Synthesis, Properties, and Structure of Tethered Molybdenum Alkylidenes

Kapil S. Lokare, Richard J. Staples, and Aaron L. Odom*

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

Received July 9, 2008

A new class of molybdenum alkylidenes has been prepared where the alkylidene is tethered to an imido ancillary ligand. The amine required for the synthesis is accessible in 38% yield in five steps from 1,3-diisopropylbenzene. The amine is then installed to generate the tethered alkylidene bis(triflate) complex, which was structurally characterized as its DME adduct. The triflates are replaced by hexafluoro-*tert*-butoxide groups using the thallium salt of the alkoxide, and the bis(alkoxide) was characterized as its quinuclidine adduct. For comparison, an alkylidene bis(alkoxide) was prepared without the tether and having a formula similar to that of the tethered system. The structures from X-ray diffraction and NMR spectroscopy of the two complexes with and without the tether but with similar formulas are compared. The tether has the apparent effect, judging from J_{CH} couplings in the alkylidene and angles in the solid-state structure, of reducing the strength of the α-agostic interaction. Four complexes were structurally characterized during this study: Mo[=N-2,4-Pr$^i_2$C$_6$H$_2$-2-CH$_2$CH$_2$CMe$_2$CH=](DME)(OTf)$_2$, Mo(OBu$^t_{F6}$)$_2$(quin)-[=N-2,4-Pr$^i_2$C$_6$H$_2$-2-CH$_2$CH$_2$CMe$_2$CH=], Mo[N(2,4-Pr$^i_2$-6-MeC$_6$H$_2$)]$_2$(neopentyl)$_2$, and Mo(OBu$^t_{F6}$)$_2$(quin)-[N(2,4-Pr$^i_2$-6-MeC$_6$H$_2$)][=C(H)Bu^t].

Introduction

Olefin metathesis continues to grow as an important methodology for the generation of new carbon−carbon bonds with applications to the synthesis of small molecules and polymers.[1] Two catalyst types have risen to preferred status for this important reaction (Chart 1): one based on ruthenium developed by the Grubbs group and one based on molybdenum by the Schrock group. Extensive synthetic effort has gone into the elaboration of both catalyst types from the groups of the catalyst's progenitors and others. At present there is a wide selection of derivatives available for specialized applications: e.g., asymmetric ring-closing reactions.[2] The R group in Schrock's catalyst is often varied in this system for various applications with R = Bu^t often used for ring-opening metathesis polymerization (ROMP)[3] and R = C(CF$_3$)$_2$Me often used for ring-closing metathesis (RCM), but many others are of utility. The effect of imido substituents on molybdenum alkylidene reactivity has also been extensively examined.[1]

Our group has been developing catalysts based on the Schrock framework for selective cyclooligomerization of cyclic olefins. In those efforts, we sought to develop a synthesis for covalent attachment of the alkylidene C$_\alpha$ carbon to an ancillary ligand on the metal center. The position of attachment decided upon was through the imido ancillary ligand. During these efforts, a catalyst was reported by Fürstner and co-workers having an alkylidene tethered to an N-heterocyclic carbene.[4] This catalyst was employed by Grubbs and co-workers in the cyclooligo-

* To whom correspondence should be addressed. E-mail: odom@cem.msu.edu.

(1) (a) Grubbs, R. H., Ed. *Handbook of Metathesis*; Wiley-VCH: Chichester, U.K., 2003. (b) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: San Diego, CA, 1997. (c) Schrock, R. R. *J. Mol. Catal. A* **2004**, *213*, 21. (d) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4592. (e) Schrock, R. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 3748.

(2) For applications in asymmetric olefin metathesis: (a) La, D. S.; Alexander, J. B.; Cefalo, D. R.; Graf, D. D.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1998**, *120*, 9720. (b) Fujimura, O.; Grubbs, R. H. *J. Org. Chem.* **1998**, *63*, 824. (c) Weatherhead, G. S.; Ford, J. G.; Alexanian, E. J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2000**, *122*, 1828. (d) Dolman, S. J.; Sattely, E. S.; Hoveyda, A. H.; Schrock, R. R. *J. Am. Chem. Soc.* **2002**, *124*, 6991. (e) Tsang, W. C. P.; Hultzsch, K. C.; Alexander, J. B.; Bonitatebus, P. J., Jr.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 2652. (f) Lee, A.-L.; Malcolmson, S. J.; Puglisi, A; Schrock, R. R.; Hoveyda, A. H *J. Am. Chem. Soc.* **2006**, *128*, 5153. (g) Sattely, E. S.; Cortez, G. A.; Moebius, D. C.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2005**, *127*, 8526. (h) Dolman, S. J.; Schrock, R. R.; Hoveyda, A. H. *Org. Lett.* **2003**, *5*, 4899. (i) Funk, T. W.; Berlin, J. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, *128*, 1840. (j) Jernelius, J. A.; Schrock, R. R.; Hoveyda, A. H. *Tetrahedron* **2004**, *60*, 7345. (k) Hultzsch, K. C.; Jernelius, J. A.; Hoveyda, A. H.; Schrock, R. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 589. (l) Cortez, G. A.; Schrock, R. R.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 4534. (m) Funk, T. W.; Berlin, J. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, *128*, 1840. (n) Berlin, J. M.; Goldberg, S. D.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2006**, *45*, 7591. For some selected applications to organic synthesis: (o) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4490. (p) Deiters, A.; Martin, S. F. *Chem. Rev.* **2004**, *104*, 2199. (q) Mohapatra, D. K.; Ramesh, D. K.; Giardello, M. A.; Chorghade, M. S.; Gurjar, M. K.; Grubbs, R. H. *Tetrahedron Lett.* **2007**, *48*, 2621. For application of olefin metathesis in the synthesis of specialized materials: (r) Anders, U.; Nuyken, O.; Buchmeiser, M. R.; Wurst, K. *Macromolecules* **2002**, *35*, 9029. (s) Buchmeiser, M. R. *J. Mol. Catal. A* **2002**, *190*, 145. (t) Kröll, R. M.; Schuler, N.; Lubbad, S.; Buchmeiser, M. R. *Chem. Commun.* **2003**, *21*, 2742. (u) Buchmeiser, M. R. *New J. Chem.* **2004**, *28*, 549. (v) Buchmeiser, M. R. *Prog. Polym. Sci.* **2005**, 176. (w) Choi, T. L.; Rutenberg, I. M.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 3839. (x) Gorodetskaya, I. A.; Choi, T.-L.; Grubbs, R. H. *J. Am. Chem. Soc.* **2007**, *42*, 12672. (y) Gabert, A. J.; Verploegen, E.; Hammond, P. T.; Schrock, R. R. *Macromolecules* **2006**, *39*, 3993. (z) Mayershofer, M. G.; Nuyken, O.; Buchmeiser, M. R. *Macromolecules* **2006**, *39*, 2452. (aa) Singh, R.; Czekelius, C.; Schrock, R. R. *Macromolecules* **2006**, *39*, 1316. (bb) Boyd, T. J.; Schrock, R. R. *Macromolecules* **1999**, *32*, 6608. (cc) Lee, J. K.; Schrock, R. R.; Baigent, D. R.; Friend, R. H. *Macromolecules* **1995**, *28*, 1966. (dd) Tassoni, R.; Schrock, R. R. *Chem. Mater.* **1994**, *6*, 744. (ee) Albagli, D.; Bazan, G. C.; Schrock, R. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 7328. (ff) Cortez, G. A.; Baxter, C. A.; Schrock, R. R.; Hoveyda, A. H. *Org. Lett.* **2007**, *9*, 2871. (gg) Singh, R.; Schrock, R. R. *Macromolecules* **2008**, *41*, 2990–2993. (hh) Hoveyda, A. H.; Zhugralin, A. R. *Nature* **2007**, *450*, 243.

10.1021/om800650v CCC: $40.75
Publication on Web 09/04/2008

merization of cyclooctene.[5] Our group reported a tethered carbene of molybdenum based on Schrock's catalyst (**1**).[6] In this paper, we will discuss the synthesis, structure, and properties of these tethered alkylidenes. These complexes are unusual metallacycles bearing two different metal−ligand multiple bonds in a ring.

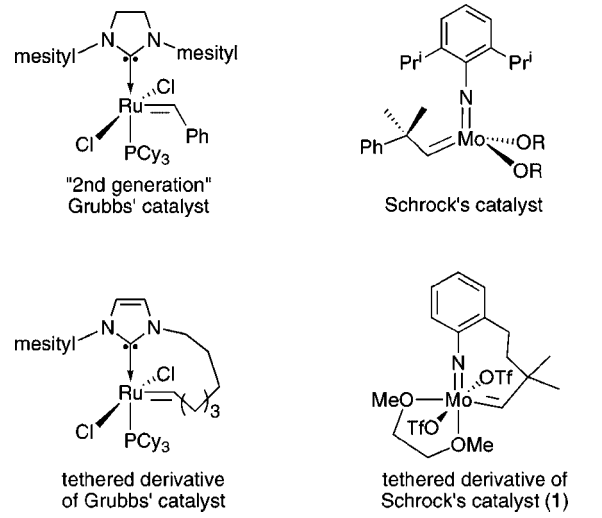
The tethered molybdenum catalyst architecture shown in Chart 1 was successful in the sense that it was stable and polymerization active as the bis(triflate). However, the bis(triflate) was quite a slow catalyst for ROMP, but this does begin to highlight the differences made by the tether, considering the untethered versions of the bis(triflate) do not seem to be as active for polymerization of norbornene.

The usual method for increasing catalyst activity in the Schrock system is to generate the alkoxide.[7] However, replacement of the triflates with alkoxides using several different techniques led to uncharacterized paramagnetic products due to decomposition. Coupled with this, the previously designed synthesis was plagued with several regiochemical issues regarding the aromatic ring and the synthesis of the tether containing a quaternary center adjacent to an olefin (Scheme 1). The result was an amine (**A**) that could be prepared on multigram scales but required careful column chromatography for purification. The tethered bis(triflate) complex **1** is prepared using the Schrock protocol with an intramolecular olefin metathesis to generate the metallacycle.[6]

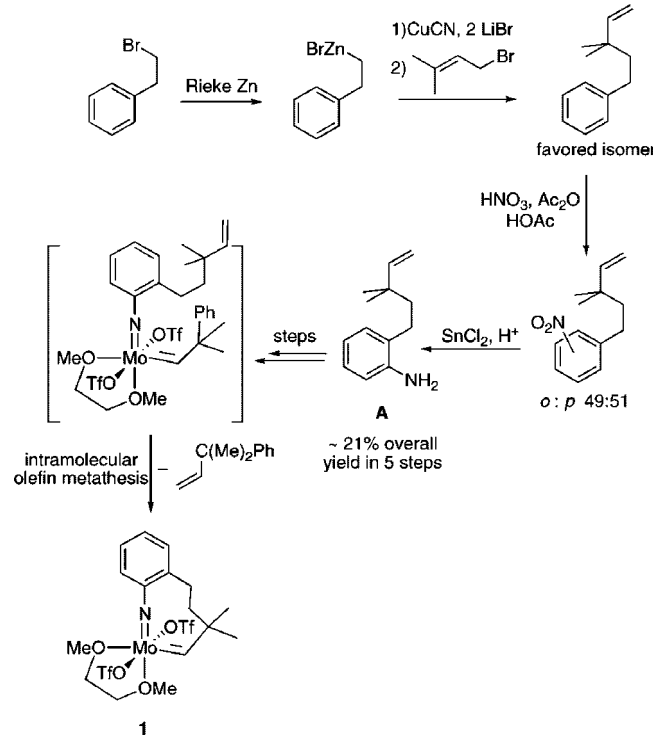
Results and Discussion

Synthesis of the Tethered Catalyst. In order in increase the stability of the resulting complex, we sought to develop a new synthetic protocol for the tethering amine with more steric protection on the aromatic ring. In addition, we sought to redesign the synthesis so that no tedious column separations were necessary and larger scales were possible.

Chart 1. Structures of Grubbs' "Second Generation" Catalyst, Schrock's Catalyst, and Tethered Derivatives



Scheme 1. Previous Tethered Alkylidene Synthesis



The new synthetic sequence is shown in Scheme 2, which takes advantage of recent developments in transition metal catalysis. The first step is selective Smith borylation[8] of 1,3-diisopropylbenzene catalyzed by iridium to generate arene boryl **B**; no other regioisomers of the product are observed. After conversion to the boronic acid **C**, Suzuki coupling using the

(3) (a) Crowe, W. E.; Mitchell, J. P.; Gibson, V. C.; Schrock, R. R. *Macromolecules* **1990**, *23*, 3534. (b) Sankaran, V.; Cummins, C. C.; Schrock, R. R.; Cohen, R. E.; Silbey, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 6858. (c) Cummins, C. C.; Schrock, R. R.; Cohen, R. E. *Chem. Mater.* **1992**, *4*, 27. (d) Fox, H. H.; Lee, J. K.; Park, L. Y.; Schrock, R. R. *Organometallics* **1993**, *12*, 759. (e) McConville, D. H.; Wolf, J. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 4413. (f) Schrock, R. R.; Krouse, S. A.; Knoll, K.; Feldman, J.; Murdzek, J. S.; Yang, D. C. *J. Mol. Catal.* **1988**, *46*, 243.

(4) (a) Fürstner, A.; Krause, H.; Ackermann, L.; Lehmann, C. W. *Chem. Commun.* **2001**, 2240. (b) Fürstner, A.; Ackermann, L.; Gabor, B.; Goddard, R.; Lehmann, C. W.; Mynott, R.; Stelzer, F.; Thiel, O. R. *Chem. Eur. J.* **2001**, *7*, 3236.

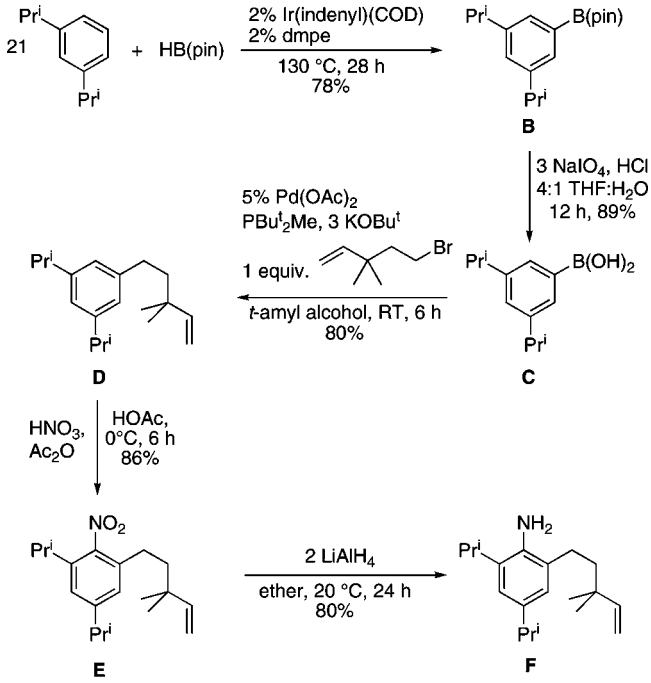
(5) (a) Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *Science* **2002**, *297*, 2041. (b) Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 8424.

(6) Ciszewski, J. T.; Xie, B.; Cao, C.; Odom, A. L. *Dalton Trans.* **2003**, 4226.

(7) For replacement of triflate with alkoxide: (a) Schrock, R. R. *Polyhedron* **1995**, *14*, 3177. Recently, other replacements have been found to be highly reactive as well. For replacement of triflate to alkyl alkoxide: (b) Sinha, A.; Schrock, R. R. *Organometallics* **2004**, *23*, 1643. (c) Sinha, A.; Lopez, L. P. H.; Schrock, R. R.; Hock, A. S.; Muller, P. *Organometallics* **2006**, *25*, 1412. (d) Rhers, B.; Salameh, A.; Baudouin, A.; Quadrelli, E. A.; Taoufik, M.; Coperet, C.; Lefebvre, F.; Basset, J.-M.; Solans-Monfort, X.; Eisenstein, O.; Lukens, W. W.; Lopez, L. P. H.; Sinha, A.; Schrock, R. R. *Organometallics* **2006**, *25*, 3554. For replacement of triflate to amido: (e) Sinha, A.; Schrock, R. R.; Muller, P.; Hoveyda, A. H. *Organometallics* **2006**, *25*, 4621. (f) Hock, A. S.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2006**, *128*, 16373. (g) Kreickmann, T.; Arndt, S.; Schrock, R. R.; Muller, P. *Organometallics* **2007**, *26*, 5702. (h) Singh, R.; Czekelius, C.; Schrock, R. R.; Muller, P.; Hoveyda, A. H. *Organometallics* **2007**, *26*, 2528. For replacement of triflate to ketiminate: (i) Tonzetich, Z. J.; Jiang, A. J.; Schrock, R. R.; Muller, P *Organometallics* **2007**, *26*, 3771. For replacement of triflate to pyrrolyl alkoxide: (j) Singh, R.; Schrock, R. R.; Muller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2007**, *129*, 12654.

(8) (a) Paul, S.; Chotana, G. A.; Holmes, D.; Reichle, R. C.; Maleczka, R. E.; Smith, M. R. *J. Am. Chem. Soc.* **2006**, *128*, 15552. (b) Holmes, D.; Chotana, G. A.; Maleczka, R. E.; Smith, M. R. *Org. Lett.* **2006**, *8*, 1407. (c) Chotana, G. A.; Rak, M. A.; Smith, M. R. *J. Am. Chem. Soc.* **2005**, *127*, 10539. (d) Maleczka, R. E.; Shi, F.; Holmes, D.; Smith, M. R. *J. Am. Chem. Soc.* **2003**, *125*, 7792. (e) Cho, J. Y.; Tse, M. K.; Holmes, D.; Malecka, R. E.; Smith, M. R. *Science* **2002**, *295*, 305. (f) Tse, M. K.; Cho, J. Y.; Smith, M. R. *Org. Lett.* **2001**, *3*, 2831. (g) Cho, J. Y.; Iverson, C. N.; Smith, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 12868. (h) Ishiyama, T.; Tkagi, J.; Ishida, K.; Miyaura, N.; Anastasi, N. R.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 390. (i) Boller, T. M.; Murphy, J. M.; Hapke, M.; Ishiyama, T.; Miyaura, N.; Hartwig, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 14263.

Scheme 2. Redesigned Amine Synthesis Used To Generate the Tethering Amino-Olefin



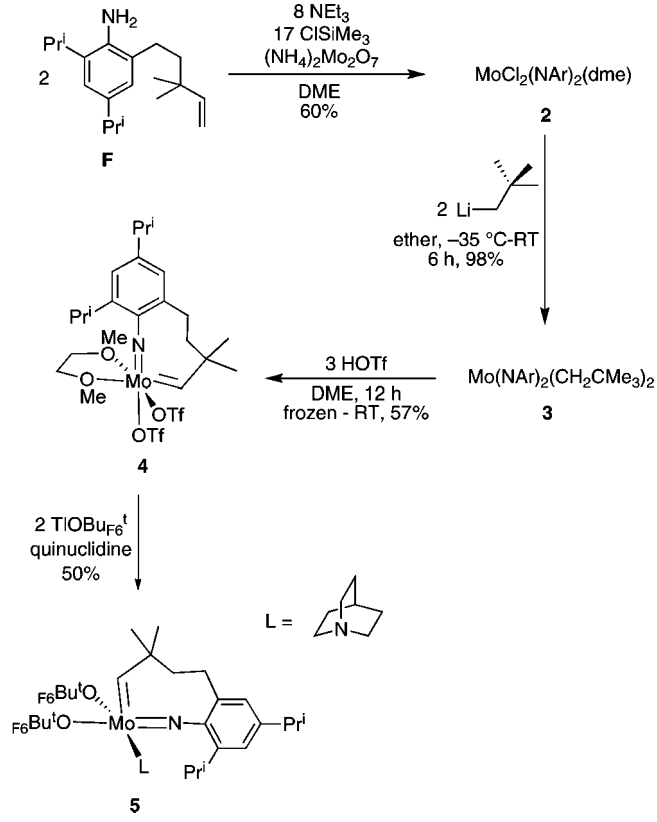
protocol developed by Fu and co-workers installs the tethering olefin.[9] The new coupling conditions allow high yields of the hydrocarbon **D** using what might otherwise be a problematic alkyl bromide containing β-hydrogens. Due to the position and size of the sterics on the aromatic ring, nitration proceeds to give the single observed product **E** with the nitro group *ortho* to the olefinic tethering group as desired. Lithium aluminum hydride reduction of nitro to amine provides the desired aniline derivative **F** in 38% overall yield for the five steps. The amino-olefin **F** has been prepared on multigram scales using this protocol, and the purification procedures essentially only involve a flush through a plug of silica gel or extractions.

Aniline derivative **F** was installed on the metal to generate bis(imido)dichloro(DME)molybdenum(VI) (**2**), which was synthesized from $(NH_4)_2Mo_2O_7$ using the procedure of Schrock and co-workers (Scheme 3).[10] Replacement of the chlorides with neopentyl groups occurs in high yield to provide $Mo(NAr)_2(Np)_2$ (**3**).

Reaction of **3** with triflic acid (HOTf) presumably produces an unobserved intermediate neopentylidene bis(triflate) complex. Formation of the metallacycle occurs by intramolecular olefin metathesis on the neopentylidene, providing **4**. In other words, triflic acid addition can be seen as initiating imido protolytic cleavage, α-abstraction on neopentyl to form neopentylidene, and intramolecular olefin metathesis in a single step.

Properties of Tethered Alkylidene Complexes. Currently, there are two molybdenum imido alkylidene bis(triflate) derivatives in the Cambridge Structural Database:[11] one untethered derivative reported by Schrock and co-workers[10a] and our previously reported tethered derivative **1**.[6] Both of these complexes have the two triflate ligands mutually trans. Often,

Scheme 3. Synthesis of the Tethered Carbene Alkoxide Catalyst 5



these molybdenum bis(triflates) exhibit spectra indicative of several isomers being present in solution. An X-ray diffraction study on the bis(triflate) **4** revealed an isomer different from that in previous structural studies with *cis* triflate ligands (Figure 1).[6,10]

The distances and angles for the metal−ligand multiple bonds in **4** are quite similar to those for the two other reported molybdenum bis(triflate) structures. The differences between the structure of **4** and these previously reported derivatives largely reside in the triflate and DME ligands. In the previously reported complexes the triflates are mutually trans, with O(triflate)−Mo−O(triflate) angles of 152.3(4) and 153.8(3)°. In **4**, the two triflates are in *cis* positions in the pseudo-octahedral compound with an O(triflate)−Mo−O(triflate) angle of 84.0(5)°.

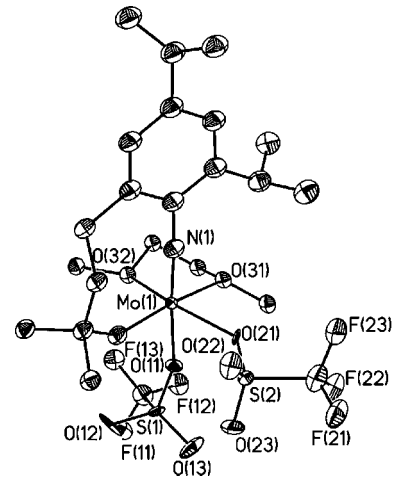


Figure 1. ORTEP representation of the structure of **4** from an X-ray diffraction study with hydrogens and ether solvent omitted.

(9) Kirchhoff, J. H.; Netherton, M. R.; Hills, I. D.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 13662.

(10) (a) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875. For a different approach to a similar complex using aryl isocyanates, see for example: (b) Bryson, N.; Youinou, M.-T.; Osborn, J. A. *Organometallics* **1991**, *10*, 3389.

(11) Cambridge Structural Database, version 5.28 (November 2006).

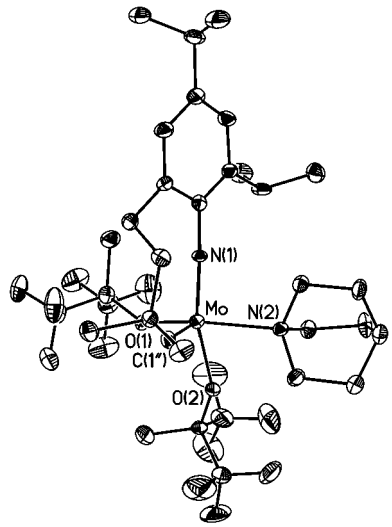


Figure 2. ORTEP representation for the structure of **5** from an X-ray diffraction study with hydrogens omitted.

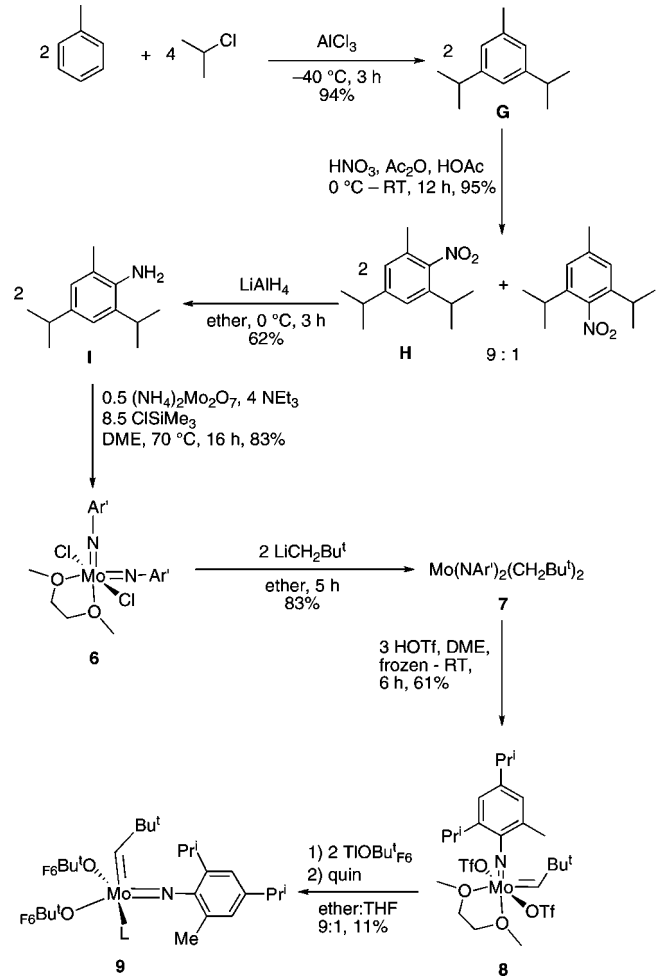
One of the triflates is *trans* to the imido group, and the other is *trans* to a DME oxygen. As would be expected, the strongly *trans*-influencing imido group provides an Mo−O(11) distance of 2.226(11) Å, and the triflate oxygen trans to a DME oxygen is significantly shorter at 2.101(11) Å. Likewise, the DME oxygen coordinated trans to the alkylidene has a much longer Mo−O bond, 2.313(12) Å, relative to that trans to triflate, 2.143(12) Å.

In solution, bis(triflate) **4** has access to several different isomers, as judged by its NMR spectroscopy. For example, at −60 °C in the ^{19}F NMR spectrum there are three pairs of resonances, which suggests the presence of three different isomers with inequivalent triflates. The other nuclei examined show similar behavior, with ^{1}H and ^{13}C NMR showing two different alkylidene resonances at room temperature, for example.

In contrast to imido alkylidenes of molybdenum not containing the tether, on replacement of the triflates in **4** by hexafluoro-*tert*-butoxide (OBu^{t}_{F6}) using $TlOBu^{t}_{F6}$ we were unable to isolate a stable product. However, $TlOBu^{t}_{F6}$ triflate metathesis (Scheme 3) in the presence of quinuclidine (quin) provides isolable $Mo(OBu^{t}_{F6})_2$(quin)(N-2,4-$Pr^{i}_2C_6H_2$-6-$CH_2CH_2CMe_2CH$=) (**5**).[12]

Complex **5** has been structurally characterized, and an ORTEP representation is shown in Figure 2. The five-coordinate complex is best described as a pseudo square pyramid with $\tau = 0.13$, where $\tau = 0$ is square pyramidal and $\tau = 1$ is trigonal bipyramidal.[13] The alkylidene carbon occupies the pseudoaxial site with angles to the remaining ligands ranging from 96 to 109°. This largest angle to the alkylidene is with the alkoxide ligand *trans* to the imido nitrogen, and the angle may be opened slightly to allow an alkylidene α-agostic interaction. The Mo−O distances are not significantly different, despite one being *trans* to imido and the other *trans* to quin. The Mo=N and Mo=C distances are typical at 1.743(4) and 1.870(5) Å, respectively. The angle subtended at N(1) is essentially linear at 175.9(4) Å.

Scheme 4. Synthesis of $Mo(OBu^{t}_{F6})_2(NAr')(=CHBu^{t})$(quin) (9)



For comparison with **5**, we prepared a close isomer not bearing the tether, $Mo(OBu^{t}_{F6})_2$(quin)(NAr′)[=C(H)Bu^{t}] (**9**), where Ar′ = C_6H_2-2,4-Pr^{i}_2-6-Me, using the protocol shown in Scheme 4. The pseudotetrahedral bis(neopentyl) intermediate **7** was also structurally characterized; see the Supporting Information for details. While **9** only differs in formula from **5** by two hydrogens, its structure (Figure 3) is different in the solid state in several ways. The five-coordinate complex is best described as a pseudo trigonal bipyramid: $\tau = 0.78$ versus 0.13 for **5**. The alkylidene carbon occupies one of the pseudoequatorial sites, and the axis is the quinuclidine nitrogen and an alkoxide with an angle subtended at Mo of 162°. The imido bends somewhat from essentially linear in **5** to 156.6(4)° in **9**. The aryl ring of the imido rotates to place the larger group toward the *syn*-alkylidene; the bending of the imido is away from this unfavorable steric interaction between imido aryl and alkylidene *tert*-butyl. However, it has been well documented that imido angles, especially of heavier congeners like molybdenum and tungsten, often have very flat potential energy surfaces associated with imido bending,[14] and it is unlikely that this imido bending results in a large energetic change relative to the linear variety found in the tethered complex.

Of greater possible consequence are the angles associated with the alkylidene (Figure 4). The alkylidene CH in Schrock's

(12) For similar adduct formation by alkylidene complexes: (a) Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; O'Regan, M. B.; Schofield, M. H. *Organometallics* **1991**, *10*, 1832. (b) Schrock, R. R.; Shifang, L.; Zanetti, N. C.; Fox, H. H. *Organometallics* **1994**, *13*, 3396. (c) Cantrell, G. K.; Geib, S. J.; Meyer, T. Y. *Organometallics* **1999**, *18*, 4250.

(13) The τ value is calculated using the equation $t = (\alpha-\beta)/60$, where α and β are the largest and next to largest angles around the metal center. For an ideal square pyramid $\tau = 0$, and $\tau = 1$ for an ideal trigonal bipyramid: (a) Alvarez, S.; Llunell, M. *Dalton Trans.* **2000**, 3288. (b) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *Dalton Trans.* **1984**, 1349. (c) Zabrodsky, H.; Peleg, S.; Avnir, D. *J. Am. Chem. Soc.* **1992**, *114*, 7843.

(14) (a) Ciszewski, J. T.; Harrison, J. F.; Odom, A. L. *Inorg. Chem.* **2004**, *43*, 3605. (b) Gibson, V. C.; Redshaw, C.; Clegg, W.; Elsegood, M. R. J. *Polyhedron* **2007**, *26*, 3161.

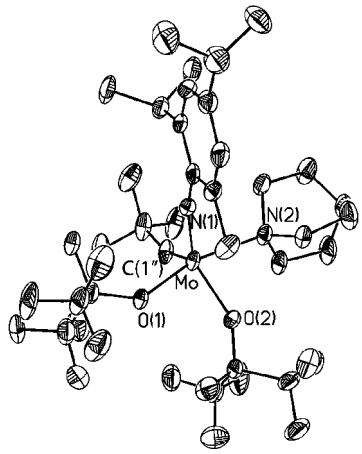


Figure 3. ORTEP representation for the structure of **9** from an X-ray diffraction study with hydrogens and ether solvent omitted.

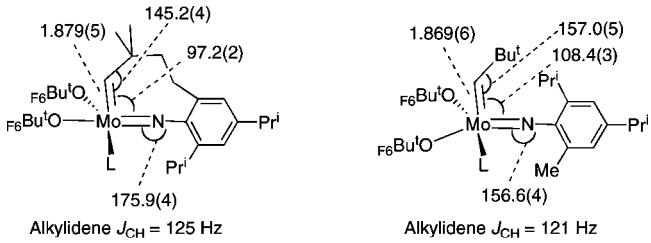


Figure 4. Structural comparisons between tethered **5** and untethered **9**. L = quinuclidine.

catalyst has an α-agostic interaction leading to larger than normal Mo−C_α−R angles and depressed J_{CH} couplings relative to common sp^2-hybridized carbons. The tether appears to reduce the Mo−C_α−R angle by about 12° relative to the untethered derivative. In addition, there is an 11° change in the N(imido)−Mo−C(alkylidene) angle, with this parameter for the cyclic derivative being significantly smaller. This leads to a rise in the alkylidene J_{CH} coupling of about 4 Hz, presumably due to a slightly reduced α-agostic interaction in the tethered complex.[15]

Concluding Remarks

The synthesis of tethered molybdenum alkylidenes has been improved to the point where these specialized catalysts can be made on relatively large scales. The required tethering aniline can be prepared as a single isomer with workup procedures not involving rigorous column chromatography. The synthesis of the bis(imido)bis(neopentyl)molybdenum(VI) proceeded through the usual route. On addition of triflic acid, an imido group was protolytically cleaved with concomitant α-abstraction to form an unobserved neopentylidene, which was trapped by the pendant olefin to generate the metallacyclic bis(triflate). Metathesis of the triflates to alkoxides was best accomplished with the thallium salts. This occurred to give an isolable hexafluoro-*tert*-butoxide complex in the presence of quinuclidine.

Structurally characterized examples of electronically similar tethered and untethered hexafluoro-*tert*-butoxide complexes provided evidence, supported by J_{CH} couplings from NMR, that the tethered derivative has a slightly attenuated α-agostic interaction. The applications of these new tethered derivatives of Schrock's catalyst to various forms of olefin metathesis are currently being explored and are very effective catalysts for common applications such as ring-closing metathesis.[16] The alternative architecture found here may provide interesting differences from untethered analogues and provide new opportunities to study the effects of these structure types on reactivity and electronic structure.

Experimental Section

General Considerations. All manipulations of air-sensitive materials were carried out in an MBraun glovebox under an atmosphere of purified nitrogen. Ethereal solvents, pentane, and toluene were purchased from Aldrich Chemical Co. and purified through alumina columns to remove water after sparging with N_2 to remove oxygen. NMR solvents (C_6D_6 and $CDCl_3$) were purchased from Cambridge Isotopes Laboratories, Inc. Deuterated benzene was distilled from purple sodium benzophenone ketyl. Deuterated chloroform was distilled from CaH_2 under dry N_2. NMR solvents were stored under sealed containers equipped with a Teflon stopcock in the drybox prior to use. Spectra were taken on Varian instruments located in the Max T. Rogers Instrumentation Facility at Michigan State University. Routine coupling constants are not reported. All NMR signals are given in ppm. Some of the assignments are tentative, due to the large number of overlapping peaks; in such cases the spectra are provided in the Supporting Information. The ^{13}C NMR assignments are based on decoupled ^{13}C, peak heights for overlapping signals, and DEPT experiments. Combustion analyses were performed by facilities in the Department of Chemistry at Michigan State University. Alumina, Celite, and silica were dried at a temperature >200 °C under dynamic vacuum for at least 16 h and then stored under an inert atmosphere. HB(Pin)[17] and Ir(Indenyl)(COD)[18] were prepared as described in the literature. Most conveniently, HB(Pin) supplied by BASF in NEt_3-stabilized form was also employed, which can be used without purification. 1,3-Diisopropylbenzene was purchased from Aldrich Chemical Co. and was distilled from purple sodium benzophenone ketyl. Sodium metaperiodate, acetic acid, acetic anhydride, triethylamine, and aluminum chloride were purchased from Spectrum Chemical Co. and used without purification. 5-Bromo-3,3-dimethylpent-1-ene was prepared as described in the literature.[19] Potassium *tert*-butoxide, $Pd(OAc)_2$, $P(^tBu)_2Me$, fuming nitric acid, triflic acid, $LiAlH_4$, and dmpe were purchased from Aldrich Chemical Co. and used without purification. *tert*-Amyl alcohol was purchased from TCI Chemical Co., distilled over magnesium turnings, stored over molecular sieves (3 Å, $^1/_{16}$ in. pellets), and degassed under nitrogen prior to use. Thallium ethoxide was purchased from Strem Chemical Co. and was degassed before use. Quinuclidine hydrochloride was purchased from Aldrich Chemical Co., was basified using K_2CO_3, and was crystallized from ether/pentane at −35 °C. 2-Chloropropane was purchased from Acros Chemical Co. and was used without purification. Neopentyllithium was prepared as described in the literature.[20]

Preparation of Thallium(I) Hexafluoro-*tert*-butoxide. In a 120 mL Erlenmeyer flask was loaded $HOBu^t_{F6}$ (1.50 g, 8.24 mmol), a stir bar, and pentane (8 mL). To the stirred solution of the alcohol was added TlOEt (2.055 g, 8.24 mmol) in pentane (10 mL). The reaction mixture was capped with a septum and stirred for 14 h.

(15) For examples of five-coordinate alkylidene J_{CH} couplings see ref 12. For general references on agostic interactions, see: Brookhart, M.; Green, M. L. H.; Parkin, G. *Proc. Natl. Acad. Sci.* **2007**, *104*, 6908. Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

(16) Lokare, K. S.; Odom, A. L. Manuscript in preparation.

(17) Tucker, E. C.; Davidson, J.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 3482.

(18) Merola, J. S.; Kacmarcik, R. T. *Organometallics* **1989**, *8*, 778.

(19) Srikrishna, A.; Dethe, D. H.; Kumar, P. R. *Tetrahedron Lett.* **2004**, *45*, 2939.

(20) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359.

Volatiles were removed under vacuum. The resulting white solid was crystallized from ether−pentane (1:1) at −35 °C, which provided 2.54 g (80%) of purified thallium alkoxide.[21] ^{1}H NMR (300 MHz, acetone-d_6): 1.60 (sept, CH_3, J_{HF} = 1.2 Hz). ^{13}C{^{1}H} NMR (75.6 MHz, acetone-d_6): 128 (q, CF_3, J_{CF} = 288.45 Hz), 77.18 (sept, C$Me(CF_3)_2$, J_{CF} = 27.55 Hz). ^{19}F NMR (282 MHz, acetone-d_6): −78.06. Mp: 155−157 °C.

Preparation of 3,5-Diisopropylphenylborane Pinacolate (B). In a glovebox, Ir(Indenyl)(COD) (416 mg, 1 mmol, 2 mol%), dmpe (146 mg, 1 mmol, 2 mol%), HBPin (6.4 g, 0.05 mol), and 1,3-diisopropylbenzene (170.4 g, 1.05 mol) were placed in a 1 L Schlenk flask equipped with a stir bar. The flask was closed with a septum, taken outside the glovebox, and stirred at room temperature for 20 min. The flask was purged with a continuous flow of purified N_2 and heated in an oil bath at 130 °C for 28 h. The reaction mixture was cooled to room temperature, poured into CH_2Cl_2 (200 mL), filtered through a short pad of silica with copious washings (CH_2Cl_2, 250 mL), and concentrated in vacuo. 1,3-Diisopropylbenzene was removed by distillation in vacuo, leaving essentially pure product, which could be crystallized from ether at 0 °C as colorless crystals (11.3 g, 0.039 mol, 78.4%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.48 (s, 2 H, *o-H*), 7.17 (s, 1 H, *p-H*), 2.89 (sept, 2 H, CH(CH$_3$)$_2$, J_{CH} = 6.9 Hz), 1.33 (s, 12 H, C(CH_3)$_2$), 1.24 (d, 12 H, CH(CH_3)$_2$, J_{CH} = 6.9 Hz). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$): 148.11, 130.42, 127.65, 83.57, 34.18, 24.84, 24.06. One aryl carbon, which we believe to be that adjacent to boron, was not located. ^{11}B NMR (96.2 MHz, $CDCl_3$): 31.15. Anal. Calcd for $C_{18}H_{29}BO_2$: C, 74.99; H, 10.16. Found: C, 74.65; H, 10.01. Mp: 120−122 °C. MS (EI): *m/z* 288 (M^+). R_f = 0.84 (SiO_2, CH_2Cl_2).

Preparation of 3,5-Diisopropylphenylboronic Acid (C). In a 250 mL round-bottom flask equipped with a stir bar was added **B** (11.0 g, 0.038 mol), THF−H_2O (4:1, 80:20 mL), and $NaIO_4$ (25 g, 0.117 mol, 3 equiv). The mixture was stirred until homogeneous, and then 2 N HCl (2 mL) was added. The reaction mixture was stirred at room temperature for 12 h. After 12 h, the reaction mixture was extracted with ethyl acetate (5 × 30 mL), and the combined organic extracts were washed with water and brine. The solution was dried with Na_2SO_4 and concentrated in vacuo to give a white solid. The solid was washed with ice-cold pentane to give the desired product as white flakes (6.97 g, 0.034 mol, 89%). The compound was used without further purification. ^{1}H NMR (300 MHz, CD_3CN): 7.46 (s, 1 H, *o-H*), 7.45 (s, 1 H, *o-H*), 7.20 (s, 1 H, *p-H*), 6.04 (s, 2 H, O*H*), 2.89 (sept, 2 H, CH(CH$_3$)$_2$, J_{CH} = 6.9 Hz), 1.23 (d, 6 H CH(CH_3)$_2$, J_{CH} = 6.9 Hz). ^{13}C{^{1}H} NMR (75.6 MHz, CD_3CN): 149.02, 130.39, 128.23, 118.31, 34.95, 24.39. ^{11}B NMR (96.2 MHz, CD_3CN): 29.60. Mp: 142−144 °C.

Preparation of 1-(3,3-Dimethylpent-4-enyl)-3,5-diisopropylbenzene (D). In a glovebox, $Pd(OAc)_2$ (316 mg, 1.41 mmol, 5 mol%) and PBu^t_2Me (452 mg, 2.82 mmol, 10 mol%) were placed in a 250 mL Schlenk flask equipped with a stir bar. The flask was closed with a septum and taken outside the glovebox. To this was added *tert*-amyl alcohol (20 mL), **C** (6.97 g, 0.034 mmol, 1.2 equiv), and KOBu^t (9.48 g, 0.084 mmol, 3 equiv). The reaction mixture was stirred at room temperature for 10 min. To this was added 5-bromo-3,3-dimethylpent-1-ene[18] (4.99 g, 0.028 mmol), and the resulting heterogeneous reaction mixture was stirred vigorously for 6 h at room temperature. The reaction was poured into hexanes (200 mL), filtered through a short pad of Celite with copious washings (hexanes, 200 mL combined), concentrated, and passed though a plug of silica gel (250−400 mesh, 400 g) to afford the desired product as a colorless oil (5.8 g, 0.022 mol, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): 6.97 (s, 1 H, *p-H*), 6.93 (s, 2 H, *o-H*), 5.96 (dd, 1 H, CH=CH$_2$, J_{CH} = 10.4 Hz, J_{CH} = 17.7 Hz), 5.06−5.09 (m, 1 H, CH=CH_2), 5.02−5.05 (m, 1 H, CH=CH_2), 2.93 (sept, 2 H, CH(CH$_3$)$_2$, J_{CH} = 6.9 Hz), 2.60−2.54 (m, 2 H, CH_2), 1.71−1.65 (m, 2 H, CH_2), 1.32 (d, 12 H, CH_3, J_{CH} = 6.9 Hz), 1.15 (s, 6 H, CH_3). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$): 149.07, 148.53, 143.31, 124.15, 122.23, 110.9, 45.10, 37.02, 34.45, 31.58, 27.01, 24.39. Anal. Calcd for $C_{19}H_{30}$: C, 88.28; H, 11.72. Found: C, 88.35; H, 12.10. MS (EI): *m/z* 258 (M^+). R_f = 0.82 (SiO_2, hexane−ethyl acetate 8:2).

Preparation of 1-(3,3-Dimethylpent-4-enyl)-3,5-diisopropyl-2-nitrobenzene (E). To a flask was added fuming HNO_3 (1.6 mL, 90%, d = 1.5), HOAc (1.5 mL), and Ac_2O (1.2 mL), and the solution was cooled to room temperature before proceeding. This solution was added dropwise to **D** (5.8 g, 0.022 mol) in 2 mL of Ac_2O. The reaction mixture was maintained at 0 °C during the addition. After the addition was complete, the mixture was stirred at 0 °C for 6 h. The reaction mixture was poured into ice-cold water (50 mL). The product was extracted with diethyl ether (4 × 25 mL), and the combined organic layers were washed with portions of $NaHCO_3$ (250 mL) until no gas formed on addition of the basic aqueous solution. The organic solution was filtered, and the separated solids were washed with ether (5 × 40 mL). The combined ether solutions were dried with $MgSO_4$. The volatiles were removed in vacuo, providing the product as a yellow oil (5.85 g, 0.019 mol, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.01 (s, 1 H, aromatic *H*), 6.95 (s, 1 H, aromatic *H*), 5.93 (dd, 1 H, CH=CH$_2$, J_{CH} = 10.5 Hz, J_{CH} = 17.7 Hz), 5.03−5.00 (m, 1 H, CH=CH_2), 4.96−4.99 (m, 1 H, CH=CH_2), 2.93 (sept, 2 H, CH(CH$_3$)$_2$, J_{CH} = 6.9 Hz), 2.66−2.59 (m, 2 H, CH_2), 1.70−1.65 (m, 2 H, CH_2), 1.28 (d, 6 H, CH_3, J_{CH} = 6.9 Hz), 1.22 (d, 6 H, CH_3, J_{CH} = 6.9 Hz), 1.08 (s, 6 H, CH_3). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$): 150.99, 147.44, 139.46, 133.64, 125.71, 123.86, 122.12, 111.22, 44.13, 36.69, 34.16, 29.02, 27.08, 26.68, 26.48, 23.81. Anal. Calcd for $C_{19}H_{29}NO_2$: C, 75.18; H, 9.65; N, 4.62. Found: C, 75.09; H, 10.03; N, 4.99. MS (EI) *m/z* = 302(M^+). R_f = 0.73 (SiO_2, hexanes:ethyl acetate 8:2).

Preparation of 2-(3,3-Dimethylpent-4-enyl)-4,6-diisopropylaniline (F). In a glovebox, $LiAlH_4$ (2.93 g, 0.077 mol, 4 equiv) and diethyl ether (100 mL) were placed in a 250 mL Schlenk flask equipped with a stir bar. The flask was closed with a rubber septum, taken outside the glovebox, and kept in a water bath to maintain the temperature between 16 and 25 °C. To the slurry was slowly added **E** (5.85 g, 0.019 mol) over a period of 1 h. After the addition was complete, the water bath was removed, and the reaction mixture was stirred overnight at room temperature. The mixture was cooled to 0 °C using an ice bath, and the excess hydride was quenched by the dropwise addition of a saturated solution of $MgSO_4$ solution. The precipitated salts were removed by filtration through Celite and washing with chloroform (200 mL). The filter cake was washed again with chloroform (3 × 50 mL). The combined organic solutions were dried to afford the desired product as a red oil (4.23 g, 0.015 mol, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): 6.86 (s, 1 H, aromatic *H*), 6.75 (s, 1 H, aromatic *H*), 5.93 (dd, 1 H, CH=CH$_2$, J_{CH} = 10.5 Hz, J_{CH} = 17.7 Hz), 5.02−5.00 (m, 1 H, CH=CH_2), 4.95−4.97 (m, 1 H, CH=CH_2), 3.49 (br s, 2 H, *NH*$_2$), 2.88 (sept, 1 H, CH(CH$_3$)$_2$, J_{CH} = 6.9 Hz), 2.77 (sept, 1 H, CH(CH$_3$)$_2$, J_{CH} = 6.9 Hz), 2.41−2.35 (m, 2 H, CH_2), 1.59−1.53 (m, 2 H, CH_2), 1.23 (d, 6 H, CH_3, J_{CH} = 6.9 Hz), 1.19 (d, 6 H, CH_3, J_{CH} = 6.9 Hz), 1.06 (s, 6 H, CH_3). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$): 147.86, 138.77, 138.64, 132.39, 126.95, 124.59, 121.05, 111.17, 41.84, 36.74, 33.58, 27.95, 27.18, 26.62, 24.35, 22.47. Anal. Calcd for $C_{19}H_{31}N$: C, 83.45; H, 11.43; N, 5.12. Found: C, 83.35; H, 11.18; N, 4.98. MS (EI): *m/z* 273 (M^+). R_f = 0.35 (SiO_2, hexanes−ethyl acetate 8:2).

Preparation of Mo(NAr)$_2$Cl$_2$(DME) (2). In a glovebox, in a 250 mL Schlenk flask was loaded $(NH_4)_2MoO_4$ (0.621 g, 1.827 mmol), DME (20 mL), and a stir bar. To the suspension was added NEt_3 (1.48 g, 0.015 mol), $ClSiMe_3$ (3.37 g, 0.031 mmol), and **F** (2 g, 0.0073 mmol). The mixture was stirred at room temperature inside

(21) For similarly prepared thallium alkoxides see: Zechmann, C. A.; Boyle, T. J.; Pedrotty, D. M.; Alam, T. M.; Lang, D. P.; Scott, B. L. *Inorg. Chem.* **2001**, *40*, 2177.

the glovebox for 1 h. After 1 h, the flask was closed with a septum, partially evacuated, and heated in an oil bath at 70 °C for 3 days. The reaction was monitored periodically by cooling the reaction mixture to room temperature, evacuating the headspace of the Schlenk flask, and taking the flask inside the glovebox. An aliquot was taken and filtered, the solvent removed, and an NMR spectrum recorded to follow the $ArNHSiMe_3/ArN(SiMe_3)_2$ peaks formed during the reaction. The reaction was allowed to proceed until these silyl amine peaks all but disappeared from the spectrum. After it was cooled to room temperature, the flask was partially evacuated and taken inside the glovebox. The solution was filtered though Celite. The volatiles of the filtrate were removed in vacuo to give a dark red viscous oil, which can be crystallized from hexamethyldisiloxane to give a brick red powder of the desired product (1.73 g, 2.17 mmol, 60%). ^{1}H NMR (300 MHz, $CDCl_3$): 6.85 (s, 2 H, aromatic *H*), 6.77 (s, 2 H, aromatic *H*), 5.81 (dd, 2 H, C*H*═CH_2, J_{CH} = 10.5 Hz, J_{CH} = 17.7 Hz), 4.91−4.82 (m, 4 H, CH═CH_2), 3.92 (s, 4 H, OCH_2), 3.80 (s, 6 H, OCH_3), 3.83 (sept, 2 H, CH(CH_3)$_2$, J_{CH} = 6.6 Hz), 2.89−2.84 (m, 4 H, CH_2), 2.79 (sept, 2 H, CH(CH_3)$_2$, J_{CH} = 6.6 Hz), 1.57−1.51 (m, 4 H, CH_2), 1.16 (d, 12 CH_3, J_{CH} = 6.6 Hz), 0.97 (d, 12 CH_3, J_{CH} = 6.6 Hz), 0.94 (s, 12 CH_3). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$): 152.80, 148.87, 147.85, 145.28, 138.99, 122.86, 120.76, 110.05, 71.15, 63.07, 42.57, 36.65, 34.23, 27.35, 26.54, 26.04, 24.65, 23.97. Anal. Calcd for $C_{42}H_{68}N_2O_2Cl_2Mo$: C, 63.07; H, 8.57; N, 3.50 Found: C, 63.35; H, 8.41; N, 3.72. Mp: 145−147 °C dec.

Preparation of Mo(NAr)$_2$(Np)$_2$ (3). In a glovebox, to a near frozen solution of **2** (1.73 g, 2.169 mmol) in ether 5 mL was added 8.7 mL of a 0.5 M solution of neopentyllithium (4.77 mmol, 2.2 equiv). The solution was warmed to room temperature and stirred for 6 h. An aliquot of the reaction mixture was filtered through Celite to remove LiCl and added to dilute nitric acid (0.25 M) solution. This solution was added to a 20 mL vial containing 50 mg of silver nitrate in 1 mL of distilled water. The absence of a white precipitate corresponding to AgCl indicated the completion of the reaction. The volatiles were removed in vacuo, and the product was redissolved in pentane and filtered through Celite to remove the lithium chloride. The volatiles of the filtrate were removed in vacuo, to give a bright red viscous oil (1.93 g, 2.131 mmol, 98%). The oil was used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): 6.79 (s, 2 H, aromatic *H*), 6.74 (s, 2 H, aromatic *H*), 5.65 (dd, 2 H, C*H*═CH_2, J_{CH} = 10.5 Hz, J_{CH} = 17.7 Hz), 4.77−4.85 (m, 4 H, CH═CH_2), 3.44 (sept, 2 H, CH(CH_3)$_2$, J_{CH} = 6.6 Hz), 2.77 (sept, 2 H, CH(CH_3)$_2$, J_{CH} = 6.6 Hz), 2.48−2.36 (m, 4 H, CH_2), 2.02 (s, 4 H, CH_2), 1.45−1.42 (m, 4 H, CH_2), 1.16 (d, 12 CH_3, J_{CH} = 6.6 Hz), 1.12 (s, 18 H, CH_3), 0.97 (d, 12 CH_3, J_{CH} = 6.6 Hz), 0.82 (s, 12 CH_3). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$): 152.19, 148.38, 145.37, 142.24, 136.60, 123.14, 120.25, 110.46, 79.17, 42.55, 36.50, 34.18, 33.47, 33.34, 27.91, 26.89, 26.53, 24.06, 23.27.

Preparation of Mo[═N-2,4-Pr$^i_2$C$_6$H$_2$-2-CH$_2$CH$_2$CMe$_2$CH═]-(DME)(OTf)$_2$ (4). In a glovebox, a near frozen solution of triflic acid (225 mg, 1.50 mmol, 3 equiv) in DME (2 mL) was added dropwise to a near frozen orange solution of **3** (453 mg, 0.5 mmol) in DME (10 mL). This solution was stirred for 24 h, and then volatiles were removed in vacuo to give a dark yellow oil. The oil was then extracted with about 15 mL of chilled toluene and filtered through Celite. The filtrate was concentrated in vacuo, and the resulting dark yellow oil was dissolved in ether and layered with pentane to obtain a bright yellow precipitate. This bright yellow precipitate was dissolved again in a minimum amount of ether and layered with an equal amount of pentane to obtain essentially pure product (190 mg, 0.256 mmol, 51%). The NMR spectroscopic data are consistent with an approximately 1.8:1 mixture of two major isomers in $CDCl_3$. The spectra are further complicated, due to the broadening of some resonances. As a result, the spectra are more complex than expected, and the assignments are difficult due to the multitude of overlapping peaks. The spectra are included in the Supporting Information, and some of the key identifiable resonances are given here. ^{1}H NMR (500 MHz, $CDCl_3$): 14.49 (s, J_{CH} = 126 Hz), 13.74 (s, J_{CH} = 121 Hz). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 333 (CH), 324 (CH). ^{19}F NMR (470 MHz, $CDCl_3$): −76.77 (major isomer), −77.88 (minor isomer). Anal. Calcd for $C_{24}H_{37}NO_8S_2F_6Mo$: C, 38.87; H, 5.03; N, 1.89 Found: C, 38.74; H, 5.23; N, 2.21. Mp: 110−112 °C dec.

Preparation of Mo[═N-2,4-Pr$^i_2$C$_6$H$_2$-2-CH$_2$CH$_2$CMe$_2$CH═]-(quin)(OBu$^t_{F6}$)$_2$ (5). In a glovebox, to a frozen solution of **4** (100 mg, 0.135 mmol) in ether−THF (9:1, 1 mL) was added a solution of quinuclidine (30 mg, 0.269 mmol) in ether−THF (9:1, 1 mL). The reaction mixture was stirred for 10 min. After 10 min, a $TlO(CF_3)_2CH_3$ (104 mg, 2 equiv, 0.269 mmol) solution was added and stirring continued for 3 h. The solvent then was removed, and the product was dissolved in pentane. The salts were removed by filtration through Celite. The product was crystallized at −35 °C from pentane as yellow crystals (56 mg, 0.07 mmol, 50.2%). Due to the fluxionality of the resulting tether and multiple isomers[15] in solution, the NMR spectrum is broad and complex. The alkylidene resonance for the quinuclidine adduct is sufficiently separated from other resonances to be assigned definitively. The spectra were scanned and are included in the Supporting Information. The assignable peaks due to the alkylidene in the major isomer are provided here. ^{1}H NMR (500 MHz, C_6D_6): 13.10 (J_{CH} = 125 Hz). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): 294.43. Anal. Calcd for $C_{33}H_{46}N_2O_2F_{12}Mo$: C, 47.98; H, 5.62; N, 3.39. Found: C, 48.50; H, 5.90; N, 3.42.

Preparation of 1-Methyl-3,5-diisopropylbenzene (G). A two-necked flask was loaded with toluene (9.21 g, 0.1 mol) and $AlCl_3$ (26.27 g, 0.2 mol, 2 equiv). This mixture was chilled to −40 °C in a dry ice/acetonitrile bath and stirred vigorously using a mechanical stirrer. To this slurry was slowly added 2-chloropropane (31.42 g, 0.4 mol, 4 equiv), and the mixture was further stirred vigorously for another 3 h. The slurry was added to ice-cold water (500 mL), and this mixture was stirred vigorously for 2 h. The product was extracted with ether (5 × 120 mL). The combined ether extracts were washed with water (2 × 100 mL) and brine (2 × 75 mL) and dried over anhydrous $MgSO_4$. After filtration, the volatiles were removed in vacuo to afford the desired product as a yellow oil (16.7 g, 0.094 mol, 94%).[22] ^{1}H NMR (300 MHz, $CDCl_3$): 6.90 (s, 3 H, aromatic *H*), 2.86 (sept, 2 H, CH(CH_3)$_2$, J_{CH} = 6.9 Hz), 2.34 (s, 3 H, CH_3), 1.26 (d, 12 H, CH_3, J_{CH} = 6.9 Hz). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$): 148.81, 137.62, 124.64, 121.78, 34.11, 24.07, 21.51. Anal. Calcd for $C_{13}H_{20}$: C, 88.54; H, 11.45. Found: C, 88.95; H, 11.80. MS (EI): *m*/*z* 176 (M^+). R_f = 0.65 (SiO_2, hexanes−ethyl acetate 8:2).

Preparation of 2-Methyl-4,6-diisopropyl-1-nitrobenzene (H). To a flask, was added fuming nitric acid (3.6 mL, 90%, d = 1.5), acetic acid (3.5 mL), and acetic anhydride (2.7 mL). The solution was cooled to room temperature. This solution was added dropwise to 1-methyl-3,5-diisopropylbenzene (8.9 g, 0.05 mol) in 4 mL of acetic anhydride. The reaction was maintained at 0 °C during the addition using an ice water bath. After the addition was complete, the mixture was stirred at 0 °C for 12 h. The reaction mixture was poured into ice-cold water (100 mL). The product was extracted with diethyl ether (5 × 50 mL), and the combined organic layers were washed with a saturated solution of $NaHCO_3$ (500 mL) until no gas formed on addition of the solution. The organic solution was filtered, and the separated solids were washed with ether (5 × 50 mL). The combined ether solutions were dried with anhydrous $MgSO_4$. The volatiles were removed in vacuo, providing the product as a light yellow oil. The compound was used without further purification (10.5 g, 0.047 mol, 95%). The compound was isolated

(22) The literature procedure led to an out-of-control exothermic reaction when attempted. The procedure was modified for a more controlled reaction: Ghiaci, M.; Asghari, J. *Synth. Commun.* **1998**, *28*, 2213.

Table 1. Structural Parameters for Mo[=N-2,4-Pr$^i_2$C$_6$H$_2$-2-CH$_2$CH$_2$CMe$_2$CH=](DME)(OTf)$_2$ (4), Mo(OBu$^t_{F6}$)$_2$(quin)[=N-2,4-Pr$^i_2$C$_6$H$_2$-2-CH$_2$CH$_2$CMe$_2$CH=] (5), Mo[N(2,4-Pr$^i_2$-6-MeC$_6$H$_2$)](neopentyl)$_2$ (7), and Mo(OBu$^t_{F6}$)$_2$(quin)[N(2,4-Pr$^i_2$-6-MeC$_6$H$_2$)][=C(H)Bu^t] (9)

	4·$^1/_2$OEt$_2$	**5**	**7**·$^1/_2$(pentane)	**9**·OEt$_2$
formula	$C_{26}H_{41}F_6MoNO_{8.5}S_2$	$C_{33}H_{46}F_{12}MoN_2O_2$	$C_{38.5}H_{66}MoN_2$	$C_{37}H_{56}F_{12}MoN_2O_3$
formula wt	777.66	826.66	652.87	900.78
space group	*Pbcn*	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	34.32(2)	17.949(2)	9.820(3)	10.550(3)
b (Å)	14.820(10)	10.2839(12)	14.543(4)	13.514(3)
c (Å)	14.379(9)	20.216(2)	15.017(4)	15.842(4)
α (deg)			94.018(5)	102.763(5)
β (deg)		102.473(3)	105.146(5)	90.020(5)
γ (deg)			107.555(5)	107.753(5)
V (Å^3)	7314(8)	3643.5(7)	1947.8(10)	2092.4(8)
Z	8	4	2	2
μ (mm^{-1})	0.546	0.453	0.362	0.403
D_{calcd} (g cm^{-3})	1.412	1.507	1.113	1.430
total no. of rflns	23075	30575	18888	18236
no. of unique rflns (R_{int})	4689 (0.1372)	5247 (0.1280)	6837 (0.0712)	6051 (0.0847)
extinction coeff		0.00057(13)		0.0010(5)
$R(F_o)$ ($I > 2\sigma$)	0.1401	0.0428	0.0702	0.0535
$R_w(F_o^2)$ ($I > 2\sigma$)	0.2882	0.0837	0.1806	0.1159

as a mixture of two isomers with the desired isomer favored 9:1. ^{1}H NMR (300 MHz, $CDCl_3$): 7.02 (s, 1 H, aromatic *H*), 6.92 (s, 1 H, aromatic *H*), 2.86 (overlapping sept, 2 H, C*H*(CH$_3$)$_2$), 2.24 (s, 3 C*H*$_3$), 1.22 (d, 6 C*H*$_3$, J_{CH} = 6.9 Hz), 1.21 (d, 6 C*H*$_3$, J_{CH} = 6.9 Hz). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$): 151.02, 139.61, 128.69, 126.53, 124.66, 122.23, 34.12, 28.99, 23.79, 23.77, 17.41. MS (EI): *m*/*z* 221 (M$^+$). R_f = 0.73 (SiO_2, hexanes−ethyl acetate 8:2).

Preparation of 2-Methyl-4,6-diisopropylaniline (I). In a glovebox, $LiAlH_4$ (3.6 g, 0.094 mol, 2 equiv) and diethyl ether (300 mL) were placed in a 500 mL Schlenk flask equipped with a stir bar. The flask was closed with a rubber septum, taken outside the glovebox, and kept in a water bath to maintain the temperature between 16 and 25 °C. To the slurry was slowly added 2-methyl-4,6-diisopropyl-1-nitrobenzene (10.5 g, 0.047 mol, 9:1 mixture of isomers from the previous step) over a period of 1 h. After the addition was complete, the water bath was removed, and the reaction mixture was stirred overnight at room temperature. The mixture was cooled to 0 °C using an ice bath, and the excess lithium aluminum hydride was quenched by the dropwise addition of a saturated solution of $MgSO_4$ solution. The precipitated salts were removed by filtration through Celite and washed with chloroform (400 mL). The filter cake was again washed with chloroform (5 × 50 mL). The combined organic solutions were dried to afford the mixture as an orange oil. Column chromatography (silica gel, 250−400 mesh, 8:2 hexane−ethyl acetate) afforded the desired product as a yellow oil (5.5 g, 0.029 mol, 62%). ^{1}H NMR (300 MHz, $CDCl_3$): 6.92 (s, 1 H, aromatic *H*), 6.84 (s, 1 H, aromatic *H*), 3.55 (s, 2 H, N*H*$_2$), 2.93 (sept, 1 H, C*H*(CH$_3$)$_2$, J_{CH} = 6.9 Hz), 2.81 (sept, 1 H, C*H*(CH$_3$)$_2$, J_{CH} = 6.9 Hz), 2.20 (s, 3 C*H*$_3$), 1.29 (d, 6 H, CH(C*H*$_3$)$_2$, J_{CH} = 6.9 Hz), 1.24 (d, 6 H, CH(C*H*$_3$)$_2$, J_{CH} = 6.9 Hz). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$): 139.25, 138.68, 131.94, 125.72, 122.17, 121.15, 33.52, 27.93, 24.35, 22.40, 18.07. MS (EI): *m*/*z* 191 (M$^+$). R_f = 0.70 (SiO_2, hexanes−ethyl acetate 8:2).

Preparation of Mo(NAr′)$_2$Cl$_2$(DME) (6). In a glovebox, a 250 mL Schlenk flask was loaded with $(NH_4)_2MoO_4$ (2.44 g, 7.18 mmol), 100 mL of DME, and a stir bar. To the suspension was added NEt_3 (5.8 g, 57 mmol), $ClSiMe_3$ (13.25 g, 122 mmol), and Ar′NH$_2$ (5.5 g, 29 mmol). The mixture was stirred at room temperature inside the glovebox for 1 h. The flask was closed with a septum, partially evacuated, and heated in an oil bath at 70 °C for 12 h. The reaction mixture gradually changed color from light yellow to orange to dark red in the first couple of hours. The reaction was monitored in a fashion similar to that discussed previously for **2**. After it was cooled to room temperature, the flask was evacuated and taken inside the glovebox. The solution was filtered though Celite. The volatiles of the filtrate were removed in vacuo to give a dark red viscous oil, which can be crystallized from ether/pentane to give a brick red powder of Mo(NAr′)$_2$(DME)Cl$_2$ (7.6 g, 11.96 mmol, 83%). ^{1}H NMR (300 MHz, $CDCl_3$): 6.86 (s, 2 H, aromatic *H*), 6.76 (s, 2 H, aromatic *H*), 3.96 (s, 4 H, OC*H*$_2$), 3.85 (s, 6 H, OC*H*$_3$), 3.78 (sept, 2 H, C*H*(CH$_3$)$_2$, J_{CH} = 6.9 Hz), 2.79 (sept, 2 H, C*H*(CH$_3$)$_2$, J_{CH} = 6.9 Hz), 2.41 (s, 6 C*H*$_3$), 1.17 (d, 12 H, CH(C*H*$_3$)$_2$, J_{CH} = 6.9 Hz), 1.03 (d, 12 CH(C*H*$_3$)$_2$, J_{CH} = 6.9 Hz). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$): 153.31, 147.79, 144.46, 134.72, 125.38, 120.83, 71.12, 63.11, 33.94, 27.61, 24.45, 23.87, 18.97. Anal. Calcd for $C_{30}H_{48}N_2O_2Cl_2Mo$: C, 56.68; H, 7.63; N, 4.41. Found: C, 56.70; H, 7.29; N, 4.41. Mp: 175−177 °C dec.

Preparation of Mo(NAr′)$_2$(CH$_2$^{t}Bu)$_2$ (7). In a glovebox, to a near frozen solution of Mo(NAr′)$_2$(DME)Cl$_2$ (2.2 g, 3.46 mmol) in 50 mL of ether was added neopentyllithium (0.541 g, 6.92 mmol, 2 equiv). The solution was warmed to room temperature and stirred for 5 h. The reaction was monitored in a fashion similar to that discussed previously for Mo(NAr)$_2$(CH$_2$^{t}Bu)$_2$. The reaction mixture was filtered through Celite to remove LiCl. The volatiles of the filtrate were removed in vacuo to give a red viscous oil, which was crystallized from ether/pentane to afford Mo(NAr′)$_2$CH$_2$^{t}Bu)$_2$ as orange microcrystals (1.78 g, 2.88 mmol, 83%). ^{1}H NMR (300 MHz, $CDCl_3$): 6.83 (s, 2 H, aromatic *H*), 6.76 (s, 2 H, aromatic *H*), 3.47 (sept, 2 H, C*H*(CH$_3$)$_2$, J_{CH} = 6.9 Hz), 2.78 (sept, 2 H, C*H*(CH$_3$)$_2$, J_{CH} = 6.9 Hz), 2.09 (s, 6 H, CH$_3$), 2.01 (s, 4 H, *CH*$_2$), 1.18 (d, 12 H, CH(C*H*$_3$)$_2$, J_{CH} = 6.9 Hz), 1.11 (s, 18 H, C*H*$_3$), 1.03 (d, 12 H, CH(C*H*$_3$)$_2$, J_{CH} = 6.9 Hz). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$): 152.84, 145.09, 141.61, 132.37, 125.01, 120.52, 78.89, 33.92, 33.47, 33.44, 28.00, 23.99, 23.27, 19.48. Anal. Calcd for $C_{36}H_{60}N_2Mo$: C, 70.08; H, 9.82; N, 4.54. Found: C, 70.27; H, 9.88; N, 4.55. Mp: 153−155 °C dec.

Preparation of Mo(NAr′)(CHBu^t)(DME)(OTf)$_2$ (8). In a glovebox, a near frozen solution of triflic acid (1.3 g, 8.64 mmol, 3 equiv) in DME (8 mL) was added to a near frozen solution of Mo(NAr′)$_2$(CH$_2$Bu^t)$_2$ (1.8 g, 2.88 mmol) in DME (30 mL). The reaction mixture was stirred for 12 h. During this period, the color changed from bright orange to dark yellow. The volatiles were removed in vacuo to give a dark yellow oil. The resulting oil was extracted with cold toluene, and the extract was filtered through a plug of Celite. The filtrate was concentrated in vacuo. The resulting dark yellow oil was dissolved in ether, layered with pentane, and allowed to stand at −35 °C until a bright yellow powder was obtained. The powder was collected by filtration and recrystallized from layered 1:1 ether−pentane to obtain the pure product (1.3 g, 1.75 mmol, 61%). By NMR spectroscopy there were two isomers visible. However, one isomer was in much higher concentration than the other. The spectral resonances for the major isomer are given. ^{1}H NMR (300 MHz, $CDCl_3$): 14.08 (s, 1 H, Mo=C*H*, J_{CH} = 121 Hz),

6.97 (s, 1 H, aromatic *H*), 6.84 (s, 1 H, aromatic *H*), 4.28 (br s, 3 H, OC*H*$_3$), 4.07 (br s, 2 H, OC*H*$_2$), 3.84 (br s, 2 H, OC*H*$_2$), 3.68 (sept, 1 H, *CH*(CH$_3$)$_2$, J_{CH} = 6.9 Hz), 3.52 (br s, 3 H, OC*H*$_3$), 2.84 (sept, 1 H, C*H*(CH$_3$)$_2$, J_{CH} = 6.9 Hz), 2.43 (s, 3 H, C*H*$_3$), 1.26 (s, 9 H, CMe$_3$), 1.21 (d, 12 H, CH(CH$_3$)$_2$, J_{CH} = 6.9 Hz). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$): 327.88, 151.98, 147.95, 142.26, 130.43, 130.04, 128.28, 128.22, 126.32, 126.12, 124.68, 124.03, 121.30, 73.18, 70.55, 66.07, 62.67, 58.56, 30.56, 28.10, 27.93, 25.26, 23.47, 22.49. ^{19}F NMR ($CDCl_3$): −76.77. Anal. Calcd for $C_{24}H_{39}NO_8S_2F_6Mo$: C, 38.75; H, 5.30; N, 1.88. Found: C, 38.32; H, 5.18; N, 2.09.

Preparation of Mo(NAr′)(CHBu^t)(quin)(OBu$^t_{F6}$)$_2$ (9). In a glovebox, to a frozen solution of Mo(NAr′)(CHBu^t)(dme)(OTf)$_2$ (700 mg, 0.942 mmol) in ether−THF (9:1, 1 mL) was added a solution of TlOBu$^t_{F6}$ (726 mg, 2 equiv, 1.883 mmol) in ether−THF (9:1, 1 mL). The reaction mixture was stirred for 3 h. Then, the solvent was removed, and the product was dissolved in pentane. The salts were filtered away through Celite, and the solvent was removed in vacuo. The product was redissolved in pentane (2 mL). To this solution was added a solution of quinuclidine (105 mg, 0.0941 mmol) in pentane (1 mL), and the reaction mixture was stirred for 40 min. After 40 min, the solution was concentrated to 1 mL and 3−4 drops of THF were added. The solution was kept in the freezer at −35 °C to afford Mo(NAr′)(CHBu^t)(quin)OBu$^t_{F6}$)$_2$ as yellow-orange crystals in 11% isolated yield (78 mg, 0.094 mmol). The NMR spectroscopic data are consistent with an approximately 1:1 mixture of two major isomers in $CDCl_3$; there are at least three minor isomers present. ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): 13.10 (s, Mo=C*H*, J_{CH} = 139.06 Hz, anti), 12.40 (s, Mo=C*H*, J_{CH} = 121 Hz, syn), 7.26−7.12 (m, aromatic), 4.46 (sept, 1 H, J_{CH} = 7.2 Hz, *CH*(CH$_3$)$_2$), 3.51 (sept, J_{CH} = 6.9 Hz, *CH*(CH$_3$)$_2$), 3.14 (t, J_{CH} = 8.1 Hz, C*H*$_2$), 2.85 (t, J_{CH} = 7.5 Hz, C*H*$_2$), 1.80 (s, C*H*), 1.46−1.60 (m, C*H*$_2$), 1.44 (br s, C*H*$_2$), 1.35−1.32 (m, C*H*$_2$), 1.30 (s, C*H*$_3$), 1.26 (s, C*H*$_2$), 1.24 (s, C*H*$_2$), 1.22−1.21 (m, C*H*$_2$), 1.19 (s, C*H*$_3$), 1.16 (s, C*H*$_3$). ^{13}C{^{1}H} NMR (75.6 MHz, $CDCl_3$): 311.04 (anti), 298.75 (syn), 153.32, 151.97, 148.15, 147.57, 146.07, 128.84, 127.85, 124.30, 123.63, 123.57, 65.88, 52.67, 49.54, 46.45, 46.40, 32.39, 31.50, 29.16, 28.61, 27.92, 26.14, 26.02, 25.58, 24.66, 24.26, 24.06, 23.94, 20.60, 19.83, 19.14, 18.60, 16.48, 15.28. Anal. Calcd for $C_{33}H_{48}N_2O_2F_{12}Mo$: C, 47.83; H, 5.84; N, 3.38. Found: C, 47.72; H, 5.72; N, 3.39. Mp: 168−170 °C.

General Considerations for X-ray Diffraction. Crystals grown from concentrated solutions at −35 °C quickly were moved from a scintillation vial to a microscope slide containing Paratone N. Samples were selected and mounted on a glass fiber in wax and Paratone. The data collections were carried out at a sample temperature of 173 K on a Bruker AXS platform three-circle goniometer with a CCD detector. The data were processed and reduced utilizing the program SAINTPLUS supplied by Bruker AXS. The structures were solved by direct methods (SHELXTL v5.1, Bruker AXS) in conjunction with standard difference Fourier techniques. Structural parameters for **4**, **5**, **7**, and **9** are given in Table 1.

Acknowledgment. We thank the Office of Naval Research, the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Department of Energy - Defense Programs, and Michigan State University for financial support of our research group. We also thank BASF for a generous gift of HBPin.

Supporting Information Available: Tables, figures, and CIF files giving results of X-ray diffraction studies and NMR spectra for Mo(NAr)$_2$(Np)$_2$ (**3**), Mo[=N-2,4-Pr$^i_2$C$_6$H$_2$-2-CH$_2$CH$_2$CMe$_2$-CH=](DME)(OTf)$_2$ (**4**), Mo[=N-2,4-Pr$^i_2$C$_6$H$_2$-2-CH$_2$CH$_2$CMe$_2$-CH=](quin)(OBu$^t_{F6}$)$_2$ (**5**), 2-methyl-4,6-diisopropyl-1-nitrobenzene (**H**), 2-methyl-4,6-diisopropylaniline (**I**), and Mo(NAr′)(CHBu^t)-(quin)(OBu$^t_{F6}$)$_2$ (**9**). This material is available free of charge via the Internet at http://pubs.acs.org.

OM800650V