

Synthesis of High Oxidation State Bimetallic Alkylidene Complexes for Controlled ROMP Synthesis of Triblock Copolymers

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An X-ray study of $[(\text{THF})(\text{R}_{\text{F6}}\text{O})_2(\text{ArN})\text{Mo}=\text{CH}]_2(1,4\text{-C}_6\text{H}_4)$ ($\text{OR}_{\text{F6}} = \text{OCMe}(\text{CF}_3)_2$; $\text{Ar} = 2,6$ -diisopropylphenyl; THF = tetrahydrofuran; **1b**), which is closely related to known $[(\text{DME})(\text{R}_{\text{F6}}\text{O})_2(\text{ArN})\text{Mo}=\text{CH}]_2(1,4\text{-C}_6\text{H}_4)$ (DME = 1,2-dimethoxyethane; **1a**), showed it to be the expected bimetallic species in which each end is approximately a trigonal bipyramidal monoadduct of a *syn* alkylidene with the THF coordinated to the *NOO* face of the metal *trans* to the $\text{Mo}=\text{C}$ bond. Treatment of **1a** with lithium *tert*-butoxide yielded $[(t\text{-BuO})_2(\text{ArN})\text{Mo}=\text{CH}]_2(1,4\text{-C}_6\text{H}_4)$ (**2**). Addition of divinylferrocene to $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{NAr})(\text{OR}_{\text{F6}})_2$ produced the bimetallic species $\{(\text{R}_{\text{F6}}\text{O})_2(\text{ArN})\text{Mo}[\text{CH}(\text{C}_5\text{H}_4)]_2\text{Fe}$ (**3**), which upon treatment with lithium *tert*-butoxide produced a related *tert*-butoxide complex (**4**). X-ray studies of **3** and **4** showed them to be “*syn/syn*” bimetallic species related to **1b**. In solution two resonances can be observed in proton NMR spectra in the alkylidene region for the “*syn/anti*” isomer of **1a**, **2**, **3**, and **4**; the total amount varies between 4 and 20% of the total. Bimetallic species **1a**, **2**, **3**, and **4** have been shown to initiate at both ends and to produce homopolymers of 4,5-dicarbomethoxynorbornadiene (DCMNBD) and methyltetracyclododecene (MTD) in a living fashion. MALDI-TOF mass spectra of ferrocene-containing species have been obtained that are consistent with the polymerization process being living. Triblock copolymers $(\text{poly}[(\text{MTD})_{x/2}(\text{DCMNBD})_y(\text{MTD})_{x/2}])$ were prepared by adding y equivalents of DCMNBD to the bimetallic initiators followed (after consumption of DCMNBD) by x equivalents of MTD. These triblocks were shown to be of relatively high purity (free of homopolymer and diblock copolymer) and to have a relatively low PDI (≤ 1.2).

Introduction

Ring-opening metathesis polymerization (ROMP) is catalyzed by a variety of alkylidene complexes.^{1,2} In many cases the propagation step is essentially irreversible (e.g., with various norbornene derivatives), and secondary metathesis reactions of double bonds in the resulting polymer chain can be slow. In these cases the polymerization becomes “living” under some specified set of conditions. In addition, if the rate of initiation and propagation are approximately the same order of magnitude or greater, then it is possible to control the average polymer length simply by controlling the number of equivalents of monomer added.³ Finally, with several catalysts, it is possible to control polymer structure in a systematic manner, i.e., to prepare all *cis* or all *trans* polymers and polymers that are isotactic or syndiotactic.^{4,5} Well-defined high oxidation state imido alkylidene complexes of molybdenum and tungsten^{6,7}

have the added advantage of reacting in a Wittig-like fashion with benzaldehydes and other reactive aldehydes (e.g., ferrocenecarboxaldehydes^{8,9}), thereby installing a capping group on the end of the polymer.

Imido alkylidene complexes of Mo or W that are living ROMP catalysts and that initiate at a rate comparable to the propagation rate are amenable to the synthesis of block copolymers. Some of the most interesting copolymers in terms of their physical properties are triblocks.^{10,11} Triblocks (e.g., $\text{A}_x\text{B}_y\text{A}_z$, where x , y , and z are the average numbers of monomers of type A or B in each block) have been synthesized via a sequential or linear method (addition of A to an initiator, then B, then A again, allowing each to be consumed) or by coupling of living homopolymers with a bifunctional central oligomer or polymer. However, such methods often have limitations, most seriously the presence of homopolymer or diblock copolymer due to (for example) incomplete coupling or catalyst degradation during the linear

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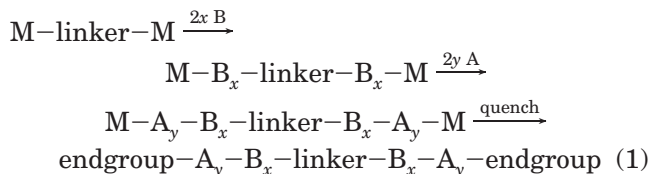
$A_xB_yA_z$ synthesis. Some purification step (e.g., selective precipitation) is then required in order to obtain relatively pure triblock. High-purity triblocks are most desirable since the presence of homopolymer or diblock copolymer in a triblock copolymer can seriously degrade the properties that might be expected in a given triblock copolymer.

Triblock copolymers of certain monomers (e.g., styrene) also can be prepared by employing "bifunctional" initiators, e.g., disodium^{12,13} or dilithio derivatives.^{10,11} Although problems related to deactivation of chain ends still exist, this method can be more reliable than the linear method for preparing high-purity triblock copolymers.

Reports of bifunctional initiators for ROMP are rare. Several years ago we reported the synthesis of some crystalline bifunctional imido alkylidene complexes, e.g., $[(R_{F6}O)_2(ArN)Mo=CHCH_2CH(OMe)]_2(1,4-C_6H_4)$ (where $OR_{F6} = OCMe(CF_3)_2$; $Ar = 2,6$ -diisopropylphenyl), $(DME)(R_{F6}O)_2(ArN)Mo(CH)_6Mo(NAr)(R_{F6}O)_2(DME)$, $(quin)(t-BuO)_2(ArN)Mo(CH)_6Mo(NAr)(O-t-Bu)_2(quin)$ (where quin is quinuclidine), and $1,4-[(DME)(R_{F6}O)_2(ArN)Mo=CH]_2(1,4-C_6H_4)$ ($DME = 1,4$ -dimethoxyethane).¹⁴ The bifunctional initiators were briefly explored as ROMP catalysts for the synthesis of poly[4,5-dicarbomethoxynorbornadiene], but no synthesis of block copolymers was undertaken. Two other examples are titanacyclobutane complexes¹⁵ and Ru catalysts of the Grubbs type that contain the $Ru=CH(1,4-C_6H_4)-CH=Ru$ unit analogous to that described above for Mo.¹⁶ In view of the ready availability and variety of many ROMP monomers, especially norbornenes and 4,5-disubstituted norbornadienes, we have returned to high oxidation state bimetallic alkylidene complexes in order to explore the potential of bimetallic ROMP initiators for the synthesis of triblock copolymers in high yield and high purity. We are especially interested in triblock copolymers in which the outer blocks are "hard" (high T_g , e.g., > 180 °C) and the inner block is "soft" (low T_g , e.g., < 20 °C).

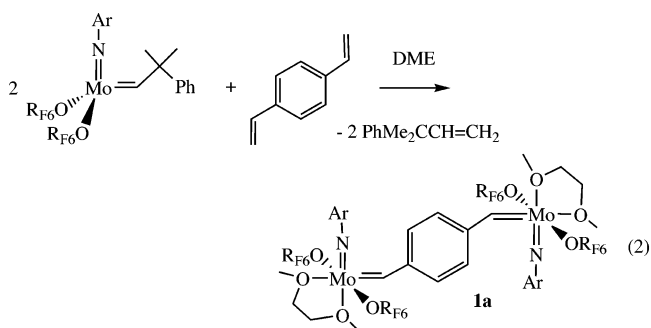
The method of synthesizing isolable bifunctional alkylidene initiators is fashioned after similar work published some time ago,¹⁴ i.e., treating a neopentylidene or neophylidene complex with a diene. Addition of monomer B would then produce a central block that would consist of primarily poly[B], with whatever "link" was employed in the bifunctional initiator located roughly in the middle of that block (eq 1). Addition of monomer A would then create the outer blocks, which would then have the same chain length on average. The outer blocks could then be capped through a Wittig-like reaction with an aldehyde. If the process involving a given catalyst under some set of conditions and monomers A and B is living, then pure triblocks copolymers should result. In this paper we prepare several bifunctional ROMP initiators of molybdenum and show them

to be catalysts for the living ring-opening metathesis polymerization of several monomers.



Results and Discussion

Synthesis of "Dibenzylidene" Complexes. The first bimetallic initiator that we prepared was one that had been reported in 1993,¹⁴ namely, $[(DME)(R_{F6}O)_2(ArN)Mo=CH]_2(1,4-C_6H_4)$, as shown in eq 2. This orange



product, **1a**, is sparingly soluble in common aliphatic or aromatic hydrocarbon solvents, but soluble in dimethoxyethane and THF. The proton NMR spectrum in C_6D_6 of the difunctional initiator showed a single alkylidene peak at 12.64 ppm. Although we could not obtain a ^{13}C NMR spectrum readily as a consequence of the low solubility of the sample, an X-ray structure of a closely related species (see below) showed the alkylidene to be in the *syn* orientation. Two smaller peaks of equal intensity (each $\sim 10\%$ of the total) were observed at 12.81 and 12.84 ppm and were invariant from sample to sample. We ascribe these alkylidene proton resonances to an isomer of **1a** in which the configuration at one metal center is different from the other. On the basis of similar observations in a related compound to be described later, we propose that $\sim 20\%$ of the compound is a species in which the orientation of the alkylidene is *anti* at one metal and *syn* at the other. Although we cannot say with certainty that the configuration at the metal is the same at the *anti* and *syn* ends in this isomer, we have no reason to suspect that is not the case.

Crystals of compound **1a** suitable for an X-ray study could not be obtained. Therefore **1a** was dissolved in THF and all solvents were removed in vacuo. A proton NMR spectrum of the resulting bright red solid in C_6D_6 was consistent with it being $[(THF)(R_{F6}O)_2(ArN)Mo=CH]_2(1,4-C_6H_4)$ (**1b**; δ H at 12.88 ppm with $J_{CH} = 125$ Hz). Recrystallization of **1b** from heptane at -30 °C yielded plates, which were suitable for an X-ray structural study.

The X-ray study (Figure 1, Tables 1 and 2) showed that **1b** is the expected bimetallic species in which each end is approximately a trigonal bipyramidal monoadduct of a *syn* alkylidene with the THF coordinated to the *NOO* face of the metal, *trans* to the $Mo=C$ bond. (Two independent molecules were found in the unit cell,

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Table 1. Crystal Data and Structure Refinement for 1b, 3, and 4^a

	1b	3	4
empirical formula	C ₅₆ H ₆₈ F ₂₄ Mo ₂ N ₂ O ₆	C ₅₈ H ₆₂ F ₂₄ FeMo ₂ N ₂ O ₄	C ₅₉ H ₈₈ FeMo ₂ N ₂ O ₄
fw	1513.00	1554.83	1137.04
temperature	100(2) K	194(2) K	373(2) K
cryst syst	triclinic	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> /2 <i>c</i>
unit cell dimens	<i>a</i> = 13.0696(19) Å <i>b</i> = 15.465(2) Å <i>c</i> = 16.682(3) Å α = 110.582(3)° β = 93.113(2)° γ = 91.248(2)°	<i>a</i> = 10.6901(11) Å <i>b</i> = 11.1070(12) Å <i>c</i> = 15.2513(17) Å α = 101.756(2)° β = 103.821(2)° γ = 106.968(2)°	<i>a</i> = 26.209(5) Å <i>b</i> = 10.958(2) Å <i>c</i> = 20.732(4) Å α = 90° β = 101.62(3)° γ = 90°
volume	3149.0(8) Å ³	1607.3(3) Å ³	5832(2) Å ³
<i>Z</i>	2	1	4
density(calcd)	1.596 Mg/m ³	1.606 Mg/m ³	1.295 Mg/m ³
absorp coeff	0.518 mm ⁻¹	0.722 mm ⁻¹	0.713 mm ⁻¹
<i>F</i> (000)	1532	782	2392
cryst size	0.28 × 0.12 × 0.04 mm ³	0.22 × 0.17 × 0.06 mm ³	0.08 × 0.08 × 0.05 mm ³
θ range for data collection	1.41 to 26.37°	2.01 to 28.33°	1.59 to 25.03°
index ranges	-16 ≤ <i>h</i> ≤ 16 -19 ≤ <i>k</i> ≤ 18 0 ≤ <i>l</i> ≤ 20	-14 ≤ <i>h</i> ≤ 14 -14 ≤ <i>k</i> ≤ 14 -18 ≤ <i>l</i> ≤ 20	-31 ≤ <i>h</i> ≤ 31 -12 ≤ <i>k</i> ≤ 13 -24 ≤ <i>l</i> ≤ 24
no. of reflns collected	55 205	27 210	32 410
no. of indep reflns	12 827 [<i>R</i> (int) = 0.0391]	7977 [<i>R</i> (int) = 0.0264]	5110 [<i>R</i> (int) = 0.0891]
completeness to θ = 26.37°	99.7%	99.4%	99.4%
absorp corr	empirical	empirical	
max. and min. transmn	0.9796 and 0.8685		0.9652 and 0.9452
no. of data/restraints/params	12 827/0/819	7977/0/416	5110/0/310
goodness-of-fit on <i>F</i> ²	1.064	1.024	1.320
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0364 <i>wR</i> 2 = 0.0925	<i>R</i> 1 = 0.0297 <i>wR</i> 2 = 0.0757	<i>R</i> 1 = 0.0826 <i>wR</i> 2 = 0.1624
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0505 <i>wR</i> 2 = 0.1031	<i>R</i> 1 = 0.0342 <i>wR</i> 2 = 0.0787	<i>R</i> 1 = 0.0923 <i>wR</i> 2 = 0.1659
largest diff peak and hole	1.371 and -0.492 e Å ⁻³	0.536 and -0.298 e Å ⁻³	1.296 and -1.931 e Å ⁻³

^a In each case the wavelength was 0.71073 Å and the refinement method was full-matrix least-squares on *F*².

Table 2. Selected Bond Lengths (Å) and Angles (deg) in 1b, 3, and 4

	1b^a		3		4
Mo(1)–N(1)	1.717(2)	Mo(1)–N(1)	1.7241(15)	Mo(1)–N(1)	1.734(5)
Mo(1)–C(1)	1.931(3)	Mo(1)–C(1)	1.9098(18)	Mo(1)–C(1)	1.912(7)
Mo(1)–O(1)	1.9395(18)	Mo(1)–O(1)	1.9309(12)	Mo(1)–O(1)	1.889(5)
Mo(1)–O(2)	1.9618(18)	Mo(1)–O(2)	1.9342(13)	Mo(1)–O(2)	1.892(5)
N(1)–Mo(1)–C(1)	100.03(11)	N(1)–Mo(1)–C(1)	98.79(7)	N(1)–Mo(1)–C(1)	99.3(3)
N(1)–Mo(1)–O(1)	115.83(9)	N(1)–Mo(1)–O(1)	110.93(6)	N(1)–Mo(1)–O(1)	113.6(2)
N(1)–Mo(1)–O(2)	114.27(9)	N(1)–Mo(1)–O(2)	119.64(6)	N(1)–Mo(1)–O(2)	116.0(2)
C(1)–Mo(1)–O(1)	102.01(10)	C(1)–Mo(1)–O(1)	105.59(6)	O(1)–Mo(1)–C(1)	108.0(3)
C(1)–Mo(1)–O(2)	98.30(9)	C(1)–Mo(1)–O(2)	107.90(7)	O(2)–Mo(1)–C(1)	109.1(3)
O(1)–Mo(1)–O(2)	120.81(8)	O(1)–Mo(1)–O(2)	112.16(6)	O(1)–Mo(1)–O(2)	110.0(2)
C(5)–N(1)–Mo(1)	171.01(19)	C(7)–N(1)–Mo(1)	174.37(13)	C(15)–N(1)–Mo(1)	166.2(5)
C(2)–C(1)–Mo(1)	141.6(2)	C(23)–O(1)–Mo(1)	142.03(12)	C(2)–C(1)–Mo(1)	137.8(5)
C(21)–O(1)–Mo(1)	141.46(17)	C(19)–O(2)–Mo(1)	148.02(13)	C(7)–O(1)–Mo(1)	140.3(4)
C(17)–O(2)–Mo(1)	140.57(17)	C(2)–C(1)–Mo(1)	139.06(13)	C(11)–O(2)–Mo(1)	141.4(4)
Mo(1)–O(3)	2.3995(19)				
N(1)–Mo(1)–O(3)	87.22(9)				
C(1)–Mo(1)–O(3)	172.49(9)				
O(1)–Mo(1)–O(3)	76.23(7)				
O(2)–Mo(1)–O(3)	76.77(7)				

^a Data for molecule 1 only. See Supporting Information for a full list of bond lengths and angles for both molecules.

the bond lengths and angles for which are similar; data for only one molecule are shown in Table 1.) This is the first structurally characterized example of a five-coordinate imido alkylidene complex in which the base is coordinated to an *NOO* face, although adducts of this type have been observed in solution by NMR methods.¹⁷ The THF is essentially *trans* to the alkylidene ligand (172.39(9)°). The imido and two alkoxide ligands are bent toward the THF ligand slightly, leading to O(3)–Mo–L angles of less than 90° (87.22(9)° when L = N(1),

76.23(7)° and 76.77(7)° when L is O(1) or O(2), respectively). The Mo=C bond length (1.931(3) Å) and Mo–C₁–C₂ angle (141.6(2)°) as well as other bond lengths and angles are not outside the norm for complexes of this general type. To our knowledge **1b** (along with **3** and **4** described below) are the first bimetallic complexes in the family of imido alkylidene complexes to be structurally characterized.

Efforts to synthesize [(*t*-BuO)₂(ArN)Mo=CH]₂(1,4-C₆H₄) (**2**) via treatment of Mo(CHCMe₂Ph)(NAr)(OCMe₃)₂ or Mo(CHCMe₃)(NAr)(OCMe₃)₂ with 0.5 equiv of *p*-divinylbenzene in C₆D₆ were not successful. A proton

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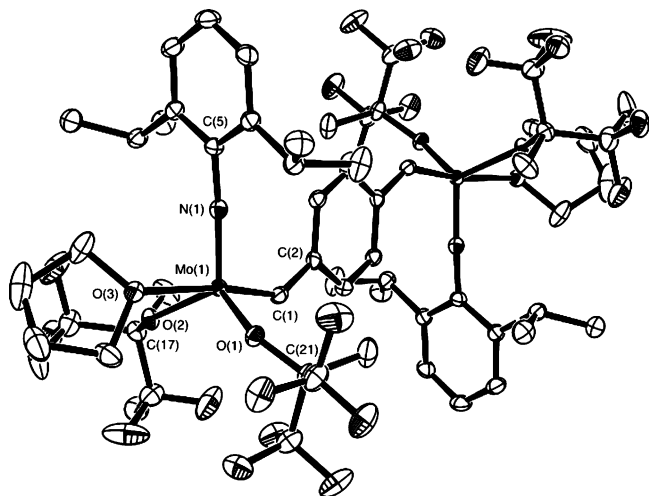


Figure 1. Thermal ellipsoid drawing of **1b**. Hydrogen atoms are omitted for clarity.

NMR spectrum in the alkylidene proton region revealed only ~30% (and slow) conversion of starting material to three different product alkylidenes with resonances at 12.10, 12.03, and 11.90 ppm. The nature of these alkylidenes is not known. Since Fox showed that alkylidene complexes containing hexafluoro-*tert*-butoxide could be converted into *tert*-butoxide catalysts in situ,¹⁴ we attempted to prepare **2** from **1a**. Reaction of **1a** with excess lithium *tert*-butoxide in C₆H₆/CH₂Cl₂ cleanly generated **2**, which could be isolated and characterized. In the proton NMR spectrum of **2** in C₆D₆ the alkylidene resonance was found at 11.91 ppm with $J_{\text{CH}} = 123$ Hz with resonances for what we propose is the “*syn/anti*” isomer at 12.10 and 12.36 ppm (14% of total).

Synthesis of Bimetallic Complexes That Contain a Ferrocene Unit. As we will show later, the presence of one or more ferrocene moieties in a ROMP polymer allows one to establish molecular weights readily via MALDI-TOF techniques. Therefore it would be desirable to incorporate a ferrocene into the bimetallic initiator. A second advantage of a ferrocene linker is a tendency to produce complexes that are more readily crystallized.

One-half equivalent of divinylferrocene was added rapidly to a solution of Mo(CHCMe₂Ph)(NAr)(OR_{F6})₂ in toluene. The solution immediately turned red, and upon cooling the solution to -30 °C, burgundy crystals of bimetallic species **3** (eq 3) were isolated. A related *tert*-

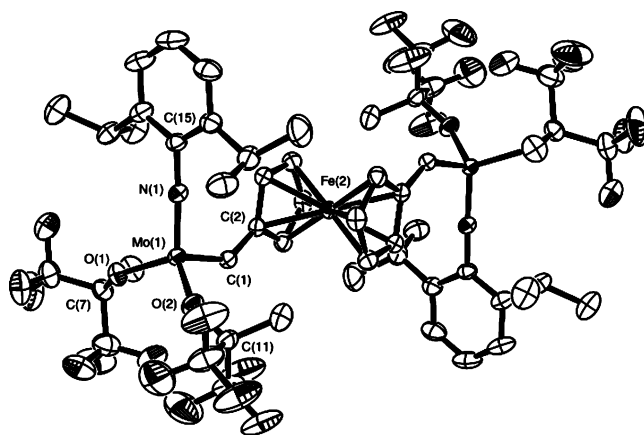
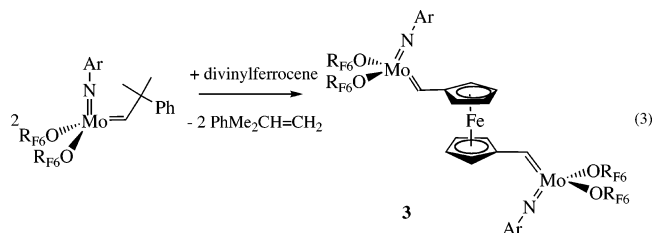


Figure 2. Thermal ellipsoid drawing of **3**. Hydrogen atoms are omitted for clarity.

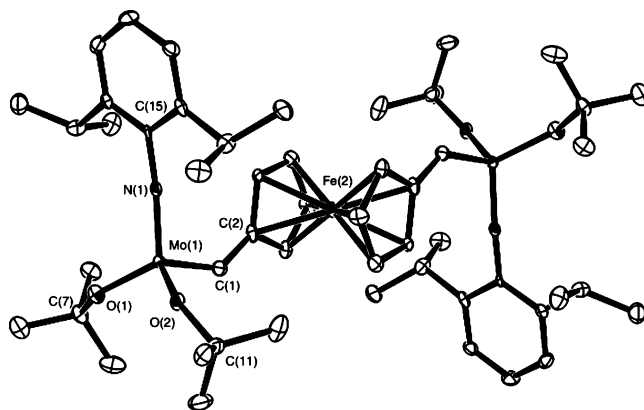


Figure 3. Thermal ellipsoid drawing of **4**. Hydrogen atoms are omitted for clarity.

butoxide were found at 13.10 ppm (6.7% of total area) and 12.68 ppm (25.8% of total area), in addition to alkylidene resonances for starting material and for **3**. We ascribe the resonances at 13.10 and 12.68 ppm to *anti* and *syn* isomers, respectively, of the monometallic ferrocenylmethylidene species, (NAr)(OR_{F6})₂Mo=CHC₅H₄-Fe(C₅H₄CH=CH₂).

Crystals suitable for X-ray studies of both **3** and **4** were isolated (Figures 2 and 3, Tables 1 and 2). One molecule of benzene was found in the crystal of **3** used for the X-ray study, while one molecule of toluene was found in the crystal of **4** used for the X-ray study. All bond lengths and angles are comparable to those found in monometallic four-coordinate structures in this class.^{18,19} In both complexes, the alkylidene is *syn* to the imido group. To our knowledge these are the only high oxidation state Mo or W ferrocenyl alkylidene complexes to be structurally characterized, although Mo[CHC₅H₄-FeCp](NAr)(O-*t*-Bu)₂ has been reported⁹ and *anti*-Re-[CHC₅H₄FeCp](C-*t*-Bu)[OCMe(CF₃)₂]₂ has been structurally characterized.²⁰

Proton and ¹³C NMR spectra of **3** and **4** are consistent with the structures found in the solid state; largely one alkylidene H_α resonance was found at 11.84 (for **4**) and 12.53 ppm (for **3**) with J_{CH} of 127 and 129 Hz, respectively (as determined by ¹³C NMR), characteristic of a

butoxide complex (**4**) can be prepared in high yield by treating **3** with lithium *tert*-butoxide. Both **3** and **4** are soluble in toluene. To confirm that these complexes were indeed bimetallic species, 1 equiv of divinylferrocene was added to Mo(CHCMe₂Ph)(NAr)(OR_{F6})₂ in 1.0 mL of C₆D₆. After 20 min two resonances for what we assign as the alkylidene formed through reaction of only one of the vinyl groups in divinylferrocene with the neo-

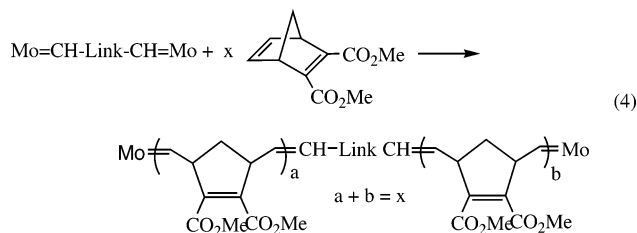
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syn orientation of the alkylidene. However, in each case two reproducible additional resonances were present in equal amounts, as observed in **1a**, **1b**, and **2**. In **4** these were found at 12.31 ppm ($J_{\text{CH}} = 154$ Hz, 4% of total area) and 11.97 ppm ($J_{\text{CH}} = 125$ Hz, 4% of total area). (The coupling constants were determined through proton NMR of a concentrated solution.) These data suggest that these resonances can be ascribed to an isomer in which one of the alkylidenes (with the alkylidene resonance at 12.31 ppm and $J_{\text{CH}} = 154$ Hz) has the *anti* orientation; the position (11.97 ppm) and J_{CH} (125 Hz) of the other resonance was characteristic of a *syn* alkylidene. Therefore the sample consisted of 92% *syn/syn* and 8% *syn/anti* isomers. Similar resonances were found for **3** at 13.03 (*anti*) and 12.64 (*syn*) ppm for the *syn/anti* isomer (each 2% of total), although the lower solubility of **3** compared to **4** and the smaller amount of the *syn/anti* isomer prevented confirmation of this assignment through a measurement of the J_{CH} values. No resonances were found for an *anti/anti* isomer in either case. The relatively low amounts of the *syn/anti* isomers of **3** and **4** that were found would suggest that the amount of *anti/anti* isomer in each case would probably be much less than 1%.

Initiation Studies. It is important to establish whether initiation for some monomer of interest takes place at approximately the same rate as propagation and whether both ends of the bifunctional initiator initiate readily. Therefore aliquots of 2 equiv of DCMNBD (4,5-dicarboxymethoxynorbornadiene) were added to solutions of the bifunctional initiators, and the alkylidene region in the proton NMR was observed. Addition of aliquots of DCMNBD to **1a** and **3** in C_6D_6 led to the disappearance of the initial alkylidene proton resonances and appearance of broadened alkylidene resonances at 12.69 ppm ($\sim 15\%$) and 12.10 ppm for the growing polymer chain (eq 4, where $\text{Mo} = \text{Mo}(\text{NAr})(\text{O}-t\text{-Bu})_2$ or $\text{Mo}(\text{NAr})(\text{OR}_{\text{F6}})_2$). Only 8 equiv of DCMNBD



(4 per Mo) were required in order to consume all of the initiator. The resonance at 12.69 ppm is proposed to be that for the *anti* isomer, while that at 12.10 ppm is proposed to be that for the *syn* isomer. Addition of aliquots of DCMNBD to **2** and **4** in C_6D_6 revealed that the initial alkylidene protons were replaced by two doublet alkylidene proton patterns at 11.71 and 11.66 ppm (2.5:1) after addition of only 4 equiv of DCMNBD (2 per Mo). This pattern is the same as that obtained using the monometallic initiator, $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{O}-t\text{-Bu})_2$, as should be the case. Since the *trans* content of poly[DCMNBD] is approximately the same, we believe that the two alkylidene resonances can be ascribed to polymer chains in which the alkylidene at the chain end contains a *trans* or a *cis* double bond between the last and the next to last monomer unit. The alkylidene itself is likely to be the average of rapidly equilibrating

Table 3. GPC Data for DCMNBD and MTD Homopolymers^a

monomer	catalyst	equiv monomer	PDI
DCMNBD	1a	100	1.03 ^b
	1a	300	1.01 ^b
	2	100	1.04 ^b
	3	50	1.01 ^b
	3	100	1.01 ^b
	3	150	1.04 ^b
	4	50	1.02 ^b
	4	100	1.05 ^b
	4	150	1.07 ^b
	MTD	1a	100
2		100	1.01 ^b
3		50	1.09
3		100	1.10
4		50	1.04
4		100	1.01

^a See Experimental Section for procedural details. Polydispersities were obtained using an RI detector versus polystyrene standards. ^b Polydispersity of precipitated polymer with yield > 95%.

anti and *syn* isomers.²¹ The main point is that initiation appears to be facile for both *tert*-butoxide and hexafluoro-*tert*-butoxide complexes, and only 4–8 equiv of DCMNBD are needed in order to initiate polymerization at both metal sites.

Polymerization Studies, Including Analyses by MALDI-TOF. Homopolymers and ABA triblock copolymers were prepared using initiators **1a**, **2**, **3**, and **4** in toluene. A typical polymerization reaction involved addition of a monomer solution to the initiator in solution, followed by continued stirring of the solution at room temperature for 1 h. To prepare triblock copolymers, the second monomer solution was then added to the reaction (after the first monomer had been completely polymerized) and the mixture stirred for another hour. All reactions ultimately were quenched through addition of excess benzaldehyde or ferrocene-carboxaldehyde. In all cases, the polymers were precipitated upon addition of methanol. Polymers were analyzed by gel permeation chromatography (GPC), and the data are summarized in Table 3.

Poly[DCMNBD]₁₀₀ prepared using **1a** as initiator had a low polydispersity index (PDI = 1.04) in contrast to poly[MTD]₁₀₀ (PDI = 1.58) as determined by GPC versus polystyrene standards. High-PDI polymers have been prepared previously with the monometallic hexafluoro-*tert*-butoxide complexes and are believed to result from circumstances where $k_p \gg k_i$.¹⁴ Triblock copolymers (Table 4) synthesized using **1a** as initiator showed a small amount of homopolymer of DCMNBD (as observed by GPC) along with the major triblock copolymer. Purity of the MTD was checked by replacing MTD by norbornene (NB) in a triblock copolymer. The triblock copolymer with NB as the outside block (PDI of triblock portion was 1.12) also showed a low molecular weight peak upon analysis by GPC. Some catalyst decomposition after formation of the inside block is the proposed reason for formation of low molecular weight homopolymer.

Initiator **2** was used to prepare homopolymers and triblock copolymers in a manner similar to that described above. The *tert*-butoxide initiator (**2**) gave poly-

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Table 4. GPC Data for MTD/DCMNBD/MTD Triblock Copolymers

catalyst	equiv DCMNBD ^a	equiv MTD ^a	PDI
1a	100	100	1.21 ^{b,c}
3	20	30	1.19
	24	30	1.13
	31	48	1.13
	50	50	1.03
	100	50	1.02
4	103	94	1.11
	50	50	1.09
	100	50	1.08

^a Per dimer. ^b Polydispersity of precipitated polymer with yield > 95%. ^c PDI for triblock copolymer peak only.

Table 5. MALDI-TOF Data Acquired for DCMNBD Homopolymers Synthesized Using 3 as the Initiator

equiv	expected M_n ($\times 10^4$)	found M_n ($\times 10^4$)	PDI
49	1.06	1.02 ^a	1.02
		1.05	1.03
		2.22	1.02
102	2.16	2.25	1.02

^a See Figure 4.

[MTD]₁₀₀ with a lower polydispersity index (PDI = 1.03) compared to poly[MTD] obtained with the hexafluoro-*tert*-butoxide catalyst (PDI = 1.58). A poly([MTD]₅₀(NB)₁₀₀(MTD)₅₀) triblock copolymer (PDI = 1.12) prepared using **2** as initiator did not contain homopolymer, which was observed in triblock copolymers prepared using **1a** as initiator. Therefore, **2** (the *tert*-butoxide catalyst) was the initiator of choice for the catalyst system containing the divinylbenzene linker.

Homopolymers of DCMNBD and MTD prepared using **3** or **4** as initiators in toluene showed low polydispersities (<1.10), as determined by GPC versus polystyrene standards (Table 3). GPC traces of poly[DCMNBD] samples prepared with **4** as the initiator showed a high molecular weight shoulder, but were unimodal when **3** was employed. Therefore the hexafluoro-*tert*-butoxide catalyst was the initiator of choice for the catalyst containing the divinylferrocene linker. Triblock copolymers of the type ABA also were prepared in toluene using the difunctional initiator **3** or **4**, which showed low polydispersities (Table 4).

Several samples of poly[DCMNBD]_x that had been prepared using **3** as initiator were examined through MALDI-TOF mass spectroscopy. The three matrixes that were investigated for MALDI included 2,5-dihydroxybenzoic acid (DHB), dithranol (DT), and *trans*-3-indoleacrylic acid (IAA). Dopants included Na⁺ (source = NaI), K⁺ (source = KCl), and Ag⁺ (source = silver trifluoroacetate). After several sample preparations and optimization of conditions, DT was found to be the most appropriate matrix for the ROMP polymers of this type. The results are presented in Table 5.

A typical MALDI spectrum of poly[DCMNBD]_x synthesized using **3** is shown in Figure 4. Two distributions are present, one centered at the expected mass, the other at approximately half the expected mass. The resolution is not sufficient to know whether the half molecular weight chains contain iron. Two possible explanations for the half molecular weight chains are (i) a significant amount of monometallic initiator was present in the catalyst, or (ii) some polymer chains are

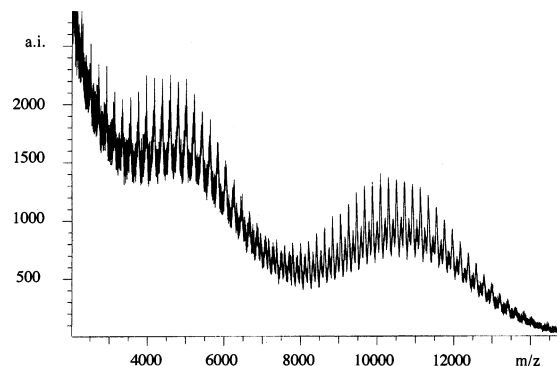


Figure 4. MALDI-TOF spectrum of poly[DCMNBD]₅₀/(CHPh)₂ synthesized using **3** as the initiator and quenching with benzaldehyde (matrix used = DT; doped with Ag⁺; $M_n = 1.02 \times 10^4$; PDI = 1.02).

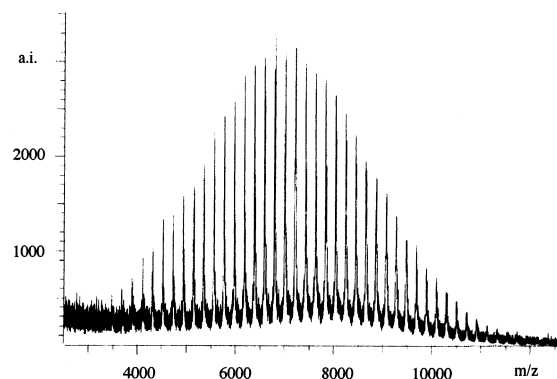


Figure 5. MALDI-TOF spectrum of poly[DCMNBD]₃₀/[(CHC₅H₄)FeCp]₂ synthesized using **2** as the initiator and quenching with ferrocenecarboxaldehyde (matrix used = DT; doped with Na⁺; $M_n = 6.8 \times 10^3$; PDI = 1.08).

fragmenting under the MALDI conditions employed. The first seems unlikely since (i) no monometallic initiator can be observed by proton NMR in the catalyst employed; (ii) if a significant amount of monometallic catalyst were present, the experimental molecular weight should be larger than that expected and observed for a living system; and (iii) the size of the half-mass peak varies depending on the MALDI conditions that were employed, and in some runs it was not present. In all four samples the distance between peaks corresponded approximately to the mass of the monomer (which for DCMNBD = 208.21 Da), the average molecular weight was approximately that expected for a living polymerization ($210.06 + n \times 208.21 + 2 \times 90.12$, where n = the number of monomers added), and the PDI (calculated from the MALDI spectrum) was analogous to that obtained by GPC methods (Table 3).

Similar studies were carried out on poly[DCMNBD]₃₀ that had been prepared using **2** as initiator. When the polymer was quenched with excess benzaldehyde, only an extremely weak signal was observed in the attempted MALDI spectra. However, when the polymer was quenched with excess ferrocenecarboxaldehyde, a significant signal was observed in the MALDI spectra. MALDI spectra of the polymer showed a single distribution ($M_n = 6.8 \times 10^3$ Da) with the molecular weight centered around the expected molecular weight (6.7×10^3 Da), as shown in Figure 5. The distance between peaks corresponds approximately to the mass of the monomer (DCMNBD = 208.21 Da), and the PDI was

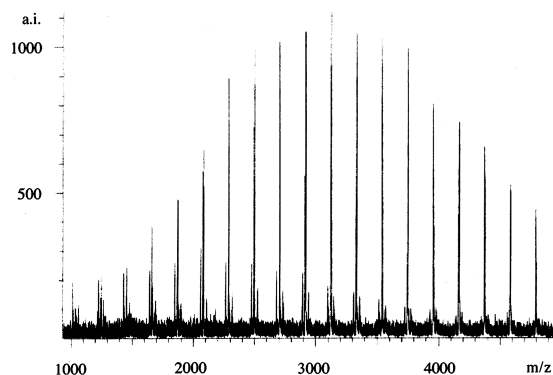


Figure 6. Spectrum of Ag^+ - and Na^+ -doped oligomer of DCMNBD synthesized with **4** and capped with benzaldehyde ($\text{poly}[\text{DCMNBD}]_{12}/(\text{CHPh})_2$). The most intense peak is the Na^+ -doped peak (matrix = DT).

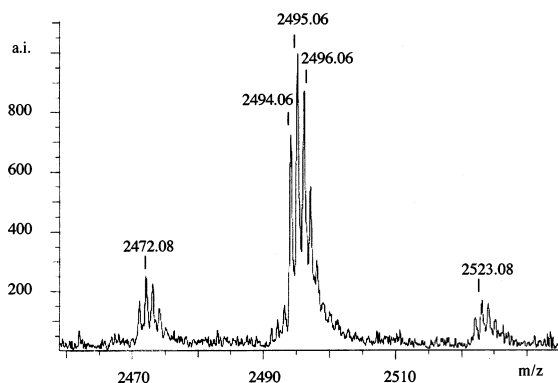


Figure 7. Expanded peak for $[\text{Fe}(\text{C}_5\text{H}_4\text{CH})_2][\text{DCMNBD}]_{10}(\text{CHPh})_2$. The three peaks correspond to H^+ , Na^+ , and Ag^+ adducts, respectively.

1.08. It is important to note that no half molecular weight chains were observed for this polymer, which further suggests that the half molecular weight chains in the polymers synthesized using **3** as the initiator can be ascribed to fragmentation at the ferrocenyl linking unit under the MALDI conditions.

An oligomer of DCMNBD (12-mer on average) was prepared by adding 12 equiv of DCMNBD to a solution of **3** in toluene. After 1 h, the solution was divided into two parts. One part was quenched with benzaldehyde to yield $\text{poly}[\text{DCMNBD}]_{12}/(\text{CHPh})_2$ and the other with ferrocenecarboxaldehyde to yield $\text{poly}[\text{DCMNBD}]_{12}/[(\text{CHC}_5\text{H}_4)\text{FeCp}]_2$ (where CHPh and $(\text{CHC}_5\text{H}_4)\text{FeCp}$ are the benzylidene and ferrocenylmethylene endgroups, respectively). Each oligomer was analyzed by MALDI. A spectrum of the $\text{poly}[\text{DCMNBD}]_{12}/(\text{CHPh})_2$ sample (doped with Na^+ and Ag^+) is shown in Figure 6. (The H^+ doped peak is also present, as in any MALDI spectrum.) The difference between any two peaks is approximately 208.21 Da, which is the molecular weight of one monomer unit. An expansion of the $[\text{Fe}(\text{C}_5\text{H}_4\text{CH})_2](\text{DCMNBD})_{10}(\text{CHPh})_2$ peak is shown in Figure 7. The distributions for the H^+ , Na^+ , and Ag^+ peaks match those expected, as shown for the Na^+ pattern in Figure 8. MALDI spectra of $\text{poly}[\text{DCMNBD}]_{12}/[(\text{CHC}_5\text{H}_4)\text{FeCp}]_2$ are analogous to those of $\text{poly}[\text{DCMNBD}]_{12}/(\text{CHPh})_2$. The expanded region of the $[\text{Fe}(\text{C}_5\text{H}_4\text{CH})_2](\text{DCMNBD})_{10}[(\text{CHC}_5\text{H}_4)\text{FeCp}]_2$ peak (Figure 9) matches closely with that of the benzaldehyde-capped polymer (Figure 7), with the difference corresponding to twice the difference in the molecular weight of the endgroups (benzylidene

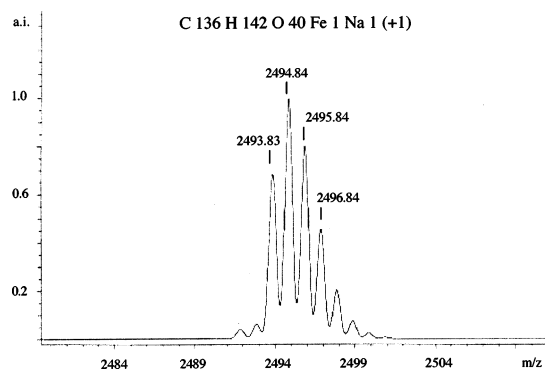


Figure 8. Expected peak distribution for $\{[\text{Fe}(\text{C}_5\text{H}_4\text{CH})_2][\text{DCMNBD}]_{10}(\text{CHPh})_2\text{Na}\}^+$.

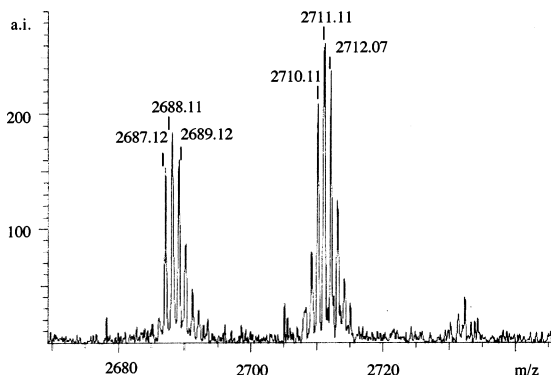


Figure 9. Expanded peak for $[\text{Fe}(\text{C}_5\text{H}_4\text{CH})_2][\text{DCMNBD}]_{10}[(\text{CHC}_5\text{H}_4)\text{FeCp}]_2$. The three peaks correspond to H^+ , Na^+ , and Ag^+ adducts, respectively (matrix = DT).

versus ferrocenylmethylene). The expected and found molecular weights differ by no more than 1 Da, and the isotopic distributions closely match for both $[\text{Fe}(\text{C}_5\text{H}_4\text{CH})_2](\text{DCMNBD})_{10}(\text{CHPh})_2$ and $[\text{Fe}(\text{C}_5\text{H}_4\text{CH})_2](\text{DCMNBD})_{10}[(\text{CHC}_5\text{H}_4)\text{FeCp}]_2$. No significant unexpected peaks were observed in any MALDI spectra of these oligomers, even the fragmented chains noted above. These data suggest that polymerization of DCMNBD by **3** as the initiator is a living process under the conditions employed and that the polymer chains are still active after the polymerization is complete. Since NMR studies discussed in the previous section suggest that both ends of the bifunctional initiator react with DCMNBD to yield the expected new alkylidenes, these polymerizations must proceed in a living fashion from the initiator in both directions with the number of monomers incorporated being statistical and on average equal in number on each side of the central linking unit, $\text{Fe}(\text{C}_5\text{H}_4\text{CH})_2$.

Conclusions

We have prepared two types of bimetallic initiators that are well-behaved initiators for the living ROMP polymerization of DCMNBD and MTD and have shown that they can be employed as initiators for the preparation of triblock copolymers in relatively high purity and with known average block size. In future studies we will explore the utility of these initiators for preparing a variety of relatively well-defined triblock copolymers.

Experimental Section

General Procedures. All manipulations were performed under dinitrogen in a glovebox or using standard Schlenk procedures unless otherwise stated. Solvents were dried using conventional procedures. Deuterated solvents were degassed and distilled from CaH₂ or sodium benzophenone ketyl. Methyltetracyclododecene (MTD) and norbornene (NB) were dried over CaH₂ and vacuum distilled. *p*-Divinylbenzene was purified as suggested in the literature²² and stored in the box freezer. Benzaldehyde was vacuum distilled and stored over molecular sieves. Commercial reagents were used without further purification unless stated otherwise. {(CH₃CHOH)-C₅H₄}₂Fe,²³ Mo(CHCMe₂Ph)(NAr)(OR_{F6})₂,²⁴ and 4,5-dicarbo-methoxynorbornadiene (DCMNBD)²⁵ were synthesized according to published procedures.

NMR spectra were recorded on a Varian INOVA 500 spectrometer. ¹H NMR chemical shifts are given in ppm versus residual protons in the deuterated solvents as follows: δ 7.27 CDCl₃, 7.16 C₆D₆, 5.32 CD₂Cl₂, and 2.09 CD₃C₆D₅. MALDI-TOF mass spectra were recorded on a Bruker Omni-Flex MALDI-TOF, and data were analyzed using Xtof Software Version 5.1.5 by Bruker Daltonics, Inc. Matrix solutions were prepared as 10 mg/mL solutions in THF. Samples were prepared as 0.1 to 1 mg/mL solutions in THF, and the matrix: sample ratio was 10:1. Dopent concentration when applicable was approximately 0.1 mg/mL. GPC analyses were carried out on a system equipped with two Waters Styragel HR 5E columns (300 mm length × 7.8 mm inner diameter) in series. HPLC grade THF was supplied at a flow rate of 1.0 mL/min with a Knauer HPLC pump K501. A Wyatt Technology mini Dawn light-scattering detector coupled with a Knauer differential refractometer was employed. Data analysis was carried out using Astrette 1.2 software (Wyatt Technology). PDI values for polymers were obtained using dn/dc = 0.110 mL/g.

[(DME)(R_{F6}O)₂(ArN)Mo=CH]₂(1,4-C₆H₄) (1a). To a stirred solution of Mo(CHCMe₂Ph)(NAr)(OR_{F6})₂ (1.2 g, 1.6 mmol) in 40 mL of DME was added *p*-divinylbenzene (125 mg, 0.96 mmol), and the reaction mixture was allowed to stir at room temperature for 12 h. The solvent was removed in vacuo, and the residue was crystallized from pentane to yield orange product; yield 1.0 g (76%): ¹H NMR (C₆D₆) δ 12.84 (s, 1H, MoCHR, *syn/anti* isomer, 10%), 12.81 (s, 1H, MoCHR, *syn/anti* isomer, 10%), 12.64 (s, 2H, MoCHR, *syn/syn* isomer, 80%). The following peaks are reported for the major isomer only: 7.0–6.8 (m, 10H, aromatic), 3.42 (sept, 4H, CH(CH₃)₂), 3.31 (s, 4H, OCH₂CH₂O), 3.12 (s, 6H, OCH₃), 1.19 (s, 12H, OCCH₃(CF₃)₂), 1.02 (d, 24H, CH(CH₃)₂). Anal. Calcd for C₅₆H₇₂F₂₄Mo₂N₂O₈: C, 43.42; H, 4.69; N, 1.81. Found: C, 43.28; H, 4.59; N, 1.76.

[(THF)(R_{F6}O)₂(ArN)Mo=CH]₂(1,4-C₆H₄) (1b). **1a** (30 mg, 0.019 mmol) was dissolved in 8 mL of THF, and the solution was stirred at room temperature for 2 h. The volatile components were removed in vacuo to give 24.3 mg of orange powder as the product (83% yield): ¹H NMR (C₆D₆) δ 13.63 (s, 1H, MoCHR, *syn/anti* isomer, 7%), 13.09 (s, 1H, MoCHR, *syn/anti* isomer, 7%), 12.88 (s, 2H, MoCHR, *syn/syn* isomer, 86%, *J*_{CH} = 125 Hz). The following peaks are reported for the major isomer only: 7.05–6.98 (m, 10H aromatic), 3.66 (sept, 4H, CH(CH₃)₂), 3.65 (s, 4H, CH₂CH₂), 1.29 (s, 4H, CH₂OCH₃), 1.18 (s, 12H, OCCH₃(CF₃)₂), 1.06 (d, 24H, CH(CH₃)₂); ¹⁹F NMR (CD₂-Cl₂, 300 MHz) δ -76.54, -76.86. Anal. Calcd for C₅₆H₆₈F₂₄Mo₂N₂O₆: C, 44.45; H, 4.53; N, 1.85. Found: C, 44.49; H, 4.59; N, 1.78.

[(*t*-BuO)₂(NAr)MoCH]₂C₆H₄ (2). Lithium *tert*-butoxide (78.8 mg, 0.985 mmol) was added to a suspension of **1a** (300 mg, 0.193 mmol) in CH₂Cl₂, and the reaction mixture was stirred at room temperature for 2 h. As the reaction progressed, the color changed from orange to dark red, and a more homogeneous solution formed. The volatiles were removed in vacuo, and the product was crystallized from pentane as a powdery red solid; yield 162 mg (89%): ¹H NMR 500 MHz (C₆D₆) δ 12.36 (s, 1H, MoCHR, *syn/anti* isomer, 7%), 12.10 (s, 1H, MoCHR, *syn/anti* isomer, 7%), 11.91 (s, 2H, MoCHR, *syn/syn* isomer, 86%). The following peaks are reported for the major isomer only: 7.14–7.05 (m, 10H, aromatic), 3.95 (sept, 4H, CH(CH₃)₂), 1.28 (s, 12H, OC(CH₃)₃), 1.16 (d, 24H, CH(CH₃)₂); ¹³C NMR (C₆D₆) δ 247.0 (d, *J*_{CH} = 123 Hz, MoCHR). Anal. Calcd for C₄₈H₇₆Mo₂N₂O₄: C, 61.23; H, 7.98; N, 3.04. Found: C, 61.37; H, 8.08; N, 3.06.

[C₅H₄(CH₂=CH)]₂Fe. (This synthesis is a modification of that reported in the literature.²⁶) A mixture of {(CH₃CHOH)-C₅H₄}₂Fe (5 g, 0.18 mol) and activated neutral alumina (50 g) in 50 mL of toluene was refluxed for 2 h. The solution was transferred into a Schlenk flask via a cannula and brought into the glovebox. The solution was then filtered through Celite, and the volatile components of the filtrate were then removed in vacuo. According to ¹H NMR spectra, the compound was approximately 75% product and 25% [Fe(C₅H₄)CMe]₂O. This mixture was used in further reactions since the presence of [Fe(C₅H₄)CMe]₂O provided no complications, and the amount of [C₅H₄(CH₂=CH)]₂Fe actually present in the mixture was known: ¹H NMR (C₆D₆): δ 6.32 (m, 1H, CHCH₂), 5.29 (m, 1H, CHCH₂), 5.04 (m, 1H, CHCH₂), 4.06 (m, 4H, CH).

[(R_{F6}O)₂(ArN)Mo=CH(C₅H₄)]₂Fe (3). The isolated divinylferrocene from above (0.27 g, 0.96 mmol) was added all at once to a yellow toluene solution (10 mL) of Mo(CHCMe₂Ph)(NAr)(OR_{F6})₂ (1.2 g, 1.6 mmol) with stirring at ambient temperature. After 1 h the solution was stored at -30 °C to yield 1.2 g of dark red crystals (83% yield): ¹H NMR (C₆D₆) δ 13.03 (s, 1H, MoCHR, *syn/anti* isomer, 2%), 12.64 (s, 1H, MoCHR, *syn/anti* isomer, 2%), 12.53 (s, 2H, MoCHR, *syn/syn* isomer, 96%). The following peaks are reported for the major isomer only: 6.99 (s, 6H, CH), 4.00 (m, 16H, C₅H₄), 3.47 (s, 4H, CH(CH₃)₂), 1.34 (s, 12H, CCH₃(CF₃)₂), 1.14 (d, 24H, CH(CH₃)₂); ¹³C NMR (C₆D₆): δ 269.10 (d, *J*_{CH} = 129 Hz, MoCHR). Anal. Calcd for C₅₄H₆₂F₂₄Mo₂N₂O₄Fe: C, 43.04; H, 4.15; N, 1.86. Found: C, 42.88; H, 4.07; N, 1.81.

[(*t*-BuO)₂(ArN)Mo=CH(C₅H₄)]₂Fe (4). Lithium *tert*-butoxide (200 mg, 2.5 mmol) was added all at once to a toluene solution (75 mL) of **3** (0.6 g, 0.40 mmol) with stirring at ambient temperature. The solution was stirred for 5 h, at which time the volatile components were removed. Pentane was added to the resulting solid, and the solution was filtered through Celite. The filtrate was concentrated and placed in the freezer overnight, during which time crystals formed; yield 0.4 g (65%): ¹H NMR (C₆D₆) δ 12.31 (s, 1H, MoCHR, *syn/anti* isomer, 4%), 11.97 (s, 1H, MoCHR, *syn/anti* isomer, 4%), 11.84 (s, 2H, MoCHR, *syn/syn* isomer, 92%). The following peaks are reported for the major isomer only: 7.09 (br s, 6H, CH), 4.25 (m, 4H, C₅H₄), 4.17 (m, 4H, C₅H₄), 3.99 (s, 4H, CH(CH₃)₂), 1.37 (s, 36H, C(CH₃)₃), 1.28 (d, 24H, CH(CH₃)₂). The following data are reported for the alkylidene region only: ¹H NMR (C₆D₅CD₃) δ 12.24 (s, 1H, MoCHR, *J*_{CH} = 154 Hz, *syn/anti* isomer, 4%), 11.90 (s, 1H, *J*_{CH} = 125 Hz, MoCHR, *syn/anti* isomer, 4%), 11.77 (s, 1H, *J*_{CH} = 130 Hz, MoCHR, *syn/syn* isomer, 92%); ¹³C NMR (C₆D₆) δ 247.05 (d, *J*_{CH} = 127 Hz, MoCHR). Anal. Calcd for C₅₄H₈₆Mo₂N₂O₄Fe: C, 60.33; H, 8.06; N, 2.61. Found: C, 60.15; H, 7.88; N, 2.54.

Observation of Monometallic Ferrocenyliene. Divinylferrocene from above (5.4 mg, 0.015 mmol) and Mo(CHCMe₂Ph)(NAr)(OR_{F6})₂ (18.2 mg, 0.0234 mmol) were each dissolved in 0.5 mL of benzene, and the solutions were mixed rapidly and placed in an NMR tube. By ¹H NMR, the various products were observed 20 min after mixing. Only the alkylidene region

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peaks are reported: ^1H NMR (C_6D_6) δ 13.10 (s, 1H, MoCH, 6.7%, monometallic species), 13.02 (s, 1H, MoCH, 6.2%, *syn/anti* isomer of **3**), 12.68 (s, 1H, MoCH, 25.8%, monometallic species), 12.64 (s, 1H, MoCH, 6.7%, *syn/anti* isomer of **3**), 12.52 (s, 1H, MoCH, 42.8%, *syn/syn* isomer of **3**), 12.14 (s, 1H, MoCH, 11.8%, unreacted starting material).

General Procedure for Polymerization to Give Homopolymers. To the catalyst solution in a given solvent was added a solution of the monomer in that solvent in one portion, and the solution was stirred at room temperature for 45 min to 1 h. The polymerization was quenched with benzaldehyde and stirred for another 45 min to 1 h. The polymer was precipitated out of methanol, filtered, and dried. For **1a** and **2** the solvent used was either DME or toluene. For **3** and **4** the solvent used was always toluene.

General Procedure for Polymerization for the Synthesis of Triblock Copolymers. The first monomer (inside block) in a given solvent was added in one portion to the catalyst solution in toluene, and the solution was stirred at room temperature for 1 h. Then a solution of the second monomer (outside block) in toluene was added in one portion and the reaction stirred for another hour. Benzaldehyde was added, and the solution was stirred for 45 min to 1 h. The polymer was precipitated by addition of methanol, filtered, and dried under vacuum.

Example of Polymerization of MTD with 1a. A solution of DCMNBD (130 mg, 0.625 mmol) in 1 mL of toluene was added in one portion to the stirred solution of **1a** (10.1 mg, 6.46×10^{-3} mmol) in 10 mL of toluene. The solution was stirred for 1 h at room temperature. Benzaldehyde (200 μL) was added to quench the reaction, and the solution was allowed to stir for another hour. The polymer was precipitated by addition of methanol (100 mL) and isolated by filtration as a white polymer (127 mg, 96%).

Example of Polymerization of MTD and DCMNBD with 1a. To the stirred solution of **1a** (10 mg, 6.46×10^{-3} mmol) in toluene (10 mL) was added a solution of DCMNBD (132 mg, 0.631 mmol) in 2 mL of toluene in one portion. The solution was stirred for 1 h at room temperature. A solution of MTD (117 mg, 0.672 mmol) in 2 mL of toluene was added in one portion, and the solution was stirred for another hour. Benzaldehyde (200 μL) was added to quench the reaction, and the solution was allowed to stir for an additional hour. The polymer was precipitated by addition of methanol (100 mL) and isolated by filtration as a white polymer (245 mg, 98%).

Synthesis of DCMNBD Oligomer Using 3, Quenched with Both Benzaldehyde and Ferrocenealdehyde. A solution of DCMNBD (208.2 mg, 12 equiv) in 10 mL of toluene was added rapidly to a solution of **3** (181 mg, 0.0069 mmol) in 75 mL of toluene. The solution was stirred for 45 min and was then split into two approximately equal portions. Two drops of benzaldehyde was added to one solution and a spatula tip of ferrocenecarboxaldehyde was added to the other to quench the reaction, and the solution was allowed to stir for an additional 45 min. A 50 mL portion of methanol was added to each solution, and the volatile components were removed. A 10 mL amount of tetrahydrofuran was added to each solution, and they were rinsed through a silica plug with additional

tetrahydrofuran. The volatile components were again removed to yield two powders, which were used in further studies.

X-ray Crystallographic Studies. Crystals were coated in Paratone-N oil in an inert atmosphere and examined under a microscope. A suitable crystal was placed on the end of a glass fiber or in a glass loop and frozen in an inert gas stream. Data were collected on a Siemens Platform three-circle diffractometer equipped with a CCD or Bruker Apex-CCD detector at low temperature. Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) was used. Integration was performed using the SAINT package and corrected for absorption effects with SADABS, unless otherwise noted. The initial solutions were obtained using direct methods, unless otherwise noted, and refined against F^2 on all data using full-matrix least squares using the SHELXTL package.²⁷ All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were 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, except for methyl groups, which were fixed at 1.5. Details of the data and refinement statistics are listed in Table 1 for all structures. Crystals of **1b** formed from a saturated heptane solution after storage at $-30 \text{ }^\circ\text{C}$ for 12 h. Compound **3** was crystallized at room temperature from a benzene solution and contains one ordered benzene of solvation. All hydrogens except H1 were placed in calculated positions and refined using a riding model. H1 was located in the difference map and refined satisfactorially.

Compound **4** was obtained from a saturated toluene solution at $-30 \text{ }^\circ\text{C}$; 1 equiv of ordered toluene was found in the crystal. During data collection the sample degraded substantially due to ice formation. Enough data were collected prior to icing to determine the structure. However, the resulting R factors are somewhat higher and the redundancy is somewhat lower than a typical data collection. The data were corrected for absorption effects using psi-scans in XPREP.

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Supporting Information Available: Fully labeled thermal ellipsoid plots, crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement parameters for **1a**, **3**, and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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