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Syntheses of Variations of Stereogenic-at-Metal Imido Alkylidene Complexes of Molybdenum

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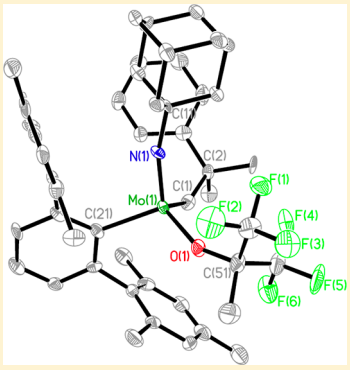
Supporting Information

ABSTRACT: In this paper we describe the syntheses of several new stereogenic-at-metal imido alkylidene complexes of molybdenum, Mo(NR)(CHR′)(X)(Y), many of which had to be prepared through selective nucleophilic displacement reactions in imido alkylidene complexes. The reported compounds include Mo(NAd)($CHCMe_2Ph$)$(MesPyr)_2$ (**1a**; MesPyr = 2-mesitylpyrrolide, Ad = 1-adamantyl), Mo(NAd)($CHCMe_2Ph$)$(2\text{-}CNPyr)_2$ (**1b**; 2-CNPyr = 2-cyanopyrrolide), Mo(NAd)($CHCMe_2Ph$)(MesPyr)(OTPP) (**2a**; OTPP = 2,3,5,6-tetraphenylphenoxide), Mo(NAd)($CHCMe_2Ph$)(MesPyr)(OBr_2Bitet) (**2b**; OBr_2Bitet = (*R*)-3,3′-dibromo-2′-(*tert*-butyldimethylsilyloxy)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2-olate), Mo(NAd)($CHCMe_2Ph$)(OHIPT)(2-Mespyr) (**2c**; HIPT = 2,6-(2,4,6-$iPr_3C_6H_2)_2C_6H_3$), Mo(NAd)($CHCMe_2Ph$)(OTf)(OHIPT) (**3**), Mo(NAd)($CHCMe_2Ph$)-(OTf)(OHIPT)(PMe_3) (**3**(PMe_3)), Mo(NAd)($CHCMe_2Ph$)(2-CNPyr)(OHIPT) (**4**), Mo(NAd)($CHCMe_2Ph$)(OHIPT)($OCMe_3$) (**5**), Mo(NR)($CHCMe_2Ph$)(OR_{F6})(OHMT) (OR_{F6} = $OCMe(CF_3)_2$; HMT = 2,6-$Mes_2C_6H_3$; R = 2,6-$iPr_2C_6H_3$ (Ar, **6a**), 2,6-$Me_2C_6H_3$ (Ar′, **6b**), 2-$iPrC_6H_4$ (Ar^{iPr}, **6c**), Ad (**6d**)), Mo(NR)($CHCMe_2Ph$)(OR_{F6})[N(H)HMT] (**7a** (R = Ar′) and **7b** (R = Ar^{iPr})), and Mo(NAd)($CHCMe_2Ph$)(OR_{F6})(HMT) (**8**). X-ray structural studies were carried out on **1b**, **2a**–**c**, **3**(PMe_3), **4**, **5**, **6d**, **7b**, and **8**. Compound **1b** is an octamer in which two η^1-pyrrolides are trans to one another at each metal center and cyano groups bind from neighboring Mo centers trans to the alkylidene and imido ligands.



INTRODUCTION

Recent advances in olefin metathesis by molybdenum,[1] tungsten,[2] and ruthenium[3] alkylidene complexes have focused on initiators in which the metal is a stereogenic center. For example, the chemistry of high-oxidation-state molybdenum or tungsten complexes of the type M(NR)(CHR′)(OR″)(Pyr), where Pyr is a pyrrolide or a substituted pyrrolide (MAP complexes) were first prepared in 2007[4,5] in the process of demonstrating that a M(NR)(CHR′)$(Pyr)_2$ complex[6,7] could act as a precursor to a bisalkoxide, a biphenolate, or a binaphtholate imido alkylidene catalyst through addition of the monoalcohol or diol to it. Recent examples of selective metathesis applications by MAP catalysts that contain a sterically demanding HIPTO ligand ($HIPTO^-$ = hexaisopropylterphenoxide = O-2,6-(2,4,6-$iPr_3C_6H_2)_2C_6H_3$) or HMTO ligand ($HMTO^-$ = hexamethylterphenoxide = O-2,6-$(mesityl)_2C_6H_3$) include *Z*-selective metathesis homocoupling of terminal olefins,[8] *Z*-selective ring-opening metathesis polymerization (ROMP) of 2,3-disubstituted norbornenes and norbornadienes,[9] *Z*-selective ring-opening/cross-metathesis reactions,[10] ethenolysis reactions[11] (including *Z*-selective ethenolysis[12]), and *Z*-selective cross-metathesis[1c] or ring-closing metathesis.[2a] Theoretical calculations by Eisenstein and co-workers[13] help explain why olefin metatheses by MAP species are relatively efficient. Isolation of 4-coordinate 14-electron methylidene species when the aryloxide is sterically demanding is consistent with the relatively long lived nature of MAP catalysts under some circumstances.[14]

Syntheses of MAP species via the "protonolysis" route is proposed to involve binding of ROH to the metal through the oxygen atom before a proton migrates to the pyrrolide, probably to the α carbon atom first to yield an intermediate pyrrolenine complex.[15] Therefore, syntheses of MAP species via the protonolysis route strongly depend upon steric factors associated with the size of the pyrrolides (so far usually parent pyrrolide or a 2,5-dimethylpyrrolide), the imido, the alkylidene, and the added ROH. Another persistent synthetic problem is that intermediate MAP species can react with a another 1 equiv of alcohol to form a bisalkoxide. In short, in our experience, many potentially useful MAP species cannot be made in pure form via "protonolysis" of bispyrrolide species. It should be noted that both bisamido[16] and dialkyl[17] complexes were explored as precursors to monoalkoxide or bisalkoxide complexes with scant success before bispyrrolides were employed as catalyst precursors to MAP complexes.

Two of the most important features of MAP complexes are that the metal is a stereogenic center and that all ligands are covalently bound to the metal. Therefore, MAP complexes are members of a larger class of stereogenic-at-metal (SAM) complexes. For example, M(D)(CHR′)(X)(Y) complexes, in theory, could be prepared where M is Mo or W, D is an imido or oxo ligand,[18] and X and Y are different monoanionic ligands

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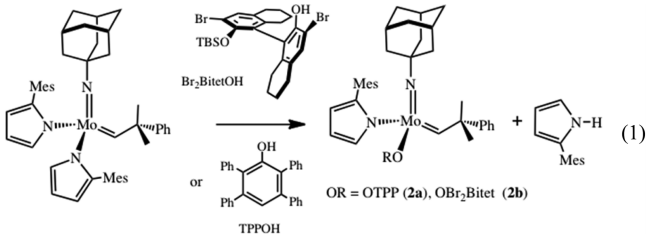
based on, for example, C (e.g., an alkyl),[15] N (e.g., an amide),[14] or O (e.g., an alkoxide). Since MAP species have demonstrated some special reactivities in olefin metathesis reactions (vide supra), other SAM complexes in addition to MAP species might exhibit special properties in metathesis reactions. However, all syntheses of M(D)(CHR′)(X)(Y) complexes cannot rely solely upon protonolysis reactions. In this paper we explore some of the problems associated with the synthesis of some new MAP variations and begin to explore possible Mo(NR)(CHR′)(X)(Y) variations in which neither X nor Y is a pyrrolide.

RESULTS AND DISCUSSION

MAP Complexes That Contain Pyrrolide Variations. Potential variations of MAP species include those that contain a sterically demanding pyrrolide: e.g., 2-mesitylpyrrolide. Mo(NAd)(CHCMe$_2$Ph)(MesPyr)$_2$ (**1a**; MesPyr = 2-mesitylpyrrolide, Ad = 1-adamantyl) can be prepared in 75% isolated yield by treating Mo(NAd)(CHCMe$_2$Ph)(OTf)$_2$(DME) with 2 equiv of Li(MesPyr) in diethyl ether. Compound **1a** is a close relative of Mo(NAd)(CHCMe$_3$)(MesPyr)$_2$, which was prepared in 25% isolated yield in a similar manner.[19] It is also related to structurally characterized Mo(NAr)(CHCMe$_2$Ph)(η^1-MesPyr)$_2$ (Ar = 2,6-diisopropylphenyl),[20] in which for steric reasons the 2-mesitylpyrrolide ligand cannot bind in an η^5 fashion, usually the observed mode of binding one of the two pyrrolides in other imido alkylidene bispyrrolide complexes.[5,21]

Mo(NAd)(CHCMe$_2$Ph)(MesPyr)$_2$ reacts with TPPOH (2,3,5,6-tetraphenylphenol) and Br$_2$BitetOH (eq 1) readily



(1)

to yield Mo(NAd)(CHCMe$_2$Ph)(MesPyr)(OTPP) (**2a**) and Mo(NAd)(CHCMe$_2$Ph)(MesPyr)(OBr$_2$Bitet) (**2b**) in 80% and 53% yields, respectively. These syntheses of **2a**,**b** are typical protonolysis methods. Compound **2b** is found as two diastereomers with syn alkylidene ^{1}H NMR shifts of 12.47 ppm (*R* diastereomer) and 13.14 ppm (*S* diastereomer). The *S* diastereomer could be isolated in pure form through crystallization from *n*-pentane. A typical observed ratio of *R* to *S* in the crude product mixture is 1:1.

Complexes **2a** and (*S*)-**2b** display distorted-tetrahedral geometries typical of MAP species (Figures 1 and 2, respectively), with bond lengths and angles similar to those found in other reported MAP complexes (Table 1). The relatively short Mo−Br distance (3.163 Å) in (*S*)-**2b** is similar to that reported (3.04 Å) for the *R* diastereomer of Mo(NAr)(CHCMe$_2$Ph)(Me$_2$Pyr)(OBr$_2$Bitet) (Me$_2$Pyr = 2,5-dimethylpyrrolide, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$).[22]

While 1 equiv of HIPTOH will react with Mo(NAd)(CHCMe$_2$Ph)(Pyr)$_2$ (Pyr = pyrrolide, 2,5-dimethylpyrrolide) to yield Mo(NAd)(CHCMe$_2$Ph)(Pyr)(OHIPT),[9a] attempts to react 1 equiv of HIPTOH with **1a** in toluene-d_8 led to no reaction, even after heating the mixtures (~0.1 M in each) to 80 °C for weeks. This result illustrates the steric limitations in certain protonolysis reactions.

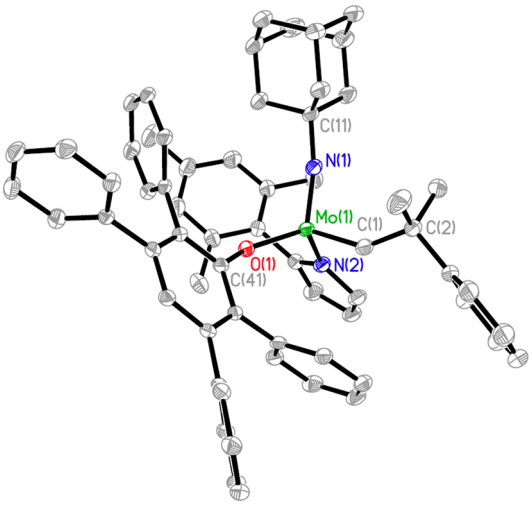


Figure 1. Thermal ellipsoid drawing of Mo(NAd)(CHCMe$_2$Ph)-(2-MesPyr)(OTPP) (**2a**) (ellipsoids at the 50% probability level). Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg) can be found in Table 1.

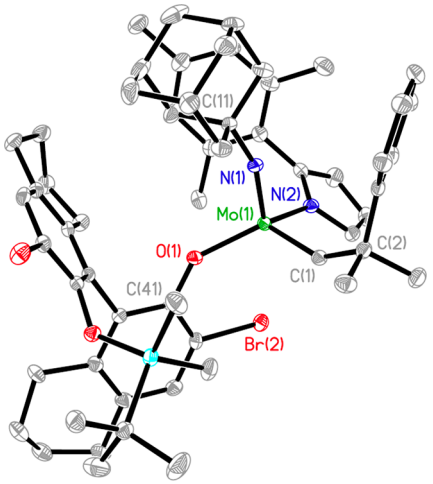


Figure 2. Thermal ellipsoid drawing of (*S*)-Mo(NAd)(CHCMe$_2$Ph)-(2-MesPyr)(OBr$_2$Bitet) ((*S*)-**2b**) (ellipsoids at the 50% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) can be found in Table 1.

In order to increase the electrophilicity of the metal center, we became interested in the possibility of employing pyrrolides that are less electron donating than the parent pyrrolide or 2,5-dimethylpyrrolide. Therefore, we explored the synthesis of MAP complexes that contain 2-cyanopyrrolide.[23]

The reaction of Mo(NAd)(CHCMe$_2$Ph)(OTf)$_2$(DME) with 2 equiv of Li(2-CNPyr) gave Mo(NAd)(CHCMe$_2$Ph)-(2-CNPyr)$_2$ (**1b**) in 55% isolated yield. Alternatively, **1b** can be obtained in 76% yield by treating Mo(NAd)(CHCMe$_2$Ph)-(Me$_2$Pyr)$_2$ with excess 2-CNPyrH (eq 2). The proton NMR

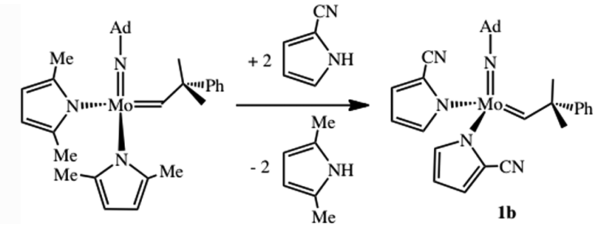


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Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) in Mo(NR)(CHR′)(OR′′)(X) Complexes

	2a	2b	2c	3(PMe$_3$)	4	5	6d	7b	8
Mo=C	1.886(2)	1.888(2)	1.8811(16)	1.8951(16)	1.883(4)	1.880(3)	1.8821(16)	1.8833(16)	1.895(5)
Mo−X	2.0527(19)	2.0608(18)	2.0551(13)	1.7413(13)	2.053(3)	1.879(2)	1.9444(12)	1.9950(13)	2.188(5)
Mo=N	1.7099(17)	1.7074(18)	1.7127(13)	2.0180(11)	1.714(3)	1.713(3)	1.7028(14)	1.7261(13)	1.703(4)
Mo−O	1.9334(14)	1.9654(15)	1.909(5)	2.1721(11)	1.906(2)	1.941(2)	1.9230(11)	1.9518(11)	1.943(5)
Mo=N−C	167.81(15)	159.50(15)	163.58(11)	168.35(11)	171.6(3)	168.73(3)	169.14(12)	173.09(12)	162.1(4)
Mo−O−C	150.88(13)	142.25(14)	169.3(10)	139.66(9)	163.00(19)	145.2(2)	154.38(10)	140.93(10)	156.2(8)
Mo−C−C	145.64(15)	144.77(16)	144.53(12)	147.17(12)	142.4(3)	145.6(3)	141.90(12)	144.78(12)	144.7(4)

spectrum of **1b** typically contains several alkylidene resonances in the range 14−15 ppm, the intensities of which vary from sample to sample. An NMR spectrum of **1b** that had been recrystallized from a mixture of THF and pentane contained only a single alkylidene resonance at 14.47 ppm. An X-ray crystallographic study of this sample showed the product to be an octamer in which 2-CNPyr bridges between metals (see below and Figure 3). Therefore, we propose that the other

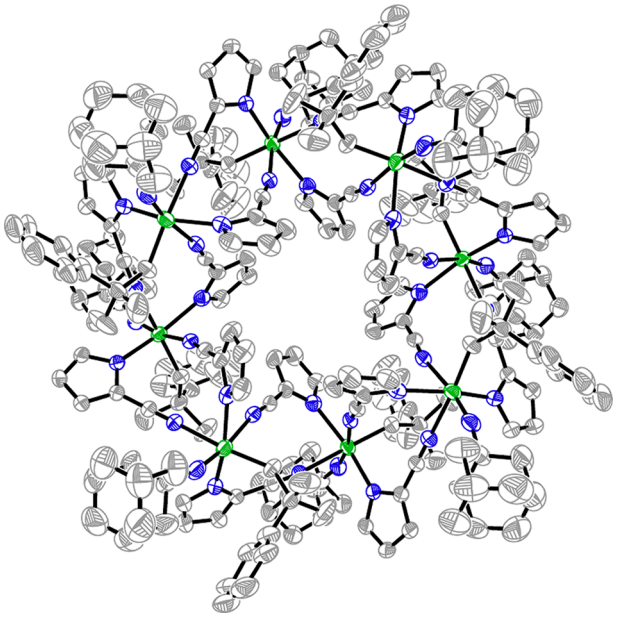


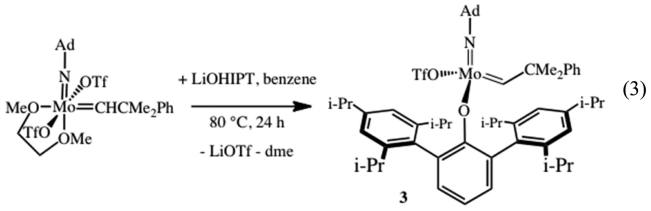
Figure 3. Thermal ellipsoid drawing of Mo(NAd)(CHCMe$_2$Ph)(2-CNPyr)$_2$ (**1b**) (ellipsoids at the 30% probability level). Hydrogen atoms, minor components of disorders, and solvent molecules are omitted for clarity. Atom colors: Mo (green); N (blue); C (gray).

alkylidene resonances observed in the initial NMR spectra arise from other oligomers of Mo(NAd)(CHCMe$_2$Ph)(2-CNPyr)$_2$ that are formed through 2-CNPyr bridges between metals.

Each molybdenum center in **1b** (Figure 3) exhibits a pseudo-octahedral geometry. The two η^1-pyrrolides are trans to one another and two cyano groups from each of the two adjacent neighboring Mo complexes are coordinated trans to the alkylidene and imido ligands. Eight bispyrrolide units of this type are linked through cyano donor interactions to yield the doughnutlike octameric structure. The bond lengths and angles in any one unit in the octamer are not unusual (see the Supporting Information). It should be noted that Mo(NAr)(CHCMe$_2$Ph)(NC$_4$H$_4$)$_2$ was found to be a dimer, {Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^5-NC$_4$H$_4$)(η^1-NC$_4$H$_4$)}{Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^1-NC$_4$H$_4$)$_2$}, in which the nitrogen in the η^5-pyrrolide bound to one Mo behaves as a donor to the other Mo.[24]

Compound **1b** reacts with Me$_3$COH, (CF$_3$)$_2$CHOH, and (CF$_3$)$_3$COH in C$_6$D$_6$ at 22 °C to give the known bisalkoxide complexes exclusively, according to NMR studies. However, **1b** does not react with 1 equiv of HIPTOH (~0.1 M in **1b** and HIPTOH) even at 100 °C over a period of days. We suspect that the sluggish reaction between **1b** and HIPTOH is a consequence of an inability of the bulky phenol to compete with the cyano donors in the octamer or various oligomers that are possible in solution (vide supra), the steric demands of the 2-cyanopyrrolides in hypothetical monomeric Mo(NAr)(CHCMe$_2$Ph)(η^1-2-CNPyr)$_2$, or the formation of the 18-electron species Mo(NAr)(CHCMe$_2$Ph)(η^1-2-CNPyr)(η^5-2-CNPyr).

Formation of a Monotriflate Monoaryloxide Complex and Reactions Thereof. The reaction between Mo(NAd)(CHCMe$_2$Ph)(OTf)$_2$(DME) and LiOHIPT in benzene at 80 °C leads to the formation of Mo(NAd)(CHCMe$_2$Ph)(OTf)(OHIPT) (**3**) in 99% yield (eq 3). Replacement of the



(3)

triflate in **3** upon reaction with LiOHIPT to yield the hypothetical Mo(NAd)(CHCMe$_2$Ph)(OHIPT)$_2$ must be slow for steric reasons. Filtration of the reaction mixture and removal of the benzene in vacuo yield **3** as a dark yellow solid that can be employed in subsequent reactions without further purification. Compound **3** shows a single resonance in its ^{19}F NMR spectrum at δ −75.4 ppm, consistent with the formation of a monotriflate species, while a single alkylidene resonance is found at 12.35 ppm in its ^{1}H NMR spectrum with a J_{CH} value (123 Hz) typical of a syn isomer.

Crystals of **3** suitable for an X-ray study could not be obtained. However, a trimethylphosphine adduct (**3**(PMe$_3$)) could be prepared readily and crystals suitable for an X-ray study obtained. As shown in Figure 4, **3**(PMe$_3$) is approximately a square pyramid with the alkylidene in the apical position and PMe$_3$ coordinated trans to the triflate ligand. The bond distances and angles in **3**(PMe$_3$) are similar to those found recently in other PMe$_3$ adducts of imido alkylidene complexes such as Mo(NAr)(CHCMe$_2$Ph)(Me$_2$Pyr)(OBr$_2$Bitet)(PMe$_3$)[25] and Mo(NAr)(CHCMe$_2$Ph)(Ph$_2$Pyr)(OR$_{F6}$)(PMe$_3$).[6] The structure of a trimethylphosphine adduct has often been viewed as analogous to that of an initial olefin adduct of an imido alkylidene complex before the TBP metallacyclobutane complex is formed. If that were the case, the imido and OHIPT ligands (N(1)−Mo(1)−O(1) = 153.63(5)° in **3**(PMe$_3$)) would end up in apical

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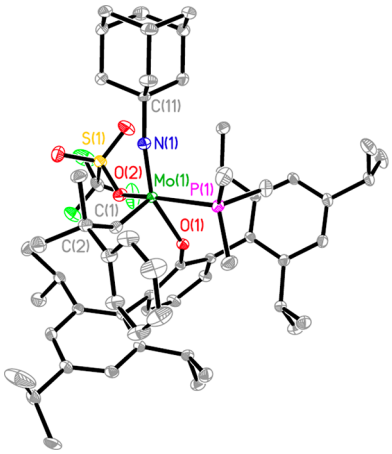


Figure 4. Thermal ellipsoid drawing of **3**(PMe_3) (ellipsoids at the 50% probability level). Hydrogen atoms and the minor component of the disorder are omitted for clarity. Selected bond lengths (Å) and angles (deg) can be found in Table 1.

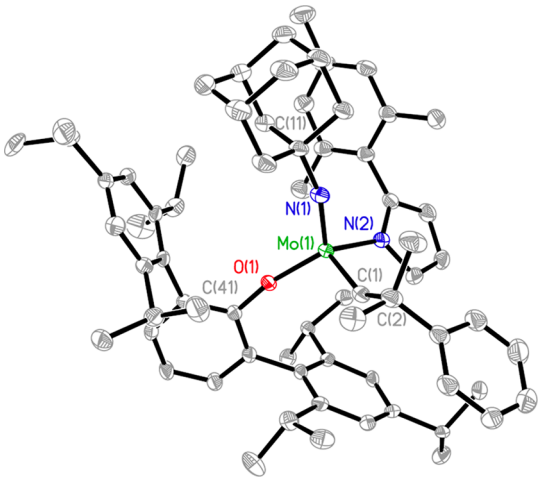
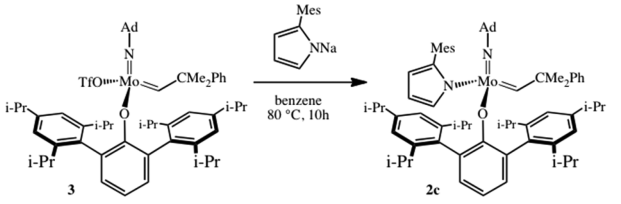


Figure 5. Thermal ellipsoid drawing of **2c** (ellipsoids at the 50% probability level). Hydrogen atoms, minor components of disorders, and the solvent molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg) can be found in Table 1.

positions in a TBP metallacyclobutane intermediate, as found in unsubstituted TBP metallacyclobutane complexes prepared from Mo or W MAP species containing one OHIPT or OBr_2Bitet ligand.[8b,9a,11]

An attempted synthesis of a monotriflate complex in a reaction between $Mo(NAr)(CHCMe_2Ph)(OTf)_2(DME)$ (Ar = 2,6-*i*$Pr_2C_6H_3$) and LiOHIPT in benzene at 80 °C led only to unidentified products. In contrast, a reaction between $Mo(NAr)(CHCMe_2Ph)(OTf)_2(DME)$ and $NaOBr_2Bitet$ led to the formation of primarily burgundy red $Mo(NAr)(CHCMe_2Ph)(OBr_2Bitet)_2$ in good yield.[26] This compound is a mixture of syn and anti isomers in solution (anti alkylidene resonance at 13.42 ppm with J_{CH} = 153.0 Hz; syn resonance at 12.90 ppm with J_{CH} = 126.0 Hz), although the X-ray structure was solved for a crystal of the pure anti isomer.[26] Attempts to prepare OHMT analogues of **3** in which NR is NAr (N-2,6-*i*$Pr_2C_2H_3$), NAr′ (N-2,6-$Me_2C_2H_3$), $NAr^{i\text{-}Pr}$ (N-2-*i*PrC_2H_4), or NAd were not successful. We propose that in the above circumstances the nucleophile attacks and deprotonates the alkylidene ligand at a rate competitive with nucleophilic attack at the metal center. We have also noted that when $Mo(NAr^M)(CHCMe_2Ph)(OTf)_2(DME)$ (Ar^M = 2-mesitylphenyl)[27] and $Mo(NAr^T)(CHCMe_3)(OTf)_2(DME)$ (Ar^T = 2-(2′,4′,6′-triisopropylphenyl)[27] were each treated with 1 equiv of LiOHIPT, the alkylidene peaks corresponding to the starting materials disappeared over time, no new alkylidene complexes were formed, and HIPTOH was observed as a product of the reaction. Clearly a fine balance of steric and electronic factors allows **3** to form in good yield. There is ample evidence in the literature that alkylidyne ligands can be formed through deprotonation of alkylidene ligands,[27] although alkylidyne complexes are rarely formed in good yield and other complications could be envisioned.

A reaction between 1 equiv of sodium 2-mesitylpyrrolide and **3** in benzene (80 °C for 10 h) led to the formation of $Mo(NAd)(CHCMe_2Ph)(OHIPT)(2\text{-}Mespyr)$ (**2c**) in 45% yield (eq 4). A single alkylidene resonance (at 12.25 ppm) with a J_{CH} characteristic of a syn species (120 Hz) is observed in the ^{1}H NMR spectrum of **2c**. A structural study of **2c** reveals it to have a slightly distorted tetrahedral geometry in which the mesityl group points away from the sterically demanding OHIPT ligand toward the relatively small adamantylimido ligand (Figure 5). Therefore, the imido ligand is bent slightly (Mo(1)−N(1)−C(11) = 163.58(11)°). It is important to note, as stated earlier, that we have not been able to prepare compound **2c** through addition of HIPTOH to $Mo(NAd)(CHCMe_2Ph)(Mespyr)_2$, at least not under the conditions we have tried so far. Therefore, **2c** must be assembled through selective nucleophilic displacements. The yield may be limited as a consequence of some competition between deprotonation of the alkylidene ligand and substitution of the triflate ligand.



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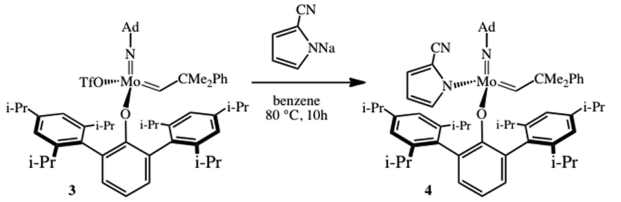
Reaction of **3** with 1 equiv of Na(2-CNPyr) in benzene at room temperature gave a complex mixture of products from which $Mo(NAd)(CHCMe_2Ph)(2\text{-}CNPyr)(OHIPT)$ (**4**) could be isolated in 25% yield (eq 5). Formation of free HIPTOH



(5)

and the relatively low yield we propose again are consequences of deprotonation of the alkylidene. The ^{1}H NMR spectrum of pure **4** is straightforward; the syn alkylidene has a J_{CH} value of 121 Hz. An X-ray study of **4** confirmed that it is a monomer (Figure 6). Evidently the steric demands of the HIPTO ligand prevent the cyano group from binding to another Mo center in this circumstance. As noted earlier, we were not able to prepare **4** by heating a mixture of **1b** and HIPTOH, although even the nucleophilic approach to **4** (eq 5) results in a low yield and is therefore borderline.

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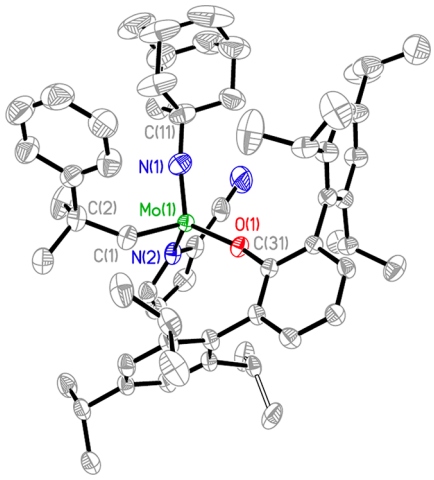
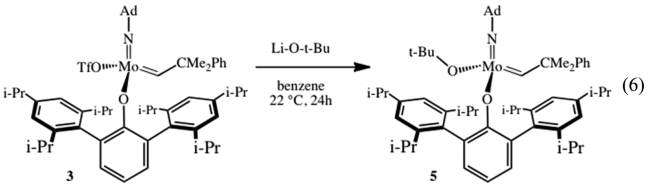


Figure 6. Thermal ellipsoid drawing of Mo(NAd)($CHCMe_2Ph$)-(2-CNPyr)(OHIPT) (**4**) (ellipsoids at the 50% probability level). Hydrogen atoms and minor components of disorders are omitted for clarity. Selected bond lengths (Å) and angles (deg) can be found in Table 1.

The reaction between 1 equiv of LiO-*t*Bu and **3** in benzene at room temperature for 1 day led to the formation of Mo(NAd)($CHCMe_2Ph$)(OHIPT)($OCMe_3$) (**5**) in 22% isolated yield (eq 6). We propose that the low yield again is a



(6)

consequence, at least in part, of competitive deprotonation of the alkylidene ligand. A single alkylidene resonance (at 11.16 ppm) with a J_{CH} value characteristic of a syn species (119 Hz) was observed in the ^{1}H NMR spectrum of **5**. A structural study reveals **5** to have the expected tetrahedral geometry (Figure 7). The Mo(1)−O(2)−C(71) angle (143.3(2)°)

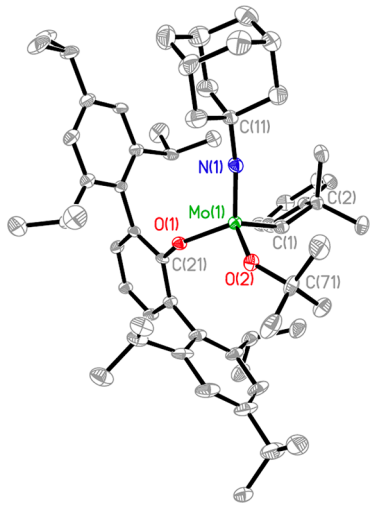


Figure 7. Thermal ellipsoid drawing of **5** (ellipsoids at the 50% probability level). Hydrogen atoms are omitted for clarity; only one independent molecule is shown. Selected bond lengths (Å) and angles (deg) can be found in Table 1.

and the Mo(1)−O(1)−C(21) angle (145.2(2)°) are essentially identical. There is no evidence for disproportionation of **5** in solution under mild conditions, perhaps because facile formation of hypothetical Mo(NAd)($CHCMe_2Ph$)($OHIPT)_2$ may be unlikely for steric reasons.

Synthesis of SAM Complexes from Bishexafluoro-*tert*-butoxide Complexes. In the previous section we noted that deprotonation of the alkylidene ligand is a likely complication of attempted nucleophilic substitutions at the metal when one or two triflate ligands are present. In past studies we noted that whereas addition of 2 equiv of $LiNPh_2$ to Mo(NAr)-($CHCMe_2Ph$)($OTf)_2$(DME) yielded Mo(NAr)($CHCMe_2Ph$)-($NPh_2)_2$ in only 35% yield after a difficult isolation,[16] Mo(NAr)($CHCMe_2Ph$)($OR_{F6})_2$ (OR_{F6} = $OCMe(CF_3)_2$) reacts with 2 equiv of $LiNPh_2$ to afford Mo(NAr)-($CHCMe_2Ph$)($NPh_2)_2$ in 78% isolated yield without formation of any significant side products. We proposed that deprotonation of the alkylidene is significantly reduced in reactions between Mo(NAr)($CHCMe_2Ph$)($OR_{F6})_2$ and amido nucleophiles. Therefore, we evaluated the possibility of employing bishexafluoro-*tert*-butoxide complexes as starting materials for making Mo(NR)($CHCMe_2Ph$)(OR_{F6})(Y) complexes.

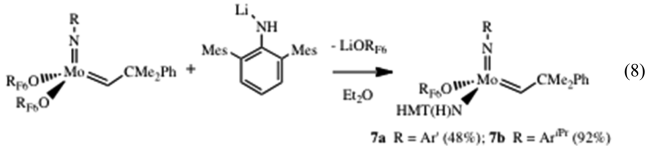
When Mo(NR)($CHCMe_2Ph$)($OR_{F6})_2$ complexes are treated with 1 equiv of LiOHMT, Mo(NR)($CHCMe_2Ph$)(OR_{F6})-(OHMT) complexes are formed where R = Ar (**6a**), Ar′ (**6b**), Ar^{iPr} (**6c**), Ad (**6d**) in moderate to good yields (43−80%, eq 7).

(7)

Complexes **6b−d** can be made without formation of any significant byproducts, except in the case of **6a**. The proton NMR spectrum of crude of **6a** shows that a substantial amount of HMTOH forms, consistent with deprotonation of the alkylidene ligand. Like **5**, compounds **6a−d** show no tendency to disproportionate under mild conditions to yield bishexafluoro-*tert*-butoxide and what are likely to be sterically crowded and currently unknown bis(OHMT) complexes. However, an example of a bis(DFTO) (DFTO = 2,6-$(C_6F_5)_2C_6H_3O$) imido alkylidene complex has recently been prepared.[28]

The structure of complex **6d** is shown in Figure 8. The HMTO ligand is oriented so that one of the mesityl groups points toward the imido group while the other points into the COO face of the tetrahedron. In this case the Mo(1)−O(1)−C(21) bond angle (145.23(12)°) and Mo(1)−O(2)−C(31) bond angle (154.38(10)°) differ in the direction one might expect.

When Mo(NR)($CHCMe_2Ph$)($OR_{F6})_2$ is treated with 1 equiv of LiN(H)HMT at 22 °C in diethyl ether, **7a** (R = Ar′) and **7b** (R = Ar^{iPr}) could be obtained cleanly (eq 8). Proton NMR



(8)

spectra of **7a,b** show only one alkylidene peak (at 11.86 ppm for **7a** and 11.72 ppm for **7b**) and one NH resonance (at 7.82 ppm for **7a** and 7.99 ppm for **7b**).

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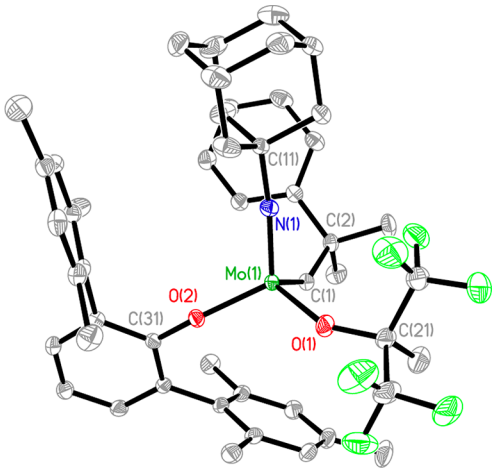


Figure 8. Solid-state structure of **6d** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) can be found in Table 1.

The reaction between Mo(NAr)(CHCMe$_2$Ph)(OR$_{F6}$)$_2$ and LiN(H)HMT leads to formation of byproducts, while in the case of Mo(NAd)(CHCMe$_2$Ph)(OR$_{F6}$)$_2$, substitution appears to be successful, according to proton NMR studies, but the compound could not be isolated in pure form readily. Compounds **7a,b** are believed to be the first examples of imido alkylidene complexes of this general type in which a primary amido ligand is present. Although we have uncovered no evidence that an α proton can migrate from an amido nitrogen to either an imido nitrogen or an alkylidene carbon atom in the same complex, we would not be surprised if some of the side products formed in reactions of this type were to result from loss of the amido proton from the amido ligand in **7** in the presence of strong nucleophiles.

The structure of **7b** is shown in Figure 9, with relevant bond distances and angles given in Table 1. The Mo(1)−N(2) bond

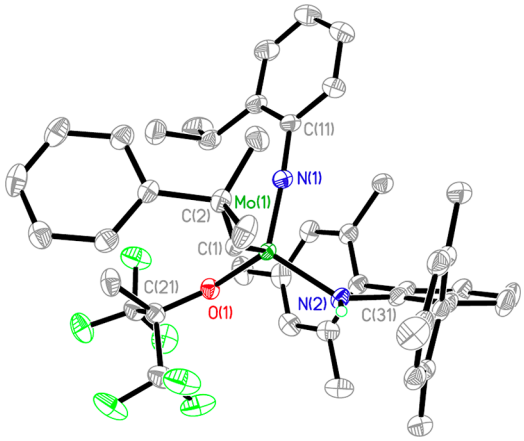
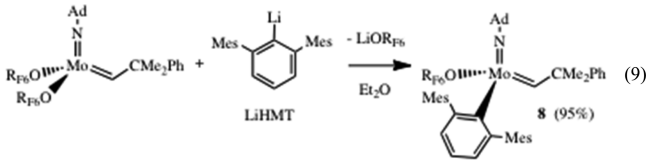


Figure 9. Solid-state structure of **7b** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity, except for the hydrogen on N(2). Selected bond lengths (Å) and angles (deg) can be found in Table 1.

distance (1.9950(13) Å) is similar to Mo−N$_{amido}$ distances in Mo(NAr)(CHCMe$_2$Ph)(NPh$_2$)$_2$ complexes[16] (2.007(3) and 2.009(3) Å), but the Mo(1)−N(2)−C(31) bond angle (133.32(11)°) is significantly larger than those of the bisamide complex (118.61(19) and 117.6(3)°), because of the steric demands of the HMT substituent in the N(H)(HMT) ligand, an N−H agostic interaction, or both.

When Mo(NAd)(CHCMe$_2$Ph)(OR$_{F6}$)$_2$ was treated with 1 equiv of LiHMT, Mo(NAd)(CHCMe$_2$Ph)(OR$_{F6}$)(HMT) (**8**) could be obtained as a crystalline yellow solid (eq 9).



(9)

A proton NMR spectrum of **8** reveals the presence of only one product, as determined by the presence of only one alkylidene resonance at 10.99 ppm (J_{CH} = 120 Hz) in its ^{1}H NMR spectrum and the set of quartets in its ^{19}F NMR spectrum.

When the imido ligand is NAr in a reaction analogous to that shown in eq 9, the steric crowding is so significant that even after 5 days of heating the mixture only 18% of a new alkylidene species is formed. When R = Ar′, the reaction reaches 90% completion after 5 days to yield two alkylidene products with alkylidene resonances at 11.7 ppm (78%) and 11.0 ppm (12%). No product analogous to **8** could be isolated in either of these reactions. When Mo(NAd)(CHCMe$_2$Ph)(OTf)$_2$(DME) is treated with 1 equiv of LiHMT, the alkylidene peak corresponding to the starting material disappears but no new alkylidene peak appears.

The structure of **8** is shown in Figure 10. The hexafluoro-*tert*-butoxide ligand is disordered. A front view of the disordered

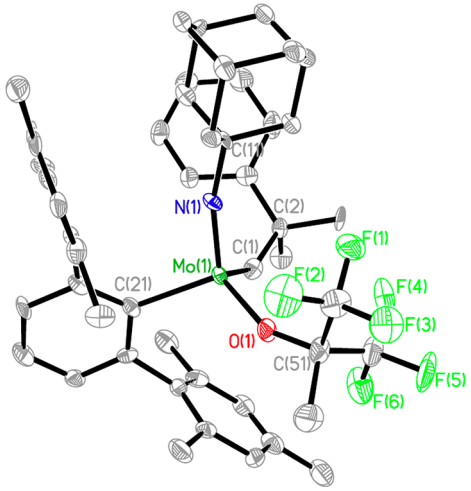


Figure 10. Solid-state structure of **8** (50% probability ellipsoids). Hydrogen atoms and minor disorder components are omitted for clarity; only one independent molecule is shown. Selected bond lengths (Å) and angles (deg) can be found in Table 1.

hexafluoro-*tert*-butoxide ligand is shown in the Supporting Information (Figure S1). The Mo(1)−C(21) bond length (2.188(5) Å) is typical of a Mo−C bond length. However, the HMT ligand creates a considerably more sterically crowded environment than an OHMT ligand, since no heteroatom is present between the Mo and C(21). No species analogous to **8** could be prepared that contains the NAr group. Compound **8** is a rare example of a SAM Mo complex that contains an carbon-based ligand singly bound to the metal. The only other examples are monoalkoxide mononeopentyl imido alkylidene complexes of Mo and W.[17]

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ROMP polymerization of 2,3-dicarbomethoxynorbornadiene has been employed as a test to determine whether a given catalyst can produce a polymer with a single structure. For example, DCMNBD (2,3-dicarbomethoxynorbornadiene) was polymerized by Mo(NAd)(CHCMe$_2$Ph)(Pyr)(OHIPT) to give a >99% cis and highly tactic poly(DCMNBD) that is proposed to be syndiotactic on the basis of formation of what could be proven to be >99% cis,syndiotactic polymer employing 2,3-dicarbomenthoxynorbornadiene.[9a] Complexes of the type Mo(NR)(CHCMe$_2$Ph)(Pyr)(OHMT) (where R = 2,6-diisopropylphenyl, 2,6-dimethylphenyl, 2-isopropylphenyl, 1-adamantyl) have also been found to yield >99% *cis,syndiotactic*-poly(DCMNBD).[27] In contrast, with the exception of **6c**, polymerization of DCMNBD with **6a**,**b**,**d**, **7a**,**b**, and **8**, did not produce highly structured poly(DCMNBD). The structures of poly(DCMNBD) samples obtained with initiators **6a** and **7b** were biased toward cis,isotactic, behavior that is not readily explicable but is not unusual for bisalkoxide species (Table 2).[29] Finally, it should be noted that polymerization of DCMNBD initiated by **8** was exceedingly slow, requiring days to consume 95% of the 100 equiv of monomer under the same conditions employed for the other initiators. We attribute the sluggishness of **8** as an initiator to the extreme steric crowding that results from the HMT group that is directly bound to the metal.

Table 2. ROMP of 2,3-Dicarbomethoxynorbornadiene (DCMNBD)[a]

cat.	[cat.] (mM)	amt of DCMNBD (equiv)	structure
Mo(NAr)(CHR′)(OR$_{F6}$) (OHMT) (**6a**)	4.6	50	>98% cis, 78% iso
Mo(NAr′)(CHR′)(OR$_{F6}$) (OHMT) (**6b**)	4.9	50	95% cis, 73% syndio
Mo(NAr^{iPr})(CHR′)(OR$_{F6}$) (OHMT) (**6c**)	4.8	50	98% cis, 95% syndio
Mo(NAd)(CHR′)(OR$_{F6}$) (OHMT) (**6d**)	4.7	50	90% cis, 76% syndio
Mo(NAr′)(CHR′)(OR$_{F6}$) [N(H)HMT] (**7a**)	4.9	50	95% cis, 71% syndio
Mo(NAr^{iPr})(CHR′)(OR$_{F6}$) [N(H)HMT] (**7b**)	4.8	50	90% cis, 54% iso
Mo(NAd)(CHR′)(OR$_{F6}$) (HMT) (**8**)	4.8	100	83% cis, 91% syndio[b]

[a]R′ = CMe$_2$Ph. [b]Five days were required to reach full conversion.

CONCLUSIONS

We have found that several stereogenic-at-metal imido alkylidene complexes can be accessed through selective nucleophilic displacement reactions in imido alkylidene complexes of molybdenum. Those that are monopyrrolide complexes could not be made through protonolysis of the required bispyrrolide. A persistent problem that is exacerbated in sterically crowded circumstances is what is proposed to be competitive deprotonation of the alkylidene ligand in competition with substitution of (usually) a triflate ligand; the product yield is consequently reduced and isolation of pure product is compromised by formation of byproducts. Several Mo(NR)(CHR′)(X)(Y) variations in which neither X nor Y is a pyrrolide could be prepared, including Mo(NR)(CHCMe$_2$Ph)(OR$_{F6}$)(Y) complexes in which Y is OHMT, N(H)HMT, or HMT (HMT = 2,6-dimesitylphenyl). Deprotonation of the alkylidene in Mo(NR)(CHCMe$_2$Ph)(OR$_{F6}$)$_2$ apparently is not facile relative to nucleophilic displacement of the OR$_{F6}$ ligand in the syntheses of Mo(NR)(CHCMe$_2$Ph)(OR$_{F6}$)(Y) complexes.

ASSOCIATED CONTENT

Supporting Information

Text, tables, figures, and CIF files giving synthesis and characterization details for all complexes and crystallographic details, fully labeled thermal ellipsoid diagrams for all crystallographically characterized species, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org. Data for the X-ray structures are also available to the public at http://www.reciprocalnet.org.

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Notes

The authors declare no competing financial interest.

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