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

Smaranda C. Marinescu, Victor W. L. Ng, Alejandro G. Lichtscheidl, Richard R. Schrock,* Peter Müller, and Michael K. Takase

Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

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)(CHCMe₂Ph)(MesPyr)₂ (1a; MesPyr = 2-mesitylpyrrolide, Ad = 1-adamantyl), Mo(NAD)(CHCMe₂Ph)(2-CNPyr)₂ (1b; 2-CNPyr = 2-cyanopyrrolide), Mo(NAD)(CHCMe₂Ph)(MesPyr)(OTPP) (2a; OTPP = 2,3,5,6-tetraphenylphenoxide), Mo(NAD)(CHCMe₂Ph)(MesPyr)(OBr₂Bitet) (2b; OB₃,Bitet = (R)-3,3'-dibromo-2,2'-((tert-butylidimethylsilyloxy)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2-olate), Mo(NAD)(CHCMe₂Ph)(OHIPT) (2c; HIPT = hexaisopropylterphenoxide = O-2,6-(2,4,6-tert-butyl)phenol), Mo(NAD)(CHCMe₂Ph)(OTf)(OHIPT) (2d; OHIPT = 2,6-(2,4,6-triisopropylphenoxide), Mo(NAd)(CHCMe₂Ph)(OHIPT)(OCMe₃) (2e; OHIPT = 2,6-(2,4,6-triisopropylphenoxide), and Mo(NAd)(CHCMe₂Ph)(OHIPT)(2-Mespyr) (2f). Isolation of 4-coordinate complexes of M(NR)(CHR′)(X)(Y), many of which had to be prepared through selective nucleophilic displacement reactions in imido alkylidene complexes. For example, Mo(NAd)(CHCMe₂Ph)(MesPyr)₂ was synthesized through selective nucleophilic displacement reactions in imido alkylidene complexes. The reported compounds include Mo(NAd)(CHCMe₂Ph)(MesPyr)₂ (1a; MesPyr = 2-mesitylpyrrolide, Ad = 1-adamantyl), Mo(NAD)(CHCMe₂Ph)(2-CNPyr)₂ (1b; 2-CNPyr = 2-cyanopyrrolide), Mo(NAD)(CHCMe₂Ph)(MesPyr)(OTPP) (2a; OTPP = 2,3,5,6-tetraphenylphenoxide), Mo(NAD)(CHCMe₂Ph)(MesPyr)(OBr₂Bitet) (2b; OB₃,Bitet = (R)-3,3'-dibromo-2,2'-((tert-butylidimethylsilyloxy)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2-olate), Mo(NAD)(CHCMe₂Ph)(OHIPT) (2c; HIPT = hexaisopropylterphenoxide = O-2,6-(2,4,6-tert-butyl)phenol), Mo(NAD)(CHCMe₂Ph)(OTf)(OHIPT) (2d; OHIPT = 2,6-(2,4,6-triisopropylphenoxide), Mo(NAd)(CHCMe₂Ph)(OHIPT)(OCMe₃) (2e; OHIPT = 2,6-(2,4,6-triisopropylphenoxide), and Mo(NAd)(CHCMe₂Ph)(OHIPT)(2-Mespyr) (2f). Isolation of 4-coordinate complexes of M(NR)(CHR′)(X)(Y), many of which had to be prepared through selective nucleophilic displacement reactions in imido alkylidene complexes. For example, Mo(NAd)(CHCMe₂Ph)(MesPyr)₂ was synthesized through selective nucleophilic displacement reactions in imido alkylidene complexes. The reported compounds include Mo(NAd)(CHCMe₂Ph)(MesPyr)₂ (1a; MesPyr = 2-mesitylpyrrolide, Ad = 1-adamantyl), Mo(NAD)(CHCMe₂Ph)(2-CNPyr)₂ (1b; 2-CNPyr = 2-cyanopyrrolide), Mo(NAD)(CHCMe₂Ph)(MesPyr)(OTPP) (2a; OTPP = 2,3,5,6-tetraphenylphenoxide), Mo(NAD)(CHCMe₂Ph)(MesPyr)(OBr₂Bitet) (2b; OB₃,Bitet = (R)-3,3'-dibromo-2,2'-((tert-butylidimethylsilyloxy)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2-olate), Mo(NAD)(CHCMe₂Ph)(OHIPT) (2c; HIPT = hexaisopropylterphenoxide = O-2,6-(2,4,6-tert-butyl)phenol), Mo(NAD)(CHCMe₂Ph)(OTf)(OHIPT) (2d; OHIPT = 2,6-(2,4,6-triisopropylphenoxide), Mo(NAd)(CHCMe₂Ph)(OHIPT)(OCMe₃) (2e; OHIPT = 2,6-(2,4,6-triisopropylphenoxide), and Mo(NAd)(CHCMe₂Ph)(OHIPT)(2-Mespyr) (2f). Isolation of 4-coordinate complexes of M(NR)(CHR′)(X)(Y), many of which had to be prepared through selective nucleophilic displacement reactions in imido alkylidene complexes. For example, Mo(NAd)(CHCMe₂Ph)(MesPyr)₂ was synthesized through selective nucleophilic displacement reactions in imido alkylidene complexes. The reported compounds include Mo(NAd)(CHCMe₂Ph)(MesPyr)₂ (1a; MesPyr = 2-mesitylpyrrolide, Ad = 1-adamantyl), Mo(NAD)(CHCMe₂Ph)(2-CNPyr)₂ (1b; 2-CNPyr = 2-cyanopyrrolide), Mo(NAD)(CHCMe₂Ph)(MesPyr)(OTPP) (2a; OTPP = 2,3,5,6-tetraphenylphenoxide), Mo(NAD)(CHCMe₂Ph)(MesPyr)(OBr₂Bitet) (2b; OB₃,Bitet = (R)-3,3'-dibromo-2,2'-((tert-butylidimethylsilyloxy)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2-olate), Mo(NAD)(CHCMe₂Ph)(OHIPT) (2c; HIPT = hexaisopropylterphenoxide = O-2,6-(2,4,6-tert-butyl)phenol), Mo(NAD)(CHCMe₂Ph)(OTf)(OHIPT) (2d; OHIPT = 2,6-(2,4,6-triisopropylphenoxide), Mo(NAd)(CHCMe₂Ph)(OHIPT)(OCMe₃) (2e; OHIPT = 2,6-(2,4,6-triisopropylphenoxide), and Mo(NAd)(CHCMe₂Ph)(OHIPT)(2-Mespyr) (2f). Isolation of 4-coordinate complexes of M(NR)(CHR′)(X)(Y), many of which had to be prepared through selective nucleophilic displacement reactions in imido alkylidene complexes. For example, Mo(NAd)(CHCMe₂Ph)(MesPyr)₂ was synthesized through selective nucleophilic displacement reactions in imido alkylidene complexes. The reported compounds include Mo(NAd)(CHCMe₂Ph)(MesPyr)₂ (1a; MesPyr = 2-mesitylpyrrolide, Ad = 1-adamantyl), Mo(NAD)(CHCMe₂Ph)(2-CNPyr)₂ (1b; 2-CNPyr = 2-cyanopyrrolide), Mo(NAD)(CHCMe₂Ph)(MesPyr)(OTPP) (2a; OTPP = 2,3,5,6-tetraphenylphenoxide), Mo(NAD)(CHCMe₂Ph)(MesPyr)(OBr₂Bitet) (2b; OB₃,Bitet = (R)-3,3'-dibromo-2,2'-((tert-butylidimethylsilyloxy)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2-olate), Mo(NAD)(CHCMe₂Ph)(OHIPT) (2c; HIPT = hexaisopropylterphenoxide = O-2,6-(2,4,6-tert-butyl)phenol), Mo(NAD)(CHCMe₂Ph)(OTf)(OHIPT) (2d; OHIPT = 2,6-(2,4,6-triisopropylphenoxide), Mo(NAd)(CHCMe₂Ph)(OHIPT)(OCMe₃) (2e; OHIPT = 2,6-(2,4,6-triisopropylphenoxide), and Mo(NAd)(CHCMe₂Ph)(OHIPT)(2-Mespyr) (2f). Isolation of 4-coordinate complexes of M(NR)(CHR′)(X)(Y), many of which had to be prepared through selective nucleophilic displacement reactions in imido alkylidene complexes. For example, Mo(NAd)(CHCMe₂Ph)(MesPyr)₂ was synthesized through selective nucleophilic displacement reactions in imido alkylidene complexes. The reported compounds include Mo(NAd)(CHCMe₂Ph)(MesPyr)₂ (1a; MesPyr = 2-mesitylpyrrolide, Ad = 1-adamantyl), Mo(NAD)(CHCMe₂Ph)(2-CNPyr)₂ (1b; 2-CNPyr = 2-cyanopyrrolide), Mo(NAD)(CHCMe₂Ph)(MesPyr)(OTPP) (2a; OTPP = 2,3,5,6-tetraphenylphenoxide), Mo(NAD)(CHCMe₂Ph)(MesPyr)(OBr₂Bitet) (2b; OB₃,Bitet = (R)-3,3'-dibromo-2,2'-((tert-butylidimethylsilyloxy)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binap...
based on, for example, C (e.g., an alkyl),\textsuperscript{15} N (e.g., an amide),\textsuperscript{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)(CHCMe₂Ph)(MesPyr)₂ (1a; MesPyr = 2-mesitylpyrrolide, Ad = 1-adamantyl) can be prepared in 75\% isolated yield by treating Mo(NAd)(CHCMe₂Ph)(OTf)₂(DME) with 2 equiv of Li(MesPyr) in diethyl ether. Compound 1a is a close relative of Mo(NAd)(CHCMe₃)(MesPyr)₂, which was prepared in 25\% isolated yield in a similar manner.\textsuperscript{19} It is also related to structurally characterized Mo(NAr)(CHCMe₂Ph)-(η⁵-MesPyr)₂ (Ar = 2,6-diisopropylphenyl),\textsuperscript{20} in which for steric reasons the 2-mesitylpyrrolide ligand cannot bind in an η⁵ fashion, usually the observed mode of binding one of the two pyrrolides in other imido alkylidene bispyrrolide complexes.\textsuperscript{5,21}

Mo(NAd)(CHCMe₂Ph)(MesPyr)₂ reacts with TPPOH (2,3,5,6-tetraphenylphenol) and Br₂BitetOH (eq 1) readily to yield Mo(NAd)(CHCMe₂Ph)(MesPyr)(OTPP) (2a) and Mo(NAd)(CHCMe₂Ph)(MesPyr)(OBr₂Bitet) (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 \(12.47 \text{ ppm} (\text{R diastereomer})\) and \(13.14 \text{ ppm} (\text{S diastereomer})\). The \(\text{S diastereomer}\) could be isolated in pure form through crystallization from \(n\)-pentane. A typical observed ratio of \(\text{R to S in the crude product mixture}\) 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)(CHCMe₂Ph)-(Me₂Pyr)(OBr₂Bitet) (Me₂Pyr = 2,5-dimethylpyrrolide, Ar = 2,6-iPr₂C₆H₃).\textsuperscript{22}

While 1 equiv of HIPTOH will react with Mo(NAd)-(CHCMe₂Ph)(Pyr)₂ (Pyr = pyrrolide, 2,5-dimethylpyrrolide) to yield Mo(NAd)(CHCMe₂Ph)(Pyr)(OHIPT),\textsuperscript{9a} attempts to react 1 equiv of HIPTOH with 1a in toluene-\(d₈\) 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.
alkylidene resonances observed in the initial NMR spectra arise from other oligomers of Mo(NAr)(CHCMe2Ph)(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 \( \eta^2 \)-pyrrolylides 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 bispyrrole 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).

Compound 1b reacts with Me3COH, (CF3)2CHOH, and (CF3)3COH in \( \text{C}_6\text{D}_6 \) 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)-(CHCMePh)(\( \eta^2 \)-2-CNPyr)2 or the formation of the 18-electron species Mo(NAr)(CHCMePh)(\( \eta^2 \)-2-CNPyr)(\( \eta^1 \)-2-CNPyr).

Formation of a Monotriphosphate Monoaloxysteryl Complex and Reactions Thereof. The reaction between Mo(NAd)-(CHCMePh)(OTf)2(DME) and LiOHIPT in benzene at 80 °C leads to the formation of Mo(NAd)(CHCMePh)(OTf)(OHIPT) (3) in 99% yield (eq 3). Replacement of the triflate in 3 upon reaction with LiOHIPT to yield the hypothetical Mo(NAd)(CHCMePh)(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 \( ^{19} \text{F} \) NMR spectrum at \( \delta \sim 75.4 \) ppm, consistent with the formation of a monotriphosphate species, while a single alkylidene resonance is found at 12.35 ppm in its \(^1\text{H} \) NMR spectrum with a \( J_{\text{CH}} \) value of 129 Hz typical of a syn isomer.

Crystals of 3 suitable for an X-ray study could not be obtained. However, a trimethylphosphine adduct (3(PMe3)) could be prepared readily and crystals suitable for an X-ray study obtained. As shown in Figure 4, 3(PMe3) is approximately a square pyramid with the alkylidene in the apical position and PMe3 coordinated trans to the triflate ligand. The bond distances and angles in 3(PMe3) are similar to those found recently in other PMe3 adducts of imido alkylidene complexes such as Mo(NAr)-(CHCMePh)(Me2Pyr)(OBr2Bitet)(PMe3) \(^{25} \) and Mo(NAr)-(CHCMePh)(Ph2Pyr)(ORF6)(PMe3). \(^{26} \) 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(PMe3)) would end up in apical

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo=C</td>
<td>1.886(2)</td>
<td>190.0(2)</td>
</tr>
<tr>
<td>Mo=X</td>
<td>2.0527(19)</td>
<td>180.0(3)</td>
</tr>
<tr>
<td>Mo=N</td>
<td>1.7099(17)</td>
<td>180.0(5)</td>
</tr>
<tr>
<td>Mo−O</td>
<td>1.9334(14)</td>
<td>180.0(2)</td>
</tr>
<tr>
<td>Mo−N−C</td>
<td>167.81(15)</td>
<td>180.0(5)</td>
</tr>
<tr>
<td>Mo−O−C</td>
<td>150.88(13)</td>
<td>180.0(4)</td>
</tr>
<tr>
<td>Mo−C−C</td>
<td>145.64(15)</td>
<td>180.0(4)</td>
</tr>
</tbody>
</table>

Figure 3. Thermal ellipsoid drawing of Mo(NAd)(CHCMePh)(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).
positions in a TBP metallacyclobutane intermediate, as found in unsubstituted TBP metallacyclobutane complexes prepared from Mo or W MAP species containing one OHIPT or OBr2Bitet ligand.8b,9a,11

An attempted synthesis of a monotriflate complex in a reaction between Mo(NAr)(CHCMe2Ph)(OTf)2(DME) (Ar = 2,6-iPr2C6H3) and LiOHIPT in benzene at 80 °C led only to unidentified products. In contrast, a reaction between Mo(NAr)(CHCMe2Ph)(OTf)2(DME) and NaOBr2Bitet led to the formation of primarily burgundy red Mo(NAr)-(CHCMe2Ph)(OBr2Bitet)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 JCH = 153.0 Hz; syn resonance at 12.90 ppm with JCH = 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-iPr2C2H3), NAr’ (N-2,6-Me2C2H3), NAr ‑Pr (N-2-iPrC2H4), 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(NAr2)(CHCMe2Ph)(OTf)2(DME) (Ar2 = 2-mesitylphenyl)27 and Mo(NAr2')(CHCMe2Ph)(OTf)2(DME) (Ar2' = 2-(2',4',6'-trisopropylphenyl)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)(CHCMe2Ph)(OHIPT)(2-Mespyr) (2c) in 45% yield (eq 4). Formation of free HIPTOH and the relatively low yield we propose again are consequences of deprotonation of the alkylidene. The 1H NMR spectrum of pure 4 is straightforward; the syn alkylidene has a JCH 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.

Figure 4. Thermal ellipsoid drawing of 3(PMe3) (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.
The reaction between 1 equiv of LiO-tBu and 3 in benzene at room temperature for 1 day led to the formation of Mo(NAd)(CHCMe2Ph)(OHIPT)(OCMe3)(5) in 22% isolated yield (eq 6). We propose that the low yield again is a 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)°) 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,Ph)(OHIPT)$_2$ may be unlikely for steric reasons.

**Synthesis of SAM Complexes from Bis(hexafluoro-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 trflate ligands are present. In past studies we noted that whereas addition of 2 equiv of LiNPh$_2$ to Mo(NAr)-(CHCMe,Ph)(OTf)$_2$(DME) yielded Mo(NAr)(CHCMe,Ph)-(NPh)$_2$ in only 35% yield after a difficult isolation, Mo(NAr)(CHCMe,Ph)(OR$_{6\text{F}}$)$_2$ (OR$_{6\text{F}}$ = OCMe(CF$_3$)$_2$) reacts with 2 equiv of LiNPh$_2$ to afford Mo(NAr)-(CHCMe,Ph)(NPh)$_2$ 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,Ph)(ORF$_6$)$_2$ and amido nucleophiles. Therefore, we evaluated the possibility of employing bis(hexafluoro-tert-butoxide complexes as starting materials for making Mo(NR)(CHCMe,Ph)(ORF$_6$)(Y) complexes.

When Mo(NR)(CHCMe,Ph)(OR$_{6\text{F}}$)$_2$ complexes are treated with 1 equiv of LiOHMT, Mo(NR)(CHCMe,Ph)(OHMT) complexes are formed where R = Ar ($^6$a), Ar’ ($^6$b), Ar$i$Pr ($^6$c), Ad ($^6$d) in moderate to good yields (43–80%, eq 7). Complexes $^6$b–$^d$ can be made without formation of any significant byproducts, except in the case of $^6$a. The proton NMR spectrum of crude of $^6$a shows that a substantial amount of HMTOH forms, consistent with deprotonation of the alkylidene ligand. Like 5, compounds $^6$a–$^d$ show no tendency to disproportionate under mild conditions to yield bis(hexafluoro-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$_6$F$_5$)$_2$C$_6$H$_3$O) imido alkylidene complex has recently been prepared. The structure of complex $^6$d is shown in Figure 8. The HMT 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,Ph)(OR$_{6\text{F}}$)$_2$ is treated with 1 equiv of LiN(H)HMT at 22 °C in diethyl ether, 7a (R = Ar’) and 7b (R = Ar$i$Pr) could be obtained cleanly (eq 8). Proton NMR 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).
The reaction between Mo(NAr)(CHCMe2Ph)(ORF6)2 and LiN(H)HMT leads to formation of byproducts, while in the case of Mo(NAd)(CHCMe2Ph)(ORF6)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 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 distance (1.9950(13) Å) is similar to Mo–N amido distances in Mo(NAr)(CHCMe2Ph)(NPh2)2 complexes (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)(CHCMePh)(ORF6)2 was treated with 1 equiv of LiHMT, Mo(NAd)(CHCMePh)(ORF6)(HMT) (8) could be obtained as a crystalline yellow solid (eq 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)(CHCMe2Ph)(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 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 a carbon-based ligand singly bound to the metal. The only other examples are monoalkoxide mononeopentyl imido alkylidene complexes of Mo and W.17

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.

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.

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.
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)(CHCMe2Ph)(Pyr)(OHIP) to give a >99% cis and highly tactic poly(DCMNBD) that is proposed to be syndiotactic based on formation of what could be proven to be >99% cis,syndiotactic polymer employing 2,3-dicarbomethoxynorbornadiene. Complexes of the type Mo(OR)(CHCMe2Ph)(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). 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,syndiotactic, behavior that is not readily explicable but is not unusual for bisalkoxide species (Table 2).59 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

<table>
<thead>
<tr>
<th>cat.</th>
<th>[cat.] (mM)</th>
<th>amnt of DCMNBD (equiv)</th>
<th>structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(NNR)(CHR)(Y)(ORF6) (HMT) (6a)</td>
<td>4.6</td>
<td>50</td>
<td>&gt;98% cis, 78% iso</td>
</tr>
<tr>
<td>Mo(NNR)(CHR)(Y)(ORF6) (HMT) (6b)</td>
<td>4.9</td>
<td>50</td>
<td>95% cis, 73% syn</td>
</tr>
<tr>
<td>Mo(NNR)(CHR)(ORF6) (HMT) (6c)</td>
<td>4.8</td>
<td>50</td>
<td>98% cis, 95% syn</td>
</tr>
<tr>
<td>Mo(NNR)(CHR)(ORF6) (HMT) (6d)</td>
<td>4.7</td>
<td>50</td>
<td>90% cis, 76% syn</td>
</tr>
<tr>
<td>Mo(NNR)(CHR)(ORF6) (HMT) (7a)</td>
<td>4.9</td>
<td>50</td>
<td>95% cis, 71% syn</td>
</tr>
<tr>
<td>Mo(NNR)(CHR)(ORF6) (HMT) (7b)</td>
<td>4.8</td>
<td>100</td>
<td>83% cis, 91% syn</td>
</tr>
</tbody>
</table>

aR’ = CMe2Ph. bFive 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 pyridine could be prepared, including Mo(NR)(CHCMe2Ph)(ORF6)(Y) complexes in which Y is OHMT, N(H)HMT, or HMT (HMT = 2,6-dimesitylphenyl). Deprotonation of the alkylidene in Mo(NR)(CHCMe2Ph)(ORF6) apparently is not facile relative to nucleophilic displacement of the ORf6 ligand in the syntheses of Mo(NR)(CHCMe2Ph)(ORF6)(Y) complexes.

REFERENCES