. ^1H NMR (C_6D_6): δ 14.23 (s, 1, CH), 7.64 (d, 2, H Ar), 6.98 (t, 2, H Ar), 6.68 and 6.66 (m, 2, H Ar), 6.58 (d, 2, H Ar), 3.84 (s, 3, OMe), 3.34 (m, 2, OCH_2), 2.92 (m, 2, OCH_2), 2.69 (s, 3, OMe), 2.35 (s, 6, Me), 1.74 (s, 6, CMe_2Ph). ^{13}C NMR (C_6D_6): δ 326.2 (d, $J_{CH} = 122$, CH), 153.9, 148.3, 140.8, 129.3, 128.3, 127.0, 126.6 (C Ar), 120.0 (q, CF_3), 73.2 (OCH_2), 69.9 (OCH_2), 65.4 (OMe), 61.4 (OMe), 58.3 (CMe_2Ph), 30.3 (CMe_2Ph), 19.5 (Me). Anal. Found: C, 39.42; H, 4.18; N, 1.92. $MoC_{36}H_{44}N_2$ calcd.: C, 39.19; H, 4.25; N, 1.90%.

3.25. *Mo(N-3,5-Me_2-C_6H_3)(CHCMe_2Ph)(OSO_2CF_3)$_2$(DME) (3d)*

The light yellow crude product was extracted with benzene and the insoluble anilinium salt was removed by filtration. The benzene was removed and the solid was recrystallized from ether. ^1H NMR (C_6D_6): δ 13.80 (s, 1, CH), 7.75 (s, 2, H Ar), 7.44 (d, 2, H Ar), 7.19 (dd, 2, H Ar), 6.99 (t, 1, H Ar), 6.54 (s, 1, H Ar), 3.26 (br s, 2, OCH_2), 3.10 (br s, 3, OMe), 3.08 (br s, 3, OMe), 2.84 (br s, 2, OCH_2), 1.97 (s, 6, Me), 1.90 (s, 6, Me); (minor isomer, 3%) 14.96 (br s, 1, CH). ^{13}C NMR (C_6D_6): δ 323.6 (d, $J_{CH} = 126$, CH), 155.6, 149.1, 139.1, 132.5, 128.7, 126.7, 126.7, 126.5 (C Ar), 120.2 (q, CF_3), 73.5 (t, OCH_2), 69.6 (t, OCH_2), 63.2 (q, OMe), 62.0 (q, OMe), 58.8 (s, CMe_2Ph), 30.7 (q, CMe_2Ph), 20.9 (q, Me).

3.26. *Mo(N-2-^{i}Pr-C_6H_4)(CHCMe_2Ph)(OSO_2CF_3)$_2$(DME) (3e)*

When 4.77 mmol of Mo(N-2-^{i}Pr-C_6H_4)$_2$(CH_2CMe_2-Ph)$_2$) was employed, about 30 ml of toluene was added to extract the product away from the anilinium salt; this mixture was stirred overnight and then was cooled prior to filtration through Celite. The salts were washed with excess toluene until all color was removed. Toluene was removed from the filtrate *in vacuo*. A small amount of ether (10 ml) was added to the brownish solids to extract soluble impurities. After 10 minutes the mixture was filtered and the solids washed with small quantities of ether until bright yellow. ^1H NMR (C_6D_6): δ (major isomer, 94%) 14.14 (s, 1, CH), 7.99 (d, 1, H Ar), 7.53 (d, 2, H Ar), 7.16 (dd, 2, H Ar), 6.92 (m, 2, H Ar), 6.80 (m, 2, H Ar), 3.76 (sept, 1, C*H*Me_2), 3.46 (s, 3, OMe), 3.26 (m, 2, OCH_2), 2.88 (m, 2, OCH_2), 2.86 (s, 3, OMe), 1.87 (s, 6, CMe_2Ph), 1.24 (d, 6, CHMe_2); δ (minor isomer, 6%, partially assigned) 15.08 (s, 1, CH), 7.38 (d, H Ar), 7.06 (m, H Ar), 3.22 (s, 3, OMe), 3.10 (m, 1, OCH_2), 2.99 (s, 3, OMe). ^{13}C (C_6D_6): δ 326.1 (CH), 153.1, 149.1, 148.9, 131.1, 130.5, 128.7, 126.9, 126.7, 126.7, 126.2 (C Ar), 120.1 (q, CF_3), 73.4 (OCH_2), 69.7 (OCH_2), 64.2 (OMe), 61.8 (OMe), 58.8 (CMe_2Ph), 30.9 (CMe_2Ph), 28.6 (*C*HMe$_2$), 23.7 (CHMe_2). Anal. Found: C, 40.13; H, 4.33; N, 1.49. $MoC_{25}H_{33}F_6NO_8S_2$ calcd.: C, 40.06; H, 4.44; N, 1.87%.

3.27. *Mo(N-2-CF_3-C_6H_4)(CHCMe_2Ph)(OSO_2CF_3)$_2$(DME) (3f)*

When 3.10 mmol of Mo(N-2-CF_3-C_6H_4)$_2$$Cl_2$(DME) was employed, about 30 ml benzene was added to the crude product and allowed to stir overnight. The anilinium triflate was removed by filtration, then solvent was removed from the filtrate *in vacuo*. The solids were recrystallized from diethyl ether. ^1H NMR (C_6D_6): δ (major isomer, 80%) 14.05 (s, 1, CH), 7.93 (d, 1, H Ar), 7.60 (d, 2, H Ar), 7.03 (dd, 2, H Ar), 6.99 (d, 1, H Ar), 6.76 (dd, 1, H Ar), 6.74 (dd, 1, H Ar), 3.48 (br, 3, OMe), 3.22 (br, 2, OCH_2), 2.84 (br, 2, OCH_2), 2.81 (br, 3, OMe), 1.79 (s, 6, CMe_2Ph); δ (minor isomer, 20%) 15.17 (s, 1, CH), 8.25 (d, 1, H Ar), 7.39 (d, 2, H Ar), 7.05 (dd, 1, H Ar), 7.04 (dd, 2, H Ar), 6.87 (dd, 1, H Ar), 6.84 (dd, 1, H Ar), 3.15 (m, 2, OCH_2), 3.04 (s, 3, OMe), 2.98 (s, 3, OMe), 2.90 (m, 1, OCH_2), 2.52 (m, 1, OCH_2), 1.94 (s, 3, CMe_2Ph), 1.53 (s, 3, CMe_2Ph). ^{13}C (C_6D_6): δ (major isomer) 325.9 (CH), 150.6, 148.3, 133.5, 132.6, 129.1, 128.6, 127.4, 126.7, 125.8, 125.6 (C Ar), 122.9 (q, CF_3 NAr), 120.1 (q, CF_3), 73.7 (OCH_2), 69.8 (OCH_2), 64.8 (OMe), 62.0 (OMe), 59.3 (CMe_2Ph), 30.6 (CMe_2Ph); (minor isomer) 334.4 (CH), 151.1, 146.0, 133.4, 132.6, 129.0, 128.8, 126.9, 126.8, 126.0, 124.6 (C Ar), 123.5 (q, CF_3 NAr), 120.3 (q, CF_3), the other triflate could not be located, 76.9, 76.1, 70.0, 61.2 (DME resonances), 59.6 (CMe_2Ph), 30.0 (CMe_2Ph), 28.6 (CMe_2Ph). ^{19}F (C_6D_6): (major isomer) -60.9 (CF_3 NAr), -76.9 (CF_3); (minor isomer) -59.5 (CF_3 NAr), -76.9 (CF_3), -77.7 (CF_3). Anal. Found: C, 35.79; H, 3.47; N, 1.52. $MoC_{23}H_{26}F_9NO_8S_2$ calcd.: C, 35.62; H, 3.38; N, 1.81%.

3.28. Mo(N-2-^{t}Bu-C_6H_4)(CHCMe$_2$Ph)(OSO$_2$CF$_3$)$_2$ (DME) (3g)

When 5.33 mmol of Mo(N-2-^{t}Bu-C_6H_4)$_2$(CH$_2$CMe$_2$Ph)$_2$ was employed, about 40 ml of toluene was added to extract the product away from the anilinium salt; this mixture stirred briefly, then was cooled prior to filtration through Celite. The salts were washed with copious amounts of toluene until the remaining solids were white. Toluene was removed from the filtrate *in vacuo*. A small amount of diethyl ether (20 ml) was added to the brownish solids to extract soluble impurities. After 15 min the mixture was filtered and the solids washed with small quantities of diethyl ether until bright yellow: ^{1}H NMR (C_6D_6): δ (major isomer, 90%) 14.24 (s, 1, CH), 8.24 (d, 1, H Ar), 7.56 (d, 2, H Ar), 7.21 (dd, 2, H Ar), 7.05–6.96 (m, 3, H Ar), 6.80 (t, 1, H Ar), 3.59 (s, 3, OMe), 3.19 (s, 2, OCH$_2$), 2.84 (s, 2, OCH$_2$), 2.74 (s, 3, OMe), 1.94 (s, 6, C*Me*$_2$Ph), 1.44 (s, 9, C*Me*$_3$); δ (minor isomer, 10%, partially assigned) 15.18 (s, 1, CH), 7.40 (d, 2, H Ar), 2.94 (s, 3, OMe), 2.08 (s, 3, C*Me*$_2$Ph), 1.52 (s, 3, C*Me*$_2$Ph), 1.50 (s, 9, C*Me*$_3$); (CD_2Cl_2): δ (major isomer, 63%) 14.10 (s, 1, CH), 7.89 (d, 1, H Ar), 7.53–7.03 (H Ar for both isomers), 4.19 (s, 3, OMe), 4.17 (m, 2, OCH$_2$), 3.88 (m, 2, OCH$_2$), 3.46 (s, 3, OMe), 1.77 (s, 6, C*Me*$_2$Ph), 1.48 (s, 9, C*Me*$_3$); δ (minor isomer, 37%, partially assigned) 14.82 (s, 1, CH), 7.53–7.03 (H Ar for both isomers), 4.06 (m, 2, OCH$_2$), 3.63 (s, 3, OMe), 3.58 (m, 1, OCH$_2$), 3.56 (m, 1, OCH$_2$), 3.51 (s, 3, OMe), 2.04 (s, 3, CHC*Me*$_2$Ph), 1.51 (s, 12, C*Me*$_2$Ph and C*Me*$_3$). ^{13}C (CD_2Cl_2): δ (major isomer) 325.2 (CH), 153.7, 148.8, 147.9, 135.2, 130.6, 128.5, 127.5–126.6 (C Ar), 119.6 (q, CF_3), 74.2 (OCH$_2$), 70.9 (OCH$_2$), 66.0 (OMe), 62.7 (OMe), 59.2 (*C*Me$_2$Ph), 36.1 (*C*Me$_3$), 30.8 (C*Me*$_2$Ph), 30.7 (C*Me*$_3$); (minor isomer) 332.3 (CH), 153.5, 148.5, 146.5, 134.8, 130.3, 129.1, 127.5–126.6 (C Ar), 77.6, 75.8, 70.6, 61.3 (DME), 58.7 (*C*Me$_2$Ph), 30.8 (C*Me*$_3$), 30.5 (C*Me*$_2$Ph), 28.8 (C*Me*$_2$Ph).

3.29. Mo(N-2-^{t}Bu-C_6H_4)(CHCMe$_3$)(OSO$_2$CF$_3$)$_2$(DME) (3h)

The product was extracted away from the anilinium triflate with benzene. The benzene was removed *in vacuo* and the product was recrystallized from dichloromethane. ^{1}H NMR (CD_2Cl_2): δ (major isomer, 85%) 13.99 (s, 1, CH), 7.92 (d, 1, H Ar), 7.45 (d, 1, H Ar), 7.31 (m, 2, H Ar), 4.27 (s, 3, OMe), 4.15 (br s, 2, OCH$_2$), 3.85 (br s, 2, OCH$_2$), 3.44 (s, 3, OMe), 1.48 (s, 9, C*Me*$_3$), 1.29 (s, 9, C*Me*$_3$); (minor isomer, 15%, partially assigned) 14.76 (s, 1, CH), 1.46 (s, 9, C*Me*$_3$), 1.28 (s, 9, C*Me*$_3$). ^{13}C NMR (C_6D_6): δ (major isomer only) 328.8 (d, J_{CH} = 117, CH), 153.9, 147.9, 134.9, 130.1, 127.1, 126.4 (C Ar), 119.7 (q, CF_3), 74.2 (OCH$_2$), 71.1 (OCH$_2$), 66.0 (OMe), 62.4 (OMe), 36.1 (*C*Me$_3$), 31.0 (CHC*Me*$_3$), 30.6 (C*Me*$_3$).

3.30. Mo(N-2-Ph-C_6H_4)(CHCMe$_3$)(OSO$_2$CF$_3$)$_2$(DME) (3i)

The product was extracted with benzene and the anilinium triflate was removed by filtration. The benzene was removed under vacuum and the pale yellow product washed with cold DME followed by diethyl ether. ^{1}H NMR ($CDCl_3$): δ (major isomer, 55%) 13.99 (s, 1, CH), 8.14–8.03 (m, 2, H Ar), 7.64 (d, 1, H Ar), 7.52–7.30 (m, 6, H Ar), 3.88 (s, 3, OMe), 3.43 (s, 3, OMe), 3.08 (m, 2, OCH$_2$), 2.80 (m, 2, OCH$_2$), 1.37 (s, 9, C*Me*$_3$); δ (minor isomer, 45%) 14.66 (s, 1, CH), 8.14–8.03 (m, 2, H Ar), 7.62 (d, 1, H Ar), 7.52–7.30 (m, 6, H Ar), 3.77 (m, 2, OCH$_2$), 3.64 (m, 2, OCH$_2$), 3.55 (s, 3, OMe), 3.40 (s, 3, OMe), 1.39 (s, 9, C*Me*$_3$). ^{13}C NMR: ($CDCl_3$) (for major and minor isomer) 337.8 (CH minor), 328.9 (CH major), 152.7, 152.6, 138.8, 138.7, 138.4, 137.1, 133.6, 132.3, 130.5, 130.3, 130.0, 129.7, 129.6, 129.1, 129.0, 128.5, 128.3, 128.1, 127.7, 127.4 (C Ar), 119.1 (q, CF_3 major), 119.3 (q, CF_3 minor), 71.8, 70.1, 65.8, 61.2, 58.9 (DME), 53.2 (*C*Me$_3$ minor), 52.6 (*C*Me$_3$ major), 30.9 (C*Me*$_3$ major and minor).

3.31. Mo(N-1-adamantyl)(CHCMe$_2$Ph)(OSO$_2$CF$_3$)$_2$-(DME) (3j)

The product was extracted with benzene and the ammonium triflate was removed by filtration. The benzene was removed *in vacuo* and the dark solid washed with cold ether to afford a white solid. ^{1}H NMR (CD_2Cl_2): δ (major isomer, 67%) 14.72 (s, 1, CH), 7.43 (d, 2, H Ar), 7.35 (dd, 2, H Ar), 7.18 (t, 1, H Ar), 3.48 (s, 4, OCH$_2$), 3.33 (s, 6, OMe), 2.23 (s, 3, C*Me*$_2$Ph), 2.20 (br m, 6, CH$_2$), 1.71 (br t, 6, CH$_2$), 1.61 (br t, 3, CH), 1.51 (s, 3, C*Me*$_2$Ph); (minor isomer, 33%) 13.87 (s, 1, CH), 7.43 (d, 2, H Ar), 7.31 (dd, 2, H Ar), 7.20 (t, 1, H Ar), 4.18 (m, 1, OCH$_2$), 4.02 (m, 2, OCH$_2$), 3.84 (s, 3, OMe), 3.70 (m, 1, OCH$_2$), 3.64 (s, 3, OMe), 2.31 (br m, 3, CH), 2.28 (br m, 6, CH$_2$), 2.09 (br d, 6, CH$_2$), 1.78 (s, 6, C*Me*$_2$Ph). ^{13}C NMR (CD_2Cl_2): δ (major isomer) 327.4 (d, J_{CH} = 128, CH), 129.0, 127.0, 126.6 (C Ar), 119.6 (q, CF_3), 72.3 (OCH$_2$), 70.4 (OCH$_2$), 61.4 (OMe), 59.0 (OMe), 43.7 (CH$_2$), 35.9 (CH$_2$), 31.3 (CH), 29.8 (C*Me*$_2$Ph), 29.7 (C*Me*$_2$Ph); (minor isomer) 318.9 (d, J_{CH} = 121, *C*HCMe$_2$Ph), 128.8, 127.0, 126.7 (C Ar), 120.1 (q, CF_3), 79.1 (OCH$_2$), 63.8 (OMe), 42.9 (CH$_2$), 35.7 (CH$_2$), 30.3 (CH), 29.8 (C*Me*$_2$Ph). Anal. Found: C, 40.73; H, 4.92; N, 1.77. $MoC_{26}H_{37}F_6NO_8S_2$ calcd.: C, 40.79; H, 4.87; N, 1.83%.

3.32. Mo(N-2,6-^{i}Pr$_2$-C_6H_3)(CHCMe$_2$Ph)(OCEt$_3$)$_2$ (4a)

^{1}H NMR (C_6D_6): δ 11.17 (s, 1, CH), 7.40 (d, 2, H Ar), 7.16 (dd, 2, H Ar), 7.05 (m, 3, H Ar), 7.05 (t, 1, H

Ar), 4.04 (sept, 2, C*H*Me$_2$), 1.69 (s, 6, C*Me*$_2$Ph), 1.52 (q, 12, CH$_2$), 1.25 (d, 12, CH*Me*$_2$), 0.87 (t, 18, Me). ^{13}C NMR (C_6D_6): δ 261.8 (d, J_{CH} = 119, CH), 153.0, 150.5, 146.0, 128.3, 126.9, 126.2, 125.9, 123.4 (C Ar), 84.1 (*C*Et$_3$), 52.6 (*C*Me$_2$Ph), 31.9 (C*Me*$_2$Ph), 31.8 (CH$_2$), 28.0 (*C*HMe$_2$), 24.4 (CH*Me*$_2$), 8.6 (Me).

3.33. Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(O-1-adamantyl)$_2$ (4b)

^{1}H NMR (C_6D_6): δ 11.33 (s, 1, C*H*CMe$_2$Ph), 7.43 (d, 2, H Ar), 7.16 (dd, 2, H Ar), 7.09 (m, 3, H Ar), 7.02 (t, 1, H Ar), 4.05 (sept, 2, C*H*Me$_2$), 2.05 (br s, 6, CH), 1.80 (m, 12, CH$_2$), 1.74 (s, 6, C*Me*$_2$Ph), 1.51 (br s, 12, CH$_2$), 1.32 (d, 12, CH*Me*$_2$). ^{13}C (C_6D_6): δ 262.2 (d, J_{CH} = 119, CH), 153.3, 149.9, 146.3, 128.3, 127.1, 126.3, 125.8, 123.2 (C Ar), 76.2 (OC), 52.6 (*C*Me$_2$Ph), 46.5 (CH), 36.6 (CH$_2$), 31.7 (CH$_2$), 31.6 (C*Me*$_2$Ph), 28.3 (*C*HMe$_2$), 24.2 (CH*Me*$_2$).

3.34. Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)[OCMe$_2$(CMe$_3$)]$_2$ (4c)

^{1}H NMR (C_6D_6): δ 11.29 (s, 1, CH), 7.41 (d, 2, H Ar), 7.17 (dd, 2, H Ar), 7.04 (m, 3, H Ar), 7.03 (t, 1, H Ar), 4.00 (sept, 2, C*H*Me$_2$), 1.70 (s, 6, C*Me*$_2$Ph), 1.26 (s, 6, Me), 1.26 (d, 12, CH*Me*$_2$), 1.06 (s, 6, Me), 1.00 (s, 18, C*Me*$_3$). ^{13}C NMR (C_6D_6): δ 263.4 (d, J_{CH} = 119, CH), 153.3, 150.3, 146.3, 128., 127.3, 126.2, 126.0, 123.3 (C Ar), 83.9 (OC), 52.9 (*C*Me$_2$Ph), 39.0 (*C*Me$_3$), 31.7 (C*Me*$_2$Ph), 28.1 (*C*HMe$_2$), 26.7 (Me), 26.3 (C*Me*$_3$), 25.5 (Me), 24.3 (CH*Me*$_2$).

3.35. Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCHMe$_2$)$_2$ (4d)

^{1}H NMR (C_6D_6): δ 11.24 (s, 1, CH), 7.40 (d, 2, H Ar), 7.17 (dd, 2, H Ar), 7.06 (m, 3, H Ar), 7.05 (t, 1, H Ar), 4.50 (sept, 2, C*H*Me$_2$), 3.99 (sept, 2, C*H*Me$_2$), 1.66 (s, 6, C*Me*$_2$Ph), 1.28 (d, 12, CH*Me*$_2$), 1.24 (s, 6, OCH*Me*Me), 1.19 (s, 6, OCHMe*Me*).

3.36. Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)[OCMe$_2$(CF$_3$)]$_2$ (4f)

^{1}H NMR (C_6D_6): δ 11.68 (s, 1, CH), 7.28 (d, 2, H Ar), 7.12 (dd, 2, H Ar), 7.02 (m, 3, H Ar), 7.01 (t, 1, H Ar), 3.74 (sept, 2, C*H*Me$_2$), 1.57 (s, 6, C*Me*$_2$Ph), 1.20 (s, 6, Me), 1.18 (s, 6, Me), 1.18 (d, 12, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 273.9 (d, J_{CH} = 120, CH), 153.4, 148.8, 146.9, 128.4, 128.4 (C Ar), 127.3 (q, CF$_3$), 126.3, 126.0, 123.3 (C Ar), 78.8 (q, OC), 53.8 (*C*Me$_2$Ph), 30.9 (C*Me*$_2$Ph), 28.5 (*C*HMe$_2$), 24.6 (CH*Me*$_2$), 23.8 (Me).

3.37. Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)[OC(CF$_3$)$_3$]$_2$ (4h)

^{1}H NMR (toluene-d_8): δ 12.87 (s, 1, CH), 7.12 (d, 2, H Ar), 7.05 (dd, 2, H Ar), 6.96 (t, 1, H Ar), 6.94 (t, 1, H Ar), 6.89 (d, 2, H Ar), 3.46 (sept, 2, C*H*Me$_2$), 1.52 (s, 6, C*Me*$_2$Ph), 1.12 (d, 12, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 298.6 (d, J_{CH} = 122, CH), 154.9, 148.9, 147.2, 130.5, 128.6, 126.9, 125.9, 123.8 (C Ar), 121.4 (q, CF$_3$), 84.1 (decet, OC), 57.4 (*C*Me$_2$Ph), 30.6 (C*Me*$_2$Ph), 29.0 (*C*HMe$_2$), 23.8 (CH*Me*$_2$). ^{19}F (C_6D_6): δ −73.8 (CF$_3$). Anal. Found: C, 41.18; H, 3.45; N, 1.60. MoC$_{30}$H$_{29}$F$_{18}$NO$_2$ calcd.: C, 41.25; H, 3.35; N, 1.60%.

3.38. Mo(N-2,6-^{i}Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)[OC(CF$_3$)$_2$CF$_2$CF$_2$CF$_3$]$_2$ (4i)

^{1}H NMR (C_6D_6): δ 12.92 (s, 1, CH), 7.14–6.89 (m, 8, H Ar), 3.49 (sept, 2, C*H*Me$_2$), 1.54 (s, 6, C*Me*$_2$Ph), 1.13 (d, 12, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 299.6 (d, J_{CH} = 122, CH), 156.1, 149.0, 147.0, 130.7, 129.0, 127.0, 125.9, 124.0 (C Ar), 57.7 (*C*Me$_2$Ph), 30.6 (C*Me*$_2$Ph), 29.0 (*C*HMe$_2$), 23.9 (CH*Me*$_2$). The ^{13}C NMR shifts for the alkoxide ligand are not listed [5]. Anal. Found: C, 38.27; H, 2.84; N, 1.37. MoC$_{34}$H$_{29}$F$_{26}$NO$_2$ calcd.: C, 38.04; H, 2.72; N, 1.30%.

3.39. Mo(N-4-Br-2,6-^{i}Pr$_2$-C$_6$H$_2$)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (4j)

^{1}H NMR (toluene-d_8): δ 12.01 (s, 1, CH), 7.26 (s, 2, H Ar), 7.13 (d, 2, H Ar), 7.04 (dd, 2, H Ar), 6.93 (t, 1, H Ar), 3.43 (sept, 2, C*H*Me$_2$), 1.49 (s, 6, C*Me*$_2$Ph), 1.15 (s, 6, OCMe(CF$_3$)$_2$), 1.04 (d, 12, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 284.9 (d, J_{CH} = 121, CH), 152.7, 148.8, 147.3, 128.6, 127.0, 126.8, 125.9, 124.1 (C Ar), 124.0 (q, CF$_3$), 123.9 (q, CF$_3$), 81.3 (sept, O*C*Me(CF$_3$)$_2$), 55.4 (*C*Me$_2$Ph), 30.3 (C*Me*$_2$Ph), 28.7 (*C*HMe$_2$), 23.3 (CH*Me*$_2$), 18.6 (OC*Me*(CF$_3$)$_2$). ^{19}F (C_6D_6): δ −78.0 (CF$_3$).

3.40. Mo(N-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe$_3$)$_2$ (4k)

^{1}H NMR (C_6D_6): δ 11.31 (s, 1, CH), 6.91 (d, 2, H Ar), 6.83 (t, 1, H Ar), 2.43 (s, 6, Me), 1.33 (s, 18, OCMe$_3$), 1.22 (s, 9, C*Me*$_3$). ^{13}C NMR (C_6D_6): δ 266.3 (d, J_{CH} = 115, CH), 156.6, 132.0, 128.0, 124.8 (C Ar), 76.6 (O*C*Me$_3$), 45.8 (*C*Me$_3$), 33.4, 32.5 (C*Me*$_3$), 19.3 (Me). Anal. Found: C, 58.50; H, 8.98; N, 3.15. MoC$_{21}$H$_{37}$NO$_2$ calcd.: C, 58.46; H, 8.64; N, 3.25%.

3.41. Mo(N-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)[OCMe$_2$(CF$_3$)]$_2$ (4l)

The reaction was performed in a 1:1 mixture of THF and diethyl ether. ^{1}H NMR (C_6D_6): δ 11.72 (s, 1, CH), 7.25 (d, 2, H Ar), 7.07 (dd, 2, H Ar), 6.93 (t, 1, H Ar), 6.81 (m, 3, H Ar), 2.24 (s, 6, Me), 1.51 (s, 6, C*Me*$_2$Ph), 1.22 (s, 6, OCMe$_2$(CF$_3$)), 1.16 (s, 6, OCMe$_2$(CF$_3$)). ^{13}C NMR (C_6D_6): δ 274.6 (CH), 156.0, 148.9, 136.5, 128.3, 127.9, 127.3 (C Ar), 126.9 (q, CF$_3$), 126.2, 126.1 (C Ar), 78.7 (q, O*C*Me$_2$(CF$_3$)), 53.1

(CMe_2Ph), 30.7 (CMe_2Ph), 24.6 ($OCMe_2(CF_3)$), 19.1 (Me): ^{19}F (C_6D_6): δ −82.4 (CF_3). Anal. Found: C, 51.67; H, 5.62; N, 2.20. $MoC_{26}H_{33}F_6NO_2$ calcd.: C, 51.92; H, 5.53; N, 2.33%.

3.42. Mo(N-2,6-Me_2-C_6H_3)(CHCMe$_3$)(O-2,6-$^iPr_2$-C_6H_3)$_2$ (4m)

^1H NMR (C_6D_6): δ 11.43 (s, 1, CH), 7.09 (d, 4, H Ar), 7.97 (t, 2, H Ar), 6.75 (m, 3, H Ar), 3.65 (sept, 4, C*H*Me_2), 2.14 (s, 6, Me), 1.29 (d, 12, CH*Me*$_2$), 1.23 (d, 12, CH*Me*$_2$), 1.00 (s, 9, CHC*Me*$_3$). ^{13}C NMR (C_6D_6): δ 277.9 (d, J_{CH} = 116, CH), 162.1, 157.1, 137.4, 135.7, 128.4, 127.0, 123.7, 122.4 (C Ar), 47.4 (*C*Me_3), 30.8 (CHC*Me*$_3$), 27.0 (*C*HMe_2), 23.0 (CH*Me*$_2$), 18.4 (Me).

3.43. Mo(N-2,6-Me_2-C_6H_3)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (4n)

^1H NMR (C_6D_6): δ 12.18 (s, 1, CH), 7.12 (d, 2, H Ar), 7.00 (dd, 2, H Ar), 6.87 (t, 1, H Ar), 6.78–6.70 (m, 3, H Ar), 2.15 (s, 6, Me), 1.43 (s, 6, C*Me*$_2$Ph), 1.16 (s, 6, OCMe(CF_3)$_2$). ^{13}C NMR (C_6D_6): δ 289.5 (CH), 156.6, 148.0, 137.2, 128.5, 128.4, 128.0, 126.5, 126.0 (C Ar), 124.3 (q, CF_3), 124.2 (q, CF_3), 81.1 (sept, O*C*Me(CF_3)$_2$), 54.6 (*C*Me_2Ph), 30.2 (C*Me*$_2$Ph), 18.9 (OC*Me*(CF_3)$_2$), 18.7 (Me). ^{19}F (C_6D_6): δ −77.9 (q, CF_3), −78.1 (q, CF_3).

3.44. Mo(N-2,6-Me_2-C_6H_3)(CHCMe$_2$Ph)[OC(CF$_3$)$_2$-CF$_2$CF$_2$CF$_3$]$_2$ (4o)

^1H NMR (C_6D_6): δ 12.86 (s, 1, CH), 7.16 (d, 2, H Ar), 6.96 (dd, 2, H Ar), 6.79 (t, 1, H Ar), 6.70 (t, 1, H Ar), 6.62 (d, 2, H Ar), 2.10 (s, 6, Me), 1.37 (s, 6, C*Me*$_2$Ph). ^{13}C NMR (C_6D_6): δ 299.2 (d, J_{CH} = 129, CH), 157.5, 147.1, 137.9, 129.3, 128.1, 127.0, 126.7 (C Ar), 56.8 (C*C*Me_2Ph), 29.9 (C*Me*$_2$Ph), 18.5 (Me). The ^{13}C NMR shifts for the alkoxide ligand are not listed [5]. Anal. Found: C, 35.61; H, 2.29; N, 1.37. $MoC_{30}H_{21}F_{26}NO_2$ calcd.: C, 35.42; H, 2.08; N, 1.38.%.

3.45. Mo(N-3,5-Me_2-C_6H_3)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (4p)

^1H NMR (C_6D_6): δ 11.91 (s, 1, CH), 7.21 (d, 2, H Ar), 7.08 (dd, 2, H Ar), 6.96 (t, 1, H Ar), 6.92 (s, 2, H Ar), 6.51 (s, 1, H Ar), 1.94 (s, 6, Me), 1.33 (s, 6, C*Me*$_2$Ph), 1.21 (s, 6, OCMe(CF_3)$_2$).

3.46. Mo(N-2-^{i}Pr-C_6H_4)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (4q)

^1H NMR (C_6D_6): δ 11.96 (s, 1, CH), 7.25 (d, 1, H Ar), 7.19 (d, 2, H Ar), 7.07 (dd, 2, H Ar), 7.00–6.83 (m, 4, H Ar), 3.47 (sept, 1, C*H*Me_2), 1.52 (s, 6, OCMe(CF_3)$_2$), 1.16 (s, 6, C*Me*$_2$Ph), 1.13 (d, 6, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 283.4 (d, J_{CH} = 121.3, CH), 155.6, 148.0, 147.0, 129.3, 128.6, 128.5, 126.6, 126.3, 126.1, 125.9 (C Ar), 124.1 (q, CF_3), 124.0 (q, CF_3), 81.2 (sept, OCMe(CF_3)$_2$), 55.1 (*C*Me_2Ph), 30.7 (C*Me*$_2$Ph), 28.6 (*C*HMe_2), 23.1 (CH*Me*$_2$), 18.8 (OC*Me*(CF_3)$_2$). ^{19}F (C_6D_6): δ −78.2 (m, CF_3). Anal. Found: C, 45.14; H, 4.27; N, 1.91. $MoC_{27}H_{29}F_{12}NO_2$ calcd.: C, 44.83; H, 4.04; N, 1.94%.

3.47. Mo(N-2-CF_3-C_6H_4)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (4r)

^1H NMR (C_6D_6): δ 11.93 (s, 1, CH), 7.19 (d, 2, H Ar), 7.11 (d, 1, H Ar), 7.06 (d, 1, H Ar), 7.04 (dd, 2, H Ar), 6.89 (t, 1, H Ar), 6.77 (dd, 1, H Ar), 6.56 (dd, 1, H Ar), 1.47 (s, 6, C*Me*$_2$Ph), 1.20 (s, 6, OCMe(CF_3)$_2$). ^{13}C NMR (C_6D_6): δ 284.7 (CH), 153.3, 147.6, 132.3, 130.3, 128.6, 127.9, 126.7, 126.3, 126.0, 125.9, 124.0 (q, CF_3), 123.9 (q, CF_3), 123.6 (q, CF_3), 81.7 (sept, O*C*Me(CF_3)$_2$), 55.4 (*C*Me_2Ph), 30.3 (C*Me*$_2$Ph), 18.6 (OC*Me*(CF_3)$_2$); ^{19}F −60.7 (CF_3), −78.0 (CF_3). Anal. Found: C, 40.14; H, 3.21; N, 2.00. $MoC_{25}H_{22}F_{15}NO_2$ calcd.: C, 40.07; H, 2.96; N, 1.87%.

3.48. Mo(N-2-^{t}Bu-C_6H_4)(CHCMe$_2$Ph)(OCMe$_3$)$_2$ (4s)

^1H NMR (C_6D_6): δ 11.05 (s, 1, CH), 7.54 (d, 1, H Ar), 7.47 (d, 2, H Ar), 7.22 (dd, 2, H Ar), 7.18 (d, 1, H Ar), 7.08–6.88 (m, 3, H Ar), 1.77 (s, 6, C*Me*$_2$Ph), 1.56 (s, 9, C*Me*$_3$), 1.27 (s, 18, OC*Me*$_3$).

3.49. Mo(N-2-^{t}Bu-C_6H_4)(CHCMe$_3$)(OCMe$_3$)$_2$ (4t)

^1H NMR (C_6D_6): δ 10.98 (s, 1, CH), 7.56 (d, 1, H Ar), 7.23 (d, 1, H Ar), 7.02 (dd, 1, H Ar), 6.91 (dd, 1, H Ar), 1.56 (s, 9, C*Me*$_3$), 1.35 (s, 18, OC*Me*$_3$), 1.31 (s, 9, C*Me*$_3$). ^{13}C NMR (C_6D_6): δ 262.7 (d, J_{CH} = 113, CH), 156.5, 144.1, 132.9, 126.7, 126.1 (C Ar), 77.0 (O*C*Me$_3$), 46.9 (*C*Me$_3$), 35.9 (*C*Me$_3$ NAr), 32.9, 32.4 (*CMe*$_3$), 30.8 (OC*Me*$_3$).

3.50. Mo(N-2-^{t}Bu-C_6H_4)(CHCMe$_2$Ph)(O-1-adamantyl)$_2$ (4u)

^1H NMR (C_6D_6): δ 11.06 (s, 1, CH), 7.63 (d, 1, H Ar), 7.46 (d, 2, H Ar), 7.26 (d, 1, H Ar), 7.18 (dd, 2, H Ar), 7.00–6.80 (m, 3, H Ar), 2.04 (br, 6, CH), 1.82 (m, 12, CH_2), 1.81 (s, 6, C*Me*$_2$Ph), 1.62 (s, 9, C*Me*$_3$), 1.50 (s, 12, CH_2). ^{13}C NMR (C_6D_6): δ 259.4 (CH), 156.7, 150.1, 144.4, 132.9, 128.3, 126.7, 126.6, 126.3, 125.9 (C Ar), 76.6 (OC), 53.0 (*C*Me_2Ph), 46.7 (CH), 36.5 (CH_2), 35.9 (*C*Me$_3$), 31.9 (CH_2), 31.6 (*C*Me$_2$Ph), 30.7 (C*Me*$_3$).

3.51. Mo(N-2-^{t}Bu-C_6H_4)(CHCMe$_3$)(O-2,6-^{i}Pr$_2$-C_6H_3)$_2$ (4v)

^1H NMR (C_6D_6): δ 11.52 (s, 1, CH), 7.83 (d, 1, H Ar), 7.18–6.83 (m, 9, H Ar), 3.72 (s, 4, C*H*Me_2), 1.39 (d, 12, CH*Me*$_2$), 1.34 (d, 12, CH*Me*$_2$), 1.22 (s, 9, C*Me*$_3$), 1.12 (s, 9, C*Me*$_3$).

3.52. Mo(N-2-'Bu-C_6H_4)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (4w)

^{1}H NMR (C_6D_6): δ 11.79 (s, 1, CH), 7.40 (d, 1, H Ar), 7.20 (d, 2, H Ar), 7.12 (d, 1, H Ar), 7.11 (dd, 2, H Ar), 7.00–6.82 (m, 3, H Ar), 1.56 (s, 6, C*Me*$_2$Ph), 1.36 (s, 9, C*Me*$_3$), 1.19 (d, 6, OCMe(CF$_3$)$_2$). ^{13}C NMR (C_6D_6): δ 281.5 (CH), 156.6, 148.0, 146.0, 133.6, 129.0, 128.6, 126.9, 126.7, 126.5, 126.0 (C Ar), 124.3 (q, CF$_3$), 124.1 (q, CF$_3$), 81.4 (sept, OCMe(CF$_3$)$_2$), 55.6 (*C*Me$_2$Ph), 35.7 (*C*Me$_3$), 30.8 (C*Me*$_2$Ph), 30.2 (C*Me*$_3$), 18.8 (OC*Me*(CF$_3$)$_2$). Anal. Found: C, 45.40; H, 4.39; N, 1.77. $MoC_{28}H_{31}F_{12}NO_2$ calcd.: C, 45.60; H, 4.24; N, 1.90%.

3.53. Mo(N-2-'Bu-C_6H_4)(CHCMe$_3$)[OCMe(CF$_3$)$_2$]$_2$ (4x)

^{1}H NMR (C_6D_6): δ 11.71 (s, 1, CH), 7.46 (d, 1, H Ar), 7.10 (d, 1, H Ar), 6.91 (dd, 1, H Ar), 6.85 (dd, 1, H Ar), 1.35 (s, 15, OCMe(CF$_3$)$_2$ and C*Me*$_3$), 1.08 (s, 9, C*Me*$_3$). ^{13}C NMR (C_6D_6): δ 284.3 (d, J_{CH} = 118.3, CH), 156.6, 145.9, 133.6, 128.9, 126.9, 126.5 (C Ar), 124.0 (q, CF$_3$), 124.0 (q, CF$_3$), 81.1 (sept, OCMe(CF$_3$)$_2$), 49.6 (*C*Me$_3$), 35.6 (*C*Me$_3$), 31.5 (C*Me*$_3$), 30.2 (C*Me*$_3$), 18.9 (OC*Me*(CF$_3$)$_2$). ^{19}F (C_6D_6): δ −77.9 (q, CF$_3$), −78.1 (q, CF$_3$). Anal. Found: C, 40.81; H, 4.23; N, 2.16. $MoC_{23}H_{28}F_{12}NO_2$ calcd.: C, 40.96; H, 4.18; N, 2.08%.

3.54. Mo(N-2-Ph-C_6H_4)(CHCMe$_3$)[OCMe(CF$_3$)$_2$]$_2$ (4y)

^{1}H NMR (C_6D_6): δ 11.83 (s, 1, CH), 7.39 (d, 1, H Ar), 7.35 (d, 2, H Ar), 7.21 (t, 2, H Ar), 7.11–7.01 (m, 2, H Ar), 6.94–6.83 (m, 2, H Ar), 1.21 (s, 6, OCMe(CF$_3$)$_2$), 0.88 (s, 9, C*Me*$_3$); ($CDCl_3$) δ 11.81 (s, 1, CH), 7.50–7.27 (m, 9, H Ar), 1.35 (s, 6, OCMe(CF$_3$)$_2$), 0.97 (s, 9, C*Me*$_3$). ^{13}C NMR ($CDCl_3$): δ 287.0 (d, J_{CH} = 117.3, CH), 154.6, 138.7, 137.8, 130.5, 129.4, 129.2, 128.4, 128.2, 127.9, 127.7 (C Ar), 123.3 (q, CF$_3$), 123.2 (q, CF$_3$), 80.5 (sept, OCMe(CF$_3$)$_2$), 48.1 (*C*Me$_3$), 31.3 (C*Me*$_3$), 18.8 (OC*Me*(CF$_3$)$_2$).

3.55. Mo(N-1-adamantyl)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (4z)

The reaction was carried out in THF. ^{1}H NMR (C_6D_6): δ (major isomer, 90%) 11.84 (s, 1, CH), 7.28 (d, 2, H Ar), 7.16 (dd, 2, H Ar), 7.02 (t, 1, H Ar), 1.91 (br d, 6, CH$_2$), 1.79 (br, 6, CH), 1.61 (s, 6, C*Me*$_2$Ph), 1.34 (br t, 6, CH$_2$), 1.20 (s, 6, OCMe(CF$_3$)$_2$); (minor isomer, 10%, partially assigned) 13.10 (s, 1, CH), 7.43 (d, 2, H$_o$), 7.20 (dd, 2, H Ar), 7.06 (t, 1, H Ar), 2.00 (br d, 6, CH$_2$), 1.84 (s, 6, C*Me*$_2$Ph). ^{13}C NMR (CD_2Cl_2): δ (major isomer, 90%) 278.3 (d, J_{CH} = 120, CH), 149.0, 128.6, 126.5, 126.4 (C Ar), 124.1 (q, CF$_3$), 124.0 (q, CF$_3$), 78.4 (NC), 51.2 (*C*Me$_2$Ph), 44.5 (CH$_2$), 35.7 (CH$_2$), 31.3 (CH), 29.9 (C*Me*$_2$Ph), 19.2 (OC*Me*(CF$_3$)$_2$); (minor isomer, 10%, partially assigned) 74.3 (NC), 43.6 (CH$_2$), 29.7, 27.9, 20.1 (OC*Me*(CF$_3$)$_2$). Anal. Found: C, 45.63; H, 4.71; N, 1.61. $MoC_{28}H_{33}F_{12}NO_2$ calcd.: C, 45.48; H, 4.50; N, 1.89%.

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