ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

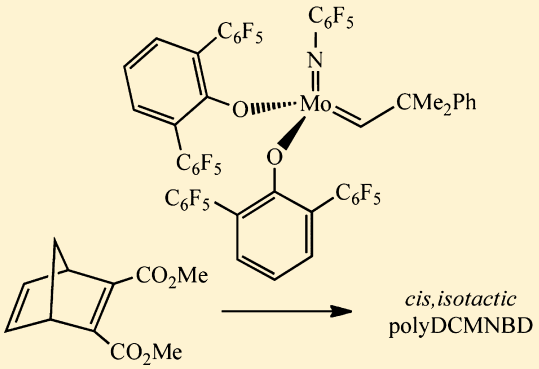
Synthesis and ROMP Chemistry of Decafluoroterphenoxide Molybdenum Imido Alkylidene and Ethylene Complexes

Jian Yuan, Richard R. Schrock,* Laura C. H. Gerber, Peter Müller, and Stacey Smith

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

Supporting Information

ABSTRACT: The bisDFTO alkylidene complexes of molybdenum Mo(NR)(CHCMe$_2$Ph)(DFTO)$_2$ (R = 2,6-i-Pr$_2$C$_6$H$_3$, 2,6-Me$_2$C$_6$H$_3$, C$_6$F$_5$, 1-adamantyl; DFTO = 2,6-(C$_6$F$_5$)$_2$C$_6$H$_3$O) and monoaryloxide monopyrrolide (MAP) complexes Mo(NR)(CHCMe$_2$Ph)(Me$_2$Pyr)(OAr) (Me$_2$Pyr = 2,5-dimethylpyrrolide; R = C$_6$F$_5$, OAr = DFTO, 2,6-dimesitylphenoxide (HMTO); R = 2,6-Me$_2$C$_6$H$_3$, OAr = DFTO) have been prepared in good yields. Addition of dicarbomethoxynorbornadiene (DCMNBD) to bisDFTO complexes yielded polymers that have a *cis,isotactic* structure. Polymerization of DCMNBD by Mo(NC$_6$F$_5$)(CHCMe$_2$Ph)(Me$_2$Pyr)(HMTO) gives a polymer that contains the expected *cis,syndiotactic* structure, but polymerization of DCMNBD by Mo(NR)(CHCMe$_2$Ph)(Me$_2$Pyr)(DFTO) (R = C$_6$F$_5$, 2,6-Me$_2$C$_6$H$_3$) generates a polymer that has a *cis,isotactic* structure, the first observation of a *cis,isotactic* polymer prepared employing a MAP initiator. Norbornene is polymerized to give what is proposed to be highly tactic *cis*-polyNBE. Addition of ethylene to Mo(NC$_6$F$_5$)(CHCMe$_2$Ph)(DFTO)$_2$ leads to formation of Mo(NC$_6$F$_5$)(CH$_2$CH$_2$)(DFTO)$_2$, which also behaves as an initiator for polymerization of DCMNBD to *cis,isotactic*-polyDCMNBD and norbornene to *cis* highly tactic polyNBE. Mo(NC$_6$F$_5$)(CH$_2$CH$_2$)(DFTO)$_2$ reacts with 3-methyl-3-phenylcyclopropene (MPCP) to give Mo(NC$_6$F$_5$)(CHCHCMePh)(DFTO)$_2$ in ~50% yield.



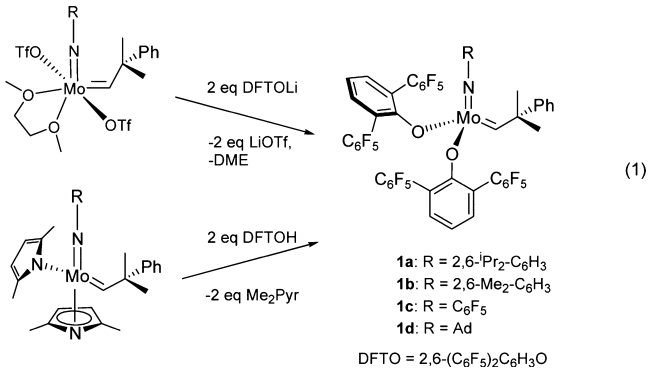
INTRODUCTION

Olefin metathesis is of continuing importance to the synthesis of organic molecules and polymers, both as a consequence of its very nature, i.e., the synthesis of C=C bonds catalytically from C=C bonds, and because of the control that can be exercised through the use of well-defined Mo, W, and Ru complexes as catalysts for that reaction.[1] In the interest of exploring variations of Mo and W olefin metathesis complexes that contain an electron-withdrawing imido ligand, we recently devised routes to pentafluorophenylimido alkylidene complexes.[2] We were especially interested in exploring high-oxidation-state monoaryloxide pyrrolide (MAP) imido alkylidene complexes of Mo and W for *Z*-selective olefin metathesis reactions.[3] In the process we introduced the 2,6-bis(pentafluorophenyl)phenoxide (decafluoroterphenoxide or DFTO) ligand, a sterically demanding but more electron withdrawing terphenoxide than either HMTO (O-2,6-(2,4,6-Me$_3$C$_6$H$_3$)$_2$C$_6$H$_3$) or HIPTO (O-2,6-(2,4,6-i-Pr$_3$C$_6$H$_3$)$_2$C$_6$H$_3$), and one that also is unlikely to be subject to any CH activation within the ligand. We failed to make MAP complexes that contain the DFTO ligand through protonation of bispyrrolide precursors as a consequence of "overprotonation" to yield M(NC$_6$F$_5$)(CHCMe$_2$Ph)(DFTO)$_2$ complexes. However, M(NC$_6$F$_5$)(CHCMe$_2$Ph)(DFTO)$_2$ complexes attracted our attention because analogous bisHMTO or bisHIPTO complexes have not been prepared and because M(NC$_6$F$_5$)(CHCMe$_2$Ph)(DFTO)$_2$ initiates polymerization of 2,3-dicarbomethoxynorbornadiene (DCMNBD) to give poly(DCMNBD) with a structure that is >99% *cis* and *isotactic*, a result that is not known for bisalkoxide or bisaryloxide imido alkylidene complexes.[4] In this paper we report the synthesis of new MAP complexes that contain the DFTO ligand along with a more thorough exploration of reactions of bisDFTO complexes that are relevant to ROMP reactions. This exploration includes the synthesis and chemistry of the ethylene complex Mo(NC$_6$F$_5$)(CH$_2$CH$_2$)(DFTO)$_2$ and a study of its behavior as an initiator for ROMP.

RESULTS AND DISCUSSION

Synthesis of BisDFTO Mo Complexes. Treatment of Mo(NR)(CHCMe$_2$Ph)(OTf)$_2$(DME) complexes with 2 equiv of DFTOLi (LiO-2,6-(C$_6$F$_5$)$_2$C$_6$H$_3$) at −30 °C in toluene gave the bisDFTO complexes Mo(NR)(CHCMe$_2$Ph)(DFTO)$_2$ (**1a**−**d**, R = 2,6-i-Pr$_2$C$_6$H$_3$, 2,6-Me$_2$C$_6$H$_3$, C$_6$F$_5$, 1-adamantyl; eq 1). These complexes also can be prepared through addition of 2 equiv of DFTOH to Mo(NR)(CHCMe$_2$Ph)(Me$_2$Pyr)$_2$ in diethyl ether at room temperature. We attribute the failure to prepare Mo(NR)(CHCMe$_2$Ph)(OR)$_2$ by either method when OR is HIPTO or HMTO to a higher pK_a for HIPTOH or HMTOH and therefore slower protonation of pyrrolide ligands or to side reactions that involve deprotonation of the

Received: March 11, 2013
Published: May 6, 2013



(1)

alkylidene[5] when $Mo(NR)(CHCMe_2Ph)(OTf)_2(DME)$ is treated with aryloxide salts.

In ^{19}F NMR spectra of **1a–d** at 20 °C, one *para*, two *meta*, and two *ortho* fluorine DFTO resonances are observed (Figure 1). The presence of two *meta* and two *ortho* resonances is

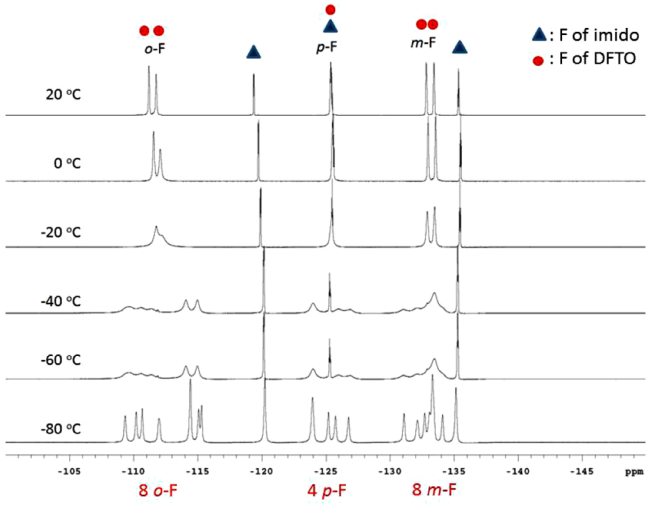
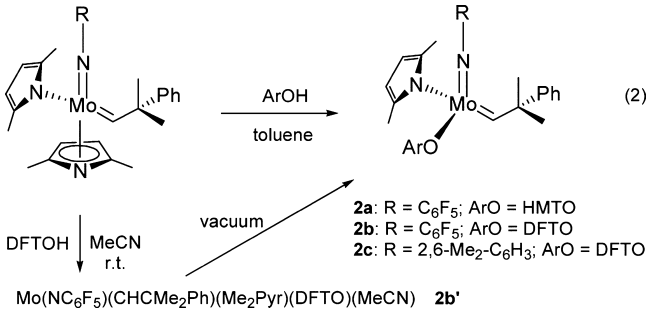


Figure 1. Variable-temperature ^{19}F NMR spectra of **1c** (in toluene-d_8).

consistent with hindered rotation of the C_6F_5 ring about the C–C connection between C_6F_5 rings and the central phenyl ring but free rotation about the Mo–O bonds on the NMR time scale. The ^{19}F NMR spectrum of **1c** at −80 °C reveals resonances (some overlapping) for eight DFTO *ortho* fluorines, eight *meta* fluorines, and four *para* fluorines, consistent with no molecular symmetry for **1c** on the NMR time scale at that temperature. An X-ray structure[2] revealed that the two DFTO ligands are oriented approximately perpendicular to each other to give an enantiomorphic atropisomer in the solid state. The DFTO ligands in the atropisomer resemble the halves of a baseball cover with the basic C_2 symmetry being reduced to C_s as a consequence of the presence of the imido and alkylidene ligands. We propose that the atropisomeric form leads to the inequivalence of all 20 DFTO fluorines on the NMR time scale. Rotation of the two DFTO ligands past one another and past the imido and alkylidene ligands creates a mirror plane on the NMR time scale at higher temperatures that coincides with the N_{imido}–Mo–C plane.

Synthesis of MAP Complexes. Treatment of $Mo(NC_6F_5)(CHCMe_2Ph)(Me_2Pyr)_2$ with 1 equiv of 2,6-dimesitylphenol (HMTOH) at 70 °C for 16 h led to formation of the MAP complex $Mo(NC_6F_5)(CHCMe_2Ph)(Me_2Pyr)(HMTO)$ in 60% yield (eq 2). However, addition of 1 equiv of DFTOH to $Mo(NC_6F_5)(CHCMe_2Ph)(Me_2Pyr)_2$ at 22 or −30 °C in



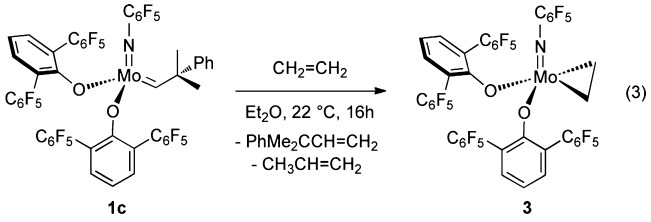
(2)

toluene followed by warming the sample to 20 °C produced a mixture of $Mo(NC_6F_5)(CHCMe_2Ph)(Me_2Pyr)_2$, $Mo(NC_6F_5)(CHCMe_2Ph)(Me_2Pyr)(DFTO)$ (**2b**), and $Mo(NC_6F_5)(CHCMe_2Ph)(DFTO)_2$ (**1c**) (~1:1:1 through integration of alkylidene resonances). In contrast, when reactions between $Mo(NC_6F_5)(CHCMe_2Ph)(Me_2Pyr)_2$ and DFTOH were carried out in *acetonitrile*, $Mo(NC_6F_5)(CHCMe_2Ph)(Me_2Pyr)(DFTO)(MeCN)$ (**2b′**) could be isolated as an orange solid in 75% yield. Proton NMR studies suggest that the acetonitrile in **2b′** dissociates readily; indeed, it can be removed by dissolving **2b′** in toluene and removing the toluene and acetonitrile in vacuo in several cycles. Compound **2b** was obtained as a red-orange solid that could be recrystallized from a mixture of diethyl ether and pentane. We propose that in the reaction between $Mo(NC_6F_5)(CHCMe_2Ph)(Me_2Pyr)_2$ and DFTOH acetonitrile is a good enough ligand to prevent over-protonation, since the oxygen of DFTOH must bind to the metal before the proton can transfer to the pyrrolide ligand. Fortunately, acetonitrile is also a poor enough ligand in this situation to be removed from **2b′** in vacuo.

An X-ray study of **2b′** revealed it to have a square-pyramidal structure ($\tau = 0.067$; $\tau = 0$ for a perfect square pyramid[6]) with the alkylidene in the apical position and acetonitrile bound *trans* to the dimethylpyrrolide (Figure 2). The Mo(1)–N(1) (1.751(1) Å) and the Mo(1)–C(1) (1.889(1) Å) distances are similar to those found in other square-pyramidal MAP adducts that contain PMe_3 or THF.[7] The alkylidene is found in the apical position of the square pyramid in all crystallographically characterized MAP adducts so far.

Synthesis of a Molybdenum Ethylene Complex. Reaction of a new alkylidene complex with ethylene is a relatively routine means of exploring the ease of formation and stability of methylidene and unsubstituted metallacyclobutane complexes.

Exposure of a diethyl ether solution of $Mo(NC_6F_5)(CHCMe_2Ph)(DFTO)_2$ (**1c**) to 1 atm of ethylene at room temperature led to a color change from orange to deep purple over a period of 16 h and formation of the ethylene complex $Mo(NC_6F_5)(CH_2CH_2)(DFTO)_2$ (**3**; eq 3), in 76% yield. At



(3)

dx.doi.org/10.1021/om400199u | Organometallics 2013, 32, 2983–2992

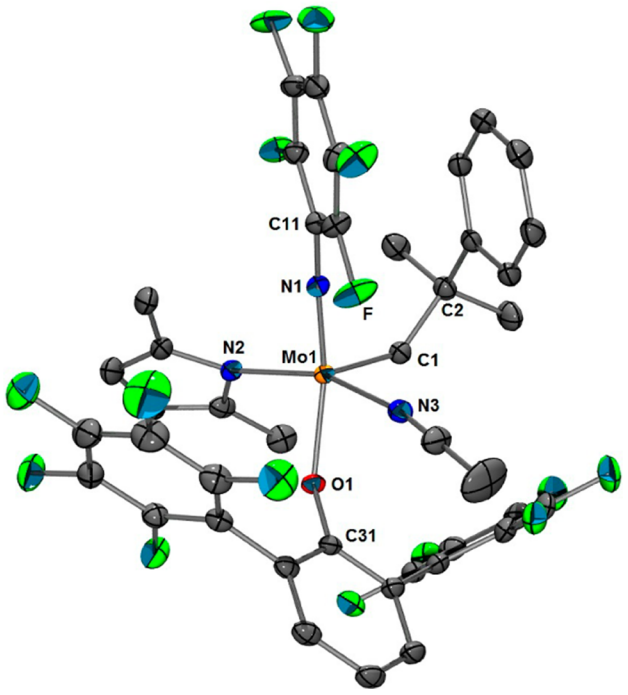


Figure 2. Thermal ellipsoid plot of the structure of **2b′**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Mo(1)−N(1) = 1.751(1), Mo(1)−C(1) = 1.889(1), Mo(1)−O(1) = 1.995(1), Mo(1)−N(2) = 2.084(1), Mo(1)−N(3) = 2.190(1), C(11)−N(1) = 1.378(1), O(1)−C(31) = 1.336(1); N(1)−Mo(1)−O(1) = 154.35(4), N(2)−Mo(1)−N(3) = 158.37(4).

room temperature the ^{1}H NMR spectrum for **3** in tol-d_8 showed two ethylene proton resonances at 1.33 and 2.48 ppm (Figure 3). At −80 °C these two resonances split into four

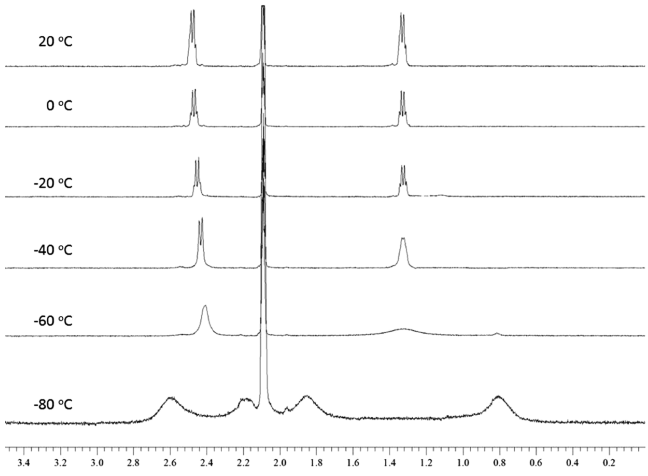


Figure 3. Variable-temperature ^{1}H NMR spectra of **3** (tol-d_8).

at δ 0.81, 1.85, 2.19, and 2.60 ppm. The ^{19}F NMR spectrum of **3** at −80 °C reveals resonances for eight *ortho* fluorines, eight *meta* fluorines, and four *para* fluorines for the two DFTO ligands, as found for **1c** (Figure 1). All data are consistent with **3** having no symmetry at −80 °C on the NMR time scale, as found for **1c**.

The structure of **3** as determined through a single-crystal X-ray diffraction study is shown in Figure 4. The Mo1−C2 bond length (2.140(4) Å) is essentially the same as the Mo1−C1

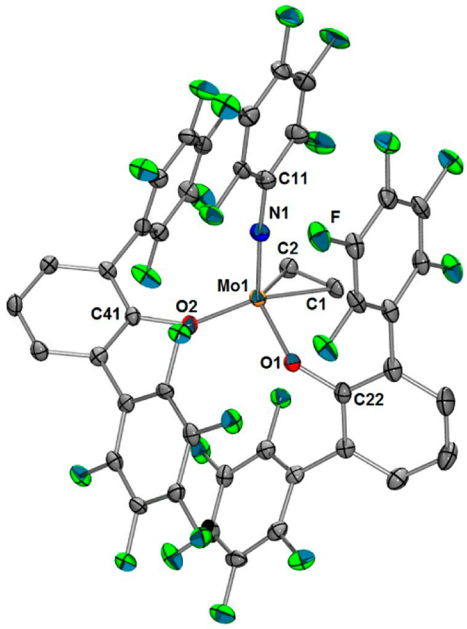


Figure 4. Thermal ellipsoid plot of **3**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Mo(1)−N(1) = 1.720(3), Mo(1)−O(2) = 1.935(3), Mo(1)−O(1) = 1.946(3), Mo(1)−C(2) = 2.140(4), Mo(1)−C(1) = 2.153(4), C(1)−C(2) = 1.415(6); N(1)−Mo(1)−O(2) = 121.37(14), N(1)−Mo(1)−O(1) = 114.79(14), O(2)−Mo(1)−O(1) = 108.45(11), C(2)−Mo(1)−C(1) = 38.49(15), C(2)−C(1)−Mo(1) = 70.3(2), C(1)−C(2)−Mo(1) = 71.2(2).

bond (2.153(4) Å). The C1−C2 bond distance is 1.415(6) Å, and the C1−Mo1−C2 angle is 38.49(15)°. The C1−C2 bond is essentially perpendicular to the Mo1−N1 bond (N1−Mo1−C1 = 97.00(15)°; N1−Mo1−C2 = 96.00(16)°). These structural features are similar to those observed for the four other Mo imido ethylene complexes in the literature.[8]

When **1c** was treated with $^{13}CH_2{=}{}^{13}CH_2$ in C_6D_6 and the reaction followed by ^{13}C NMR, **1c** was fully converted into a mixture of a TBP metallacyclobutane complex, $Mo(NC_6F_5)(^{13}CH_2{}^{13}CH_2{}^{13}CH_2)(DFTO)_2$ (**4***), and $^{13}CH_2{=}CHCMe_2Ph$ in 5 min. After 15 min, resonances for $Mo(NC_6F_5)(^{13}CH_2{}^{13}CH_2)(DFTO)_2$ (**3***) and $^{13}CH_2{=}{}^{13}CH^{13}CH_3$ could be observed; after 24 h conversion to **3*** and $^{13}CH_2{=}{}^{13}CH^{13}CH_3$ was complete. According to proton NMR spectra the amount of propylene was less than 1 equiv, as a consequence of some being lost into the head space. A ^{13}C NMR spectrum of isolated **3*** under ∼0.5 atm of $^{13}CH_2{}^{13}CH_2$ at room temperature showed that two carbon resonances were present at δ 82.9 and 39.9 ppm (with a second-order coupling pattern), consistent with formation of a small amount of the metallacyclopentane complex $Mo(NC_6F_5)(^{13}CH_2{}^{13}CH_2{}^{13}CH_2{}^{13}CH_2)(DFTO)_2$ (∼2%; Figure 5).[9] We propose that $Mo(NC_6F_5)(^{13}CH_2{}^{13}CH_2{}^{13}CH_2)(DFTO)_2$ rearranges to $Mo(NC_6F_5)(^{13}CH_2{=}{}^{13}CH^{13}CH_3)(DFTO)_2$ and that propylene is then *displaced* (most likely) by ethylene to give $Mo(NC_6F_5)(^{13}CH_2{}^{13}CH_2)(DFTO)_2$ and free propylene. The mechanism of rearrangement is proposed to consist of β hydride elimination in the metallacyclobutane complex to give an intermediate allyl hydride followed by reductive elimination. Formation of an alkyl intermediate through CH activation in either the DFTO or the NC_6F_5 ligand is not possible. However, migration of the β hydride in the metallacyclobutane to the

dx.doi.org/10.1021/om400199u | *Organometallics* 2013, 32, 2983−2992

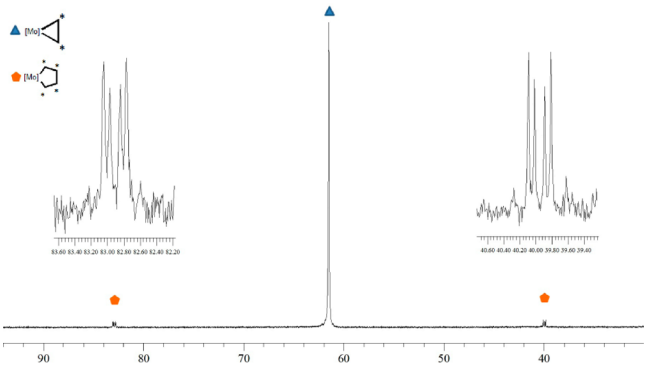


Figure 5. ^{13}C NMR spectrum of $Mo(NC_6F_5)(^{13}CH_2{=}^{13}CH_2)(DFTO)_2$ and $^{13}CH_2{=}^{13}CH_2$ in C_6D_6 at room temperature ([Mo] = $Mo(NC_6F_5)(DFTO)_2$).

imido nitrogen to give an intermediate Mo(IV) complex, $Mo(NHC_6F_5)(^{13}CH_2{}^{13}CH{}^{13}CH_2)(DFTO)_2$, cannot be ruled out.

Polymerization of DCMNBD Initiated by 1. We often employ polymerization of 2,3-dicarbomethoxynorbornadiene (DCMNBD) as a means of assessing the potential stereoselectivity of a given initiator. We noted in a communication that DCMNBD was polymerized by initiator **1c** to give *cis,isotactic* polymer.[2] Addition of 100 equiv of DCMNBD to **1a,b,d** also led to the formation of poly(DCMNBD). As shown in Table 1, only initiators **1b,c** produce a polymer with a highly

Table 1. Poly(DCMNBD) Formed Employing $Mo(NR)(CHCMe_2Ph)(DFTO)_2$ Initiators

compd	R	cis (%)	tacticity (%)
1a	2,6-i-$Pr_2C_6H_3$	89	72 *iso*
1b	2,6-$Me_2C_6H_3$	>98	>98 *iso*
1c	C_6F_5	>98	>98 *iso*
1d	adamantyl		atactic

regular >98% *cis*, >98% *isotactic* structure, on the basis of the chemical shift of the methylene carbon (C(7)) at 38.7 ppm in $CDCl_3$;[10] this contrasts with a chemical shift for C(7) of 38.0 ppm in *cis,syndiotactic*-poly(DCMNBD).[3b] Formation of *cis,isotactic*-poly(DCMNBD) employing an imido alkylidene bisalkoxide initiator is not known.[4] However, polymerization of DCMNBD initiated by W(CH-t-Bu)(O)(O-2,6-$Ph_2C_6H_3)_2(PPh_2Me)$ has been reported to produce >95% *cis*, >95% *isotactic* poly(DCMNBD).[11] Initiators that contain chiral biphenolate and binaphtholate ligands produce *cis,isotactic*-poly(DCMNBD) through enantiomorphic site control.[4] Only atactic polymer was formed employing initiator **1d**, either isolated or prepared in situ. The lower efficiency of forming a *cis,isotactic* polymer with initiator **1a** is likely to be a consequence of too much steric hindrance.

GPC analyses of *cis,isotactic*-poly(DCMNBD) made from 50, 100, 200, and 800 equiv of DCMNBD in $CHCl_3$ at room temperature with initiator **1c** (Table 2) showed that the polydispersity of each sample is relatively low and decreases as the polymer length increases, both of which suggest that the polymerization is relatively well-behaved. (For a neophylidene initiator k_p often is greater than k_i and PDI values therefore are higher than when k_p and k_i are comparable.) The relationship between the number of equivalents of monomer employed and the number average molecular weight of the polymers

Table 2. GPC Studies of Poly(DCMNBD) Prepared with 1c as the Initiator[a]

n	conversion (%)	M_n	PDI
50	>98	7000	1.19
100	>98	13000	1.17
200	>98	24000	1.15
800	>98	88000	1.10

[a] M_n in $CHCl_3$ vs polystyrene; *n* = equivalents of monomer added.

measured in $CHCl_3$ versus polystyrene standards is linear with an R^2 value of 0.9999 (Figure S1 in the Supporting Information).

Polymerization of DCMNBD by bisDFTO initiators **1b,c** to yield *cis,isotactic*-poly(DCMNBD) would seem to require that the monomer attack the same side of a M=C bond in each step. We tentatively suggest that *cis,isotactic*-poly(DCMNBD) forms through a type of chain end control where one diastereomer is created through interlocking of the terphenoxide ligands in combination with the chirality of the last inserted monomer; reaction of the other diastereomer is not competitive. The failure of **1d** to yield *cis,isotactic*-poly(DCMNBD) suggests that the nature of the imido group is a significant part of the puzzle that is not yet understood.

Polymerization of DCMNBD Initiated by 2a–c. Addition of 100 equiv of DCMNBD to **2a** led to consumption of the monomer and formation of polymer within 30 min. The polymer is >98% *cis,syndiotactic* (Table 3), as is the poly-

Table 3. Poly(DCMNBD) Formed with Initiators $Mo(NR)(CHCMe_2Ph)(Me_2Pyr)(OAr)$ (2a–c)

initiator	R	ArO	cis (%)	tacticity (%)
2a	C_6F_5	HMTO	>98	>98 *syndio*
2b′	C_6F_5	DFTO	92	atactic
2b	C_6F_5	DFTO	95	91 *iso*
2c	2,6-$Me_2C_6H_3$	DFTO	>98	96 *iso*

(DCMNBD) produced employing Mo(NAd)($CHCMe_2Ph$)(Pyr)(OHIPT)[3b] as an initiator. The polymer obtained with **2b′** is largely *cis* but relatively atactic, presumably solely as a consequence of the presence of 1 equiv of acetonitrile. To our surprise, treatment of **2b** with 100 equiv of DCMNBD led to the formation of a new polymer that has a 95% *cis* and 91% *isotactic* structure, while poly(DCMNBD) prepared with **2c** as the initiator was found to contain ~98% *cis* and 96% *isotactic* dyads. Formation of *cis,isotactic* polymer with a MAP initiator has never been observed, although formation of *trans,isotactic*-poly[(+)-2,3-dicarbomethoxynorbornene] employing a MAP initiator has been reported recently.[3l] The change in tacticity upon changing from HMTO (in **2a**) to DFTO (in **2b**) is striking, as is the disruption of the tacticity of the poly(DCMNBD) in the presence of 1 equiv of acetonitrile (in **2b′**).

Poly(DCMNBD) made from 50, 100, and 200 equiv of monomer in $CHCl_3$ with initiator **2b** was analyzed by GPC (Table 4). In comparison to the polymer produced by initiator **1c** (Table 2), the polydispersities of each of the samples are relatively high and increase as the polymer length increases. The relationship between the number of equivalents of monomer employed and the number average molecular weight of the polymers measured in $CHCl_3$ versus polystyrene standards is also linear, with an R^2 value of 0.99 (Figure S2 in the Supporting Information). The molecular weights of these

dx.doi.org/10.1021/om400199u | *Organometallics* 2013, 32, 2983–2992

Table 4. GPC Studies of Poly(DCMNBD) Samples Using 2b as an Initiator[a]

n	conversion (%)	M_n	PDI	n'	n/n'
50	>99	28000	1.19	242	0.21
100	>99	55000	1.20	490	0.20
200	>99	90000	1.26	817	0.24

[a] M_n in $CHCl_3$ vs polystyrene; n = equivalents of monomer added; n' = the required equivalents of monomer to produce the same M_n with initiator **1c**.

polymers are about 5 times what they are when **1c** is employed as the initiator, as can be seen from the data in Table 2; the ratio n/n' is ~0.2, where n' would be the required number of equivalents to produce an observed M_n employing initiator **1c**.

Formation of largely *cis,isotactic*-poly(DCMNBD) by **2b,c** contrasts dramatically with the *cis,syndiotactic*-poly(DCMNBD) formed when **2a** is employed as an initiator. In fact, we can explain formation of *cis,isotactic*-poly(DCMNBD) only if the "rule" concerning approach of the monomer *trans* to a pyrrolide ligand does not hold in this situation or if we invoke a turnstile rotation of a metallacyclobutane intermediate followed by a rotation of the alkylidene ligand, as shown in Scheme 1. We have entertained the possibility that a *propagating species generated from* **2b** disproportionates to yield bispyrrolide and bisDFTO complexes and that the *cis,isotactic* structure arises through selective polymerization of DCMNBD by the bisDFTO complex so formed. However, a mixture of **1c** and $Mo(NC_6F_5)(CHCMe_2Ph)(Me_2Pyr)_2$ (1:1) in C_6D_6 did not give any **2b** at room temperature or upon heating to 50 °C for 16 h. Also, the data in Table 4 would suggest that the amount of disproportionation would have to be ~20%. It should be noted that $Mo(NAr)(CHCMe_2Ph)(Me_2Pyr)(OC_6F_5)$ has been found to yield a mixture of $Mo(NAr)(CHCMe_2Ph)(Me_2Pyr)_2$ plus $Mo(NAr)(CHCMe_2Ph)(OC_6F_5)_2$ in solution.[12] We conclude that disproportionation of a *propagating species generated from* **2b** cannot be rejected out of hand, but it seems unlikely at this stage.

ROMP Initiated by $Mo(NC_6F_5)(CH_2CH_2)(DFTO)_2$ (3). When $Mo(NC_6F_5)(CH_2CH_2)(DFTO)_2$ was treated with 50 equiv of DCMNBD in $CDCl_3$ in a J. Young tube, a trace amount of polymer was observed after 16 h at room temperature. When the reaction mixture was heated for 4 h at 50 °C, 48% of the monomer was consumed. The reaction was monitored by ^1H NMR, and conversion vs time is shown in Figure 6. All monomer was consumed after 16 h at 50 °C in a Schlenk flask when ethylene was removed in a flow of nitrogen gas. ^{13}C NMR analysis of the poly(DCMNBD) showed that the

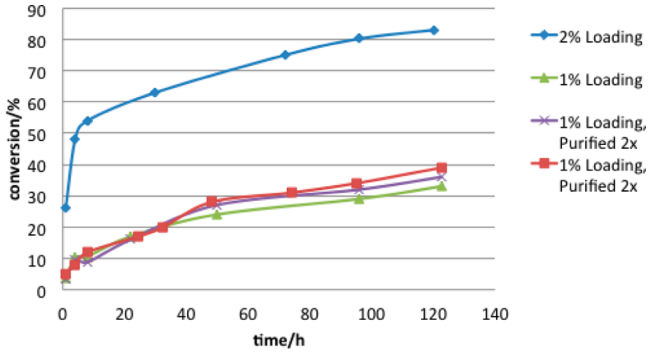


Figure 6. Consumption of DCMNBD in $CDCl_3$ by **3** at 50 °C. Blue diamonds imply 2% catalyst loading, green triangles imply 1% catalyst loading, and red squares and purple crosses are 1% catalyst loading with **3** that had been exposed to ethylene to remove any alkylidene impurities.

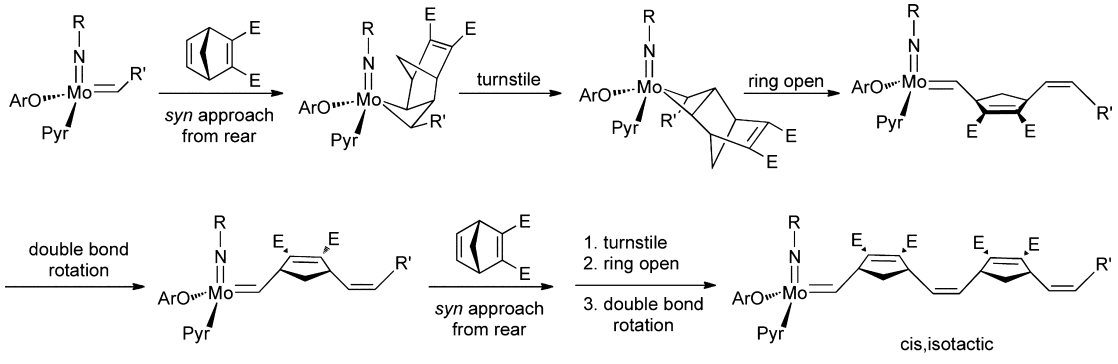
polymer is >99% *cis* and *isotactic*. The same phenomenon was observed when 1% catalyst was employed, even when samples of **3** were exposed multiple times to ethylene and recovered. Therefore, the evidence argues against the possibility that the polymerization can be ascribed to a trace of residual alkylidene complex. Since *cis,isotactic*-poly(DCMNBD) is formed employing $Mo(NC_6F_5)(CHCMe_2Ph)(DFTO)_2$ as an initiator, it seems highly likely that the initiator for the polymerization is a bisDFTO complex and that the initiator is generated from DCMNBD itself.

Addition of 1 equiv of DCMNBD to $Mo(NC_6F_5)(CH_2CH_2)(DFTO)_2$ led to formation of a red-orange crystalline product in 57% yield with the apparent composition $Mo(NC_6F_5)(CH_2CH_2)(DCMNBD)(DFTO)_2$ (**5**).

The ^1H NMR spectrum showed four triplet of doublet resonances (12, 4 Hz) at δ 1.43, 1.77, 2.72, and 3.07 ppm for the ethylene protons, which is indicative of a product with no symmetry. An X-ray diffraction study showed that the DCMNBD has bonded to Mo through the carbonyl groups in the two esters (O1 and O3, Figure 7), rather than forming a "mixed" metallacyclopentane from DCMNBD and ethylene. One ester is *trans* to the ethylene ligand, while the other is *trans* to the imido group. The two DFTO ligands are *trans* to each other. The bond lengths and angles are unsurprising. The Mo1–C1 distance (2.187(1) Å) is slightly shorter than the Mo1–C2 distance (2.195(1) Å), and the C1–C2 distance is 1.416(2) Å.

The synthesis of six-coordinate **5** suggests that the steric limits associated with, or imposed by, two terphenoxide ligands

Scheme 1. A Mechanism That Leads to *cis,isotactic*-Poly(DCMNBD)



dx.doi.org/10.1021/om400199u | Organometallics 2013, 32, 2983–2992

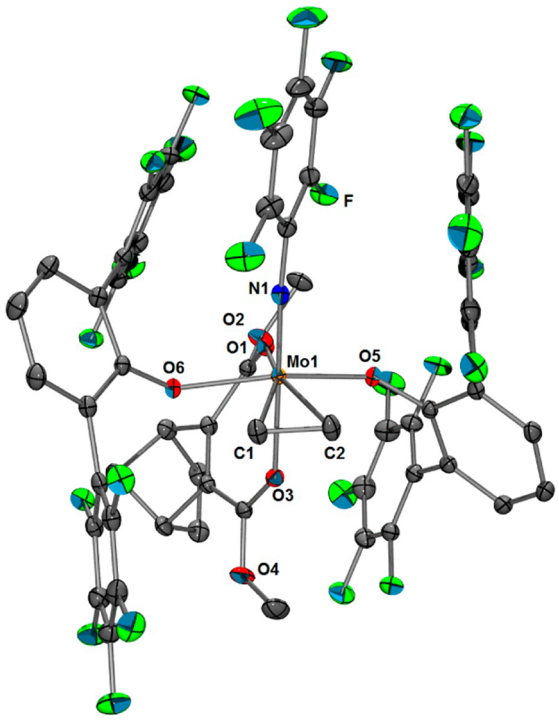


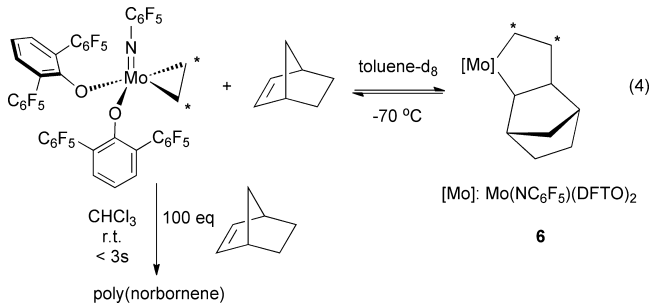
Figure 7. Thermal ellipsoid plot of **5**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): C(1)−C(2) = 1.416(2), Mo(1)−C(1) = 2.187(1), Mo(1)−C(2) = 2.195(1), Mo(1)−N(1) = 1.7290(9), Mo(1)−O(1) = 2.1983(8), Mo(1)−O(3) = 2.2198(8), Mo(1)−O(5) = 2.0664(7), Mo(1)−O(6) = 2.1041(7); N(1)−Mo(1)−O(3) = 178.92(4), O(5)−Mo(1)−O(6) = 148.94(3), C(1)−Mo(1)−C(2) = 37.70(4).

are difficult to predict, although the electron-withdrawing DFTO ligands should encourage adduct formation. It also should be noted that bisaryloxide catalysts have been employed in macrocyclizations that give trisubstituted double bonds,[3k] which suggests that crowded bisaryloxide catalysts may turn out to have some special properties in metathesis reactions that have been overlooked. In any case, coordination of the esters in DCMNBD to the metal almost certainly impedes formation of an initiator from DCMNBD.

Addition of 100 equiv of DCMNBD to $Mo(NC_6F_5)(^{13}CH_2{}^{13}CH_2)(DFTO)_2$ led to the formation of ∼50% yield of polymer in 8 h at 50 °C in $CDCl_3$. The ^{13}C NMR spectra exhibit one ^{13}C resonance at δ 116.1 ppm along with others expected for naturally abundant ^{13}C in the polymer. A 2D $^{13}C-^{1}H$ HMBC experiment (Figure S3, Supporting Information) confirmed that the ^{13}C resonance at 116.1 ppm is that in a $PCH{=}{}^{13}CH_2$ group (P = polymer) at one end of the poly(DCMNBD); the magnitudes of the coupling of the two protons in the $^{13}CH_2$ group to a third olefinic proton were found to be 17 Hz (J_{trans}) and 7 Hz (J_{cis}). We propose, in part on the basis of results to be described later, that the $PCH{=}{}^{13}CH_2$ group results from a *back reaction* between liberated $^{13}CH_2{}^{13}CH_2$ and a growing polymer chain, *not* through formation of $Mo(NC_6F_5)(^{13}CH_2)(DFTO)_2$ as the initiator.

Addition of 100 equiv of norbornene to **3** at room temperature led to formation of poly(norbornene) in seconds. The ^{13}C NMR spectrum of the polymer in $CDCl_3$ showed only four sharp resonances (at 134.00, 42.83, 38.72, and 33.34 ppm), characteristic of pure cis poly(NBE).[13] Samples prepared with initiators **1c** and **2a** were identical with those prepared with initiator **3**. The widths of the resonances at half height are ∼9 Hz at 125 MHz, which are unusually narrow. It seems unlikely, but not impossible, that the samples made with **1c** and **2a** are each highly tactic but have *different* tacticities (expected to be *iso* and *syndio*, respectively), since at least one additional resonance in a 125 MHz ^{13}C NMR experiment, most likely near that at 38.72 ppm, should be present if polymers with two different tacticities are formed. In early work on poly(NBE) ^{13}C NMR spectra,[13] Ivin and co-workers decided that fine structure due to tacticity differences, at least in the relatively low frequency ^{13}C NMR experiments at that time, could not be detected. However, a second explanation of the result obtained here is that the *cis* highly tactic poly(NBE) samples produced with initiators **1c** and **2a** are *both isotactic*. This possibility would require that the "rule" concerning formation of syndiotactic polymers with HMTO MAP species breaks down for norbornene, just as it did when *cis,isotactic*-poly(DCMNBD) was formed with initiators **2b,c**. Whether the tacticity of poly(NBE) is *iso* or *syndio* cannot be determined through NMR studies, since no chiral element is present in the polymer.[4] As far as we are aware, this is the first time that pure >98% *cis* and (we propose) highly (>98%) tactic poly(norbornene) has been prepared.

Addition of 1 equiv of norbornene to $Mo(NC_6F_5)(^{13}CH_2{}^{13}CH_2)(DFTO)_2$ at −78 °C in toluene-d_8 showed that, after 1 h at −70 °C, 69% of the ethylene complex was converted to the "mixed" metallacyclopentane complex **6** (eq 4). The $^{13}CH_2$ resonances in the metallacycle were observed as

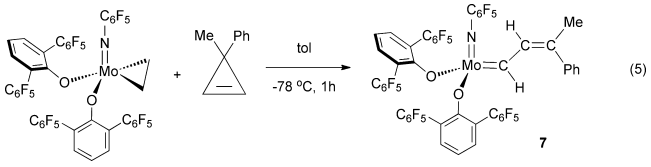


(4)

first-order doublets at δ 84.7 and 46.6 ppm ($^{1}J_{CC}$ = 37 Hz) in the ^{13}C NMR spectrum at −70 °C, consistent with one isomer of **6** being formed. When the temperature was raised to −50 °C, the concentration of **6** decreased while the concentrations of **3** and poly(norbornene) increased. After 1 h at −50 °C, all the norbornene had been consumed and the ethylene complex **3** was observed as the only Mo species to contain a ^{13}C label: i.e., no $PCH{=}{}^{13}CH_2$ group was detected in this experiment. As in reactions between **3** and DCMNBD, ethylene does not appear to be involved in formation of the initiator.

Treatment of **3** with 1 equiv of a mixture of labeled and unlabeled 3-methyl-3-phenylcyclopropene (MPCP; two parts of unlabeled MCPC to one part in which one CH is ^{13}C labeled) at −78 °C led to an immediate color change from purple to orange and formation of $Mo(NC_6F_5)(CHCH{=}CMePh)(DFTO)_2$ (**7**; eq 5) upon warming the sample to room temperature. Since one-third of the MPCP was monolabeled with ^{13}C in an olefinic position, the alkylidene proton resonance consists of a doublet at δ 12.10 ppm (d, $^{3}J_{HH}$ = 9 Hz) along with two ^{13}C satellites ($^{1}J_{CH}$ = 130 Hz, $^{3}J_{HH}$ = 9 Hz) in a ratio of 1:4:1 (Figure 8), consistent with **7** being a mixture of $[Mo]{=}{}^{13}CHCH{=}C(Me)Ph$, $[Mo]{=}CH{}^{13}CH{=}C(Me)$-

dx.doi.org/10.1021/om400199u | *Organometallics* 2013, 32, 2983−2992



(5)

Ph, and [Mo]=CHCH=C(Me)Ph in one isomeric form (where [M] = $Mo(NC_6F_5)(DFTO)_2$). (The isomer shown in eq 5 is arbitrary.) A similar coupling pattern was observed for the β-hydrogen at δ 8.33 ppm ($^1J_{CH}$ = 159 Hz, $^3J_{HH}$ = 9 Hz). The origin of the minor resonances at 12.20, 8.65, and 8.15 ppm (inter alia) has not been identified. In the ^{13}C NMR spectrum, the alkylidene carbon resonance was found at δ 264.5 ppm and the β-carbon resonance was found at δ 136.0 ppm. The vinyl alkylidene **7** rapidly initiates ROMP of MPCP at −78 °C or room temperature to yield atactic poly(MPCP).[3d] We propose that MPCP replaces ethylene in **3** to give a MPCP complex that then rearranges to form the vinyl alkylidene complex **7**. A single experiment employing **3**, unlabeled ethylene, and trimethoxybenzene as an internal standard showed that $Mo(NC_6F_5)(CHCH{=}CMePh)(DFTO)_2$ was formed in 50% yield. We propose that some MPCP is polymerized in the process. Ready conversion of **3** into an alkylidene is analogous to the results of reactions between 3,3-diphenylcyclopropene and complexes that contain Ti(II) and Zr(II),[14] W(IV),[15] and Ru(II).[16]

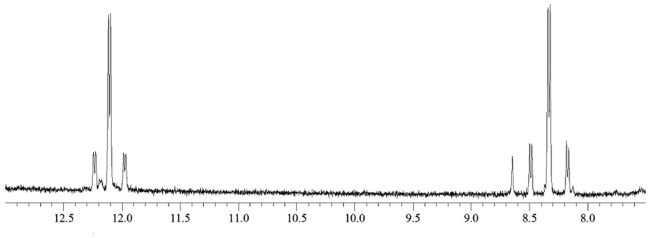


Figure 8. ^1H NMR spectrum of **7** in C_6D_6.

The ROMP of DCMNBD with **3** to give *cis,isotactic*-poly(DCMNBD), strongly suggests that some $Mo(NC_6F_5)(ODFT)_2(CRR')$ initiator is formed from DCMNBD. The ROMP of norbornene by **3** also suggests that some initiator forms from norbornene. These results can be added to others in the last several years that employ Mo(IV) or W(IV) initiators for metathesis reactions.[17] Evidence in the literature that stretches over several decades suggests that a norbornylidene complex can form from a norbornene via a 1,2-shift of an olefinic hydrogen.[18] However, to our knowledge no pure norbornylidene complex has ever been prepared. The closest is formation of a mixture of $(Silox)_3M(norbornene)$ (Silox = t-Bu_3SiO; M = Nb, Ta) and $(Silox)_3M(norbornylidene)$ as part of a study of isomerization of $(Silox)_3M(alkene)$ complexes to $(Silox)_3M(alkylidene)$ complexes via formation of intermediate alkyl complexes through CH activation in a Silox ligand.[19]

CONCLUSIONS

This first exploration of DFTO alkylidene complexes suggests that they can behave quite differently from complexes that contain superficially similar terphenoxides such as HMTO. $Mo(NR)(CHCMe_2Ph)(DFTO)_2$ complexes have no HMTO or HIPTO analogues and behave in a ROMP reaction as if the metal were chiral. Some observations can be ascribed to the electron-withdrawing ability of the DFTO ligand in combination with dramatic steric bulk. However, formation of *cis,isotactic*-poly(DCMNBD) from both MAP initiators **2b,c**, as well as apparently identical *cis* and highly tactic poly(norbornene) samples employing initiators **1c** and **2a**, suggest that the "rule" concerning formation of syndiotactic polymers from MAP initiators requires rethinking and testing. Finally, ROMP polymerization initiated by the ethylene complex **3** appears to proceed via an alkylidene formed from the monomer itself.

EXPERIMENTAL SECTION

General Considerations. All manipulations were conducted under a nitrogen atmosphere in a glovebox under nitrogen or through Schlenk techniques. All glassware was dried in an oven prior to use. Ether, pentane, toluene, dichloromethane, toluene, and benzene were degassed with dinitrogen and passed through activated alumina columns under nitrogen. All dried and deoxygenated solvents were stored over molecular sieves in a nitrogen- or argon-filled glovebox. NMR spectra were recorded on a 500 MHz spectrometer. Chemical shifts for ^1H spectra were referenced to the residual ^1H resonances of the deuterated solvent (^1H NMR C_6D_6 δ 7.16 ppm, $CDCl_3$ δ 7.26 ppm, toluene-d_8 7.09, 7.01, 6.97, 2.08 ppm; ^{13}C NMR C_6D_6 δ 128.06 ppm, $CDCl_3$ δ 77.16 ppm, toluene-d_8 20.43 ppm) and are reported as parts per million relative to tetramethylsilane. Midwest Microlab, Indianapolis, IN, provided elemental analyses. The following abbreviations refer to the multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. Other abbreviations include Ar′ = 2,6-$Me_2C_6H_3$, Ad = 1-adamantyl, and Ar = 2,6-i-$Pr_2C_6H_3$. $Mo(NC_6F_5)(CHCMe_2Ph)(OTf)_2(DME)$,[2] $Mo(NC_6F_5)(CHCMe_2Ph)(Me_2Pyr)_2$,[2] $Mo(NAr')(CHCMe_2Ph)(OTf)_2(DME)$,[3c] $Mo(NAr')(CHCMe_2Ph)(Me_2Pyr)_2$,[2] $Mo(NC_6F_5)(CHCMe_2Ph)(DFTO)_2$,[2] $Mo(NAd)(CHCMe_2Ph)(Me_2Pyr)_2$,[7a] and DFTOH[2] were prepared as described in the literature. All the other reagents were used as received unless noted otherwise.

$Mo(NAr)(CHCMe_2Ph)(DFTO)_2$ (1a). $Mo(NAr)(CHCMe_2Ph)(Me_2Pyr)_2$ (100 mg, 0.159 mmol) was dissolved in benzene (5 mL). DFTOH (136 mg, 0.320 mmol) was added at room temperature, and the mixture was heated at 100 °C for 16 h. The solvent was removed to give an orange oily product. The residue was recrystallized from a mixture of diethyl ether and pentane to give a yellow solid (174 mg, 87%): ^1H NMR (500 MHz, C_6D_6, 20 °C) δ 11.69 (s, 1H, Mo=CH), 6.97 (m, 3H), 6.84 (d, 8 Hz, 5H), 6.76 (d, $^3J_{HH}$ = 8 Hz, 2H), 6.68 (m, 4H), 1.90 (sept, $^3J_{HH}$ = 7 Hz, 2H), 1.36 (s, $^3J_{HH}$ = 6 Hz), 0.84 (s, 12H); ^{19}F NMR (282 MHz, C_6D_6, 20 °C) δ −137.8 (m, 4F), −139.2 (m, 4F), −154.6 (m, 4F), −161.2 (m, 4F), −161.7 (m, 4F); $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 20 °C) δ 288.7 (s, 1C, Mo=C), 164.5, 147.6, 14.7 (d, $^1J_{CF}$ = 252 Hz), 141.4 (d, $^1J_{CF}$ = 250 Hz), 138.3 (d, $^1J_{CF}$ = 254 Hz), 134.8, 133.5, 125.6 (d, 50 Hz), 124.3 (d, 52 Hz), 122.5, 121.2, 118.3, 113.0, 56.8, 29.3, 28.3. Anal. Calcd for $C_{58}H_{30}F_{20}MoNO_2$: C, 55.65; H, 2.81; N, 1.12. Found: C, 55.39; H, 2.93; N, 1.14.

$Mo(NAr')(CHCMe_2Ph)(DFTO)_2$ (1b). $Mo(NAr')(CHCMe_2Ph)(OTf)_2(DME)$ (Ar′ = 2,6-$Me_2C_6H_3$; 100 mg, 0.121 mmol) was suspended in toluene (5 mL), and the mixture was cooled to −30 °C. DFTOLi (110.4 mg, 0.255 mmol) was added at −30 °C, and the temperature was allowed to rise to 22 °C. After 1 h, the solvent was removed in vacuo, the dark oily residue was extracted with CH_2Cl_2, and the solvent was removed again in vacuo. Pentane (2 mL) was added and the mixture was stirred for 30 min. The resulting yellow precipitate was filtered off and dried in vacuo; yield 115 mg (79%) of a yellow solid; ^1H NMR (500 MHz, C_6D_6, 20 °C) δ 11.39 (s, 1H, Mo=CH), 6.91 (d, $^3J_{HH}$ = 7.5 Hz, 4H), 6.83 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 6.75 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 6.72 (m, 3H), 6.54 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 6.43 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 1.49 (s, 6H), 1.02 (s, 6H); ^{19}F NMR (282 MHz, C_6D_6, 20 °C) δ −138.9 (d, $^3J_{FF}$ = 23 Hz, 4F), −139.7 (d, $^3J_{FF}$ = 23 Hz, 4F), −154.7 (t, $^3J_{FF}$ = 23 Hz, 4F), −161.7 (m, 4F), −162.0 (m, 4F); $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6, 20 °C) δ 286.0 (s, 1C, Mo=C), 164.7, 156.3, 147.3, 144.7 (dm, $^1J_{CF}$ = 249 Hz), 141.5 (dm, $^1J_{CF}$ =

dx.doi.org/10.1021/om400199u | *Organometallics* 2013, 32, 2983−2992

252 Hz), 138.3 (dm, $^1J_{CF}$ = 252 Hz), 135.9, 125.5, 121.7, 117.8, 112.7 (m), 55.2, 29.5, 17.5. Anal. Calcd for $C_{54}H_{27}F_{20}MoNO_2$: C, 54.15; H, 2.27; N, 1.17. Found: C, 53.83; H, 1.96; N, 0.99.

Mo(NAd)(CHCMe$_2$Ph)(DFTO)$_2$ (1d). Mo(NAd)(CHCMe$_2$Ph)-(Me$_2$Pyr)$_2$ (100 mg, 0.177 mmol) was suspended in diethyl ether (5 mL). DFTOH (151 mg, 0.354 mmol) was added at room temperature. After 1 h, the solvent was removed to give a yellow oil. Pentane (1 mL) was added, and the mixture was stirred for 30 min. The yellow precipitate was filtered off and dried in vacuo to give a yellow solid (190 mg, 88%): ^{1}H NMR (500 MHz, C_6D_6, 20 °C) δ 11.08 (s, 1H, Mo=CH), 7.02 (m, 6H), 6.92 (t, $^3J_{HH}$ = 12 Hz, 1H), 6.77 (t, $^3J_{HH}$ = 12 Hz, 2H), 6.58 (d, $^3J_{HH}$ = 12 Hz, 2H), 1.57 (s, 2H), 1.14 (s, 6H), 1.08 (s, 6H), 0.97 (s, 6H); ^{19}F NMR (282 MHz, C_6D_6, 20 °C) δ −139.6 (m, 4F), −140.1 (m, 4F), −155.1 (t, $^3J_{FF}$ = 21 Hz, 4F), −162.1 (m, 4F), −162.5 (m, 4F); ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 20 °C) δ 280.0 (s, 1C, Mo=C), 162.967, 149.5, 144.7 (d, $^1J_{CF}$ = 247 Hz), 141.4 (d, $^1J_{CF}$ = 254 Hz), 138.2 (d, $^1J_{CF}$ = 247 Hz), 133.7 (m), 126.5, 121.6, 117.8, 115.0, 112.7, 78.8, 53.1, 50.1, 43.6 (m), 35.1 (m), 31.6, 29.7 (m). Anal. Calcd for $C_{56}H_{33}F_{20}MoNO_2$: C, 54.78; H, 2.71; N, 1.14. Found: C, 54.82; H, 2.61; N, 1.20.

Mo(NC$_6$F$_5$)(CHCMe$_2$Ph)(Me$_2$Pyr)(HMTO) (2a). Mo(NC$_6$F$_5$)-(CHCMe$_2$Ph)(Me$_2$Pyr)$_2$ (300 mg, 0.502 mmol) was dissolved in benzene (5 mL). HMTOH (183 mg, 0.557 mmol) was added, and the mixture was heated to 70 °C. After 16 h, the solvent was removed in vacuo to give a dark oily product. The residue was recrystallized from a mixture of pentane and diethyl ether to give an orange solid; yield 259 mg (60%): ^{1}H NMR (500 Hz, C_6D_6, 20 °C) δ 11.08 (s, 1H, Mo=CH), 7.24 (d, ^3J = 8 Hz, 2H), 6.94 (m, 3H), 6.88(m, 2H), 6.79 (s, 2H), 6.73 (s, 2H), 6.69 (m, 1H), 6.07 (s, 2H), 2.05 (d, J = 10.5 Hz, 12H), 1.98 (br, 12H), 1.36 (d, J = 11.3 Hz, 6H); ^{19}F NMR (282 Hz, C_6D_6, 20 °C) δ −145.7 (d, 2F, ^3J = 23 Hz, o-Ar), −159.4 (t, 1F, ^3J = 24 Hz, p-Ar), −165.0 (t, 2F, ^3J = 23 Hz, m-Ar); ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 20 °C) δ 295.3 (s, 1C, Mo=C), 157.9, 148.4, 143.0(d, $^1J_{CF}$ = 245 Hz), 139.4(d, $^1J_{CF}$ = 260 Hz), 136.9, 136.8, 136.4, 135.5 (d, $^1J_{CF}$ = 235 Hz), 135.2, 134.7, 131.9, 129.8, 129.1, 127.3, 126.0, 123.4, 109.7, 155.5, 34.4, 32.5, 28.6, 22.7, 21.1, 19.9, 16.8, 14.4. Anal. Calcd for $C_{46}H_{45}F_5MoN_2O_2$: C, 66.34; H, 5.45; N, 3.36. Found: C, 66.27; H, 5.49; N, 3.33.

Mo(NC$_6$F$_5$)(CHCMe$_2$Ph)(Me$_2$Pyr)(DFTO) (2b). Mo(NC$_6$F$_5$)-(CHCMe$_2$Ph)(Me$_2$Pyr)$_2$ (300 mg, 0.491 mmol) was dissolved in MeCN (10 mL), and DFTOH (209 mg, 0.491 mmol) was added as a solid at room temperature. After 16 h, the solvent was removed in vacuo to give an orange oily product. Diethyl ether (1 mL) was added, and the mixture was stirred for 30 min to give an orange solid of Mo(NC$_6$F$_5$)(CHCMe$_2$Ph)(Me$_2$Pyr)(DFTO)(MeCN) (356 mg, 75%). The solid was dissolved in toluene, and the solvent was removed in vacuo. This step was repeated 10 times to remove MeCN and give **2b** as a red foam (341 mg): ^{1}H NMR (500 MHz, C_6D_6, 20 °C) δ 11.64 (br, 1H, Mo=CH), 7.13 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 6.99 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 6.88 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 6.79 (brt, $^3J_{HH}$ = 7 Hz, 2H), 6.60 (brt, $^3J_{HH}$ = 7 Hz, 1H), 5.68 (br, 2H), 2.01 (br, 6H), 1.29 (br, 3H), 1.05 (s, 3H); ^{19}F NMR (282 MHz, C_6D_6, 20 °C) δ −140.0 (br, 2F), −140.4 (br, 2F), −148.0 (d, $^3J_{FF}$ = 20 Hz, 2F), −154.7 (br, 2F), −156.5 (t, $^3J_{FF}$ = 20 Hz, 1F), −162.1 (br, 2F), −162.8 (br, 2F), −163.8 (m, 2F); ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 20 °C) δ 298.8 (br, Mo=C), 165.3, 147.6, 144.6 (dm, $^1J_{CF}$ = 246 Hz), 142.8 (dm, $^1J_{CF}$ = 241 Hz), 141.4 (dm, $^1J_{CF}$ = 246 Hz), 140.5 (dm, $^1J_{CF}$ = 246 Hz), 138.4 (dm, $^1J_{CF}$ = 249 Hz), 137.4 (dm, $^1J_{CF}$ = 251 Hz), 133.9, 133.6, 131.3 (t, 15 Hz), 126.7, 126.4, 122.1, 117.7, 112.3, 110.2, 55.7, 29.1, 15.7 (br); ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C) δ 11.59 (br, 1H, Mo=CH), 7.37 (d, $^3J_{HH}$ = 7 Hz, 2H), 7.19 (t, $^3J_{HH}$ = 8 Hz, 1H), 7.12 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 7.06 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 6.93 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 5.73 (br, 2H), 2.00 (br, 6H), 1.41 (s, 3H), 1.25 (s, 3H); ^{19}F NMR (282 MHz, $CDCl_3$, 20 °C) δ −139.4 (br, 2F), −140.1 (br, 2F), −147.2 (d, $^3J_{FF}$ = 20 Hz, 2F), −154.4 (br, 2F), −155.8 (t, $^3J_{FF}$ = 20 Hz, 1F), −161.9 (br, 2F), −162.5 (br, 2F), −163.3 (m, 2F). The foamlike solid was recrystallized from a mixture of acetonitrile, diethyl ether, and pentane to give analytically pure orange crystals of Mo(NC$_6$F$_5$)-(CHCMe$_2$Ph)(Me$_2$Pyr)(DFTO)(MeCN)(Et$_2$O)$_{0.5}$: ^{1}H NMR (500 MHz, C_6D_6, 20 °C) δ 12.13 (br, 1H, Mo=CH), 7.08 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 7.01 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 6.83 (t, $^3J_{HH}$ = 7.5 Hz, 3H), 6.67 (brt, $^3J_{HH}$ = 7 Hz, 1H), 5.83 (br, 2H), 3.25 (q, $^3J_{HH}$ = 7 Hz, 2H), 2.06 (br, 6H), 1.30 (s, 3H), 1.19 (s, 3H), 1.12 (t, $^3J_{HH}$ = 7 Hz, 3H), 0.62 (br, 3H); ^{19}F NMR (282 MHz, C_6D_6, 20 °C) δ −140.3 (br, 4F), −147.9 (d, $^3J_{FF}$ = 20 Hz, 2F), −154.9 (br, 2F), −156.1 (t, $^3J_{FF}$ = 20 Hz, 1F), −162.1 (br, 2F), −162.7 (br, 2F), −163.7 (m, 2F). Anal. Calcd for $C_{44}H_{31}F_{15}MoN_3O_{1.5}$: C, 52.50; H, 3.10; N, 4.17. Found: C, 52.82; H, 3.29; N, 4.04.

Mo(NAr′)(CHCMe$_2$Ph)(Me$_2$Pyr)(DFTO) (2c). Mo(NAr′)-(CHCMe$_2$Ph)(Me$_2$Pyr)$_2$ (130 mg, 0.242 mmol) was suspended in toluene (5 mL). The suspension was cooled to −30 °C, and DFTOH (103 mg, 0.242 mmol) was added at −30 °C. The mixture was warmed to room temperature. After 1 h, the solvent was removed in vacuo to give a dark red oily product. Pentane (2 mL) was added, the mixture was stirred for 30 min to give a homogeneous reddish solution, and MeCN (3 drops) was added. The brownish precipitate was recrystallized from a mixture of ether and pentane to give **2c** as a yellow solid; yield 162 mg (76%): ^{1}H NMR (500 MHz, C_6D_6, 20 °C) δ 12.08 (s, 1H, Mo=CH), 7.13 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 6.99 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 6.91 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 6.88 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 6.82 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 6.61 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 6.53 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 5.85 (br, 2H), 1.93 (br, 6H), 1.69 (br, 6H), 1.30 (s, 3H), 1.24 (s, 3H); ^{19}F NMR (282 MHz, C_6D_6, 20 °C) δ −139.8 (dm, $^3J_{FF}$ = 23 Hz, 2F), −140.6 (dm, $^3J_{FF}$ = 23 Hz, 2F), −153.9 (t, $^3J_{FF}$ = 23 Hz, 2F), −161.7 (m, 4F); ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, 20 °C) δ 294.6 (s, 1C, Mo=C), 164.9, 155.8, 147.2, 144.7 (dm, $^1J_{CF}$ = 242 Hz), 141.2 (dm, $^1J_{CF}$ = 252 Hz), 138.2(dm, $^1J_{CF}$ = 247 Hz), 133.7 (d, J_{CF} = 22 Hz), 121.8, 117.6, 115.9, 112.5, 109.9 (br), 100.9, 55.2, 30.6, 17.6, 14.2. Crystals of **2c′**, the MeCN adduct, were obtained from a mixture of diethyl ether and MeCN. Anal. Calcd for $C_{42}H_{32}F_{10}MoN_2O$: C, 58.22; H, 3.89; N, 4.64. Found: C, 58.51; H, 4.19; N, 4.26.

Mo(NC$_6$F$_5$)(CH$_2$CH$_2$)(DFTO)$_2$ (3). Mo(NC$_6$F$_5$)(CHCMe$_2$Ph)-(DFTO)$_2$ (138 mg, 0.119 mmol) was dissolved in ether (10 mL). The Schlenk bomb was freeze−pump−thawed three times. Ethylene (1 atm) was added. After the mixture was stirred at room temperature for 16 h, the orange solution turned dark purple. The solvent was removed, and pentane (1 mL) was added. The mixture was stirred to 30 min to give a purple solid, cooled to −30 °C overnight, and filtered. The purple solid was washed with cold pentane and dried in vacuo; yield 105 mg (76%): ^{1}H NMR (500 MHz, tol-d_8, 20 °C) δ 6.95 (d, ^3J = 8 Hz, 4H), 6.78 (t, ^3J = 8 Hz, 2H), 2.48 (dt, J = 8 Hz, J = 5 Hz, 2H, CH$_2$=CH$_2$), 1.33 (dt, J = 8 Hz, J = 5 Hz, 2H, CH$_2$=CH$_2$); ^{19}F NMR (282 MHz, tol-d_8, 20 °C) δ −140.7 (d, $^3J_{FF}$ = 22 Hz, 8F, o-F), −150.7 (d, $^3J_{FF}$ = 25 Hz, 2F, o-F of NC$_6$F$_5$), −154.8 (m, 5F), −162.3 (m, 10F); ^{13}C{^{1}H} NMR (125 MHz, tol-d_8, 20 °C) δ 161.5, 144.4 (dm, $^1J_{CF}$ = 246 Hz, 8C, DFTO), 142.9 (dm, $^1J_{CF}$ =253 Hz, 2C, NC$_6$F$_5$), 141.2 (dm, $^1J_{CF}$ = 255 Hz, 4C, DFTO), 140.5 (dm, $^1J_{CF}$ = 255 Hz, 1C, NC$_6$F$_5$), 138.2 (dm, $^1J_{CF}$ = 253 Hz, 8C, DFTO), 137.3 (dm, $^1J_{CF}$ = 255 Hz, 2C, NC$_6$F$_5$), 133.8 (m), 122.5 (m), 118.2, 112.3 (td, 9 Hz, 4 Hz), 61.1 (CH$_2$=CH$_2$); ^{1}H NMR (500 MHz, tol-d_8, −80 °C) δ 7.05 (br, 4H), 6.81 (br, 2H), 2.60 (br, 1H), 2.19 (br, 1H), 1.85 (br, 1H), 0.81 (br, 1H); ^{19}F NMR (282 MHz, tol-d_8, −80 °C) δ −140.0 (1F), −141.2 (1F), −142.1 (1F), −142.3 (1F), −143.3 (4F), −151.5 (1F), −152.0 (2F), −154.5 (2F), −154.8 (2F), −159.7 (1F), −161.4 (1), −162.4 (5F), −163.5 (2F), −164.2 (1F). Anal. Calcd for $C_{44}H_{10}F_{25}MoNO_2$: C, 45.74; H, 0.87; N, 1.21. Found: C, 45.79; H, 1.06; N, 1.26.

Mo(NC$_6$F$_5$)(CH$_2$CH$_2$)(DCMNBD)(DFTO)$_2$ (5). Mo(NC$_6$F$_5$)-(CH$_2$=CH$_2$)(DFTO)$_2$ (40 mg, 0.0341 mmol) was dissolved in C_6D_6 (0.5 mL). DCMNBD (7.1 mg, 0.0341 mol) was added as a solution in C_6D_6 (0.071 mL, 100 mg/mL). After 16 h, reddish orange crystals were formed (27 mg, 57%): ^{1}H NMR (500 MHz, C_6D_6, 20 °C) δ 7.16 (d, J = 8 Hz, 2H), 7.10 (br, 2H), 6.89 (br, 2H), 6.79 (br, 1H), 6.72 (t, J = 8 Hz, 1H), 3.91 (s, 1H), 3.85 (s, 1H), 3.73 (s, 3H), 3.07 (td, J = 12 Hz, J = 4 Hz, 1H, CH$_2$=CH$_2$), 2.72 (td, J = 12 Hz, J = 4 Hz, 1H, CH$_2$=CH$_2$), 2.39 (s, 3H, OMe), 2.45 (d, 8 Hz, 1H), 1.94 (d, 8 Hz, 1H), 1.77 (td, J = 12 Hz, J = 4 Hz, 1H, CH$_2$=CH$_2$), 1.43 (td, J = 12 Hz, J = 4 Hz, 1H, CH$_2$=CH$_2$); ^{19}F NMR (282 MHz, C_6D_6,

dx.doi.org/10.1021/om400199u | Organometallics 2013, 32, 2983−2992

20 °C) δ −133.3 (br, 1F), −137.3 (br, 1F), −140.9 (s, 2F), −145.3 (br, 1F), −150.5 (s, 1F), −151.5 (s, 1F), −152.0 (s, 1F), 154.6 (s, 1F), −156.2 (s, 1F), −157.0 (m, 2F), −158.9 (br, 2F), −162.3 (bs, 4F), −163.9 (m, 4F). Compound **5** slowly decomposes in the solid state at room temperature and therefore could not be analyzed.

Observation of Mo(NC$_6$F$_5$)(^{13}CH$_2$^{13}CH$_2$^{13}CH$_2$)(DFTO)$_2$ (4*). Mo(NC$_6$F$_5$)(CHCMe$_2$Ph)(DFTO)$_2$ (10 mg) was dissolved in C$_6$D$_6$ (0.5 mL) in a J. Young NMR tube. The solution was freeze−pump−thawed three times. ^{13}CH$_2$=^{13}CH$_2$ (<1 atm) was added. After 5 min, all of the starting material was consumed and **4*** was formed in addition to Mo(NC$_6$F$_5$)(^{13}CH$_2$^{13}CH$_2$^{13}CH$_2$)(DFTO)$_2$: ^{1}H NMR (500 MHz, C$_6$D$_6$, 20 °C) δ 3.67 (brd, J_{CH} = 165 Hz, 2H, α-H), 3.55 (brd, J_{CH} = 155 Hz, 2H, α-H), −0.72 (brd, J_{CH} = 154 Hz, 1H, β-H), −1.33 (brd, J_{CH} = 154 Hz, 1H, β-H); ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 20 °C) δ 102.5 (C$_\alpha$), −3.1 (C$_\beta$).

Mo(NC$_6$F$_5$)(^{13}CH$_2$^{13}CH$_2$^{13}CH$_2$^{13}CH$_2$)(DFTO)$_2$ (Observation). Mo(NC$_6$F$_5$)(^{13}CH$_2$^{13}CH$_2$)(DFTO)$_2$ (10 mg, 0.00852 mmol) was dissolved in C$_6$D$_6$ (0.5 mL) in a J. Young NMR tube. The solution was freeze−pump−thawed three times. ^{13}CH$_2$=^{13}CH$_2$ was added through vacuum transfer. After 2 days, about 1% ^{13}C-labelled Mo(NC$_6$F$_5$)-(^{13}CH$_2$^{13}CH$_2$^{13}CH$_2$^{13}CH$_2$)(DFTO)$_2$ was formed: ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 20 °C) δ 82.9 (m, AA′BB′, C$_\alpha$), 39.9 (m, AA′BB′, C$_\beta$).

Mo(NC$_6$F$_5$)(^{13}CH$_2$^{13}CH$_2$-norbornene)(DFTO)$_2$ (Observation). Mo(NC$_6$F$_5$)(^{13}CH$_2$^{13}CH$_2$)(DFTO)$_2$ (10 mg, 0.00852 mmol) was dissolved in toluene-d_8 (0.5 mL) in a septum-capped tube and cooled to −78 °C. Norbornene (0.8 mg, 0.00852 mmol) was added as a solution in toluene-d_8 (0.5 mL) drop by drop. The NMR tube was inserted into a −70 °C NMR. After 1 h, 69% of the product was formed: ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 20 °C) δ 84.7 (d, $^1J_{CC}$ = 37 Hz, MoC$_\alpha$), 46.6 ppm (d, $^1J_{CC}$ = 37 Hz, C$_\beta$).

Mo(NC$_6$F$_5$)(CHCHCMePh)(DFTO)$_2$ (Observation). Mo(NC$_6$F$_5$)-(CH$_2$CH$_2$)(DFTO)$_2$ (10 mg, 0.00853 mmol) was dissolved in toluene (4 mL), and the solution was cooled to −78 °C. MPCP (1.11 mg, 0.00853 mmol) was added dropwise as a solution in toluene (1 mL). The purple color changed to orange immediately. After 1 h, the mixture was warmed to room temperature and the solvent removed to give an oily orange product (12 mg): ^{1}H NMR (500 MHz, C$_6$D$_6$, 20 °C) δ 12.10 (dd, $^1J_{CH}$ = 130 Hz, $^3J_{HH}$ = 9 Hz, MoCH), 8.33 (dd, $^1J_{CH}$ = 159 Hz, $^3J_{HH}$ = 9 Hz, β-H), the other resonances overlap with polymer resonances; ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 20 °C) δ 264.5 (s, C$_\alpha$), 136.0 (s, C$_\beta$).

Procedure for ROMP of DCMNBD. The initiator (1 mg) was dissolved in CDCl$_3$ (0.5 mL). DCMNBD (100 equiv) was added as a solution in CDCl$_3$ (0.5 mL). After 30 min, benzaldehyde (0.1 mL) was added to the mixture. The reaction mixture became deep green within 5 min and was stirred for 1 h. The entire mixture was added dropwise to 100 mL of vigorously stirred methanol. A fine white solid formed immediately. After 2 h the polymer was filtered off, rinsed with MeOH, and dried in vacuo.

Measurement of Conversion of DCMNBD by 3. DCMNBD (50 mg, 0.240 mmol) and an internal standard of anthracene were dissolved in CDCl$_3$ in a J. Young NMR tube. A ^{1}H NMR spectrum was obtained. A 12.0 mM solution of **3** was prepared, and 0.2 mL (2.4 μmol) was added to the NMR tube. The tube was inverted to mix, and the tube was then heated to 50 °C. ^{1}H NMR spectra were obtained over 120 h. Conversion was measured by integration of the olefinic resonance of DCMNBD against the anthracene internal standard.

■ ASSOCIATED CONTENT

Supporting Information

Figures S1−S3 and text, tables, and CIF files giving crystallographic details and data for **2b′**, **3**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for R.R.S.: rrs@mit.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

R.R.S. thanks the National Science Foundation (CHE-1111133) and the Department of Energy (DE-FG02-86ER13564) for supporting this research. The Department of Chemistry thanks the NSF (CHE-9808061) for funds to purchase a 500 MHz NMR instrument and an X-ray diffractometer (CHE-0946721).

■ REFERENCES

(1) (a) Schrock, R. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 3748. (b) Grubbs, R. H. *Angew. Chem., Int. Ed.* **2006**, *45*, 3760. (c) *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, Germany, 2003; Vols. *1*−*3*. (d) Schrock, R. R. *Chem. Rev.* **2009**, *109*, 3211.

(2) Yuan, J.; Schrock, R. R.; Müller, P.; Axtell, J. C.; Dobereiner, G. E. *Organometallics* **2012**, *31*, 4650.

(3) (a) Ibrahem, I.; Yu, M.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 3844. (b) Flook, M. M.; Jiang, A. J.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 7962. (c) Jiang, A. J.; Zhao, Y.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 16630. (d) Flook, M. M.; Gerber, L. C. H.; Debelouchina, G. T.; Schrock, R. R. *Macromolecules* **2010**, *43*, 7515. (e) Flook, M. M.; Ng, V. W. L.; Schrock, R. R. *J. Am. Chem. Soc.* **2011**, *133*, 1784. (f) Meek, S. J.; O'Brien, R. V.; Llaveria, J.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2011**, *471*, 461. (g) Marinescu, S. C.; Schrock, R. R.; Müller, P.; Takase, M. K.; Hoveyda, A. H. *Organometallics* **2011**, *30*, 1780. (h) Yu, M.; Ibrahem, I.; Hasegawa, M.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2012**, *134*, 2788. (i) Townsend, E. M.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2012**, *134*, 11334. (j) Wang, C.; Yu, M.; Kyle, A. F.; Jacubec, P.; Dixon, D. J.; Schrock, R. R.; Hoveyda, A. H. *Chem. Eur. J.* **2013**, *19*, 2726. (k) Wang, C.; Haeffner, F.; Schrock, R. R.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2013**, *52*, 1939. (l) Flook, M. M.; Börner, J.; Kilyanek, S.; Gerber, L. C. H.; Schrock, R. R. *Organometallics* **2012**, *31*, 6231.

(4) Schrock, R. R. *Dalton Trans.* **2011**, *40*, 7484.

(5) Marinescu, S. C.; Ng, V. W. L.; Lichtscheidl, A. G.; Schrock, R. R.; Müller, P.; Takase, M. K. *Organometallics* **2012**, *31*, 6336.

(6) Addison, A. W.; Rao, T. J.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

(7) (a) Marinescu, S. C.; Singh, R.; Hock, A. S.; Wampler, K. M.; Schrock, R. R.; Müller, P. *Organometallics* **2008**, *27*, 6570. (b) Jiang, A. J.; Simpson, J. H.; Müller, P.; Schrock, R. R. *J. Am. Chem. Soc.* **2009**, *131*, 7770. (c) Marinescu, S. C.; Schrock, R. R.; Li, B.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 58.

(8) (a) Jiang, A. J.; Schrock, R. R.; Müller, P. *Organometallics* **2008**, *27*, 4428. (b) Marinescu, S. C.; King, A. J.; Schrock, R. R.; Singh, R.; Müller, P.; Takase, M. K. *Organometallics* **2010**, *29*, 6816. (c) Tsang, W. C. P.; Jamieson, J. Y.; Aeilts, S. A.; Hultzsch, K. C.; Schrock, R. R.; Hoveyda, A. H. *Organometallics* **2004**, *23*, 1997.

(9) Tsang, W. C. P.; Jamieson, J. Y.; Aeilts, S. A.; Hultzsch, K. C.; Schrock, R. R.; Hoveyda, A. H. *Organometallics* **2004**, *23*, 1997.

(10) McConville, D. H.; Wolf, J. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 4413.

(11) O'Donoghue, M. B.; Schrock, R. R.; LaPointe, A. M.; Davis, W. M. *Organometallics* **1996**, *15*, 1334.

(12) Singh, R. Ph.D. thesis, Massachusetts Institute of Technology, 2008.

(13) Ivin, K. H.; Laverty, D. T.; Rooney, J. J. *Makromol. Chem.* **1977**, *178*, 1545.

(14) Binger, P.; Müller, P.; Benn, R.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 610.

(15) (a) De la Mata, F. J.; Grubbs, R. H. *Organometallics* **1996**, *15*, 577. (b) Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 8130.

(16) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974.
(17) (a) Schrock, R. R.; Lopez, L. P. H.; Hafer, J.; Singh, R.; Sinha, A.; Müller, P. *Organometallics* **2005**, *24*, 5211. (b) Schrock, R. R.; Duval-Lungulescu, M.; Tsang, W. C. P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2004**, *126*, 1948.
(18) Bencze, L.; Bíró, N.; Szabó-Ravasz, B.; Mihichuk, L. *Can. J. Chem.* **2004**, *82*, 499.
(19) Hirsekorn, K. F.; Veige, A. S.; Marshak, M. P.; Koldobskaya, Y.; Wolczanski, P. T.; Cundari, T. R.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **2005**, *127*, 4809.