Synthesis of Five- and Six-Coordinate Alkylidene Complexes of the Type Mo(CHR)(NAr)[OCMe(CF$_3$)$_2$]$_2$S$_x$ and Their Use as Living ROMP Initiators or Wittig Reagents

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Received October 13, 1992

Addition of a slight excess of 4-methoxy-1-hexene to Mo(CHCMe$_2$Ph)(NAr)(OR$_{F6}$)$_2$ (**1a**) or Mo(CHCMe$_3$)(NAr)(OR$_{F6}$)$_2$ (**1b**) in pentane (OR$_{F6}$ = OCMe(CF$_3$)$_2$) yielded crystalline, red-orange *anti*-Mo[CHCH$_2$CH(OMe)CH$_2$CH$_3$](NAr)(OR$_{F6}$)$_2$ (**2**). A similar reaction was used to prepare the difunctional complex *anti*-[(ArN)(OR$_{F6}$)$_2$Mo=CHCH$_2$CH(OMe)]$_2$C$_6$H$_4$ (**3**). Styrene reacts with **1a** or **1b** in DME over a period of 12 h to afford orange *syn*-Mo(CHPh)(NAr)-(OR$_{F6}$)$_2$(DME) (**4**) in good yield. 4-(Dimethylamino)styrene and 2,4,6-trimethoxystyrene react analogously to yield dark red *syn*-Mo(CH-4-C$_6$H$_4$-NMe$_2$)(NAr)(OR$_{F6}$)$_2$ (DME) (**5**) and red *anti*-Mo[CH-2,4,6-C$_6$H$_2$-(OMe)$_3$](NAr)(OR$_{F6}$)$_2$(DME) (**6**). **4** also can be synthesized from Mo-(NAr)$_2$Cl$_2$(DME) via Mo(NAr)$_2$(CH$_2$Ph)$_2$ and Mo(CHPh)(NAr)(OTf)$_2$(DME). The reaction between 1 and 0.5 equiv of octatetraene in DME afforded *syn*-(DME)(R$_{F6}$O)$_2$(ArN)Mo(CH)$_6$-Mo(NAr)(OR$_{F6}$)$_2$(DME) (**9a**). A related complex, *syn*-(Et$_2$O)(R$_{F6}$O)$_2$(ArN)Mo(CH)$_6$Mo(NAr)-(OR$_{F6}$)$_2$(Et$_2$O) (**9b**), could be prepared directly in diethyl ether or by dissolving **9a** in diethyl ether. *anti*-(THF)(R$_{F6}$O)$_2$(ArN)Mo(CH)$_6$Mo(NAr)(OR$_{F6}$)$_2$(THF) (**9c**) was observed upon dissolving **9a** in THF. Addition of 4 equiv of LiO-*t*-Bu and 2 equiv of quinuclidine (quin) to **9a** yields metallic green (quin)(*t*-BuO)$_2$(ArN)Mo(CH)$_6$Mo(NAr)(O-*t*-Bu)$_2$(quin) (**9d**). 1,4-Divinylbenzene reacts smoothly with **1a** or **1b** to give another conjugated difunctional alkylidene complex, 1,4-[(DME)(R$_{F6}$O)$_2$(ArN)MoCH]$_2$C$_6$H$_4$ (**10a**). Mo(CH$_2$)(NAr)(OR$_{F6}$)$_2$(DME) (**11a**) could be generated and observed by ^{1}H NMR upon adding an excess of ethylene to a solution of **1b** in DME-d_{10} in a septum-sealed NMR tube. Addition of 2,2′-bipyridine (bpy) to **11a** yielded isolable Mo(CH$_2$)(NAr)(OR$_{F6}$)$_2$(bpy) (**11b**). 2,3-Dicarbomethoxynorbornadiene (100 equiv) could be polymerized in a living manner in DME using **1b**, **4**, **5**, **9a**, **9b**, or **10a** as the initiator. 2,3-Bis(trifluoromethyl)norbornadiene (100 equiv) was also polymerized in a living manner by **1a** in DME. Addition of an excess of LiO-*t*-Bu (8 equiv) to a solution of **3** in toluene, followed by 200 equiv of methyltetracyclododecene (MTD), gave low-polydispersity poly-MTD (M_w/M_n = 1.03) in 93% yield. Complexes **4**, **5**, **9a**, **9b**, and **10a** react cleanly with pivaldehyde or benzaldehyde in CD$_2$Cl$_2$ or DME. A combination of Wittig reactions was used to prepare the di-*tert*-butyl-capped polyenes (*t*-Bu)(CH=CH)$_n$(*t*-Bu) (n = 4, 6, 8). The techniques described here should expand the opportunities for making polymers via living ROMP reactions and, in particular, should allow one to introduce conjugated sequences with a known, fixed length into a variety of polymers and to attach functional groups to both ends of a polymer.

Introduction

Alkylidene complexes of the type M(CHR)(NAr)(OR′)$_2$ (M = Mo,[1,2] W;[3] Ar = 2,6-diisopropylphenyl) are readily accessible, well-defined metathesis catalysts. (The Mo-(CHCMe$_2$Ph)(NAr)(O-*t*-Bu)$_2$ catalyst is now commercially available from Strem Chemicals, Inc.) When OR′ = O-*t*-Bu, these catalysts do not react rapidly with ordinary internal olefins but do react rapidly with norbornenes and norbornadienes. Therefore, they are useful initiators for living ring-opening metathesis polymerization (ROMP)[4] reactions to give polymers in which the initial alkylidene ligand is introduced at the beginning of the polymer chain.[5-7] For example, Mo(CHFc)(NAr)(O-*t*-Bu)$_2$ (Fc = ferrocenyl) has been used to prepare redox-active polymers with redox-active end groups.[8] Since polymerizations can be terminated in a Wittig-like capping reaction with a functionalized benzaldehyde,[9] it is now possible, in theory, to control the nature of the groups at both ends of a ROMP polymer, including polyenes.[10-12] Such control is crucial to the synthesis of potentially interesting materials such

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as push–pull polyenes.[13-15] Therefore, it is important to develop routes to new alkylidene initiators for living polymerization reactions. A potential secondary benefit is that initiators other than a neopentylidene or neophylidene complex may have a lower ratio of the rate of propagation to the rate of initiation.[6,7,16-18] Finally, it would be desirable in some circumstances to develop a difunctional (bimetallic) initiator in order to synthesize a polymer by growing the polymer chain in two directions at the same time.[19]

The most straightforward way to prepare new monosubstituted alkylidene complexes of the same basic type is via a metathesis reaction between a neopentylidene or neophylidene complex and a terminal olefin. It is most desirable that the metathesis reaction be essentially quantitative and relatively fast and that the new alkylidene complex be stable and isolable. *tert*-Butoxide complexes are not suitable in general since they react only slowly with terminal olefins and the new monosubstituted alkylidene complexes are often unstable. Hexafluoro-*tert*-butoxide complexes are much more reactive,[20] but living polymerization of a norbornene or disubstituted norbornadiene requires that metathesis of the disubstituted double bonds in the polymer chain be slow on the time scale of polymerization. Therefore, conditions must be found where a new alkylidene complex can be prepared readily in a metathesis reaction but remains useful for a living polymerization reaction.

Four-coordinate alkylidene complexes are inherently unstable toward bimolecular decomposition.[21] Five- or six-coordinate base adducts are much more stable[22] but also much less reactive.[22-24] For example, quinuclidine has been used to stabilize unsubstituted vinyl alkylidene complexes such as *cis*- and *trans*-M(CHCH=CHMe)(NAr)(OR_{F6})$_2$(quinuclidine) (M = Mo, W; OR_{F6} = OCMe(CF_3)$_2$).[22] Adducts of methylene complexes can be observed, e.g., W(CH_2)(NAr)(OR_{F6})$_2$(PMe_3),[25,26] W(CH_2)(NAr)[OC(CF_3)$_2$($CF_2CF_2CF_3$)]$_2$(PMe_3),[25,26] and Mo(CH_2)(NAr)(OR_{F6})$_2$(PMe_3).[27] Intramolecular coordination of a base also can be an effective means of stabilizing alkylidene complexes. For example, W(CH-*o*-C_6H_4-OMe)(NAr)(OR_{F6})$_2$(THF) is stabilized by both intramolecular and intermolecular base coordination.[28] Coordinating solvents such as THF are also basic enough to temper the metathetic activity of these complexes toward internal olefins, especially complexes that contain more electron-withdrawing alkoxides.[23,24] Since a neopentylidene or neophylidene complex might not coordinate a donor ligand as strongly as a complex containing a relatively small alkylidene,[29] a metathesis reaction between a neophylidene or neopentylidene complex and a terminal olefin in the presence of a weakly coordinating base might yield a stable new alkylidene complex that would then not react readily with internal olefinic bonds of the type found in polymers prepared by ROMP. One might expect benzylidene complexes to be among the more stable and easily made in a metathetical reaction, and the ready availability of functionalized styrenes would allow one to prepare a variety of functionalized benzylidene complexes. W(CH-*t*-Bu)(NAr)(OR_{F6})$_2$ is known to react with *cis*-β-methylstyrene to yield W(CHPh)(NAr)(OR_{F6})$_2$[25] as a crystalline, isolable material, but the analogous Mo complex, Mo(CHPh)(NAr)[$OCMe_2(CF_3)$]$_2$, although it could be observed in situ,[2] could not be isolated.[30] Molybdenum benzylidene complexes also are generated in situ when styrene is employed as a chain transfer reagent in ROMP reactions, terminating the polymerization and regenerating the catalyst.[31] A molybdenum *tert*-butyl imido benzylidene complex also has been reported.[32]

In this paper we report the synthesis of a number of new Mo(VI) alkylidene hexafluoro-*tert*-butoxide complexes that are stabilized by external or internal Lewis base coordination, including several difunctional alkylidene complexes. We also demonstrate the utility of the alkylidene complexes prepared in this work for ROMP in dimethoxyethane (DME) and Wittig-like reactions with aldehydes, and show that hexafluoro-*tert*-butoxide complexes can be converted into *tert*-butoxide catalysts in situ in order to take advantage of the mild nature of *tert*-butoxide catalysts for living ROMP reactions.

Results and Discussion

Synthesis of New Alkylidene Complexes. Addition of a slight excess of 4-methoxy-1-hexene to a solution of yellow Mo($CHCMe_2Ph$)(NAr)(OR_{F6})$_2$ (**1a**) or Mo($CHCMe_3$)(NAr)(OR_{F6})$_2$ (**1b**) in pentane (OR_{F6} = OCMe(CF_3)$_2$) yields crystalline, red-orange Mo[$CHCH_2CH(OMe)CH_2CH_3$](NAr)(OR_{F6})$_2$ (**2**) in good yield (eq 1). A related difunctional alkylidene complex (**3**; eq 2) can be prepared in a similar manner in 2 h from **1a** and the appropriate α,ω-diene. NMR data for **2** and **3** and other alkylidene complexes described later are summarized in Table I. NMR spectra of **2** and **3** suggest that no plane of symmetry is present in either complex, and the J_{CH_α} value (158 Hz) suggests that the alkylidene is the anti rotamer[2,22] in each case. The structure shown in eq 1 (or a related square-pyramidal species containing an axial imido ligand) is consistent with these data. To our knowledge, no five-coordinate complex of this type has been structurally characterized, although six-coordinate W(CH-*o*-C_6H_4-OMe)(NAr)(OR_{F6})$_2$(THF) has been shown to have a structure related to that shown in eq 1 in which the THF

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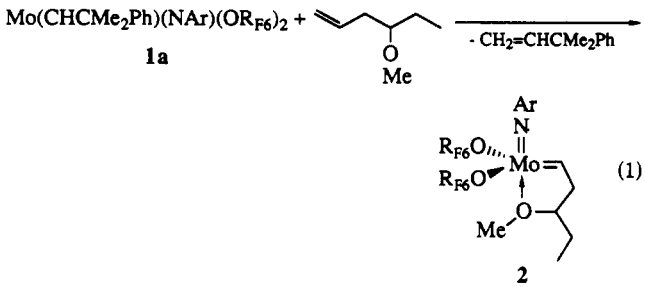
Table I. Selected ^1H and ^{13}C NMR Data for Mo(VI) Alkylidene Complexes

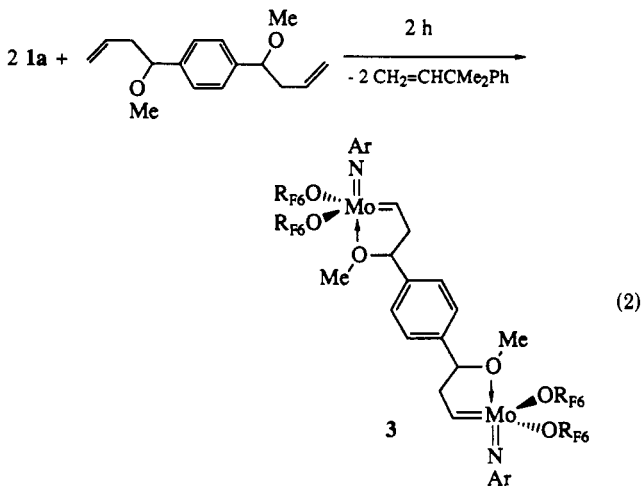
alkylidene complex	$\delta(H_\alpha)^a$	$\delta(C_\alpha)^a$	$^1J_{CH}$ (Hz)
$Mo(CHCMe_2Ph)(NAr)(OR_{F6})_2$ (**1a**)[b]	12.12	284.9	121
$Mo(CHCMe_3)(NAr)(OR_{F6})_2$ (**1b**)[b]	12.06	288.2	117
$Mo(CHCH_2CH(OMe)CH_2Me)(NAr)(OR_{F6})_2$ (**2**)	12.35	273.0	157
$[(R_{F6}O)_2(ArN)MoCHCH_2CH(OMe)]_2C_6H_4$ (**3**)	12.38	272.2	158
$Mo(CHPh)(NAr)(OR_{F6})_2(DME)$ (**4**)	12.95	271.7	126
$Mo[CH\text{-}4\text{-}C_6H_4(NMe_2)](NAr)(OR_{F6})_2(DME)$ (**5**)	12.60	269.2	124
$Mo[CH\text{-}2,4,6\text{-}C_6H_2(OMe)_3](NAr)(OR_{F6})_2(DME)$ (**6**)	13.16	255.7	159
$Mo(CHPh)(NAr)(OTf)_2(DME)$ (**8**)	15.05, 14.44	315.3, 308.4	131, 127
$(DME)(R_{F6}O)_2(ArN)Mo(CH)_6Mo(NAr)(OR_{F6})_2(DME)$ (**9a**)	12.53	267.5	127
$(Et_2O)(R_{F6}O)_2(ArN)(Mo(CH)_6Mo(NAr)(OR_{F6})_2(OEt_2)$ (**9b**)	12.53	267.4	132
$(THF)(R_{F6}O)_2(ArN)Mo(CH)_6Mo(NAr)(OR_{F6})_2(THF)$ (**9c**)	12.41	271.5	152
$(quin)(t\text{-}BuO)_2(ArN)Mo(CH)_6Mo(NAr)(O\text{-}t\text{-}Bu)_2(quin)$ (**9d**)[c]	11.70	255.5	
$1,4\text{-}\{(DME)(R_{F6}O)_2(ArN)MoCH\}_2C_6H_4$ (**10a**)[d]	12.94	279.1	125
$1,4\text{-}\{(THF)(R_{F6}O)_2(ArN)MoCH\}_2C_6H_4$ (**10b**)[c]	12.93		124
$Mo(CH_2)(NAr)(OR_{F6})_2(DME)$ (**11a**)[d]	12.56, 11.99		(J_{HH} = 6.0)
$Mo(CH_2)(NAr)(OR_{F6})_2(bpy)$ (**11b**)	13.26, 12.92	285.5	139 (J_{HH} = 3.9)

[a] Chemical shifts reported in CD_2Cl_2 unless otherwise noted. [b] In C_6D_6. [c] In THF-d_8. [d] Observed in situ in DME-d_{10}.

is bound trans to the W=C bond.[28] Five-coordinate monoadducts of imido alkylidene complexes of this type



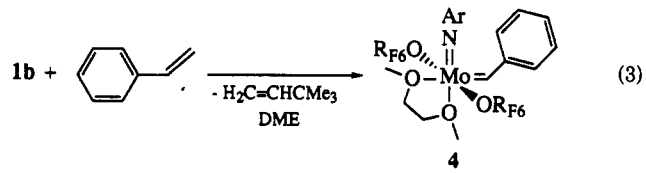
(1)



(2)

normally have the donor ligand in an axial position and the alkylidene and imido ligands in equatorial positions.[22]

Styrene reacts cleanly with **1a** or **1b** in DME over a period of 12 h to afford orange $Mo(CHPh)(NAr)(OR_{F6})_2$(DME) (**4**) in good yield (eq 3). Productive metathesis to give stilbene is slow under these conditions. For example, when 47 equiv of styrene in DME was added to **4** in DME (3.7 mM), only 8.3 equiv of *trans*-stilbene was obtained after 14 h. Several analogous benzylidene complexes that contain π-donating groups have also been prepared. 4-(Dimethylamino)styrene and 2,4,6-trimethoxystyrene react with **1a** or **1b** to yield dark red $Mo[CH\text{-}4\text{-}C_6H_4\text{-}NMe_2]$-$(NAr)(OR_{F6})_2$ (DME) (**5**) and red $Mo[CH\text{-}2,4,6\text{-}C_6H_2$-$(OMe)_3](NAr)(OR_{F6})_2$(DME) (**6**), respectively. All three benzylidene complexes are stable and crystalline and are red (versus the yellow color of **1**), consistent with the conjugated nature of the alkylidene.[10,22] Isolable benzylidene complexes could not be prepared in diethyl ether or THF directly from **1b**, $Mo(CH\text{-}t\text{-}Bu)(NAr)[OCMe_2$-$(CF_3)]_2$, or $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$. Metathesis re-



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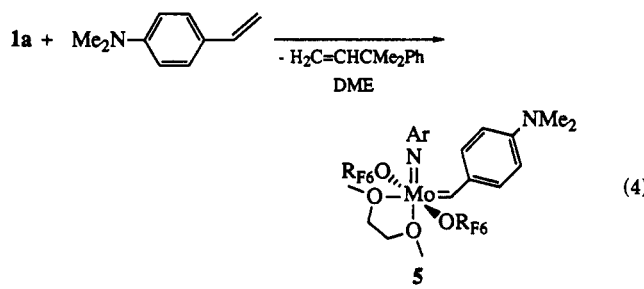
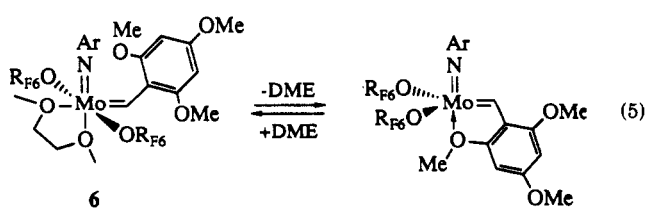


(4)

actions in the presence of 4-(dimethylamino)pyridine or quinuclidine (quin) did not yield stable adducts of benzylidene complexes.

On the basis of the relatively low value for J_{CH_α} in **4** and **5** (Table I), and by analogy with the structure of Mo-$(CH\text{-}t\text{-}Bu)(NAr)(OTf)_2(DME)$ (OTf = O_3SCF_3),[2] the complexes are believed to be the syn rotamers with the overall structures shown in eqs 3 and 4. In each species DME exchanges readily at room temperature with free DME. (Low-temperature ^1H NMR experiments could not be carried out due to the low solubility of these complexes in most solvents.) In contrast, the alkylidene ligand in **6** is in the anti orientation in solution (J_{CH_α} = 159 Hz; Table I), consistent with coordination of an *o*-methoxy group to the metal, probably in a five-coordinate species analogous to the type proposed for **2** and **3** (eq 5). Dimethoxyethane



(5)

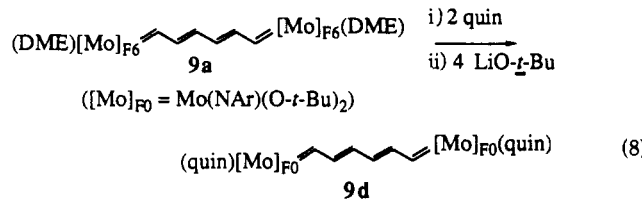
cannot be removed in vacuo from solid samples of **6**, however, so we presume that DME is bound to give a six-coordinate species in the solid state. The Mo(VI) analog of $W(CH\text{-}o\text{-}C_6H_4\text{-}OMe)(NAr)(OR_{F6})_2(THF)$[28] could not

be prepared directly in THF or diethyl ether by the metathetical methods employed here.

A universal catalyst precursor that contains a benzylidene ligand could be prepared directly in four steps from ammonium molybdate, one of which involves an α-hydrogen-abstraction reaction in a dibenzyl complex. $Mo(NAr)_2Cl_2(DME)$[1,2] reacts cleanly with 2 equiv of KCH_2Ph[33] to give $Mo(NAr)_2(CH_2Ph)_2$ (**7**). Treatment of **7** with 3 equiv of triflic acid afforded $Mo(CHPh)(NAr)(OTf)_2(DME)$ (**8**), which is isolated as a mixture of isomers, according to NMR studies. Two alkylidene resonances are observed in a 1:1 ratio at 15.05 and 14.44 ppm (in CD_2Cl_2; a 1:6 ratio at 15.33 and 14.70 ppm in C_6D_6). The isopropyl methyl groups in one isomer are all equivalent, consistent with a structure containing a freely rotating imido phenyl group and trans triflates. In the other isomer, the isopropyl methyl groups are diastereotopic, which suggests that the triflates are cis to one another. The ratio of the two isomers is solvent-dependent. In C_6D_6, 86% of the mixture consists of the symmetric isomer. This synthetic route is analogous to that used to prepare neopentylidene (R = Me) and neophylidene (R = Ph) complexes of the type $Mo(CHCMe_2R)(NAr)(OTf)_2(DME)$, which are universal precursors to virtually any dialkoxide complex.[2] The success of the α-hydrogen abstraction to give **8** is surprising in view of the reluctance with which benzyl groups were found to undergo clean α-hydrogen-abstraction reactions in the early tantalum alkylidene chemistry.[34] Evidently the triflate ligands in the presumed intermediate, $Mo(NAr)(CH_2Ph)_2(OTf)_2$, make the metal electrophilic enough to initiate α-hydrogen abstraction via an agostic H_α interaction in one of the benzyl groups, while coordination of dimethoxyethane after the benzylidene ligand is formed protects the benzylidene complex against bimolecular decomposition. Since the α-hydrogen-abstraction reaction is known to be accelerated by coordinating ligands, another strong possibility is that dimethoxyethane also accelerates α-hydrogen abstraction in $Mo(NAr)(CH_2Ph)_2(OTf)_2$ by coordinating to the relatively electrophilic metal.

A metathesis reaction between **1a** or **1b** and 0.5 equiv of octatetraene in DME afforded $[(DME)(R_{F6}O)_2(ArN)Mo]_2(CH)_6$ (**9a**; eq 6). The solution changes from yellow to deep red as the reaction goes to completion, consistent with formation of a conjugated alkylidene complex.[22,29] The six-coordinate structure of **9a** shown in eq 6 is proposed on the basis of the observed stoichiometry, the stability of the compound in solution and in the solid state (see below), and the similarities between the ^1H NMR data for **9a** and those for **4**, **5**, and **6**. However, **9a** must be in equilibrium in solution with free DME and a four-coordinate alkylidene complex, on the basis of the reactivity of the complex toward norbornenes and norbornadienes (see below), as well as the fact that the DME ligand in **9a** can be replaced easily by diethyl ether or THF to give monoadduct **9b** or **9c** (eq 7). Complex **9b** can be prepared directly from **1a** and octatetraene in ether in 66% yield. **9c** could not be prepared directly in THF, because the initial metathesis step is too slow. All three complexes (**9a–c**) are isolable, crystalline species that are stable at 25 °C in solution and in the solid state. The value of J_{CH_α} for **9c** (152 Hz) is indicative of an anti orientation of the alkylidene with respect to the imido ligand, while J_{CH_α} values for **9a** (132 Hz) and **9b** (127 Hz) are more consistent with their being syn rotamers.

Addition of 4 equiv of LiO-*t*-Bu and 2 equiv of quinuclidine (quin) to **9a** yields metallic green $(quin)(t\text{-}BuO)_2(ArN)Mo(CH)_6Mo(NAr)(O\text{-}t\text{-}Bu)_2(quin)$ (**9d**; eq 8).



(8)

9d is much less stable than **9a–c** in the solid state; samples of crystalline **9d** decompose even at −40 °C over a period of days. We propose that quinuclidine is not bound strongly because of the more electron-donating nature of the alkoxide ligands. Nevertheless, **9d** can be used immediately after it is prepared, for example, to synthesize discrete polyenes (see below).

1,4-Divinylbenzene also reacts smoothly with **1a** or **1b** to give another difunctional alkylidene complex, $1,4\text{-}[(DME)(R_{F6}O)_2(ArN)MoCH]_2C_6H_4$ (**10a**; eq 9). **10a** can be isolated as a crystalline, bright orange solid which is soluble in DME and THF but is nearly insoluble in other common solvents. Proton and carbon NMR data (Table I) suggest that the structure of **10a** is analogous to that proposed for **4**; there is only one aryl proton resonance for the alkylidene aryl group, as one would expect for the structure depicted in eq 9 in which rotation about the C_α–C_{ipso} bond is fast on the NMR time scale. The value for J_{CH_α} (125 Hz) is consistent with a syn orientation of the alkylidene with respect to the imido ligand. An isolable

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(34) Schrock, R. R. *Alkylidene Complexes of the Earlier Transition Metals*; Plenum: New York, 1986.

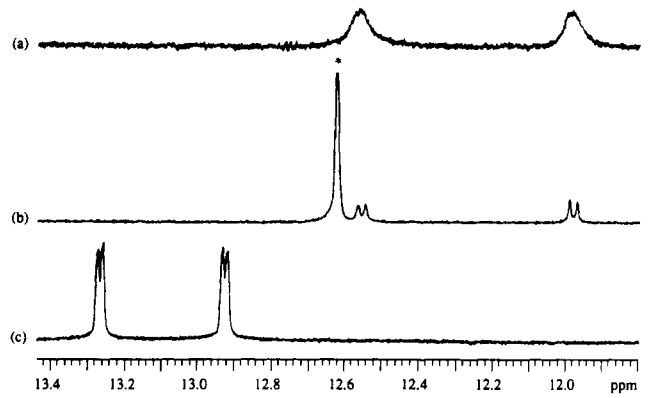
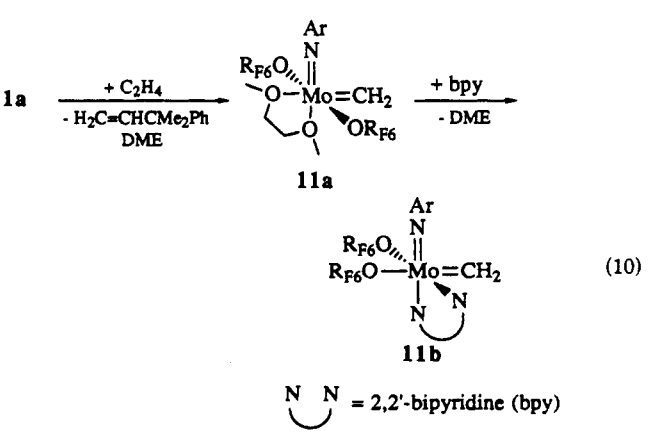


Figure 1. ^{1}H NMR alkylidene region of (a) $Mo(CH_2)(NAr)(OR_{F6})_2(DME)$ (**9a**) in DME-d_{10} under excess ethylene, (b) sample in (a) after ethylene was removed, showing $Mo(CHCMe_3)(NAr)(OR_{F6})_2$ (**1b**) and **9a**, (c) $Mo(CH_2)(NAr)(OR_{F6})_2(bpy)$ (**9b**) in CD_2Cl_2 (the asterisk denotes **1b**).

THF adduct (**10b**) can be prepared from **10a** simply by dissolving **10a** in THF. However, as in the case of **9a**, metathesis with divinylbenzene proceeds too slowly to prepare **10b** directly from **1a** or **1b** in THF. The DME ligand in **10a** (and in **4**, **5**, or **6**) is not displaced by diethyl ether, as found in the case of **9a**, which suggests that DME is the preferred donor ligand for benzylidene complexes.

It is interesting to note that productive metathesis is relatively slow in all reactions mentioned so far, and methylene complexes have not been observed. However, $Mo(CH_2)(NAr)(OR_{F6})_2(DME)$ (**11a**) can be generated and observed by ^{1}H NMR upon adding an excess of ethylene to a solution of **1b** in DME-d_{10} in a septum-sealed NMR tube. Two broad resonances at 12.54 and 11.96 ppm are observed for the syn and anti methylene protons of **11a** (Figure 1a), along with resonances for free ethylene, which is also broad, and neohexene. When free ethylene was removed from this sample in vacuo, ca. 90% of **1b** was regenerated and the residual methylene resonances for **11a** (ca. 10% of the mixture) could be observed as two sharp doublets at 12.56 and 11.99 ppm (J_{HH} = 6.0 Hz) (Figure 1b). Presumably some neohexene is also removed upon removing the ethylene so that a mixture of **1b** and **11a** is obtained instead of pure **1b**. We propose that in the presence of excess ethylene the methylene complex is reacting with ethylene at a rate of the order of the NMR time scale. Consequently, the resonances for the methylene and ethylene protons are broadened. The methylene complex can be generated in DME from **1b** on a preparative scale under a pressure of ethylene and trapped as a highly crystalline and stable 2,2′-bipyridine (bpy) adduct (**11b**) in 65% isolated yield (eq 10). The alkoxides are inequivalent in **11b**, and it has no plane of symmetry (according to NMR data). The methylene protons appear as sharp doublets (J_{HH} = 3.9 Hz; Figure 1c). One possible structure for **11b** is shown in eq 10.



(10)

Table II. GPC and Yield Data for Poly(2,3-dicarbomethoxynorbornadiene)$_{100}$ Prepared in DME

catalyst	M_n[a]	M_w/M_n[a]	yield (%)
1b	16 400	1.04[b]	86
4	16 200	1.06	94
5	15 200	1.03	90
9a	13 400	1.18	93
9b	14 500	1.12	98
10a	14 500	1.06	94

[a] Determined by GPC versus polystyrene standards. [b] The reaction was quenched after 90 min. An analogous reaction which was allowed to run for 16 h yielded a polymer whose properties were identical with those of the polymer obtained after 90 min.

ROMP and Wittig Reactions. 2,3-Dicarbomethoxynorbornadiene (100 equiv) is polymerized smoothly in DME using **1b**, **4**, **5**, **9a**, **9b**, or **10a** as the initiator. Both the monomer and the polymer are soluble in DME. The polymerization could be quenched with benzaldehyde to yield a polymer in high yield that was shown to have a low polydispersity (M_w/M_n; Table II). The polydispersities of the polymers prepared from **9a** and **9b** were larger due to a small amount of double- and half-molecular-weight polymer that was present. The half-molecular-weight polymer might arise in a reaction in which one end of the difunctional catalyst is incompletely initiated or has been terminated in some side reaction (e.g., with oxygen). The double-molecular-weight polymer is relatively common in polymerization reactions of this type and may arise from reactions that involve oxygen.[35] The polymerization is rapid (complete after 1 h), and ^{13}C NMR shows this polymer to be 98% cis. In order to confirm that there is no secondary metathesis of the polymer chain, a polymerization reaction mixture was stirred for 16 h before being quenched; the cis/trans content, tacticity, and yield of the polymer was unchanged (87% yield, M_w/M_n = 1.04).

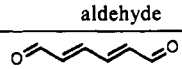
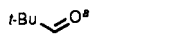
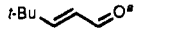
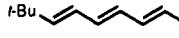
2,3-Bis(trifluoromethyl)norbornadiene (100 equiv) also was successfully polymerized in DME using **1a** to give a low-polydispersity polymer (1.08) in high yield (94%). The cis/trans content (97% cis) and tacticity of the polymer was determined by ^{13}C NMR to be identical with that prepared using **1a** in THF.[24]

A metathesis study of *cis*-2-pentene (500 equiv) in DME using **1a** was undertaken in order to confirm that the metathesis activity of this complex in DME toward ordinary internal olefins is relatively low. After 17 h, the mixture of 2-butenes, 2-pentenes, and 3-hexenes suggested that the reaction had progressed ca. 35% of the way toward equilibrium. In comparison equilibrium was reached in 2 min in toluene.[2] The ability of THF to moderate the reactivity of the analogous tungsten complex has already been noted.[23] A typical double bond in a ROMP polymer would be more sterically protected than that in 2-pentenes and also is often deactivated by electron-withdrawing substituents such as CO_2Me or CF_3 groups.[6]

Methyltetracyclododecene (MTD) can be polymerized using the hexafluoro-*tert*-butoxide initiators, but poly-MTD having a relatively high polydispersity is obtained in THF. For example, polymerization of 100 equiv of MTD by **3** in THF for 10 min followed by capping with

(35) Feast, W. J.; Gibson, V. C.; Khosravi, E.; Marshall, E. L.; Mitchell, J. P. *Polymer* **1992**, *33*, 872.

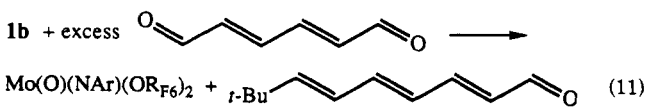
Table III. Polyenes (*n*-ene) Prepared from Wittig-like Reactions with Various Aldehydes and Alkylidene Complexes

alkylidene complex	aldehyde	*t*-Bu(=CH)$_n$-*t*-Bu (*n*-ene)
1b[a]		4-ene
9d		4-ene
9d		6-ene
9d		10-ene

[a] Two equivalents employed.

benzaldehyde gave (MTD)$_{50}$CHCH$_2$CH(OMe)C$_6$H$_4$CH(OMe)CH$_2$CH(MTD)$_{50}$ in 78% yield which had a polydispersity of 1.35. In this case, internal coordination of the methoxy group could slow the rate of initiation significantly relative to propagation and lead to a higher polydispersity than would otherwise be expected. An analogous reaction in which **1a** was employed as the initiator gave a polymer with a polydispersity of 1.2 after 1 h of reaction. Addition of an excess of LiO-*t*-Bu (8 equiv) to a solution of **3** in toluene, followed by 200 equiv of MTD, gave low-polydispersity poly-MTD (M_w/M_n = 1.03) in 93% yield after quenching with benzaldehyde. Similar results were obtained by starting with **1a**. The presence of LiOR$_{F6}$ or LiO-*t*-Bu did not seem to effect the polymerization reaction. For example, 200 equiv of MTD was added to a mixture of **9a** and excess LiO-*t*-Bu in toluene without isolating the less reactive bis(*tert*-butoxide) complex, and the reaction was quenched with benzaldehyde. The polymer (PhCH)(MTD)$_{100}$(CH)$_6$(MTD)$_{100}$(CHPh), which was obtained in 94% yield, had a polydispersity of 1.05. The UV/vis spectrum of this polymer is consistent with the presence of the tetraene unit.[10,12] Addition of 200 equiv of norbornene to **9d** followed by quenching with pivaldehyde yielded low-polydispersity (PhCH)(norbornene)$_{100}$(CH)$_6$(norbornene)$_{100}$(CHPh) (PDI = 1.07), consistent with a more controlled (living) polymerization in the presence of 1 equiv of quinuclidine per metal. These studies suggest that even polymerization of norbornene itself or MTD can be controlled under some conditions and secondary metathesis limited, or if that is not the case, that a less reactive *tert*-butoxide catalyst can be prepared and used in situ.

Another important aspect of polymerization reactions is termination of the reaction with aldehydes in a Wittig-like reaction.[5] Complexes **4**, **5**, **9a**, **9b**, and **10a** react cleanly with pivaldehyde or benzaldehyde in CD_2Cl_2 or DME. The reactions of **9a** and **9b** were complete after 20 min, according to proton NMR spectra, and no side products were observed. Reactions in DME were complete after 1 h and also showed no evidence of side products. Interestingly, treatment of **1b** with excess *trans,trans*-2,4-hexadiene-1,6-dialdehyde affords 8,8-dimethylnona-*trans,trans,trans*-2,4,6-trienal in good yield (eq 11). We have



(11)

also found that reactions between **9d** and aldehydes in THF are quantitative and that di-*tert*-butyl-capped polyenes, (*t*-Bu)(CH=CH)$_n$(*t*-Bu) (n = 4, 6, 8),[10,12] can be prepared in a stoichiometric reaction in high yield (Table III). The 4-ene can be prepared by adding excess pivaldehyde to **9d** or 0.5 equiv of *trans,trans*-2,4-hexadiene-1,6-dialdehyde to **1b**. This synthesis of discrete all-trans polyenes is more convenient and efficient than polymerization methods, which require low-temperature chromatography under an inert atmosphere of a distribution of polyenes with different chain lengths.[10,12] Variations of the reactions shown in Table III have been used to prepare the known all-trans di-*tert*-butyl-capped polyenes that contain up to 12 double bonds.[36]

Conclusions

We have shown that a variety of Mo(VI) hexafluoro-*tert*-butoxide alkylidene complexes can be prepared if they are stabilized by internal or external coordination of a base, that they can be employed as living ROMP initiators, and that they react smoothly with a variety of aldehydes in Wittig-like reactions. DME appears to be the preferred external base for stabilizing alkylidene complexes, yet the DME is labile and the alkylidene complexes therefore react with especially reactive olefins such as norbornenes and norbornadienes. A methylene complex can also be stabilized in DME, which suggests that bimolecular decomposition of intermediate methylene complexes is relatively slow. Dimethoxyethane may also play an important role in accelerating and controlling α-hydrogen-abstraction reactions in dibenzyl complexes. We have also shown that in circumstances when hexafluoro-*tert*-butoxide initiators are not entirely satisfactory for synthesizing low-polydispersity polymers, *tert*-butoxide initiators can be prepared in situ and employed in ROMP reactions. The techniques described here should expand the opportunities for making polymers via living ROMP reactions and, in particular, should allow one to introduce conjugated sequences with a known, fixed length into a variety of polymers and to attach functional groups to both ends of the polymer. Future work will be directed toward determining what other types of monomers can be polymerized in a living fashion and what functionalities can be tolerated.

Experimental Section

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques unless otherwise specified. Silica gel (Merck grade 60, 3 × 40 cm) was dried (at ~130 °C) in vacuo overnight. Pentane was washed with sulfuric/nitric acid (95/5 v/v), sodium bicarbonate, and water, stored over calcium chloride, and distilled from sodium benzophenone ketyl under nitrogen. Reagent grade diethyl ether, tetrahydrofuran, toluene, benzene, and 1,2-dimethoxyethane were distilled from sodium benzophenone ketyl under nitrogen. Reagent grade dichloromethane was distilled from calcium hydride under nitrogen. Toluene used for polymerizations was stored over a Na/K alloy. DME and polymerization grade THF were vacuum-transferred a second time from sodium benzophenone ketyl. Benzene-d_6 and CD_2Cl_2 were sparged with argon and stored over molecular sieves (4 Å). THF-d_8 and DME-d_{10} were vacuum-distilled from Na/benzophenone. HPLC grade solvents were used in GPC and HPLC runs and were degassed prior to use. HPLC spectra were run using a Hewlett-Packard 1090M HPLC equipped with a 250-mm reverse-phase (C18) Econosil analytical column purchased from Alltech Associates. Gel permeation chromatography (GPC) was carried out using Shodex KF-802.5, 803, 804, 805, and 800P columns, a Knauer differential refractometer, and a Viscotek H-500 differential refractometer/viscometer on samples 0.1–0.3% w/v in THF which were filtered through a Millex-SR 0.5-μm filter in

(36) Park, L. Y. Ph.D. Thesis, MIT, 1991.

order to remove particulates. GPC columns were calibrated versus polystyrene standards (Polymer Laboratories Ltd.) which ranged from 1206 to 1.03×10^6 MW. The GPC data were analyzed using Unical 4.03 (Viscotek). UV/vis spectra were recorded on a Hewlett-Packard 8451A diode array spectrophotometer in the range of 190–820 nm. NMR data were obtained at 300 MHz (^{1}H) and 75.43 MHz (^{13}C) and are listed in parts per million downfield from tetramethylsilane for proton and carbon. Coupling constants are listed in hertz. Spectra were obtained at 25 °C unless otherwise noted. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN analyzer.

All chemicals used were reagent grade and purified by ordinary methods. Pivaldehyde (Aldrich) was distilled and passed over alumina before use. Quinuclidine and 2,2′-bipyridine (Aldrich) were recrystallized from diethyl ether prior to use. 1,4-Divinylbenzene (Aldrich) was purified as described in the literature.[37] $Mo(NAr)_2Cl_2(DME)$,[1] $Mo(CHCMe_2Ph)(NAr)(OTf)_2(DME)$,[2] 4,4-dimethyl-*trans*-2-pentenal,[38] *p*-Me_2N-$C_6H_4CHCH_2$,[39] KCH_2Ph,[33] *trans,trans*-1,3,5,7-octatetraene,[40] and *trans,trans*-2,4-hexadiene-1,6-dialdehyde[41] were prepared by literature methods.

$Mo(CHCMe_2Ph)(NAr)(OR_{F6})_2$ (1a). $LiOCMe(CF_3)_2$ (459 mg, 2.44 mmol) was added to a cold (−30 °C) solution of $Mo(CHCMe_2Ph)(NAr)(OTf)_2(DME)$ (0.966 g, 1.22 mmol) in 50 mL of diethyl ether. The reaction mixture was warmed to room temperature while it was stirred over a period of 1 h. The solvents were removed in vacuo, the resulting solid was extracted with pentane, and the mixture was filtered. The pentane was removed in vacuo to yield a dark yellow solid. Recrystallization of the solid from pentane at −40 °C produced 802 mg of yellow crystalline product (86%): ^{1}H NMR (C_6D_6) δ 12.12 (s, 1, $MoCHCMe_2Ph$), 7.19–6.92 (m, 8, aromatic), 3.56 (sept, 2, $CHCMe_2$), 1.53 (s, 6, $OCMe(CF_3)_2$), 1.18 (d, 12, $CHMe_2$), 1.17 (s, 6, $MoCHCMe_2Ph$); ^{13}C NMR (C_6D_6) δ 284.9 (d, J = 121, $MoCHR$), 154.0 (s, C_{ipso} NAr), 148.0 (s, C_o NAr), 147.6 (s, C_{ipso} Ph), 129.6 (d, C_p NAr), 128.6 (d, C_o Ph), 126.7 (d, C_p Ph), 125.9 (d, C_m Ph), 124.2 (q, $^1J_{CF}$ = 289, $OCMe(CF_3)_2$), 124.1 (q, $^1J_{CF}$ = 289, $OCMe(CF_3)_2$), 123.5 (d, J = 159, C_m NAr), 81.3 (sept, $^3J_{CF}$ = 29, $OCMe(CF_3)_2$), 55.4 (s, $MoCHCMe_2Ph$), 30.4 (q, J = 133, $MoCHCMe_2Ph$), 28.7 (d, J = 130, $CHMe_2$), 23.8 (q, J = 127, $CHMe_2$), 18.8 (q, J = 130, $OCMe(CF_3)_2$). Anal. Calcd for $MoC_{30}H_{35}F_{12}NO_2$: C, 47.07; H, 4.61; N, 1.83. Found: C, 47.06; H, 4.56; N, 1.95.

$CH_3CH_2CH(OMe)CH_2CH{=}CH_2$. Allylmagnesium bromide (1.0 M in ether, 100 mmol) in 100 mL of ether was added to a solution of propanal (5.81 g, 100 mmol) in 200 mL of ether at 0 °C over a period of 1 h. The mixture was warmed up to room temperature and stirred for 1 h. A saturated aqueous solution of NH_4Cl (200 mL) was added, and the organic layer was separated and dried over $MgSO_4$. 4-Hydroxy-1-hexene (5.36 g, 54%) was obtained by distilling the residue at 110 °C.

4-Hydroxy-1-hexene (5.36 g, 53.5 mmol) in 20 mL of ether was added to Na (1.29 g, 53.5 mmol) suspended in 100 mL of ether. The solution was stirred for 1 h and refluxed for 2 h or until all the Na had disappeared. Dimethyl sulfate (9.29 g, 73.7 mmol) was added over a period of 20 min at 25 °C, and the mixture was stirred for 3 h. $[NH_4]OH$ (5 mL, 15 N) was then added to decompose the excess dimethyl sulfate. The reaction mixture was worked up with water and washed several times until the pH was neutral. The organic layer was separated and dried over $MgSO_4$. The solvent was removed in vacuo, and the residue was distilled at 112 °C to give 4-methoxy-1-hexene (3.77 g, 61%): ^{1}H NMR (C_6D_6) δ 5.93–5.75 (m, 1, $=CH-$), 5.10–5.00 (m, 2, $CH_2{=}$), 3.12 (s, 3, OCH_3), 3.00–2.87 (m, 1, $-CHOMe-$), 2.30–2.07 (m, 2, $=CHCH_2-$), 1.50–1.38 (m, 2, $-CH_2CH_3$), 0.85 (t, 3, $-CH_3$).

$CH_3CH_2CH(OMe)CH_2CH{=}Mo(NAr)(OR_{F6})_2$ (2). 4-Methoxy-1-hexene (47 mg, 410 μmol) was added to a solution of **1a** (0.20 g, 296 μmol) in 7 mL of pentane. The color changed quickly from yellow to orange-red. After the mixture was stirred for 2 h, the solvent and 3-methyl-3-phenylbutene were removed in vacuo. The solid product was recrystallized from ether/pentane to yield orange-red crystals (0.13 g, 66%): ^{1}H NMR (C_6D_6) δ 12.35 (dd, 1, $MoCHR$), 7.12–6.90 (m, 3, H_{aryl}), 4.38–4.20 (sept, 2, $CHMe_2$), 4.00–3.87 (m, 1, $-CH(OMe)-$), 3.63–3.48 (m, 1, $-CH_aH_b-$), 3.20 (s, 3, OMe), 3.08–2.95 (m, 1, $-CH_aH_b-$), 1.52–1.39 (m, 2, $-CH_2-$), 1.36 (s, 3, $OCMe(CF_3)_2$), 1.35 (d, 6, $CHMe_2$), 1.32 (d, 6, $CHMe_2$), 1.25 (s, 3, $OCMe(CF_3)_2$), 0.54 (t, 3, $-CH_3$); ^{13}C NMR (CD_2Cl_2) δ 273.0 (d, J = 158, $MoCHR$), 152.0 (s, C_{ipso}), 147.3 (s, C_o), 128.1 (d, J = 161, C_p), 124.7 (q, $^1J_{CF}$ = 293, $OCMe(CF_3)_2$), 124.5 (q, $^1J_{CF}$ = 293, $OCMe(CF_3)_2$), 123.5 (d, J = 160, C_m), 83.3 (d, J = 144, $-CH(OMe)-$), 81.4 (m, $OCMe(CF_3)_2$), 56.3 (q, J = 137, OMe), 46.3 (t, J = 128, $-CH_2-$), 28.8 (d, J = 131, $CHMe$), 25.1 (q, J = 131, $CHMe_2$), 23.3 (q, J = 131, $CHMe_2$), 24.6 (t, J = 127, $-CH_2-$), 20.0 (q, J = 126, $OCMe(CF_3)_2$), 19.8 (q, J = 126, $OCMe(CF_3)_2$), 19.8 (q, J = 126, $OCMe(CF_3)_2$), 8.6 (q, J = 126, $-CH_3$). Anal. Calcd for $C_{26}H_{35}F_{12}NO_3Mo$: C, 42.58; H, 4.81; N, 1.91. Found: C, 42.42; H, 4.55; N, 1.97.

$CH_2{=}CHCH_2CH(OMe)C_6H_4CH(OMe)CH_2CH{=}CH_2$. Allylmagnesium chloride (2.0 M, 72 mmol, 36 mL) was added dropwise to a solution of terephthaldehyde (4.02 g, 30 mmol) in 150 mL of benzene and 150 mL of THF. After the mixture was stirred for 3.5 h, it was worked up with a saturated aqueous solution of NH_4Cl at 0 °C. The organic layer was separated and washed with a saturated $NaHCO_3$ solution, rinsed twice with water, and dried over $MgSO_4$. Solvent was removed in vacuo to yield a red oily liquid (5.19 g, 74%). Colorless crystals of the dialcohol were obtained after purification by column chromatography (silica gel, THF/hexane = 1/2).

A solution of the dialcohol (1.67 g, 7.65 mmol) in 15 mL of THF was added to a suspension of NaH (0.50 g, 16.7 mmol) in 15 mL of THF. Dihydrogen was generated, and the color changed to greenish yellow upon refluxing the mixture over a period of 1 h. The mixture was cooled down to 25 °C using a water bath, and dimethyl sulfate was added slowly. After being stirred for 3 h, the reaction mixture was worked up as described above. The product (1.65 g, 88%) was purified by column chromatography (silica gel, Et_2O/hexane = 2/3): ^{1}H NMR (C_6D_6) δ 7.30 (s, 4, H_{aryl}), 5.87–5.72 (m, 2, $=CH-$), 5.10–4.98 (m, 4, $CH_2{=}$), 4.21–4.15 (dd, 2, $-CH(OMe)-$), 3.20 (s, 6, OMe), 2.62–2.35 (m, 4, $-CH_2-$); ^{13}C NMR (CD_2Cl_2) δ 141.6 (C_{ipso}), 135.5 ($-CH{=}$), 127.0 (C_o), 116.8 ($CH_2{=}$), 83.8 ($-CH(OMe)-$), 56.8 ($-OMe$), 42.8 ($-CH_2-$).

$[(R_{F6}O)_2(NAr)Mo{=}CHCH_2CH(OMe)]_2C_6H_4$ (3). To a solution of **1a** (1.50 g, 2.01 mmol) in 50 mL of pentane was added $CH_2{=}CHCH_2CH(OMe)C_6H_4CH(OMe)CH_2CH{=}CH_2$ (0.248 g, 1.00 mmol). After the reaction mixture was stirred for 1.5 h (the color changed from yellow to red), solvent and side products were removed in vacuo over a period of 2 h. The orange-red residue was dissolved in a minimum amount of pentane (about 15 mL) and orange crystals (0.93 g, 67%) were obtained upon cooling the solution: ^{1}H NMR (CD_2Cl_2) δ 12.38 (dd, 2, $MoCHR$), 7.55 (s, 4, H_{aryl}), 7.20 (s, 6, imido H_{aryl}), 5.15 (dd, 2, $-CH(OMe)-$), 4.40–4.25 (m, 2, $-CH_aH_b-$), 4.15 (sept, 4, $CHMe_2$), 3.65–3.50 (m, 2, $-CH_aH_b-$), 3.35 (s, 6, $-OMe$), 1.56 (s, 6, $OCMe(CF_3)_2$), 1.36 (d, 12, $CHMe_2$), 1.33 (d, 12, $CHMe_2$), 1.31 (s, 6, $OCMe(CF_3)_2$); ^{13}C NMR (CD_2Cl_2) δ 272.2 (d, J = 158, $MoCHR$), 152.1 (s, C_{ipso} NAr), 147.4 (s, C_o NAr), 139.5 (s, C_{ipso} Ph), 128.8 (d, J = 159, C_o Ph), 128.3 (d, J = 161, C_p NAr), 124.8 (q, $^1J_{CF}$ = 286, $OCMe(CF_3)_2$), 124.4 (q, $^1J_{CF}$ = 286, $OCMe(CF_3)_2$), 123.6 (d, J = 158, C_m Ph), 85.3 (d, J = 148, $-CH(OMe)-$), 81.8 (sept, $^2J_{CF}$ = 23, $OCMe(CF_3)_2$), 81.2 (sept, $^2J_{CF}$ = 23, $OCMe(CF_3)_2$), 57.0 (q, J = 148, OMe), 49.8 (t, J = 131, $-CH_2-$), 28.9 (d, J = 130, $CHMe_2$), 25.2 and 23.3 (q, J = 128, $CHMe_2$), 20.1 (q, J = 132, $OCMe(CF_3)_2$), 20.0 (q, J = 132, $OCMe(CF_3)_2$). Anal. Calcd for $C_{54}H_{64}F_{24}O_6N_2Mo_2$: C, 43.68; H, 4.34; N, 1.89. Found: C, 44.06; H, 4.45; N, 1.78.

$Mo(CHPh)(NAr)(OR_{F6})_2(DME)$ (4). **1b** (0.300 g, 0.426 mmol) was dissolved in 15 mL of DME, and styrene (45 μL, 0.426 mmol) was added. After 1 h the solvents were removed in vacuo and the residue was recrystallized from ether to afford 0.23 g (0.283 mmol) of the orange product (66%): ^{1}H NMR (CD_2Cl_2)

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δ 12.95 (s, 1, MoC*H*R), 7.36–7.05 (m, 8, H_{aryl}), 3.56 (sept, 2, C*H*Me$_2$), 3.50 (s, 4, CH_2OMe), 3.34 (s, 6, CH$_2$O*Me*), 1.46 (s, 6, OC*Me*(CF$_3$)$_2$), 1.14 (d, 12, CH*Me*$_2$); ^{13}C NMR (CD$_2$Cl$_2$) δ 271.7 (d, J = 126, MoCHR), 154.1 (s, C_{ipso} NAr), 148.6 (s, C_o NAr), 145.1 (s, C_{ipso} Ph), 130.2 (d, J = 161, C_p NAr), 129.7 (d, J = 161, C_p Ph), 128.6 (d, J = 161, C_o Ph), 128.0 (d, J = 157, C_m Ph), 124.3 (q, $^1J_{CF}$ = 290, OCMe(*C*F$_3$)$_2$), 124.1 (q, $^1J_{CF}$ = 290, OCMe(*C*F$_3$)$_2$), 123.9 (d, J = 158, C_m NAr), 81.9 (sept, $^2J_{CF}$ = 29, O*C*Me(CF$_3$)$_2$), 72.4 (t, J = 143, *C*H$_2$OMe), 59.1 (q, J = 138, CH$_2$O*Me*), 29.1 (d, J = 129, *C*HMe$_2$), 23.6 (q, J = 127, CH*Me*$_2$), 19.3 (q, J = 130, OC*Me*(CF$_3$)$_2$). Anal. Calcd for $MoC_{31}H_{39}F_{12}NO_4$: C, 45.77; H, 4.83; N, 1.72. Found: C, 45.95; H, 4.68; N, 1.76.

Metathesis of Styrene. 4 (30 mg, 0.037 mmol) was dissolved in 10 mL of DME, and styrene was added (182 mg, 1.732 mmol). The solution was stirred for 14 h, 100 μL of *t*-BuCHO was added, and the volatiles were removed in vacuo. The solid was dissolved in pentane and the solution passed through a column of Al_2O_3. *trans*-Stilbene was isolated upon evaporation of the solvent (55 mg, 35%) and was analyzed by ^{1}H NMR and UV/vis spectroscopy.

Mo[CH-4-C$_6$H$_4$-NMe$_2$](NAr)(OR$_{F6}$)$_2$(DME) (5). 1a (0.600 g, 0.784 mmol) was dissolved in 15 mL of DME, and 4-(dimethylamino)styrene (0.115 g, 0.781 mmol) was added. After 12 h the solvents were removed from the red reaction mixture in vacuo and the residue was recrystallized from dichloromethane to afford 0.524 g (0.611 mmol) of the dark red product (78%): ^{1}H NMR (CD$_2$Cl$_2$) δ 12.60 (s, 1, MoC*H*R), 7.32 (t, 1, NAr H_p), 7.23 (d, 2, NAr H_m), 7.19 (d, 2, benzylidene H_o), 6.52 (d, 2, benzylidene H_m), 3.60 (sept, 2, C*H*Me$_2$), 3.50 (s, 4, CH_2OMe), 3.34 (s, 6, CH$_2$O*Me*), 2.99 (s, 6, N*Me*$_2$), 1.43 (s, 6, OC*Me*(CF$_3$)$_2$), 1.17 (d, 12, CH*Me*$_2$); ^{13}C NMR (CD$_2$Cl$_2$) δ 269.2 (d, J = 124, MoCHR), 154.1 (s, C_{ipso} NAr), 151.5 (s, C_{ipso} Ph), 148.2 (s, C_o NAr), 135.1 (s, C_p Ph), 129.8 (d, J = 159, C_p NAr), 129.3 (d, J = 159, C_o Ph), 124.2 (q, $^1J_{CF}$ = 289, OCMe(*C*F$_3$)$_2$), 123.6 (d, J = 159, C_m NAr), 111.1 (d, J = 141, C_m Ph), 81.4 (sept, $^2J_{CF}$ = 31, O*C*Me(CF$_3$)$_2$), 72.2 (t, J = 140, *C*H$_2$OMe), 59.1 (q, J = 141, CH$_2$O*Me*), 40.2 (q, J = 135, N*Me*$_2$), 28.9 (d, J = 129, *C*HMe$_2$), 23.6 (q, J = 126, CH*Me*$_2$), 19.3 (q, J = 131, OC*Me*(CF$_3$)$_2$). Anal. Calcd for $MoC_{33}H_{44}F_{12}NO_4$: C, 46.27; H, 5.18; N, 3.27. Found: C, 45.97; H, 4.96; N, 3.49.

2,4,5-Trimethoxystyrene. A 6.3-mL amount of a 1.6 M (10.2 mmol) *n*-butyllithium solution was added to 75 mL of ether at room temperature. Solid triphenylmethylphosphonium bromide (3.64 g, 10.2 mmol) was added over 5 min. The solution turned yellow as it was stirred for 4 h. 2,4,6-Trimethoxybenzaldehyde (2.00 g, 10.2 mmol) was added to the mixture, which was stirred overnight. The solution was filtered, washed with water, and dried over $MgSO_4$. The solution was filtered and was passed through a short column of silica. The ether was removed in vacuo. The resulting liquid was filtered to remove the crystalline aldehyde; 460 mg was obtained (23%): ^{1}H NMR (C$_6$D$_6$) δ 7.45 (dd, 1, RC*H*CH$_2$), 6.42 (dd, 1, RCHC*H*$_2$), 6.05 (s, 2, aromatic), 5.58 (dd, 1, RCHC*H*$_2$), 3.34 (s, 3, para O*Me*), 3.29 (s, 6, ortho O*Me*).

Mo[CH-2,4,5-C$_6$H$_2$-(OMe)$_3$](NAr)(OR$_{F6}$)$_2$(DME) (6). 1b (0.100 g, 0.142 mmol) was dissolved in 15 mL of DME, and 2,4,6-trimethoxystyrene (27 mg, 0.139 mmol) was added. The solution was stirred for 1 h and became red. The volatiles were removed in vacuo, and the solid was recrystallized from CH_2Cl_2 to afford 83 mg of an orange product (65%): ^{1}H NMR (C$_6$D$_6$) δ 13.16 (s, 1, MoC*H*R), 7.04 (d, 2, NAr H_m), 6.98 (t, 1, NAr H_m), 6.98 (t, 1, NAr H_p), 6.10 (s, 1, benzylidene H_m), 5.98 (s, 1, benzylidene H_m), 4.43 (sept, 2, C*H*Me$_2$), 3.75 (s, 3, O*Me*), 3.33 (s, 4, CH_2OMe), 3.29 (s, 3, O*Me*), 3.12 (s, 3, O*Me*), 3.11 (s, 6, CH$_2$O*Me*), 1.43 (d, 12, CH*Me*$_2$), 1.20 (s, 6, OC*Me*(CF$_3$)$_2$); ^{13}C NMR (CD$_2$Cl$_2$) δ 255.7 (d, J = 159, MoCHR), 162.5 (s, C_{ipso} Ph), 158.3 (s, C_o Ph), 152.5 (s, C_{ipso} NAr), 148.2 (s, C_o NAr), 147.0 (s, C_p Ph), 128.1 (d, J = 164, C_p NAr), 124.3 (q, $^1J_{CF}$ = 289, OCMe(*C*F$_3$)$_2$), 124.1 (q, $^1J_{CF}$ = 289, OCMe(*C*F$_3$)$_2$), 123.3 (d, J = 160, C_m NAr), 116.1 (s, C_o Ph), 92.2 (d, J = 161, C_m Ph), 89.6 (d, J = 156, C_m Ph), 81.3 (sept, $^2J_{CF}$ = 26, O*C*Me(CF$_3$)$_2$), 72.2 (t, J = 140, *C*H$_2$OMe), 59.0 (q, J = 145, CH$_2$O*Me*), 57.5 (q, J = 140, O*Me*), 56.4 (q, J = 149, O*Me*), 56.3 (q, J = 149, O*Me*), 29.0 (d, J = 131, *C*HMe$_2$), 24.1 (q, J = 126, CH*Me*$_2$), 19.4 (q, J = 129, OC*Me*(CF$_3$)$_2$). Anal. Calcd for $MoC_{34}H_{45}F_{12}NO_7$: C, 45.19; H, 5.02; N, 1.55. Found: C, 44.79; H, 4.94; N, 1.52.

Mo(NAr)$_2$(CH$_2$Ph)$_2$ (7). Mo(NAr)$_2$Cl$_2$(DME) (1.9 g, 3.13 mmol) was dissolved in 40 mL of diethyl ether and the solution was chilled to −40 °C. KCH$_2$Ph (0.815 g, 6.26 mmol) was added slowly as a solid over 2 min, followed by 5 mL of THF. After the mixture was stirred for 12 h, the volatiles were removed in vacuo and the solid was redissolved in ether. The mixture was filtered through Celite and concentrated in vacuo for crystallization at −40 °C. A red crystalline product was obtained (1.49 g, 76%): ^{1}H NMR (C$_6$D$_6$) δ 7.01–6.93 (m, 16, H_{aryl}), 3.75 (sept, 4, C*H*Me$_2$), 2.83 (s, 4, MoC*H*$_2$Ph), 1.13 (d, 24, CH*Me*$_2$); ^{13}C NMR (C$_6$D$_6$) δ 153.6 (s, C_{ipso} NAr), 143.5 (s, C_o NAr), 137.1 (s, C_{ipso} Ph), 130.8 (d, J = 158, C_o Ph), 129.6 (d, J = 159, C_m Ph), 126.8 (d, J = 159, C_p Ph), 125.9 (d, J = 158, C_p NAr), 122.7 (d, J = 155, C_m NAr), 47.9 (t, J = 136, Mo*C*H$_2$Ph), 28.6 (d, J = 127, *C*HMe$_2$), 23.6 (q, J = 127, CH*Me*$_2$). Anal. Calcd for $C_{38}H_{48}N_2Mo$: C, 72.59; H, 7.69; N, 4.46. Found: C, 72.56; H, 7.71; N, 4.79.

Mo(CHPh)(NAr)(OTf)$_2$(DME) (8). Mo(NAr)$_2$(CH$_2$Ph)$_2$ (0.556 g, 0.88 mmol) was dissolved in 15 mL of DME and cooled to −40 °C. Triflic acid (0.400 g, 2.65 mmol) was added in 1 mL of DME. The solution was stirred for 16 h, and the color changed from red to dark yellow. The DME was removed in vacuo, and the solid was extracted with cold (−30 °C) toluene (60 mL). The suspension was filtered through Celite, and the toluene was removed in vacuo. The product was crystallized from ether to give a yellow product (0.345 g, 55%). There were two isomers by NMR, the ratio of which changed in different solvents. In C$_6$D$_6$, 86% of the mixture was the major isomer with equivalent isopropyl methyl groups, and in CD$_2$Cl$_2$, the isomers are observed in a 1:1 ratio: ^{1}H NMR δ (CD$_2$Cl$_2$) 15.05 (s, 1, MoC*H*Ph), 14.44 (s, 1, MoC*H*Ph), 7.39–7.10 (H_{aryl}), 4.36 (b), 4.16 (s), 4.12 (b), 4.08 (m), 3.91 (b), 3.78 (s), 3.64 (m), 1.16 (d, 6, C*H*Me$_2$), 1.08 (d, 12, C*H*Me$_2$), 0.98 (d, 6, C*H*Me$_2$); ^{13}C NMR δ 315.3 (MoCHPh), 308.4 (MoCHPh), 152.5, 149.9 (q, $^1J_{CF}$ = 337, CF$_3$), 149.7 (q, $^1J_{CF}$ = 337, CF$_3$), 131.9, 131.4, 131.2, 130.9, 129.6, 129.4, 128.6, 128.1, 124.4, 124.2, 119.6 (q, $^1J_{CF}$ = 317, CF$_3$), 119.5 (q, $^1J_{CF}$ = 317, CF$_3$), 77.6, 76.0, 73.8, 71.4, 66.1, 63.4, 62.0, 28.6, 28.4, 24.4, 23.9, 23.7. Anal. Calcd for $C_{25}H_{33}NO_8F_6S_2Mo$: C, 40.06; H, 4.44; N, 1.87. Found: C, 40.36; H, 4.52; N, 1.60.

(DME)(R$_{F6}$O)$_2$(NAr)Mo(CH)$_6$Mo(NAr)(OR$_{F6}$)$_2$(DME) (9a). To a solution of 1a (98 mg, 132 μmol) in 4 mL of DME was added the solution of octatetraene (7 mg, 66 μmol) in 1 mL of DME at 25 °C. After the mixture was stirred for 1 h (color changed from yellow to dark red), solvent was removed in vacuo and the residue was dissolved in pentane. The insoluble brown powder was filtered and recrystallized from pentane/CH_2Cl_2 to yield dark red crystals (52 mg, 52%): ^{1}H NMR (CD$_2$Cl$_2$) δ 12.53 (d, 2, MoC*H*R), 7.80 (m, 2, H_β), 7.35–7.20 (m, 6, H_{aryl}), 5.50–5.40 (m, 2, H_γ), 3.62–3.48 (sept, 4, C*H*Me$_2$), 3.50 (s, 8, –OCH_2–), 3.35 (s, 12, –O*Me*), 1.40 (s, 12, OC*Me*(CF$_3$)$_2$), 1.20 (d, 24, CH*Me*$_2$); ^{13}C NMR (CD$_2$Cl$_2$) δ 267.5 (d, J = 127, MoCHR), 153.4 (s, C_{ipso}), 148.6 (s, C_o), 145.5 (d, J = 156, C_β), 130.2 (d, J = 161, C_p), 124.3 (d, J = 135, C_γ), 123.7 (q, $^1J_{CF}$ = 247, OCMe(*C*F$_3$)$_2$), 123.6 (d, J = 160, C_m), 81.8 (sept, $^2J_{CF}$ = 20, O*C*Me(CF$_3$)$_2$), 72.2 (d, J = 145, –OCH_2–), 59.1 (q, J = 140, O*Me*), 29.0 (d, J = 129, *C*HMe$_2$), 23.6 (q, J = 127, CH*Me*$_2$), 19.0 (q, J = 132, OC*Me*(CF$_3$)$_2$). Anal. Calcd for $C_{54}H_{72}F_{24}N_2O_8Mo_2$: C, 42.53; H, 4.76; N, 1.84. Found: C, 42.97; H, 4.76; N, 1.77.

(Et$_2$O)(R$_{F6}$O)$_2$(NAr)Mo(CH)$_6$Mo(NAr)(OR$_{F6}$)$_2$(Et$_2$O) (9b). This complex was prepared by two routes as described below. (a) To a solution of 1a (98 mg, 132 μmol) in 4 mL of Et$_2$O was added the solution of octatetraene (7 mg, 66 μmol) in 1 mL of Et$_2$O at 25 °C. The color changed quickly to dark red, and a precipitate formed. After the mixture was stirred for 1 h, the precipitate was collected and rinsed with cold pentane to give a dark brown powder (65 mg, 66%). (b) The DME ligand in 9a was easily replaced by dissolving the compound in Et$_2$O, generating the ether adduct quantitatively: ^{1}H NMR (CD$_2$Cl$_2$) δ 12.52 (d, 2, MoC*H*R), 7.80 (m, 2, H_β), 7.35–7.10 (m, 6, H_{aryl}), 5.52–5.35 (m, 2, H_γ), 3.65–3.35 (m, 12, –C*H*Me$_2$ and –OCH_2–), 1.40 (s, 12, OC*Me*(CF$_3$)$_2$), 1.20 (d, 24, –CH*Me*$_2$), 1.15 (t, 12, OCH$_2$*Me*); ^{13}C

NMR (CD_2Cl_2) δ 267.4 (d, J = 132, Mo*C*HR), 153.4 (s, C_{ipso}), 148.6 (s, C_o), 145.5 (d, J = 157, C_β), 130.2 (d, J = 161, C_p), 124.3 (d, J = 153, C_γ), 123.8 (q, $^1J_{CF}$ = 276, OCMe(*C*F_3)$_2$), 123.6 (d, J = 161, C_m), 81.6 (sept, $^2J_{CF}$ = 32, O*C*Me(CF_3)$_2$), 66.0 (t, J = 146, –O*C*H_2–), 29.0 (d, J = 131, *C*HMe$_2$), 23.6 (q, J = 129, CH*Me*$_2$), 19.0 (q, J = 133, OC*Me*(CF_3)$_2$), 15.4 (q, J = 127, OCH_2*Me*).

(THF)(R_{F6}O)$_2$(NAr)Mo(CH)$_6$Mo(NAr)(OR_{F6})$_2$(THF) (9c). The DME ligand in **9a** was also easily replaced by dissolving the compound in THF, generating the THF adduct quantitatively: ^{1}H NMR (CD_2Cl_2) δ 12.41 (d, 2, Mo*C*HR), 7.78 (m, 2, H_β), 7.35–7.15 (m, 6, H_{aryl}), 5.37 (m, 2, H_γ), 3.73 (m, 8, –OCH_2–), 3.63 (m, 4, *C*HMe$_2$), 1.79 (m, 8, –OCH$_2$CH_2–), 1.32 (s, 12, OC*Me*(CF_3)$_2$), 1.19 (d, 24, CH*Me*$_2$); ^{13}C NMR (CD_2Cl_2) δ 271.5 (d, J = 152, Mo*C*HR), 153.1 (s, C_{ipso}), 148.5 (s, C_o), 146.4 (d, J = 156, C_β), 129.8 (d, J = 161, C_p), 124.4 (q, $^1J_{CF}$ = 283, OCMe(*C*F_3)$_2$), 124.2 (d, J = 155, C_γ), 123.6 (d, J = 162, C_m), 81.6 (sept, $^2J_{CF}$ = 29, O*C*Me(CF_3)$_2$), 69.3 (t, J = 147, –O*C*H_2–), 28.8 (d, J = 128, *C*HMe$_2$), 25.8 (t, J = 133, –OCH$_2$*C*H_2–), 23.7 (q, J = 127, CH*Me*$_2$), 18.6 (q, J = 132, OC*Me*(CF_3)$_2$).

(quin)(Me$_3$CO)$_2$(NAr)Mo(CH)$_6$Mo(NAr)(OCMe$_3$)$_2$(quin) (9d). Quinuclidine (1 mL of a 2.2 mg/mL stock solution in CH_2Cl_2, 2 equiv) was added to a solution of **9a** (15 mg, 9.8 μmol) in 1 mL of CH_2Cl_2. The reaction mixture was stirred for 10 min. A solution of LiO-*t*-Bu (1 mL of a 3.4 mg/mL stock solution in CH_2Cl_2, 39.2 μmol) was added, and the mixture was stirred for 40 min. The solvent was removed in vacuo, and the residue was extracted with pentane. A brown powder was collected and was washed with cold pentane. Although the reaction proceeded quantitatively, on the basis of the ^{1}H NMR spectrum of the crude mixture, the isolated compound was not pure owing to the instability of the product and the contamination of alkoxides: ^{1}H NMR (THF-d_8) δ 11.70 ppm (b, 2, H_α-vinyl alkylidene), 7.55 (b, 2, H_β-vinyl alkylidene), 7.10 (b, 6, H_m and H_p), 5.28 (b, 2, H_γ-vinyl alkylidene), 3.96 (b, 4, *C*HMe$_2$), 2.90 (b, 12, H_α-quin), 1.52 (b, 12, H_β-quin), 1.22 (bs, 18, C*Me*$_3$), 1.99 (bd, 12, CH*Me*$_2$); ^{13}C NMR δ 255.5 (C_α), 147 (tentatively assigned to C_β), 122.8 (tentatively assigned to C_γ). More extensive characterization of **7d** has been difficult due to its thermal instability.

1,4-[(DME)(R_{F6}O)$_2$(NAr)MoCH]$_2$C$_6$H$_4$ (10a). **1b** (0.300 g, 0.426 mmol) was dissolved in 8 mL of DME, and divinylbenzene was added (27 mg, 0.207 mmol). After it was stirred for 12 h, the solution turned orange. The solvents were removed in vacuo, the solid was washed with CH_2Cl_2, and the orange product was collected by filtration. Additional product was collected by crystallization from CH_2Cl_2; yield 0.247 g (70%): ^{1}H NMR (DME-d_{10}) δ 12.94 (s, 2, Mo*C*HR), 7.36 (t, 2, imido H_p), 7.18 (d, 4, imido H_m), 7.10 (s, 4, alkylidene H_o), 3.58 (sept, 4, *C*HMe$_2$), 1.24 (s, 12, OC*Me*(CF_3)$_2$), 1.02 (d, 24, CH*Me*$_2$); ^{13}C NMR (DME-d_{10}) δ 279.1 (d, J = 125, Mo*C*HR), 154.3 (s, C_{ipso} NAr), 148.8 (s, C_o NAr), 146.5 (s, C_{ipso} Ph), 131.0 (d, J = 162, C_p NAr), 128.8 (d, J = 161, C_o Ph), 124.3 (q, $^1J_{CF}$ = 290, OCMe(*C*F_3)$_2$), 124.1 (q, $^1J_{CF}$ = 290, OCMe(*C*F_3)$_2$), 124.5 (d, J = 160, C_m NAr), 82.3 (sept, $^2J_{CF}$ = 28, O*C*Me(CF_3)$_2$), 29.0 (d, J = 130, *C*HMe$_2$), 23.9 (q, J = 125, CH*Me*$_2$), 18.7 (q, J = 130, OC*Me*(CF_3)$_2$). Anal. Calcd for $MoC_{31}H_{39}F_{12}NO_4$: C, 43.42; H, 4.68; N, 1.81. Found: C, 43.30; H, 4.60; N, 1.73.

1,4-[(THF)(R_{F6}O)$_2$(NAr)MoCH]$_2$C$_6$H$_4$ (10b). **10b** was observed upon dissolving **10a** in THF-d_8: ^{1}H NMR (THF-d_8) δ 12.93 (s, 2, Mo*C*HR), 7.33 (t, 2, imido H_p), 7.18 (d, 4, imido H_m), 7.10 (s, 4, alkylidene H_o), 3.62 (sept, 4, *C*HMe$_2$), 1.24 (s, 12, OC*Me*(CF_3)$_2$), 1.02 (d, 24, CH*Me*$_2$).

Observation of Mo(CH$_2$)(NAr)(OR_{F6})$_2$(DME) (11a). **1b** (0.020 g, 0.028 mmol) was dissolved in 600 μL of DME-d_{10} in a septum-sealed NMR tube. Two milliliters of ethylene was injected into the tube via a syringe, pressurizing the system with ethylene. The ^{1}H NMR spectrum of the methylene complex **11a** was taken, showing two broad H_α resonances at 12.54 and 11.96 ppm. The ethylene was then removed in vacuo, and the ^{1}H NMR spectrum was taken again, showing that most of the alkylidene had reverted to the neopentylidene **1b**, although approximately 12% of the methylene was still present. The two H_α resonances for the methylene complex were sharp doublets at 12.56 and 11.99 ppm (J_{HH} = 6.0).

Mo(CH$_2$)(NAr)(OR_{F6})$_2$(bpy) (11b). **1b** (0.150 g, 0.196 mmol) was dissolved in 5 mL of DME in a 20-mL vial sealed with a septum. A 20-mL amount of ethylene was bubbled into the stirring solution via syringe, pressurizing the system with ethylene. After 5 min, a solution of 2,2′-bipyridine (30 mg, 0.196 mmol) in 2 mL of DME was added via syringe and stirred for 5 min. The solvents were removed in vacuo, and the product was recrystallized from methylene chloride layered with pentane (1:1) to afford yellow crystals of **11b** (0.104 g, 65%): ^{1}H NMR (CD_2Cl_2) δ 13.26 (d, 1, J_{HH} = 3.9, Mo*C*H_2), 12.92 (d, 1, J_{HH} = 3.9, Mo*C*H_2), 9.24 (m, 1, bpy), 8.67 (m, 1, bpy), 8.15–7.95 (m, 4, bpy), 7.66 (m, 1, bpy), 7.35 (m, 1, bpy), 6.97–6.90 (m, 3, NAr), 4.36 (sept, 2, *C*HMe$_2$), 1.41 (s, 3, OC*Me*(CF_3)$_2$), 1.20 (s, 3, OCMe(CF_3)$_2$), 1.10 (d, 6, CH*Me*$_2$), 0.79 (d, 6, CH*Me*$_2$); ^{13}C NMR (CD_2Cl_2) δ 285.5 (t, J = 139, Mo*C*H_2), 159.3 (d, J = 186, bpy), 154.5 (s, C_{ipso}), 152.2 (s, bpy), 150.3 (d, J = 187, bpy), 149.3 (d, J = 187, bpy), 148.8 (s, C_o), 140.0 (d, J = 167, bpy), 139.6 (d, J = 166, bpy), 126.4 (d, J = 160, C_p), 126.2 (q, $^1J_{CF}$ = 288, OCMe(*C*F_3)$_2$), 125.7 (d, J = 166, bpy), 125.4 (q, $^1J_{CF}$ = 290, OCMe(*C*F_3)$_2$), 125.2 (q, $^1J_{CF}$ = 289, OCMe(*C*F_3)$_2$), 124.9 (q, $^1J_{CF}$ = 289, OCMe(*C*F_3)$_2$), 123.0 (d, J = 157, C_m), 122.7 (d, J = 166, bpy), 121.6 (d, J = 166, bpy), 80.1 (sept, $^2J_{CF}$ = 27, O*C*Me(CF_3)$_2$), 79.2 (sept, $^2J_{CF}$ = 27, O*C*Me-(CF_3)$_2$), 28.0 (d, J = 131, *C*HMe$_2$), 25.3 (q, J = 126, CH*Me*$_2$), 23.3 (q, J = 126, CH*Me*$_2$), 18.6 (q, J = 129, OC*Me*(CF_3)$_2$), 17.5 (q, J = 129, OC*Me*(CF_3)$_2$). Anal. Calcd for $MoC_{31}H_{33}F_{12}N_3O_2$: C, 46.34; H, 4.14; N, 5.23. Found: C, 46.59; H, 4.33; N, 4.86.

Poly(2,3-dicarbomethoxynorbornadiene)$_{100}$. **1a** (10 mg, 0.013 mmol) was dissolved in 4 mL of DME. The monomer (270 mg, 1.3 mmol) was dissolved in 1 mL of DME and added all at once to a stirring solution of the catalyst. After 90 min, 8 μL of benzaldehyde was added to terminate the reaction. The polymer was precipitated in hexanes and dried in vacuo to give 231 mg of polymer (86%). Polymerizations involving the other catalysts were conducted under similar conditions.

Poly(2,3-bis(trifluoromethyl)norbornadiene)$_{100}$. **1a** (5 mg, 0.007 mmol) was dissolved in 4 mL of DME. 2,3-Bis(trifluoromethyl)norbornadiene (149 mg, 0.70 mmol) was dissolved in 1 mL of DME and added all at once to a stirring solution of the catalyst. After 16 h, 5 μL of benzaldehyde was added. After 1 h, the polymer was precipitated in hexanes and dried in vacuo to afford 140 mg of polymer (94%).

Metathesis of *cis*-2-Pentene by 1a in DME. **1a** (4 mg, 0.005 mmol) was dissolved in 2 mL of DME, *cis*-2-pentene (282 μL, 500 equiv) was added, and the solution was stirred for 17 h. An aliquot was quenched by passing it through Al_2O_3. GLC analysis showed it to consist of a mixture of 2-butenes, 2-pentenes, and 3-hexenes. The less volatile components were used to assess activity; the ratio of 2-pentenes to 3-hexenes was found to be 1:0.13.

(MTD)$_{100}$CHCH$_2$CH(OMe)C$_6$H$_4$CH(OMe)CH$_2$CH(MTD)$_{100}$. To the solution of **3** (10 mg, 6.7 μmol) in 5 mL of toluene was added LiO-*t*-Bu (5 mg, 53.6 μmol, 100% excess), and the mixture was stirred for 1 h. A 200-equiv amount of MTD (234 mg, 1.34 mmol) was added all at once, and after 10 min the reaction mixture was capped with benzaldehyde (reaction time 1 h). The polymer was precipitated in 100 mL of methanol and dried in vacuo to yield 219 mg (93%) with a polydispersity of 1.03.

(MTD)$_{100}$(CH)$_6$(MTD)$_{100}$. The same procedure was used as described above to make this polymer. A white polymer was obtained with a polydispersity of 1.05 (94% yield).

Reactions with Aldehydes. Complexes **4**, **5**, **9a**, **9b**, and **10a** were each treated with pivaldehyde and benzaldehyde, and the expected coupled products were obtained quantitatively. The general procedure was dissolving alkylidene complexes in CH_2Cl_2 or DME followed by adding appropriate aldehydes (in 10% excess) and removing the metal oxo product by passing through silica gel column (ether eluent).

8,8-Dimethylnona-*trans,trans,trans*-2,4,6-trienal. **1b** (0.150 g, 0.308 mmol) was dissolved in 5 mL of THF. A solution of

trans,trans-2,4-hexadiene-1,6-dialdehyde (0.068 g, 0.615 mmol) in 5 mL of THF was added, and the solution was stirred for 1 h. The solvent was then removed in vacuo. The solids were extracted with pentane, and the soluble material was chromatographed on silica gel. Pentane was used to elute any di-*tert*-butyl-capped decapentaene that had formed. Ether was then used to elute the desired product. The solvent was then evaporated and the product obtained in 65% yield: ^{1}H NMR (C_6D_6) δ 9.44 (d, 1, H_a), 6.49 (dd, 1), 6.15 (dd, 1), 5.99 (dd, 1), 5.6–5.8 (overlapping multiplets, 3), 0.91 (s, 9, CMe_3).

(*t*-Bu)(CH=CH)$_4$(*t*-Bu) (4-ene). 9d (125 mg, 0.110 mmol) was dissolved in 10 mL of THF, and excess pivaldehyde (~5 equiv) was then added. The solution was stirred for 45 min, turning light orange. The solvent was removed in vacuo, and the resulting solids were taken up in pentane; this solution was passed through a column of silica gel in order to remove the metal–oxo complex. The product was isolated as a white solid in essentially quantitative yield (22 mg, 0.101 mmol, 92%). This compound and other polyenes were identified by UV/vis and HPLC.[12]

(*t*-Bu)(CH=CH)$_6$(*t*-Bu) (6-ene). 9d (85 mg, 0.116 mmol) was dissolved in THF, and 0.5 equiv of hexa-2,4-diene-1,6-dialdehyde (6.4 mg, 0.0580 mmol) was added. After the mixture was stirred for 1 h, the solvents were stripped away, leaving an orange solid. This material was purified by chromatography on a column of silica gel; the product was eluted with pentane. The product was isolated as a yellow solid in 15-mg yield (0.550 mmol, 94%).

(*t*-Bu)(CH=CH)$_{10}$(*t*-Bu) (10-ene). 9d (90 mg, 0.079 mmol) was dissolved in 5–10 mL of THF. A 2-fold excess of 8,8-dimethylnona-2,4,6-trienal (26 mg, 0.160 mmol) was dissolved in 5 mL of THF and added to the solution. After the mixture was stirred for 1 h, an orange solid material had precipitated from the solution. The solvents were stripped away and the solids extracted with pentane. The remaining solid material was identified as the desired product (27 mg, 0.072 mmol, 91%).

Acknowledgment. R.R.S. thanks the National Science Foundation (Grant CHE 91 22827) and the Director, Office of Basic Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy (Contract DE-FG02-86ER13564) for supporting polyene research.

OM920630C