Initiators of the Type Mo(NAr)(CHR′)(OR′′)$_2$ for the Controlled Polymerization of Diethyldipropargylmalonate

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The reaction between Mo(NAr)(*trans*-CHCH═CHMe)[OCMe(CF$_3$)$_2$]$_2$(quin) (Ar = 2,6-*i*-Pr$_2$-C$_6$H$_3$; quin = quinuclidine) and lithium *tert*-butoxide yields Mo(NAr)(*trans*-CHCH═CHMe)(O-*t*-Bu)$_2$(quin) (**1**). The *achiral*,*syn* isomer could be isolated and was shown in an X-ray study to be a trigonal bipyramid in which quinuclidine is coordinated *trans* to a *syn* butenylidene group. A base-free species (**2**) that contains a five-membered ring as part of a trienylidene unit could be obtained by treating Mo(NAr)(CHCMe$_2$R)-[OCMe(CF$_3$)$_2$]$_2$ (R = Me, Ph) with diethyl 3-(2-methylprop-1-enyl)-4-vinylcyclopent-3-ene-1,1-dicarboxylate (**B**) in pentane. The *tert*-butoxide analogue of **2** (**3**) was obtained straightforwardly and was shown in an X-ray study to be the *syn* alkylidene isomer. The reaction between 1-methylidene-5,5-bis(carboxyethyl)cyclohex-1-ene and Mo(NAr)(CHCMe$_3$)[OCMe(CF$_3$)$_2$]$_2$ gave Mo(NAr)[1-methylidene-5,5-bis(carboxyethyl)cyclohex-1-ene)][OCMe(CF$_3$)$_2$]$_2$ (**5a**), which could be treated with LiO-*t*-Bu to yield an analogous *tert*-butoxide species (**5b**). An X-ray structure of a sample of **5b** that retained 2 equiv of LiOCMe(CF$_3$)$_2$ showed it to be a dimeric species in which two Mo complexes were joined through a Li$_4$O$_4$ heterocubane-type structure binding to one ester oxygen in each of the Mo species. Reactions between diethyldipropargylmalonate (DEDPM) and **1**, **3**, or **5b** showed initiation to be smooth with k_p/k_i values less than 1 and to yield oligomers that were consistent with formation of polymers that contain largely five-membered rings. All reactions can be followed by proton NMR spectra of the alkylidene proton region, and all appear to be living polymerizations under the conditions employed. A Wittig-like reaction between diethyl 3-formyl-4-(2-methylprop-1-enyl)cyclopent-3-ene-1,1-dicarboxylate (**A**) and **2** yielded a symmetric pentaene (**C**) as an ivory-colored solid. The heptaene (**D**) and the nonaene (**E**) could be isolated from reactions between 1 equiv of DEDPM and **3** in CH$_2$Cl$_2$ in the presence of 1 equiv of quinuclidine at −30 °C followed by quenching with aldehyde **A**.

Introduction

Polyacetylene (all *trans*) is the simplest π-conjugated organic polymer. It is highly conductive when doped, particularly when oriented, and possesses a high third-order susceptibility ($\chi^{(3)}$). It is also unstable toward oxidation by oxygen and insoluble in common organic solvents. Soluble and more air-stable substituted polyenes have been prepared through polymerization of substituted phenylacetylenes[1−5] or 4,4-disubstituted 1,6-heptadiynes.[6−8] Although such polyenes are no longer highly conductive in the solid state, they still have desirable electronic, linear or nonlinear optical, and electrochemical (photoconductive or photorefractive) properties.

We have shown that Mo(NR)(CHR′)(OR′′)$_2$ complexes can be designed that will initiate the polymerization of both substituted phenylacetylenes such as *ortho*-TMSphenylacetylene[9] and 4,4-disubstituted 1,6-heptadiynes such as diethyldipropargylmalonate (DEDPM).[10] To maximize a given property of poly[1,6-heptadiynes], it is most desirable to design catalysts that will yield polymers with a single regular structure and with the narrowest possible molecular weight distribution through a living polymerization. We showed that polymerization of DEDPM could be carried out in a living manner with well-defined imido alkylidene catalysts[11] of the type Mo(NAr)-(CHCMe$_2$Ph)(OR$_{F6}$)$_2$ (Ar = 2,6-*i*-Pr$_2$-C$_6$H$_3$, OR$_{F6}$ = OCMe-(CF$_3$)$_2$) to give polyenes that contain a mixture of five- or six-membered rings, on the basis of comparison of ^{13}C NMR spectra of polymers with those of model cyclic monomers.[10,12] Five- or six-membered rings are formed as a consequence of initial addition of the first triple bond to give an α- or a β-substituted molybdacyclobutene intermediate, respectively (Scheme 1). HPLC procedures have been developed that have allowed oligomers that contain both five- and six-membered rings to be separated according to their chain lengths and absorption spectra to be obtained at room-temperature solutions and in glasses at 77 K.[13] The proposal that a greater degree of steric hindrance around the metal would force β-addition led to the design of

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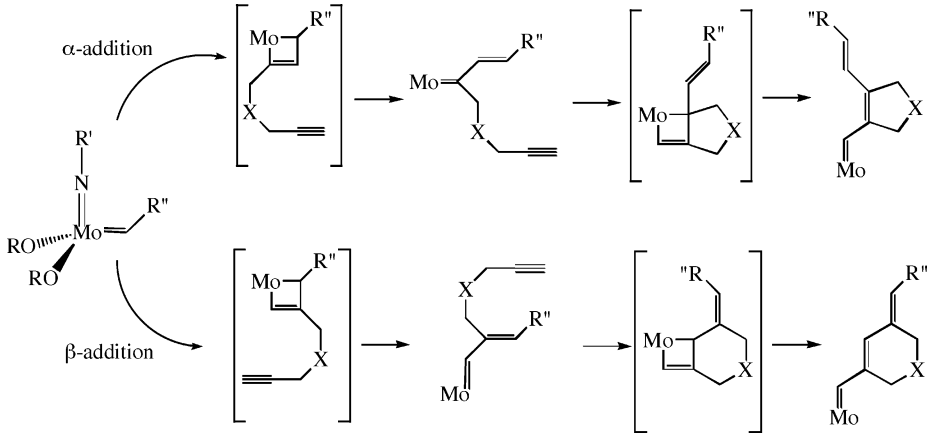
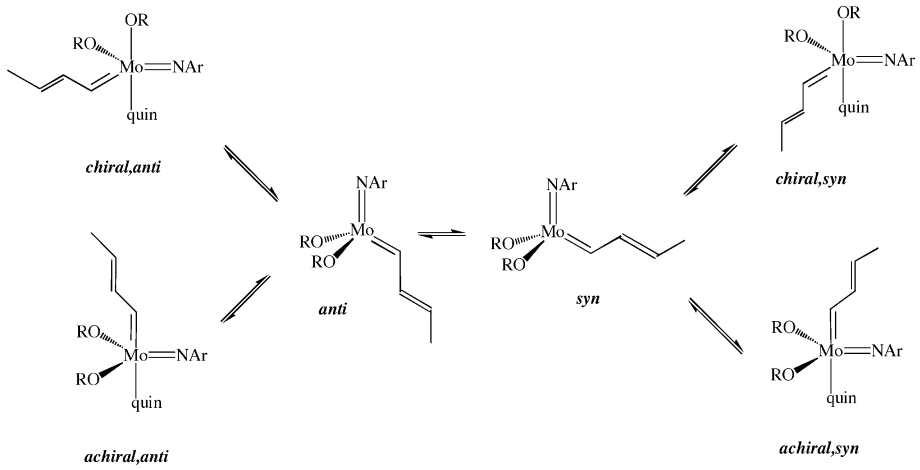
Scheme 1. Reaction of Mo(NR)(CHR′)(OR″)$_2$ with 1,6-Heptadiyne Derivatives (e.g., X = C(CO$_2$Et)$_2$)



Scheme 2. Possible Isomers of Mo(NAr)(*trans*-CHCH═CHMe)(OR)$_2$ and Mo(NAr)(*trans*-CHCH═CHMe)(OR)$_2$(quin)



catalysts that contain carboxylates, in particular Mo(NAd)(CHCMe$_2$Ph)(O$_2$CCPh$_3$)$_2$ (Ad = 1-adamantyl). The carboxylate catalysts in fact will polymerize DEDPM to yield polyenes that contain all six-membered rings.[14] Most recently Buchmeiser has shown that polyenes that contain largely (>95%) five-membered rings can be prepared using Mo(NAr)(CHCMe$_2$Ph)(O-*t*-Bu)$_2$ catalysts.[15,16] Polyenes that contain largely (>95%) five-membered rings also can be prepared with new types of Ru catalysts, although these processes do not appear to be living.[17] The alternating *cis/trans* 1,2-(cyclopent-1-enylene)vinylenes produced when Mo(NAr)(CHCMe$_2$Ph)(O-*t*-Bu)$_2$(quin) is employed as an initiator were characterized by M_n(experimental)/M_n(calculated) ratios between 1.5 and 2 (according to light scattering at 690 nm), PDI values between 1.15 and 1.26 (according to GPC), and a λ_{max} as high as 591 nm. There is a possibility that five- and six-membered rings are formed through selective reaction with *syn* or *anti* alkylidene isomers,[18] although this has not been elucidated fully. Connected with the *syn/anti* issue is the issue concerning donors such as quinuclidine, which slow polymerization overall and appear to bind more strongly to *anti* isomers than to *syn* isomers. Typically, more five-membered rings have been found in polymers prepared in the presence of quinuclidine.[15,16]

In all polymerizations reported so far the rate of propagation is much higher than the rate of initiation, a fact that limits maximum control over the chain length of such polymers and information concerning the origin of five- and six-membered rings in the polyene. Therefore it would be desirable to prepare and employ relatively stable initiators that react with 1,6-heptadiynes at a rate that is approximately the same as, or is faster than, the rate of propagation to give polyenes. In this paper we show how to prepare catalysts that are rapid initiators and explore their reactions with diethyldipropargylmalonate (DEDPM) to yield oligomers of DEDPM that contain >95% five-membered rings.

Results and Discussion

Synthesis and Solid-State Structure of a Butenyl Initiator. In view of the fact that the propagating species in a cyclopolymerization of a 1,6-heptadiyne is a vinyl-substituted primary alkylidene (Scheme 1), it seemed sensible to attempt to employ vinylalkylidenes as initiators. However, known four-coordinate vinylalkylidene complexes must be stabilized toward bimolecular coupling of alkylidenes to yield reduced Mo species. For example, Mo(NAr)(*trans*-CHCH═CHMe)[OCMe(CF$_3$)$_2$]$_2$(quin) (quin = quinuclidine) is a known species that may be prepared by treating Mo(NAr)(CHCMe$_3$)[OCMe(CF$_3$)$_2$]$_2$ with several equivalents of 1,3-pentadiene in the presence of excess quinu-

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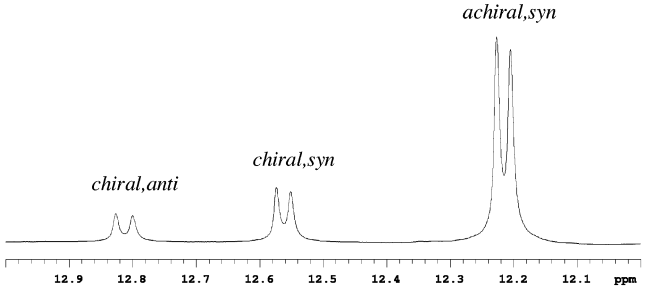

Figure 1. 500 MHz ^{1}H NMR (−70 °C, $C_6D_5CD_3$) spectrum of the alkylidene H_α resonances of Mo(NAr)(*trans*-CHCH═CHMe)-(O-*t*-Bu)$_2$(quin).

clidine, but quinuclidine-free Mo(NAr)(*trans*-CHCH═CHMe)-[OCMe(CF$_3$)$_2$]$_2$ appears to be unstable.[19] We prepared Mo-(NAr)(*trans*-CHCH═CHMe)[OCMe(CF$_3$)$_2$]$_2$(quin) and confirmed that alkylidene resonances for three isomers are observed in the proton NMR spectrum in CD_2Cl_2. They are the *chiral,anti* isomer ($\delta H_\alpha = 13.04$ ppm), the *chiral,syn* isomer ($\delta H_\alpha = 12.90$ ppm), and the *achiral,syn* isomer ($\delta H_\alpha = 12.55$ ppm). Four possible adduct structures are shown in Scheme 2. *Achiral,anti* isomers have not been observed in compounds of this general type. Two alternative possible structures in which the base is *trans* to the imido ligands are not shown. As we found previously, the initial ratio of isomers that is obtained in a typical synthesis varies with reaction conditions, and the initial mixture then evolves toward a final mixture of isomers. The *syn* isomers appear to reach a steady-state concentration most rapidly, while the *syn* and *anti* isomers equilibrate more slowly. In past studies it has been postulated that *syn* and *anti* isomers interconvert through loss of the base and rotation of the alkylidene in the four-coordinate species and that a base binds more strongly to *anti* isomers.[19] This is the reason *anti* adducts equilibrate with *syn* adducts relatively slowly.

The *tert*-butoxide analogue of the vinylalkylidene species Mo-(NAr)(*trans*-CHCH═CHMe)(O-*t*-Bu)$_2$(quin) (**1**) can be prepared via addition of an excess (4 equiv) of LiO-*t*-Bu to Mo(NAr)-(*trans*-CHCH═CHMe)[OCMe(CF$_3$)$_2$]$_2$(quin). (Excess LiO-*t*-Bu ensures that Mo(NAr)(*trans*-CHCH═CHMe)[OCMe(CF$_3$)$_2$]$_2$-(quin) reacts completely in a practical amount of time.) Compound **1** decomposes slowly in CD_2Cl_2 over a period of several hours and more rapidly in $CHCl_3$. Mo(NAr)(*trans*-CHCH═CHMe)(O-*t*-Bu)$_2$(quin) is not indefinitely stable even in benzene. After 14 h in C_6D_6 at room temperature, the integral value of each alkylidene resonance was only 37% of the original value compared to an internal standard. We propose that the base dissociates from the more electron rich metal center to yield Mo(NAr)(*trans*-CHCH═CHMe)(O-*t*-Bu)$_2$, which then decomposes bimolecularly as a consequence of its lower coordination number to yield MeCH═CHCH═CHCH═CHMe and unidentified reduced metal species.[20] Mo(NAr)(*trans*-CHCH═CHMe)(O-*t*-Bu)$_2$(quin) is stable when stored as a solid at −30 °C for several months.

At 20 °C in toluene-d_8 the ^{1}H NMR spectrum of Mo(NAr)-(*trans*-CHCH═CHMe)(O-*t*-Bu)$_2$(quin) reveals a broadened doublet alkylidene H_α resonance for the *achiral,syn* isomer at 12.11 ppm with a $^1J_{CH}$ coupling constant of 122 Hz ($^3J_{HH} = 11$ Hz). The proton NMR spectrum in toluene-d_8 is consistent with a complex that has a mirror plane; that is, a single broadened septet is observed at 4.15 ppm corresponding to two equivalent

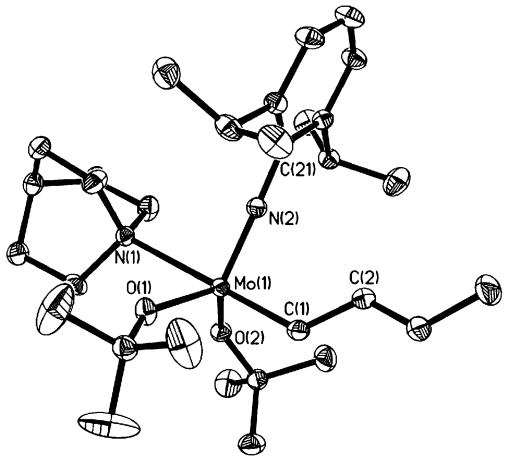

Figure 2. Thermal ellipsoid drawing of *achiral,syn* Mo(NAr)-(*trans*-CHCH═CHMe)(O-*t*-Bu)$_2$(quin) (**1**) at the 50% probability level. Hydrogen atoms are omitted for clarity.

isopropyl methine protons, a doublet is observed at 1.34 ppm corresponding to 12 equivalent isopropyl methyl protons, and a large singlet is observed at 1.38 ppm corresponding to 18 equivalent *tert*-butyl methyl protons. The resonances for bound and free quinuclidine are broadened, which suggests that bound and free quinuclidine exchange readily, although not rapidly enough on the NMR time scale to lead to coalescence of resonances. The weak quinuclidine coordination is a consequence of the greater electron-donating ability of *tert*-butoxide groups versus hexafluoro-*tert*-butoxide groups. At 20 °C, the *chiral,anti* isomer ($\delta H_\alpha = 12.70$ ppm, $^1J_{CH} = 142$ Hz in C_6D_5-CD_3) is present to the extent of ∼9% in solution at equilibrium, and this equilibrium is readily established as a consequence of the quinuclidine base being relatively labile. Addition of 10 equiv of quinuclidine to Mo(NAr)(*trans*-CHCH═CHMe)(O-*t*-Bu)$_2$(quin) in C_6D_6 does not significantly affect the ratio of isomers present in solution.

At −70 °C three isomers are present (Figure 1), the *chiral,-anti* isomer (10%; $H_\alpha = 12.81$ ppm), the *chiral,syn* isomer (18%; $H_\alpha = 12.56$ ppm), and the *achiral,syn* isomer (72%; $H_\alpha = 12.22$ ppm). Pairs of septets for the isopropyl methine proton resonances of the two minor products are observed at 3.71 and 4.60 ppm for the *chiral,syn* isomer and at 3.80 and 4.71 ppm for the *chiral,anti* isomer. Upon warming the sample, the *chiral,-syn* isomer resonance at 12.56 ppm disappears and the 91:9 equilibrium of *achiral,syn* to *chiral,anti* isomers is restored.

Successive recrystallizations of the mixture of isomers from pentane yielded large dark purple crystals of Mo(NAr)(*trans*-CHCH═CHMe)(O-*t*-Bu)$_2$(quin). This species was shown to be the *achiral,syn* isomer in an X-ray study (Tables 1 and 2, Figure 2), i.e., a trigonal bipyramid in which quinuclidine is coordinated *trans* to a *syn* butenylidene group. Although other *achiral,syn* adducts of this type have been observed in NMR spectra,[19] this is only the second structure of an adduct of a Mo(NR)(CHR′)-(OR″)$_2$ compound to be reported in which the base is *trans* to the alkylidene. The other is [(THF)(R$_{F6}$O)$_2$(ArN)Mo═CH]$_2$(1,4-C_6H_4) (OR$_{F6}$ = OCMe(CF$_3$)$_2$).[21] The reader should refer to Table 2 for bond distances and angles, all of which are within the expected ranges.

Synthesis and Solid-State Structure of a Model Five-Membered-Ring Initiator. The most desirable initiator would be one that is analogous to that formed through polymerization

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Table 1. Crystal Data and Structure Refinement[a] for Mo(NAr)(*trans*-CHCH═CHMe)(O-*t*-Bu)$_2$(quin) (1), Mo(NAr)(CH[5])(O-*t*-Bu)$_2$ (3), and Mo(CH[6])(NAr)(O−t-Bu)$_2$·2LiOR$_{F6}$ (5b)

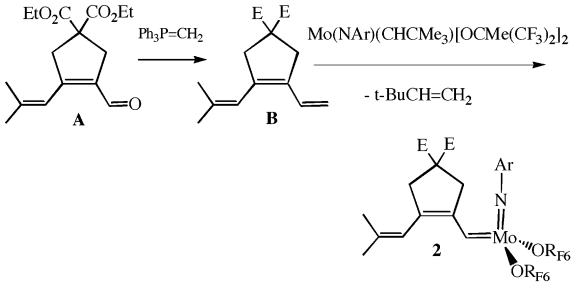
empirical formula	$C_{31}H_{54}MoN_2O_2$	$C_{36}H_{57}MoNO_6$	$C_{41}H_{59}F_{12}Li_2MoNO_8$
fw	582.70 g/mol	695.77 g/mol	1031.71 g/mol
cryst syst	monoclinic	triclinic	orthorhombic
space group	*Pn*	$P\bar{1}$	$Cmc2_1$
unit cell dimens	$a = 9.3667(3)$ Å	$a = 9.5227(13)$ Å	$a = 45.308(2)$ Å
	$b = 10.5520(4)$ Å	$b = 11.7582(16)$ Å	$b = 10.0831(4)$ Å
	$c = 16.3250(4)$ Å	$c = 19.324(2)$ Å	$c = 21.3920(9)$ Å
	$\alpha = 90°$	$\alpha = 95.113(4)°$	$\alpha = 90°$
	$\beta = 91.0640(10)°$	$\beta = 102.926(4)°$	$\beta = 90°$
	$\gamma = 90°$	$\gamma = 113.726(4)°$	$\gamma = 90°$
volume	1613.24(9) Å^3	1891.3(4) Å^3	9772.9(7) Å^3
Z	2	2	8
density (calcd)	1.200 g/cm^3	1.222 g/cm^3	1.402 g/cm^3
absorption coeff	0.433 mm^{-1}	0.387 mm^{-1}	0.361 mm^{-1}
F(000)	624	740	4256
θ range for data collection	1.93 to 30.03°	1.93 to 28.28°	1.80 to 29.57°
index ranges	$-13 \le h \le 13$	$-12 \le h \le 12$	$-62 \le h \le 62$
	$-14 \le k \le 14$	$-15 \le k \le 15$	$-14 \le k \le 14$
	$-22 \le l \le 22$	$-25 \le l \le 25$	$-29 \le l \le 29$
no. of reflns collected	36 482	38 735	106 930
no. of indep reflns	9391 [$R_{int} = 0.0383$]	9388 [$R_{int} = 0.0446$]	13844 [$R_{int} = 0.0670$]
max. and min. transmn	0.9662 and 0.9580	0.9885 and 0.9623	0.9893 and 0.9478
no. of data/restraints/params	9391/2/336	9388/0/411	13 844/456/706
goodness-of-fit on F^2	1.041	1.043	1.042
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0313$	$R_1 = 0.0355$	$R_1 = 0.0349$
	$wR_2 = 0.0679$	$wR_2 = 0.0809$	$wR_2 = 0.0731$
R indices (all data)	$R_1 = 0.0361$	$R_1 = 0.0448$	$R_1 = 0.0484$
	$wR_2 = 0.0699$	$wR_2 = 0.0847$	$wR_2 = 0.0784$
largest diff peak and hole	0.947 and −0.226 e·Å^{-3}	0.742 and −0.421 e·Å^{-3}	0.594 and −0.261 e·Å^{-3}

[a] In all structures the wavelength was 0.71073 Å, the temperature 100(2) K, and the refinement method full-matrix least-squares on F^2.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for 1, 3, and 5b

Mo(NAr)(*trans*-C$_4$H$_6$)(O-*t*-Bu)$_2$(quin) (**1**)		Mo(NAr)(CH[5])(O-*t*-Bu)$_2$ (**3**)		Mo(NAr)(CH[6])(O-*t*-Bu)$_2$ (**5b**)	
Mo(1)−C(1)	1.952(2)	Mo(1)−C(1)	1.9217(19)	Mo(1)−C(1)	1.911(2)
Mo(1)−N(2)	1.7440(17)	Mo(1)−N(2)	1.7333(16)	Mo(1)−N(1)	1.7345(19)
Mo(1)−O(1)	1.9139(15)	Mo(1)−O(1)	1.8840(13)	Mo(1)−O(1)	1.8897(16)
Mo(1)−O(2)	1.9233(14)	Mo(1)−O(2)	1.8791(14)	Mo(1)−O(2)	1.8845(16)
Mo(1)−N(1)	2.4955(19)	N(2)−Mo(1)−C(1)	99.91(8)	N(1)−Mo(1)−C(1)	101.02(9)
N(2)−Mo(1)−C(1)	93.08(8)	O(1)−Mo(1)−O(2)	111.26(6)	O(1)−Mo(1)−O(2)	112.26(7)
N(2)−Mo(1)−O(1)	120.97(8)	O(1)−Mo(1)−C(1)	107.27(7)	O(1)−Mo(1)−C(1)	107.02(8)
N(2)−Mo(1)−O(2)	116.88(8)	O(2)−Mo(1)−C(1)	108.42(7)	O(2)−Mo(1)−C(1)	108.41(8)
O(1)−Mo(1)−O(2)	115.97(6)	N(2)−Mo(1)−O(1)	115.04(7)	N(1)−Mo(1)−O(1)	112.57(8)
N(1)−Mo(1)−C(1)	178.70(8)	N(2)−Mo(1)−O(2)	113.92(7)	N(1)−Mo(1)−O(2)	114.59(8)
Mo(1)−N(2)−C(21)	172.47(16)	Mo(1)−C(1)−C(2)	135.48(14)	Mo(1)−C(1)−C(2)	138.18(17)
Mo(1)−C(1)−C(2)	128.99(18)	Mo(1)−N(2)−C(25)	175.60(13)	Mo(1)−N(1)−C(31)	168.12(17)

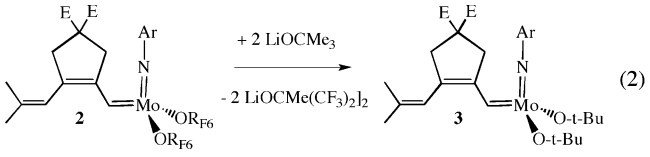
of DEDPM. For this reason we prepared triene **B** (eq 1) through a Wittig reaction with **A**, an aldehyde that is readily formed in a Ru-catalyzed cyclization reported by Trost.[22−24] (Trost reported the dimethyl ester of this compound.) **B** was isolated in 57% yield after column chromatography on silica gel as a colorless crystalline solid; it appears to be stable in air at room temperature for at least several days. It was added to Mo(NAr)(CHCMe$_2$R)[OCMe(CF$_3$)$_2$]$_2$ (R = Me, Ph) in pentane to give **2** (eq 1) as a flaky, orange-yellow solid that has a relatively low



(1)

solubility in pentane. Only the *syn* isomer is observed in solution, with the H$_\alpha$ resonance appearing at 12.79 ppm ($^1J_{CH}$ = 120 Hz) and the H$_\delta$ resonance appearing at 5.96 ppm in CD_2Cl_2. Unlike Mo(NAr)(*trans*-CHCH═CHMe)[OCMe(CF$_3$)$_2$]$_2$(quin), **2** is stable as a base-free species toward bimolecular coupling of alkylidenes.

Addition of 2.5 equiv of LiO-*t*-Bu to **2** in a minimal amount of pentane yielded the analogous *tert*-butoxide species, Mo(NAr)(CH[5])(O-*t*-Bu)$_2$ (**3**, eq 2). Compound **3** can be crystallized from pentane and thereby freed of the LiOCMe(CF$_3$)$_2$ byproduct. The *syn* isomer is the only one observed in solution, with H$_\alpha$ appearing at 11.87 ppm and H$_\delta$ at 6.01 ppm in CD_2Cl_2.



(2)

An X-ray structure of **3** confirmed that it is a *syn* alkylidene complex in which the angles between the ligands range from 107.27(7)° to 115.04(7)° (Tables 1 and 2, Figure 3). The

(22) Trost, B. M.; Older, C. M. *Organometallics* **2002**, *21*, 2544.
(23) Trost, B. M.; Rudd, M. T. *J. Am. Chem. Soc.* **2002**, *124*, 4178.
(24) Trost, B. M.; Rudd, M. T. *J. Am. Chem. Soc.* **2005**, *127*, 4763.

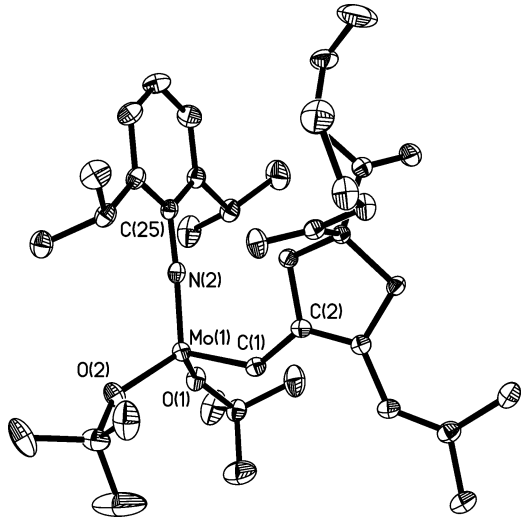
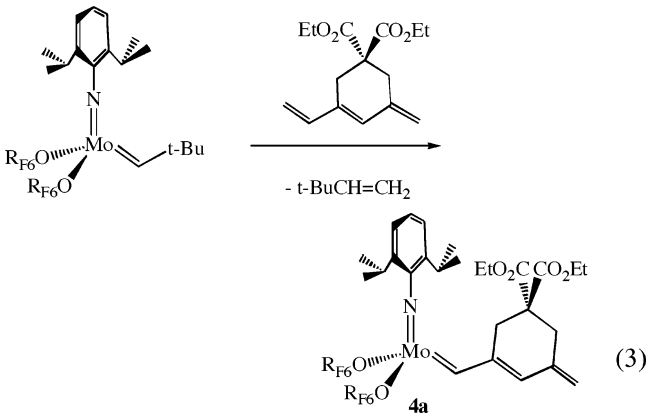


Figure 3. Thermal ellipsoid drawing of Mo(CH[5])(NAr)(O-*t*-Bu)$_2$ **(3)** at the 50% probability level. Hydrogen atoms are omitted for clarity.

alkylidene substituent appears to be relatively demanding sterically, with the Mo−C(1)−C(2) bond angle (135.48(14)°) being larger than the Mo−C(1)−C(2) bond angle of 128.99(18)° in the solid-state structure of **1**. The isopropyl groups on the imido ligand are turned away from the esters in the alkylidene substituent. The Mo−N_{imido}, Mo−O(1), Mo−O(2), and Mo−C(1) bond distances of 1.7333(16), 1.8840(13), 1.8791(14), and 1.9217(19) Å, respectively, are all shorter than the corresponding distances (1.7440(17), 1.9139(15), 1.9233(14), and 1.952(2) Å) in the structure of **1**, presumably as a consequence of the lower coordination number of **3**.

Addition of quinuclidine to a solution of **3** produced an equilibrium mixture that is composed of 71% of the base-free, *syn* isomer (11.87 ppm in CD_2Cl_2) and 29% of the base-bound *chiral,anti* isomer (H_α = 12.33 ppm in CD_2Cl_2 with $^1J_{CH}$ = 144 Hz). Resonances are observed for both bound and free quinuclidine, although they are broadened, consistent with exchange of bound and free quinuclidine on the order of the NMR time scale. The quinuclidine adduct of **3** is more stable than Mo(NAr)(*trans*-CHCH═CHMe)(O-*t*-Bu)$_2$(quin) in solution; 70% of the initial alkylidene remained after 14 h at 22 °C in C_6D_6. The quinuclidine adduct of **3** could not be crystallized however; apparently the greater lability of quinuclidine in **3**, compared to **1**, simply prevents formation of a strong enough adduct, at least under the conditions examined so far.

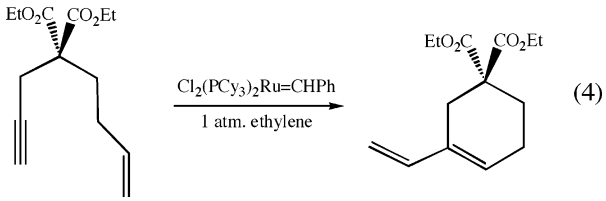
Synthesis and Solid-State Structure of a Six-Membered-Ring Initiator. It has been reported that 1-vinyl-3-methylene-5,5-bis(carboxyethyl)cyclohex-1-ene is formed when DEDPM is added to a solution of Mo(NAr)(CHCMe$_3$)[OCMe(CF$_3$)$_2$]$_2$ in the presence of ethylene.[10] This reaction has been reproduced, although the yield of the triene is relatively low after column chromatography. It was reported as a yellow solid, but we are now certain that it is a colorless oil with limited stability in air at room temperature. Therefore it must be used shortly after it is prepared. It also was reported that this triene reacts with Mo(NAr)(CHCMe$_3$)[OCMe(CF$_3$)$_2$]$_2$ to produce Mo(NAr)[1-methylidene-3-methylen-5,5-bis(carboxyethyl)cyclohex-1-ene)][OCMe(CF$_3$)$_2$]$_2$ (**4a**; eq 3). We have been able to reproduce this result also, although we have been able to isolate **4a** in only low (<12%) yield. Over a period of 1 to 24 h in pentane, DME, or toluene, no more than 45% of the starting neopentylidene complex is consumed. Several impurities are formed during this time, some of which are believed to arise from decomposition of the triene itself.



(3)

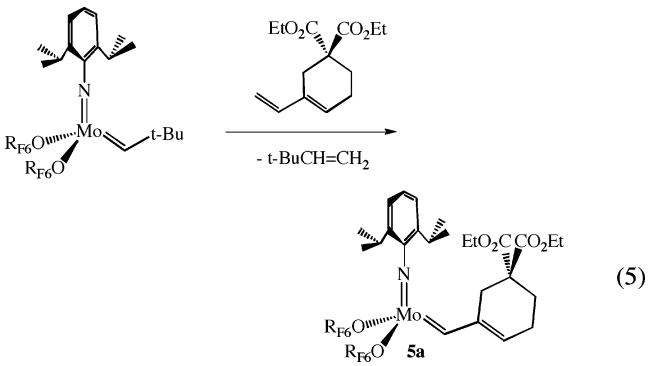
Addition of 2.1 equiv of lithium *tert*-butoxide to **4a** in CD_2Cl_2 yields its *tert*-butoxide analogue, **4b**, and LiOCMe(CF$_3$)$_2$, according to ^{1}H NMR spectroscopy. Unfortunately, we have not been able to isolate **4b**. The alkylidene H_α resonance for **4b** is observed at 11.59 ppm in CD_2Cl_2, and the vinyl proton H_γ resonance of the six-membered ring is observed at 5.59 ppm. Addition of 1 equiv of quinuclidine did not affect the chemical shift of the alkylidene H_α resonance for **4b**.

To prepare isolable initiators that contain a six-membered ring, we turned to the synthesis of a related cyclohexene that lacks the exo-methylene group found in 1-vinyl-3-methylene-5,5-bis(carboxyethyl)cyclohex-1-ene, namely, 1-methylidene-5,5-bis(carboxyethyl)cyclohex-1-ene, which can be prepared through an enyne reaction employing Cl$_2$(PCy$_3$)$_2$Ru═CHPh as a catalyst (eq 4).[25] The resulting diene appears to be much more



(4)

stable than 1-vinyl-3-methylene-5,5-bis(carboxyethyl)cyclohex-1-ene and can be stored at room temperature for short periods of time (1 to 2 days). It reacts readily with Mo(NAr)(CHCMe$_3$)[OCMe(CF$_3$)$_2$]$_2$ to produce Mo(NAr)[1-methylidene-5,5-bis(carboxyethyl)cyclohex-1-ene)][OCMe(CF$_3$)$_2$]$_2$ (Mo(NAr)(CH[6])[OCMe(CF$_3$)$_2$]$_2$, **5a**) in good yield (eq 5). The H_α resonance



(5)

for **5a** appears at 12.52 in CD_2Cl_2 (cf. 12.44 ppm reported for

(25) Mori, M.; Sakakibara, N.; Kinoshita, A. *J. Org. Chem.* **1998**, *63*, 6082.

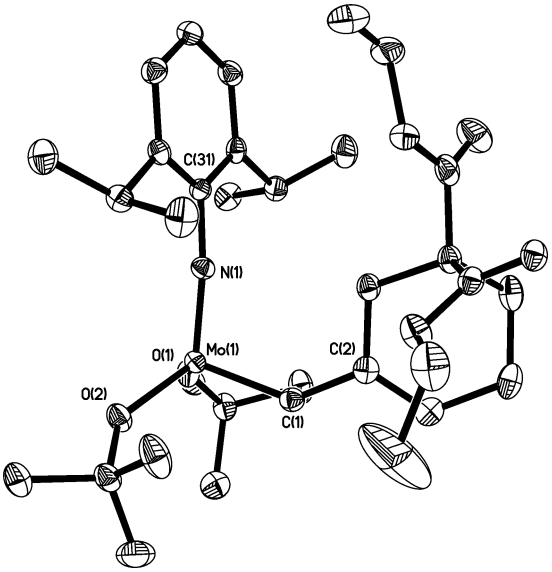
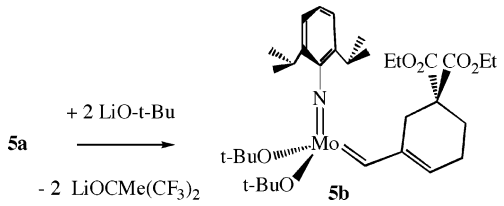


Figure 4. Thermal ellipsoid drawing of Mo(CH[6])(NAr)(O-*t*-Bu)$_2$ (**5b**) at the 50% probability level. Hydrogen atoms are omitted for clarity.

4a) with a $^1J_{CH}$ value of 125 Hz suggestive of a *syn* alkylidene. As with **2**, **5a** shows limited solubility in pentane and may be crystallized readily.

Addition of 2 equiv of LiO-*t*-Bu to **5a** yields **5b** (eq 6). Samples of **5b** prepared in this fashion retain both equivalents of LiOCMe(CF$_3$)$_2$, even after repeated crystallizations from pentane. Compound **5b** may be prepared free of the lithium



(6)

salt by treating **5a** with 2 equiv of TlO-*t*-Bu, but we have not been able to isolate **5b** prepared in this manner, i.e., free of lithium alkoxide. This observation suggests that the lithium salt may aid in crystallization, e.g., by coordinating to an ester functionality. The LiOCMe(CF$_3$)$_2$ present in **5b** does not affect the appearance of the NMR spectra, as the alkylidene H$_\alpha$ resonance shows the same chemical shift as that in samples prepared by treating **5a** with TlO-*t*-Bu. The H$_\alpha$ resonance for **5b** appears at 11.67 ppm in CD_2Cl_2 with a $^1J_{CH}$ = 119 Hz, again suggestive of a *syn* alkylidene. This chemical shift value should be compared to that of **4b** (11.59 ppm) and **3** (11.87 ppm).

Crystals of **5b**·2LiOR$_{F6}$ suitable for X-ray diffraction were grown from a saturated heptane solution. The solid-state structure of the Mo-containing portion of **5b**·2LiOR$_{F6}$ is depicted in Figure 4. As expected, the alkylidene is *syn* and the C(1)−C(2) single bond is transoid, as in **3**. The structure contains 2 equiv of LiOR$_{F6}$ per Mo in the form of a Li_4O_4 heterocubane-type structure coordinating to one ester in each of two Mo catalyst molecules (see Figures S7 and S8 in the Supporting Information). The bond lengths and angles about Mo are similar to those of **3** (Tables 1 and 2). The isopropyl groups of the aryl imido are found in slightly different orientation than observed in **3**.

NMR Studies of Reactions of DEDPM with Initiators. Addition of 0.2 to 5 or more equivalents of DEDPM to Mo(NAr)(*trans*-CHCH=CHMe)(O-*t*-Bu)$_2$(quin) in CD_2Cl_2 at 22 °C led to the consumption of the initiator and the appearance of alkylidene resonances for various insertion products. Upon addition of ∼3 equiv of DEDPM to a solution of Mo(NAr)(*trans*-CHCH=CHMe)(O-*t*-Bu)$_2$(quin), the pale red solution became deep red over a period of 10 s. Proton NMR spectra suggest that the initial alkylidene is almost completely consumed. The ratios of the rate constants for propagation versus initiation (k_p/k_i) at 22 °C in experiments in which between 1.06 and 2.53 equiv of DEDPM had been added were calculated as described in the literature[26] and found to be 0.39 in CD_2Cl_2 (average of five runs; range = 0.36−0.44) and 0.55 in C_6D_6 (average of five runs; range = 0.53−0.61). The value in CD_2Cl_2 did not change significantly when the monomer was added to the initiator at −30 °C (k_p/k_i = 0.41).

In contrast, addition of 3 equiv of DEDPM to Mo(NAr)(CHCMe$_3$)(O-*t*-Bu)$_2$ in CD_2Cl_2 in the presence of 1 equiv of quinuclidine led to consumption of only 69% of the initiator and a value of k_p/k_i = 5.8. Values of k_p/k_i of this magnitude or greater are typical for polymerizations that involve an initial neopentylidene or neophylidene species.[15,16]

When Mo(NAr)(*trans*-CHCH=CHMe)(O-*t*-Bu)$_2$(quin) was treated with 1−3 equiv of DEDPM at −30 and 0 °C, proton NMR spectra similar to that shown in Figure 5a were obtained. Sharp alkylidene resonances to the left of the doublet at 11.85 ppm for the initiator are insertion products in which a five-membered ring is next to the metal (Mo=CH(5) species), while resonances to the right of the doublet at 11.85 ppm near 11.5 ppm are insertion products in which a six-membered ring is next to the metal (Mo=CH(6) species). This assignment is based on the chemical shifts of alkylidene protons in the isolated Mo=CH(5) and Mo=CH(6) compounds described above and experiments described below that involve Mo(NAr)(*trans*-CHCH=CHMe)[OCMe(CF$_3$)$_2$]$_2$(quin). The broad resonances between 12.6 and 12.7 ppm in Figure 5a are proposed to be quinuclidine adducts of two isomers of the first insertion product, Mo=CH-(5)(CHCH=CHMe), in which the bound quinuclidine is exchanging readily with free quinuclidine (see later).

Addition of 10 equiv of DEDPM to Mo(NAr)(*trans*-CHCH=CHMe)(O-*t*-Bu)$_2$(quin) led to NMR spectra that contained a relatively large alkylidene resonance for Mo=CH(5) species at 12.02 ppm and a relatively small alkylidene resonance for Mo=CH(6) species at 11.54 ppm (Figure 5b). Note that the broad resonances between 12.6 and 12.7 ppm in Figure 5a are absent in Figure 5b. The resonance for Mo=CH(6) species at 11.54 ppm amounts to between 8 and 12% of the total amount of propagating species, i.e., ∼10% of the propagating species contain a six-membered ring adjacent to the metal (Figure 5b). Although warmer temperatures reportedly yield greater percentages of six-membered rings,[15] we found that the percentages of six-membered rings adjacent to the metal in the alkylidene chain did not differ significantly when initiations were performed at −30 °C. Polymer chains prepared in bulk polymerizations contain >95% five-membered rings. Therefore formation of ∼10% six-membered rings in oligomers may be the consequence of low concentrations of DEDPM or simply more favorable formation of six-membered rings in the early stages of polymerization, i.e., until the growing polymer attains some significant bulk.

The following experiments clearly establish the region in which the alkylidene resonances for Mo=CH(6) species are

(26) Bazan, G.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378.

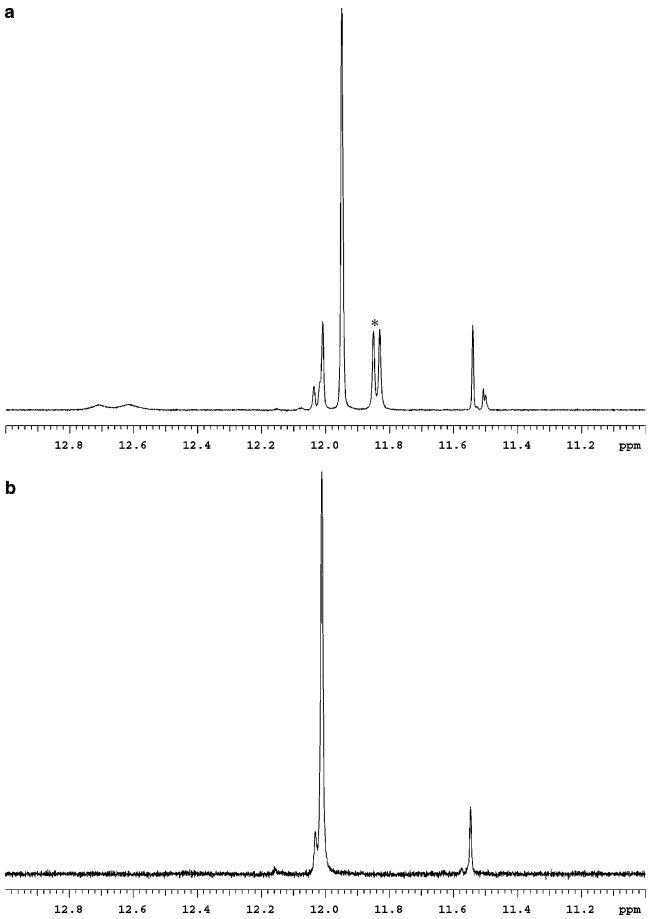


Figure 5. (a) 500 MHz ^{1}H NMR spectrum (CD_2Cl_2, 22 °C) of the alkylidene region of a sample of Mo(NAr)(*trans*-CHCH═CHMe)-(O-*t*-Bu)$_2$(quin) after addition of 1.10 equiv of DEDPM. The ***** denotes the initial alkylidene species. (b) 500 MHz ^{1}H NMR spectrum (CD_2Cl_2, 22 °C) of the alkylidene region of a sample of Mo(NAr)(*trans*-CHCH═CHMe)(O-*t*-Bu)$_2$(quin) after addition of 10 equiv of DEDPM.

found. From 0.78 to 2.40 equiv of DEDPM was added to Mo-(NAr)(*trans*-CHCH═CHMe)[OCMe(CF$_3$)$_2$]$_2$(quin) at 22 °C. After all monomer had been consumed, 8 equiv of excess LiO-*t*-Bu was added in order to convert any hexafluoro-*tert*-butoxide species into *tert*-butoxide species. A spectrum in which 1.10 equiv of DEDPM was employed is shown in Figure 6. The majority of insertion products have alkylidene proton resonances to the right of the initiator doublet (at 11.85 in CD_2Cl_2), between 11.5 and 11.6 ppm, corresponding to Mo═CH(6) species. Polymers prepared with Mo(NAr)(CH-*t*-Bu)[OCMe(CF$_3$)$_2$]$_2$ as the initiator in the presence of quinuclidine contain ∼50% each of five- and six-membered rings.[10] However, between 75 and 85% of the products in Figure 6 contain a six-membered ring adjacent to the metal. As discussed above and shown in Figure 5b, more six-membered rings are found in oligomers than in bulk polymers if *tert*-butoxide initiators are employed. Therefore the phenomenon of forming more six-membered rings early in the polymerization appears to be characteristic of polymerizations by both *tert*-butoxide and hexafluoro-*tert*-butoxide catalysts.

In experiments involving initiation of DEDPM polymerization by Mo(NAr)(*trans*-CHCH═CHMe)[OCMe(CF$_3$)$_2$]$_2$(quin) followed by addition of LiO-*t*-Bu, values for k_p/k_i were found to be 1.25 in both CD_2Cl_2 and C_6D_6 with a range of 1.10−1.46. Slower initiation may be attributed to tighter binding of quinuclidine to the initiator relative to the propagating species

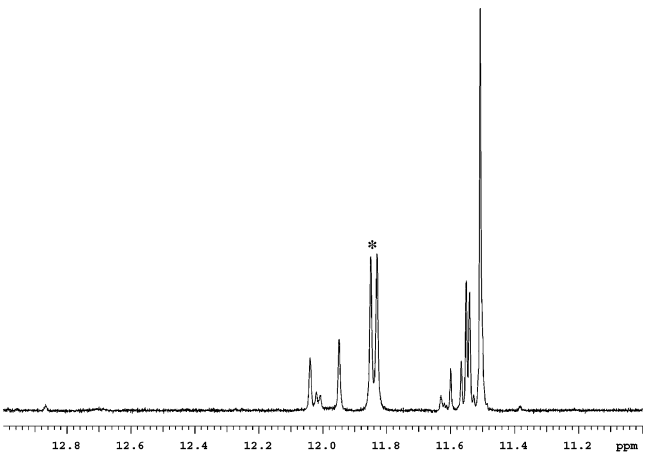


Figure 6. 500 MHz ^{1}H NMR spectrum (CD_2Cl_2, 22 °C) of the alkylidene region of a sample of Mo(NAr)(*trans*-CHCH═CHMe)-[OCMe(CF$_3$)$_2$]$_2$(quin) after addition of 1.1 equiv of DEDPM followed by the addition of excess LiO-*t*-Bu. The ***** denotes the initial alkylidene species.

when the catalyst contains OCMe(CF$_3$)$_2$ ligands rather than the more electron-donating O-*t*-Bu ligands.

On the basis of experiments in which various equivalents of DEDPM are added to Mo(NAr)(*trans*-CHCH═CHMe)(O-*t*-Bu)$_2$(quin) in CD_2Cl_2 it is clear that the resonance at 11.95 ppm (Figure 5a) can be ascribed to the first insertion product. The first insertion product alkylidene H$_\alpha$ protons are observed as two separate singlets at 12.40 and 12.38 ppm in the spectrum in C_6D_6. We propose that two resonances are found since two isomers of the five-membered-ring first insertion product are possible; that is, the double bond between C$_\delta$ and C$_\epsilon$ may have either a *cis* or *trans* configuration. Resonances for the first insertion product decrease in intensity as more DEDPM is added, and resonances for two second insertion products (at 12.01 and 12.02) and alkylidene resonances for propagating species that contain three or more monomers (at 12.04 ppm, Figures 5a and 5b) are formed. Two propagating species alkylidene H$_\alpha$ peaks are observed in a ratio of about 10 to 1 at 12.02 and 12.04 ppm in CD_2Cl_2, respectively, and at 12.49 and 12.52 ppm in C_6D_6, respectively, for the second insertion product. The larger of these resonances represents the Mo═CH(5)(5)P propagating species (P = the growing polymer chain; (5) represents an inserted monomer that forms a five-membered ring); we propose that the smaller alkylidene resonance corresponds to the Mo═CH(5)(6)P propagating species. When Mo-(NAr)(*trans*-CHCH═CHMe)[OCMe(CF$_3$)$_2$]$_2$(quin) is employed as the initiator and the OCMe(CF$_3$)$_2$ ligands are replaced with O-*t*-Bu, the peak at 12.02 ppm in CD_2Cl_2 (12.49 ppm in C_6D_6) is smaller than the peak at 12.04 in CD_2Cl_2 (12.52 ppm in C_6D_6), supporting the identification of these alkylidene H$_\alpha$ peaks as the Mo═CH(5)(5)P and Mo═CH(5)(6)P propagating species, respectively. Since the Mo═CH(5)(6)P to Mo═CH(5)(5)P ratio is approximately the same as the Mo═CH(6) to Mo═CH(5) ratio, the reactivities of Mo═CH(6) and Mo═CH(5) species toward DEDPM evidently are approximately the same.

The broadened alkylidene H$_\alpha$ peaks at 12.6 and 12.7 ppm in CD_2Cl_2 (13.2 and 13.3 ppm in C_6D_6) in the spectra of reactions initiated by Mo(NAr)(*trans*-CHCH═CHMe)(O-*t*-Bu)$_2$(quin) we propose correspond to the quinuclidine-bound *chiral,anti* isomers of the first insertion product, Mo═CH(5)(CHCH═CHMe). Two resonances are present as a consequence of approximately equal amounts of a *cis* and a *trans* double bond between C(4) and C(5)); isomers are not observed when a different initiator is employed where no isomers are possible (see later), and

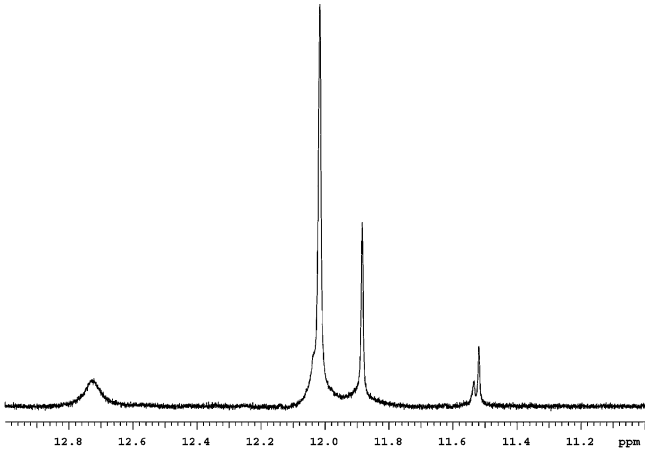


Figure 7. 500 MHz ^{1}H NMR spectrum (CD_2Cl_2, 22 °C) of the alkylidene region of a sample of Mo(CH[5])(NAr)(O-*t*-Bu)$_2$ after addition of 1.1 equiv of DEDPM. The peak at 11.88 ppm is assigned to the alkylidene proton for the initiator.

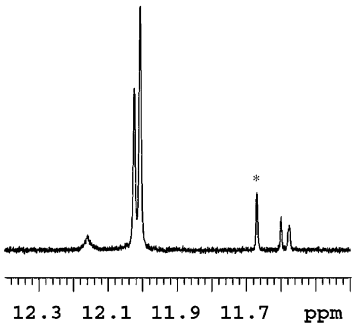


Figure 8. 500 MHz ^{1}H NMR spectrum (CD_2Cl_2, 22 °C) of the alkylidene region of a sample of Mo(CH[6])(NAr)(O-*t*-Bu)$_2$ after addition of 1.9 equiv of DEDPM. The * denotes the initial alkylidene species.

quinuclidine adducts are not observed in second insertion products such as Mo=CH(5)(5)(CHCH=CHMe), as a consequence of the increased steric bulk of an alkylidene in a second insertion product. When Mo(NAr)(*trans*-CHCH=CHMe)[OCMe(CF$_3$)$_2$]$_2$(quin) is employed as the initiator and the OCMe(CF$_3$)$_2$ ligands of the initiation products are replaced with O-*t*-Bu ligands, the broad resonances near 12.7 ppm are greatly reduced in intensity (Figure 6). Apparently quinuclidine does not bind to Mo=CH(6) species as readily as it does to Mo=CH(5)-(CHCH=CHMe) species, which was also suggested in NMR studies with the isolated species described above. The resonances near 12.7 ppm are also virtually absent in Figure 5b, since only second or higher insertion products are present.

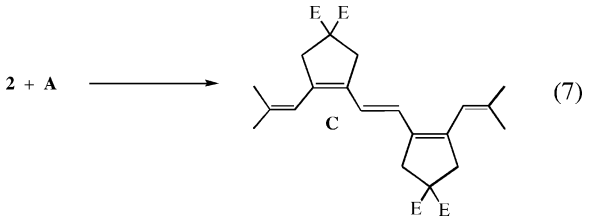
Identification of insertion products in which a six-membered ring in the alkylidene chain is adjacent to the metal center is much more complicated than the identification of insertion products in which a five-membered ring in the alkylidene chain is adjacent to the metal center, as a consequence of additional C=C isomers being possible.[27] Consequently, the many H_α alkylidene peaks observed in the ^{1}H NMR spectra of these reactions (e.g., as in Figure 6) cannot be identified readily.

Compound **3** in the presence of quinuclidine behaves in a manner similar to **1** as an initiator (Figure 7; cf. Figure 5a). Cyclopolymerization of 1 equiv of DEDPM by **3** to form a five-membered ring produces only one isomer of the first insertion product. Therefore only one quinuclidine adduct of a *chiral,-anti* isomer of the first insertion product is found with a resonance at 12.73 ppm (Figure 7). The rate of propagation relative to initiation (k_p/k_i) was calculated to be 0.36 in CD_2Cl_2 at 22 °C, which is similar to that obtained for Mo(NAr)(*trans*-CHCH=CHMe)(O-*t*-Bu)$_2$(quin) (0.39).

Unfortunately, the presence of a five-membered ring adjacent to the metal in the alkylidene ligand does not appear to enhance α-selectivity of initiation. When **3** in the presence of quinuclidine was employed as the initiator in reactions with 0.2 to 1 equiv of DEDPM in CD_2Cl_2 at 22 or −30 °C, approximately 10% of the initiation products contained a six-membered ring adjacent to the metal in the alkylidene chain.

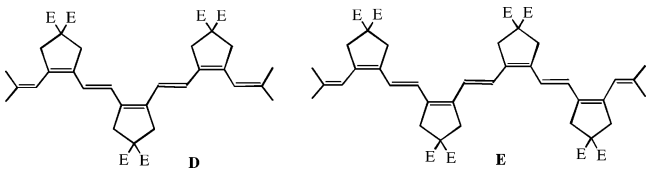
Results obtained with **5b** as the initiator were similar to those obtained with **3** as the initiator. The alkylidene region for the reaction of **5b** with 1.9 equiv of DEDPM is shown in Figure 8. The spectrum shows 5−10% propagating Mo=CH(6)P species, as found with **3** as the initiator. The ratio of k_p/k_i for **5b** was calculated to be 0.60 in CD_2Cl_2 at 22 °C, a value that is slightly larger than that found for both **1** and **3**.

Synthesis of Symmetric Oligomers that Contain all Five-Membered Rings. Addition of **A** (eq 1) to **2** yielded the "dimer" pentaene **C** (eq 7). The pentaene is an ivory-colored solid with limited stability in air. The NMR features of **C** are consistent with the structure shown in eq 7. Two olefinic resonances are found at 6.35 and 5.99 ppm and two ring methylene resonances at 3.32 and 3.20 ppm. (See Figure S1 for a ^{1}H NMR spectrum.)



(7)

Oligomers also could be isolated from actual "polymerization" reactions. Addition of 1 equiv of DEDPM to **3** in the presence of quinuclidine in CH_2Cl_2 at −30 °C followed by quenching with aldehyde **A** led to a mixture of molybdenum oxo products and "symmetric oligomers" analogous to **C**. This mixture was washed with pentane, and the pentane-soluble components were separated on a silica gel column. This yellow-colored mixture contained **C** and the "trimer" (**D**), as well as molybdenum oxo byproducts and oligomers containing at least one six-membered ring. Very little **C** was recovered in this experiment, but approximately 20 wt % of **D** was recovered. Proton NMR spectra show three ring CH_2 singlet resonances at 3.28, 3.31, and 3.36 ppm in $CDCl_3$ and three olefinic resonances at 6.55, 6.44, and 6.03 ppm (see Figure S2) for **D**. Compound **D** also has limited stability in air, decomposing as a solid or in solution after a few minutes of exposure.



Approximately 6% yield by weight of higher molecular weight red-colored oligomers was removed from the pentane-insoluble portion through ether extraction. The ether-soluble orange oligomers were separated by silica gel column chromatography. An air-sensitive tetramer (**E**) could be isolated cleanly in 56% yield. The four singlet resonances representing four ring CH_2 protons in **E** are observed at 3.29, 3.35, 3.37, and 3.39

(27) Tonzetich, Z. J. Unpublished observations.

ppm in the ^{1}H NMR spectrum in $CDCl_3$, and the four expected olefin resonances are found at 6.63, 6.56, 6.47, and 6.03 ppm (see Figure S3).

Conclusions

We have been able to prepare and isolate four-coordinate vinyl alkylidene initiators that resemble closely the vinyl alkylidene propagating species in a cyclopolymerization of diethyldipropargylmalonate (DEDPM). These species behave as smooth initiators for the cyclopolymerization of DEDPM in a living manner with *tert*-butoxide catalysts to yield polyenes that contain largely five-membered rings. For reasons that are not yet understood, more six-membered rings form in the early stages of a polymerization using either a *tert*-butoxide or hexafluoro-*tert*-butoxide initiator. We have shown that a symmetric "dimer" (pentaene **C**) can be prepared by treating an initiator with an aldehyde and that the symmetric "trimer" (heptaene **D**) and "tetramer" (nonaene **E**) can be isolated from an actual "polymerization" reaction (using 1 equiv of DEDPM) after quenching the reaction with aldehyde **A**. These results suggest (inter alia) that although oligomers larger than **E** are not likely to be isolated via column chromatography of oligomer mixtures, we should be able to prepare longer oligomers using variations of the stoichiometric Wittig reaction that produced pentaene **C**. This possibility has been realized for ester derivatives other than ethyl esters[28] and will be reported in due course.

Experimental Section

General Comments. All manipulations of air- and moisture-sensitive materials were performed in oven-dried (200 °C) glassware under an atmosphere of nitrogen on a dual-manifold Schlenk line or in a Vacuum Atmospheres glovebox. HPLC grade organic solvents were sparged with nitrogen and dried by passage through activated alumina (for diethyl ether, toluene, pentane, THF, and methylene chloride) followed by passage through Q-5 supported copper catalyst (for benzene) prior to use, then stored over 4 Å Linde-type molecular sieves. Benzene-d_6 and toluene-d_8 were dried over sodium/benzophenone ketyl and vacuum-distilled. Methylene chloride-d_2 was dried over CaH_2, vacuum distilled, and stored over 4 Å Linde-type molecular sieves. Chloroform-d_1 was used as received. NMR spectra were recorded on a Varian 500 or Varian 300 spectrometer. Chemical shifts for ^{1}H and ^{13}C spectra were referenced to the residual ^{1}H/^{13}C resonances of the deuterated solvent (^{1}H: $CDCl_3$, δ 7.26; C_6D_6, δ 7.16; CD_2Cl_2, δ 5.32; C_7D_8, δ 2.09. ^{13}C: $CDCl_3$, δ 77.23; C_6D_6, δ 128.39; CD_2Cl_2, δ 54.00) and are reported as parts per million relative to tetramethylsilane. ^{19}F NMR spectra were referenced externally to fluorobenzene (δ −113.15 ppm upfield of $CFCl_3$). High-resolution mass spectrometry measurements were performed at the MIT Department of Chemistry Instrument Facility, and elemental analyses were performed by H. Kolbe Microanalytics Laboratory, Mülheim an der Ruhr, Germany. MALDI-ICR-FTMS spectra were obtained by L. Amundson and Professor E. A. Stemmler at Bowdoin College.

Mo(CHCMe$_2$R)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (R = Me, Ph),[29] Mo(*trans*-CHCHCHMe)(NAr)[OCMe(CF$_3$)$_2$]$_2$(quin),[19] and diethyl dipropargylmalonate (DEDPM)[30] were prepared according to published procedures. Synthetic details for all organic compounds other than **B** can be found in the Supporting Information. LiOCMe(CF$_3$)$_2$ and LiO-*t*-Bu were prepared by addition of *n*-BuLi (1.6 M in hexanes, Aldrich) to a pentane solution of the corresponding alcohols (Aldrich). Quinuclidine was purchased from Aldrich and sublimed prior to use.

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Diethyl 3-(2-methylprop-1-enyl)-4-vinylcyclopent-3-ene-1,1-dicarboxylate, B. An oven-dried flask was charged with 0.860 g (2.13 mmol) of MePPh$_3$I and 50 mL of THF. To the suspension was added 0.076 g (1.93 mmol) of NaH (60.8 wt % dispersion in mineral oil). The mixture was allowed to stir at room temperature for 3 h, during which time it became bright yellow in color. To the mixture was added a solution of 0.505 g (1.72 mmol) of **A** in 15 mL of THF. The reaction was then allowed to stir at room temperature overnight. The THF was removed in vacuo and the residue treated with Et_2O, causing precipitation of NaI and OPPh$_3$. The Et_2O solution was decanted away from the solids, washed three times with water, and dried over $MgSO_4$. The Et_2O was removed in vacuo and the compound purified by silica gel chromatography (20% Et_2O/hexanes) to give a colorless crystalline solid; yield 0.287 g (57%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.57 (dd, 1, $^3J_{cis}$ = 10.5 Hz, $^3J_{trans}$ = 18.0 Hz, −C*H*═CH$_2$), 5.90 (br s, 1, Me$_2$C═C*H*−), ∼5.11 and ∼5.06 (m, second order, 2, ═C*H*$_2$), 4.20 (q, 4, OC*H*$_2$), 3.28 (s, 2, C*H*$_2$), 3.16 (s, 2, C*H*$_2$), 1.82 (s, 3, *Me*), 1.75 (s, 3, *Me*), 1.25 (t, 6, OCH$_2$C*H*$_3$); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 172.29, 137.04, 135.83, 133.51, 130.99, 119.15, 114.34, 61.80, 57.83, 44.67, 39.91, 27.43, 20.40, 14.25; IR (neat) cm^{-1} 2978, 1731, 1665, 1633, 1616, 1445, 1365, 1261, 1188, 1069, 895, 857; HRMS (EI, [M]$^+$) calcd for $C_{17}H_{24}O_4$ 292.1669, found 292.1667.

Mo(NAr)(*trans*-CHCHCHMe)(O-*t*-Bu)$_2$(quin) (1). To a solution of 2.654 g (3.32 mmol) of Mo(NAr)(*trans*-CHCHCHMe)-[OCMe(CF$_3$)$_2$]$_2$(quin) in 25 mL of pentane was added 1.064 g (13.3 mmol) of LiO-*t*-Bu as a solid in one portion. The mixture was stirred for 1 h at room temperature. The solution volume was concentrated in vacuo to ∼10 mL and stored at −30 °C for 12 h. Colorless crystals of LiO-*t*-Bu and LiOCMe(CF$_3$)$_2$ precipitated first and were filtered off. The solution was then concentrated to saturation and stored at −30 °C for another 12 h. Large, dark purple crystals of the desired compound formed and were collected by decanting the mother liquor. Three additional crystallizations yielded mixtures of purple and colorless crystals that were separated mechanically; yield 1.565 g (81%): ^{1}H NMR (500 MHz, C_6D_6) (*achiral,syn* isomer) δ 12.11 (d, 1, $^1J_{CH}$ = 121 Hz, MoC*H*$_\alpha$), 8.00 (br t, 1, *H*$_\beta$), 7.10 (m, 3, Ar*H*), 4.77 (dq, 1, *H*$_\gamma$), 4.17 (sep, 2, C*H*Me$_2$), 2.88 (m, 6, quin *H*$_\alpha$), 1.78 (d, 3, *Me*), 1.39 (s, 18, O-*t*-*Bu*), 1.34 (d, 12, CH*Me*$_2$), 1.27 (m, 1, quin H$_\gamma$), 1.26 (m, 6, quin H$_\beta$); (*chiral,anti* isomer) δ 12.49 (d, 1, $^1J_{CH}$ = 142 Hz, MoC*H*$_\alpha$), 8.14 (br t, 1, *H*$_\beta$), 2.04 (d, 3, *Me*); ^{13}C{^{1}H} NMR (125 MHz, C_6D_6) (*achiral,syn* isomer) δ 262.75 (MoC$_\alpha$), 152.44, 146.61 (br, *C*$_\beta$ or *C*$_\gamma$), 144.13 (br, *C*$_\beta$ or *C*$_\gamma$), 127.59, 123.70, 117.21, 77.07 (O*C*Me$_3$), 48.39 (br, quin *C*$_\alpha$), 32.56 (OC*Me*$_3$), 28.54, 27.07, 24.53, 21.64, 16.85. Anal. Calcd for $C_{31}H_{54}MoN_2O_2$: C, 63.90; H, 9.34; N, 4.81. Found: C, 63.67; H, 9.52; N, 4.77.

Mo(NAr)(CH[5])(OCMe(CF$_3$)$_2$)$_2$ (2). A solution of **B** (0.359 g, 1.23 mmol) in 3 mL of pentane was added to a stirred suspension of Mo(NAr)(CHCMe$_3$)(OCMe(CF$_3$)$_2$)$_2$ (0.683 g, 1.17 mmol) in 10 mL of pentane. The mixture was stirred at room temperature for 30 min, during which time the suspension became homogeneous, and then an orange-yellow solid precipitated from solution. The precipitate was collected by filtration and dried in vacuo. The mother liquor was concentrated and a second batch of fluffy solid obtained as before; yield 0.847 g (84%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 12.79 (s, 1, $^1J_{CH}$ = 120 Hz, MoC*H*$_\alpha$), 7.19 (t, 1, *p*-Ar*H*), 7.19 (d, 2, *m*-Ar*H*), 5.96 (s, H, C*H*$_\delta$), 4.00 (q, 4, OC*H*$_2$), 3.71 (s, 2, C*H*$_2$), 3.51 (sep, 2, C*H*Me$_2$), 3.21 (s, 2, C*H*$_2$), 1.96 (s, 3, *Me*), 1.91 (s, 3, *Me*), 1.42 (s, 6, *Me*-OR$_{F6}$), 1.19 (d, 12, CH*Me*$_2$), 1.07 (t, 6, OCH$_2$C*H*$_3$); ^{19}F NMR (470 MHz, CD_2Cl_2) δ −78.50. Anal. Calcd for $C_{36}H_{45}F_{12}MoNO_6$: C, 47.43; H, 4.98; N, 1.54. Found: C, 47.55; H, 4.87; N, 1.48.

Mo(NAr)(CH[5])(O-*t*-Bu)$_2$ (3). To a suspension of 0.421 g (0.468 mmol) of Mo(NAr)(CH[5])[OCMe(CF$_3$)$_2$]$_2$ in 5 mL pentane was added a solution of 0.094 g (1.17 mmol) of LiO-*t*-Bu in 3 mL of pentane. Upon addition of the LiO-*t*-Bu, the suspension became

homogeneous and acquired a deep red color. The mixture was stirred at room temperature for 15 min. The solution was concentrated to 2 mL and stored at −30 °C for 12 h. A dark red solid precipitated and was collected via filtration; yield 0.104 g (33%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 11.87 (s, 1, $^1J_{CH}$ = 118 Hz, MoCH_α), 7.12 (m, 3, Ar*H*), 6.01 (s, 1, CH_δ), 3.97 (m, 4, OCH_2), 3.74 (sep, 2, C*H*Me$_2$), 3.61 (s, 2, CH_2), 3.21 (s, 2, CH_2), 1.92 (s, 3, *Me*), 1.90 (s, 3, *Me*), 1.29 (s, 18, O-*t*-*Bu*), 1.18 (d, 12, CH*Me*$_2$), 1.06 (t, 6, OCH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2) δ 236.50 (MoC_α), 172.76 (*C*O), 153.64, 146.59 (C_δ), 143.47, 136.17, 127.44, 123.20, 121.07, 119.93, 78.35, 61.95, 57.93 (C_{quat} of [5]-ring), 46.21, 43.76, 32.07 (C*Me*$_3$), 28.57, 28.03, 23.98, 20.21, 14.23. Anal. Calcd for $C_{36}H_{57}MoNO_6$: C, 62.14; H, 8.26; N, 2.01. Found: C, 61.97; H, 8.16; N, 1.94.

Mo(NAr)(CH[6])[OCMe(CF$_3$)$_3$]$_2$ (5a). A solution of 0.505 g (0.718 mmol) of Mo(CH-t-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ in 20 mL of pentane was treated with a solution of 0.20 g (0.79 mmol) of diethyl 3-vinylcyclohex-3-ene-1,1-dicarboxylate in 5 mL of pentane. The solution was allowed to stir at room temperature for 3 h, during which time the color changed from yellow to brown. All volatiles were removed in vacuo, and the residue was dissolved in a minimal amount of pentane. The solution was set aside at −25 °C for 18 h, during which time the compound precipitated as fluffy, orange-red crystals; yield 0.404 g (65%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 12.52 (s, 1, $^1J_{CH}$ = 125 Hz, MoCH_α), 7.26 (t, 1, *p*-Ar*H*), 7.17 (d, 2, *m*-Ar*H*), 5.32 (m, 1, CH_γ), 3.98 (m, 2, OCH_2), 3.85 (m, 2, OCH_2), 3.52 (sep, 2, C*H*Me$_2$), 2.87 (s, 2, CH_2), 2.52 (br m, 2, CH_2), 1.97 (t, 2, CH_2), 1.43 (s, 6, *Me*-OR$_{F6}$), 1.19 (d, 12, CH*Me*$_2$), 1.05 (t, 6H, OCH$_2$C*H*$_3$); ^{19}F NMR (470 MHz, CD_2Cl_2) δ −78.40, −78.53. Anal. Calcd for $C_{33}H_{41}F_{12}MoNO_6$: C, 45.47; H, 4.74; N, 1.61. Found: C, 45.68; H, 4.67; N, 1.56.

Mo(NAr)(CH[6])(O-*t*-Bu)$_2$·[LiOCMe(CF$_3$)$_2$]$_2$ (5b). To a suspension of 1.075 g (1.23 mmol) of Mo(CH[6])(NAr)[OCMe(CF$_3$)$_3$]$_2$ in 35 mL of pentane was added 0.202 g (2.52 mmol) of LiO-*t*-Bu as a solid in one portion. The solution became deep red within 5 min and was allowed to stir at room temperature for an additional 30 min. The volatiles were removed in vacuo, and the residue was dissolved in a minmal amount of pentane. The solution was set aside at −25 °C for 2 days, during which time the compound crystallized as red needles; yield 1.082 g (85%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 11.67 (s, 1, $^1J_{CH}$ = 119 Hz, MoCH_α), 7.10 (m, 3, *m* and *p* Ar*H*), 5.15 (br t, 1, CH_γ), 3.96 (m, 2, OCH_2), 3.83 (m, 2, OCH_2), 3.74 (sep, 2, C*H*Me$_2$), 2.85 (s, 2, CH_2), 2.42 (br m, 2, CH_2), 1.95 (t, 2, CH_2), 1.29 (s, 18, OC*Me*$_3$), 1.78 (d, 12, CH*Me*$_2$), 1.01 (t, 6, OCH$_2$C*H*$_3$); ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2) δ 249.85 (MoC_α), 172.42 (*C*O), 153.42, 146.68, 142.64, 127.38, 123.20, 116.19, 78.36, 61.81, 54.58 (C_{quat} of [6]-ring), 36.29, 32.17 (C*Me*$_3$), 28.57, 27.65, 24.02, 22.27, 14.21 (OCH$_2$*C*H$_3$). Anal. Calcd for $C_{41}H_{59}F_{12}Li_2MoNO_8$: C, 47.73; H, 5.76; N, 1.36. Found: C, 47.66; H, 5.81; N, 1.41.

Pentaene C. To a solution of 0.303 g (0.33 mmol) of **2** in 10 mL of diethyl ether was added a solution of 0.100 g (0.34 mmol) of **A** in 5 mL of ether. The reaction was allowed to stir at room temperature for 60 min. The solution was filtered through a plug of silica gel, washed with 1 M HCl, and dried over $MgSO_4$. The crude material was then purified by chromatography on silica gel (40% Et_2O/hexanes) to yield the desired material as a pale yellow solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.35 (s, 2, C*H*), 5.99 (br s, 2, C*H*), 4.20 (q, 8, OCH_2), 3.32 (s, 4, CH_2), 3.20 (s, 4, CH_2), 1.87 (s, 6, *Me*), 1.80 (s, 6, *Me*), 1.25 (t, 12, OCH$_2$C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.21, 137.03, 135.81, 133.75, 123.37, 119.34, 61.83, 58.00, 44.61, 40.13, 27.72, 20.59, 14.22; MALDI-ICR-FTMS [M + Na$^+$] calcd for $C_{22}H_{44}NaO_8$ 579.2934, found 579.3033.

Heptaene D: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.55 (d, 2, C*H*), 6.44 (d, 2, C*H*), 6.03 (s, 2, C*H*), 4.23 (m, 12, OCH_2), 3.36 (s, 4, CH_2), 3.31 (s, 4, CH_2), 3.28 (s, 4, CH_2), 1.90 (s, 6, *Me*), 1.82 (s, 6, *Me*), 1.28 (m, 18, OCH$_2$C*H*$_3$); MALDI-ICR-FTMS [M + Na$^+$] calcd for $C_{45}H_{60}NaO_{12}$ 815.3982, found 815.4211.

Nonaene E: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.63 (s, 2, C*H*), 6.56 (d, 2, C*H*), 6.47 (d, 2, C*H*), 6.03 (s, 2, C*H*), 4.29 (m, 16, OCH_2), 3.39 (s, 4, CH_2), 3.37 (s, 4, CH_2), 3.35 (s, 4, CH_2), 3.29 (s, 4, CH_2), 1.90 (s, 6, *Me*), 1.83 (s, 6, *Me*), 1.28 (m, 24, OCH$_2$C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.27, 172.19, 137.70, 137.30, 136.90, 135.76, 133.74, 125.07, 122.99, 121.68, 119.38, 62.07, 61.95, 57.34, 58.14, 44.80, 41.61, 41.50, 40.19, 27.87, 20.73, 14.29; MALDI-ICR-FTMS [M + Na$^+$] calcd: 1052.20, found 1052.54.

General Procedure for Initiation Reactions. If required, quinuclidine adducts were formed by treating the specified catalyst with 1.1 equiv of quinuclidine for 15 min at room temperature. Separate solutions containing the initiator (2 to 30 mM) and DEDPM in equal volumes of solvent were prepared and mixed at the specified temperature (total volume = 0.8 mL for NMR scale experiments). Products of initiation reactions (employing less than 3 equiv of DEDPM) were observed after 10 min.

Crystal Structures. Low-temperature diffraction data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), performing φ- and ω-scans. All structures were solved by direct methods using SHELXS[31] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[32] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups). Details of the data quality and a summary of the residual values of the refinements are listed in Table 2.

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Supporting Information Available: Experimental procedures for organic compounds other than **B**, proton NMR spectra for **C**, **D**, and **E** (Figures S1, S2, and S3), and fully labeled thermal ellipsoid drawings for Mo(*trans*-CHCH=CHMe)(NAr)(O-*t*-Bu)$_2$-(quin), Mo(CH[5])(NAr)(O-*t*-Bu)$_2$, and Mo(NAr)(CH[6])(O-*t*-Bu)$_2$·2LiOCMe(CF$_3$)$_2$ (Figures S4−S8). This material is available free of charge via the Internet at http://pubs.acs.org. Data for the structures are also available to the public at http://www.reciprocalnet.org/ (numbers 05086, 05136, and 05248, respectively).

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