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Synthesis of Bifunctional Imido Alkylidene BisPyrrolide Complexes of Molybdenum and Their Conversion into Bifunctional Imido Alkylidene Diolate Complexes That Can Be Employed as ROMP Initiators

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Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract: Addition of four equivalents of lithium 2,5-dimethylpyrrolide to a solution of $[Mo(NAr)(OR_{F6})_2(CHC_5H_4)]_2Fe$ ($OR_{F6} = OCMe(CF_3)_2$) in dichloromethane led to $[Mo(NAr)(Me_2Pyr)_2(CHC_5H_4)]_2Fe$ (**2**; Me_2Pyr = 2,5-dimethylpyrrolide) and lithium hexafluoro-*tert*-butoxide, which crystallizes out upon cooling the reaction mixture to −35 °C. Attempts to prepare parent pyrrolide complexes analogous to **2** resulted in the formation of a mixture of two products. The one that could be isolated contains one equivalent of lithium pyrrolide per molybdenum, that is $[Mo(NAr)(Pyr)_3(CHC_5H_4)]_2FeLi_2$ (**3**). The X-ray structure obtained shows it to be a dimer of dimers in which each lithium atom is bound to three pyrrolides. Addition of four equivalents of lithium 2,5-dimethylpyrrolide to $[Mo(NAr)(OR_{F6})_2]_2(DME)_2(CH\text{-}1,4\text{-}C_6H_4CH)$ (**1b**) in cold DME produced $[Mo(NAr)(Me_2Pyr)_2]_2(CH\text{-}1,4\text{-}C_6H_4CH)$ (**4**) in good yield, in which the bridging alkylidene is derived from 1,4-divinylbenzene. Three equivalents of (*S*)-H_2[Biphen] are required for a clean reaction with **3** to form $[Mo(NAr)(Biphen)(CHC_5H_4)]_2Fe$ (**5**) (H_2[Biphen] = 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diol), Li_2[Biphen], and two equivalents of pyrrole. Reactions involving **4** with the chiral diols are the best behaved. Brown $[Mo(NAr)(Benz_2Bitet)]_2(CH\text{-}1,4\text{-}C_6H_4CH)$ (**6**) can be isolated upon addition of (*R*)-$H_2[Benz_2Bitet]$ ($H_2[Benz_2Bitet]$ = (3,3′-dibenzhydryl-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diol) to **4**, while addition of (*R*)-$H_2[Mes_2Bitet]$ ($H_2[Mes_2Bitet]$ = 3,3′-dimesityl-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diol) to **4** yields $[Mo(NAr)(Mes_2Bitet)]_2(CH\text{-}1,4\text{-}C_6H_4CH)$ (**7**). Compounds **5**, **6**, and **7** were employed as initiators for the polymerization of 2,3-dicarbomethoxynorbornadiene (DCMNBD) and 2,3-bis(trifluoromethyl)norbornadiene (NBDF6).

Keywords: lithium · metathesis · molybdenum · ring-opening polymerization · triblock polymers

Introduction

Some of the most interesting copolymers in terms of their physical properties are triblocks.[1] Triblocks (e.g., $A_xB_yA_z$, where x, y, and z are the average numbers of monomers of type A or B in each block) have been synthesized using a "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. Such methods have limitations, however, most seriously the presence of homopolymers or diblock copolymers. Purification through selective precipitation of the triblock copolymer is then required. A "bifunctional" approach to triblocks has been employed (e.g., disodium[2] or dilithio derivatives[1]) in order to synthesize triblocks from monomers that are prone to anionic polymerization (e.g., styrene). A bifunctional approach can be more reliable than the linear method for preparing high purity triblock copolymers since the triblock grows from the "inside out," that is, produces the central B block first and then the A blocks, and involves fewer opportunities for errors. High purity triblocks are most desirable since the presence of homo- or diblock copolymers in a triblock copolymer often degrade the properties of a given pure triblock copolymer.

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Reports of bifunctional initiators for ring-opening metathesis polymerization (ROMP) are rare.[3] Recently we published examples of isolable bifunctional alkylidene initiators for ROMP, for example $[Mo(NAr)(OR)_2(CHC_5H_4)]_2Fe$ species (where Ar = 2,6-diisopropylphenyl; OR = $OCMe_3$ or $OCMe(CF_3)_2$), and showed them to be catalysts for the living ROMP of several monomers.[4] This approach was employed for the preparation of ABA triblock copolymers using the divinylferrocene-linked complexes, where the inner blocks of the triblock copolymers were functionalized by liquid crystal mesogens.[5] So far, the number of bifunctional catalysts that can be prepared by this method has been limited to catalysts where OR is hexafluoro-*tert*-butoxide (OR_{F6}) or *tert*-butoxide. We sought a more general approach to bifunctional ROMP catalysts, including asymmetric catalysts.[6] Since we have shown that bisalkoxide catalysts can be prepared from bispyrrolide complexes, Mo(NR)(CHR′)(pyrrolide)$_2$,[7] upon addition of an alcohol, we decided to explore the possibility of preparing bifunctional bispyrrolide species that could be employed as precursors to bifunctional bisalkoxide or diolate complexes. We report here the synthesis of three pyrrolide complexes of the type $[Mo(NAr)(X)_2]_2$(linker) (where X = pyrrolide or 2,5-dimethylpyrrolide and the linker is an alkylidene derived from divinylbenzene or divinylferrocene) and the reaction of these complexes with various chiral diols. We demonstrate that bifunctional diolate complexes (isolated and prepared in situ) can be employed as initiators for the ROMP polymerization of 2,3-dicarbomethoxynorbornadiene (DCMNBD) and (2,3-bistrifluoromethylnorbornadiene (NBDF6).

Results and Discussion

Synthesis and Characterization of Bifunctional Bispyrrolide Complexes

We have found that bispyrollide complexes are relatively unreactive toward olefins. Therefore it is not possible to prepare $[Mo(NAr)(Me_2Pyr)_2(CHC_5H_4)]_2Fe$ (for example) through addition of divinylferrocene to Mo(NAr)(CHCMe$_2$Ph)(Me$_2$Pyr)$_2$. Therefore $[Mo(NAr)(OR_{F6})_2(CHC_5H_4)]_2Fe$ (**1a**) must be prepared first and lithium 2,5-dimethylpyrrolide added to it (Equation 1; OR_{F6} = OCMe(CF$_3$)$_2$) in dichloromethane.

$$\underset{\mathbf{1a}}{[Mo(NAr)(OR_{F6})_2(CHC_5H_4)\}_2Fe} \xrightarrow[\text{- 4 LiOR}_{F6}]{\text{4 LiMe}_2\text{Pyr}} \underset{\mathbf{2}}{[Mo(NAr)(Me_2Pyr)_2(CHC_5H_4)]_2Fe} \quad (1)$$

Four equivalents of lithium 2,5-dimethylpyrrolide are required to form a clean product, $[Mo(NAr)(Me_2Pyr)_2(CHC_5H_4)]_2Fe$ (**2**, where Me$_2$Pyr = 2,5-dimethylpyrrolide). When the reaction mixture is cooled to −35 °C, lithium hexafluoro-*tert*-butoxide crystallizes from solution and can be removed by filtration. Compound **2** appears to be unstable in the solid state at 22 °C over a period of days, evidenced by a color change, even in vacuo, and variable results for elemental analyses. Contamination by traces of lithium hexafluoro-*tert*-butoxide does not appear to be the cause since no LiOCMe(CF$_3$)$_2$ could be detected by ^{19}F NMR.

X-ray quality crystals of **2** were grown from diethyl ether. The solid state structure is shown in Figure 1. Crystallographic data can be found in Table 1 and relevant bond lengths and angles can be found in Table 2. The Mo−N$_{Ar}$−C$_{ipso}$ bond angle is almost linear at 178.77(13)°. The geometry of the molybdenum center is pseudotetrahedral with one of the 2,5-dimethylpyrrolide ligands being bound in an η^5-manner and the other in an η^1-manner. The alkylidene is oriented *syn* with respect to the imido ligand and the Mo(1)−C(1)−C(2) angle is 136.21(13)°. The electron count at the metal is 18. Two other compounds of this general type that contain one η^5- and one η^1-pyrrolide have been characterized crystallographically, namely W(NAr)(CHCMe$_2$Ph)(η^5-Me$_2$Pyr)(η^1-Me$_2$Pyr)[8] and Mo(NAd)(CHCMe$_2$Ph)(η^5-Me$_2$Pyr)(η^1-Me$_2$Pyr) (Ad = 1-adamantyl).[9]

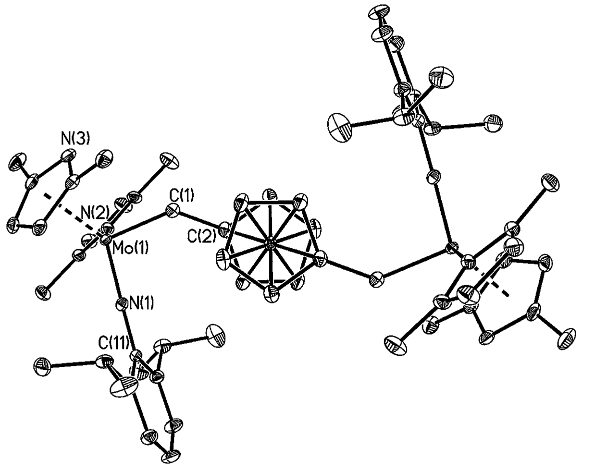


Figure 1. Thermal ellipsoid drawing of **2**. Solvent molecules and hydrogen atoms have been removed for clarity. (Only half the molecule is labelled since the two ends are identical.)

The alkylidene resonance for compound **2** is found at 13.1 ppm in the ^{1}H NMR spectrum (C$_6$D$_6$) with J_{CH} = 136 Hz, which is approximately half-way between typical coupling constants for *syn* (~125 Hz) and *anti* (~145 Hz) isomers. Variable temperature ^{1}H NMR studies (in C$_6$D$_5$CD$_3$) reveal free rotation of the imido aryl groups and rapid interconversion of the η^1- and η^5-bound pyrrolides at high temperature (60 °C). At room temperature, the pyrrolide resonances and the methine and methyl resonances of the arylimido groups are broadened almost into the baseline. At −30 °C, the spectrum begins to sharpen, and two alkylidene resonances are observed in a 1:0.7 ratio (at 13.01 and 12.94 ppm, respectively). We ascribe these two resonances to *meso* and the *rac* dimeric forms (as a consequence of chirality at each Mo) of the two diastereomers when interconversion of the η^1- and η^5-bound pyrrolides on the molybde-

Table 1. Crystallographic details for **3** and **2**.

Compound	**3**	**2**
Empirical formula	$C_{177}H_{193}Fe_2Li_4Mo_4N_{16}$	$C_{64}H_{86}FeMo_2N_6O$
Molar mass [g mol^{-1}]	3067.69	1203.12
Compound ID	07025	07035
Temperature [K]	100(2)	100(2)
λ [Å]	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P21/n$
Unit cell dimensions		
a [Å]	14.8816(18)	10.1779(13)
b [Å]	15.647(2)	28.119(4)
c [Å]	34.236(4)	11.5174(15)
α [°]	101.630(2)	90
β [°]	96.790(2)	114.802(2)
γ [°]	93.384(2)	90
Volume [Å^3]	7725.4(17)	2992.1(7)
Z	2	2
ρ_{calcd} [Mg/m^3]	1.319	1.335
Absorption coefficient [mm^{-1}]	0.556	0.697
$F(000)$	3198	1260
Crystal size [mm^3]	$0.10\times0.06\times0.04$	$0.15\times0.10\times0.04$
Range of θ [°]	1.58–24.71	1.45–29.57
Index ranges	$-17\leq h\leq17$	$-14\leq h\leq14$
	$-18\leq k\leq18$	$-39\leq k\leq39$
	$-39\leq l\leq40$	$-15\leq l\leq15$
Reflections collected	95875	57968
Independent reflections	26348 [$R_{int}=0.1108$]	8375 [$R_{int}=0.0632$]
Completeness [%] to θ [°]	99.9, $\theta=29.57$	100.0, $\theta=29.57$
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9781 and 0.9465	0.9726 and 0.9026
Data/restraints/parameters	26348/9334/2133	8375/35/369
GoF on F^2	1.005	1.028
Final R indices [I > 2 σ(I)]	$R1=0.0517$, $wR2=0.1028$	$R1=0.0292$, $wR2=0.0663$
R indices (all data)	$R1=0.1075$, $wR2=0.1244$	$R1=0.0406$, $wR2=0.0718$
Largest diff. peak and hole [e Å^{-3}]	1.101, −0.649	0.560, −0.562

Table 2. Selected bond lengths (Å) and angles (°) for **2** and **3**. (Distances are given for only one of the four independent Mo atoms in **3**.)

Compound	**2**	**3**
Mo(1)−C(1)	1.9523(17)	1.885(4)
Mo(1)−N(1)	1.7455(14)	1.721(3)
Mo(1)−N(2)	2.0915(14)	2.129(3)
Mo(1)−N(3)	2.4352(15)	2.162(4)
Mo(1)−N(4)	n/a	2.158(3)
Mo(1)−C(1)−C(2)	136.21(13)	141.3(3)
Mo(1)−N(1)−C(11)	178.77(13)	164.8(3)

num is slow on the NMR timescale. At −60 °C, there are eight ferrocene resonances and four methine resonances.

Attempts to prepare parent pyrrolide complexes analogous to **2** resulted in the formation of a mixture of two products. The one that could be isolated in pure form is a species that contains one equivalent of lithium pyrrolide per molybdenum, that is, $[Mo(NAr)(Pyr)_3(CHC_5H_4)]_2FeLi_2$ (**3**; Pyr = $NC_4H_4^-$; Equation 2). The complex was isolated as bright red crystals. A single alkylidene resonance at 14.01 ppm was observed in the ^{1}H NMR spectrum. X-ray quality crystals of **3** (Table 1) were grown from a hot benzene solution as the solution slowly returned to room temperature. Compound **3** also appeared to be thermally unstable over a period of days and yielded variable and irreproducible elemental analyses.

In the solid state, **3** is a dimer of the bifunctional "ate" complex shown in Equation 2. The dimer contains four molybdenum atoms, four lithium atoms, and two iron atoms. A drawing of the metal atom core can be found in Figure 2 and relevant bond lengths and angles can be found in Table 2. From the two-dimensional view shown, the lithium atoms form the corners of a square and the four molybdenum atoms are located on the four edges of the square. The iron atoms are located in the center of the square, and the molybdenum atoms associated with each ferrocene-linker are on opposite edges. Each lithium atom is coordinated to three pyrrolides, two of which are coordinated to one molybdenum atom, while the third is coordinated to a neighboring molybdenum atom. The alkylidene ligand adopts a *syn* conformation with respect to the imido group, and the Mo(1)−C(1)−C(2) angle is 141.3(3)°. The bond lengths and angles are comparable to other crystallographically characterized ferrocene-linked complexes of this nature.[4] The geometry around the molybdenum center is between trigonal bipyramidal and square pyramidal. The cyclopentadienyl rings of ferrocene are almost eclipsed. The two substituents on the cyclopentadienyl rings are related by a torsion angle of approximately 55° (Figure 2b), as opposed to the ~180° observed in other divinylferrocene-linked structures.[4] We attribute this difference to the requirements for forming the tetramolybdenum complex in the solid state.

$$[Mo(NAr)(OR_{F6})_2(CHC_5H_4)]_2Fe \xrightarrow[-\ 4\ LiOR_{F6}]{6\ LiPyr} \underset{\mathbf{3}}{[Mo(NAr)(Pyr)_3(CHC_5H_4)]_2FeLi_2} \qquad (2)$$

The ^{1}H NMR spectrum of **3** at room temperature reveals broad resonances associated with the pyrrolide protons. The J_{CH} value for the alkylidene proton is 124 Hz, indicating that in solution the alkylidene is oriented *syn* to the imido ligand, as observed in the solid state. Variable temperature ^{1}H NMR spectroscopic studies ($C_6D_5CD_3$) reveal that only one H_α resonance is observed in the temperature interval between −80 °C and 60 °C. At −80 °C all four methyl imido

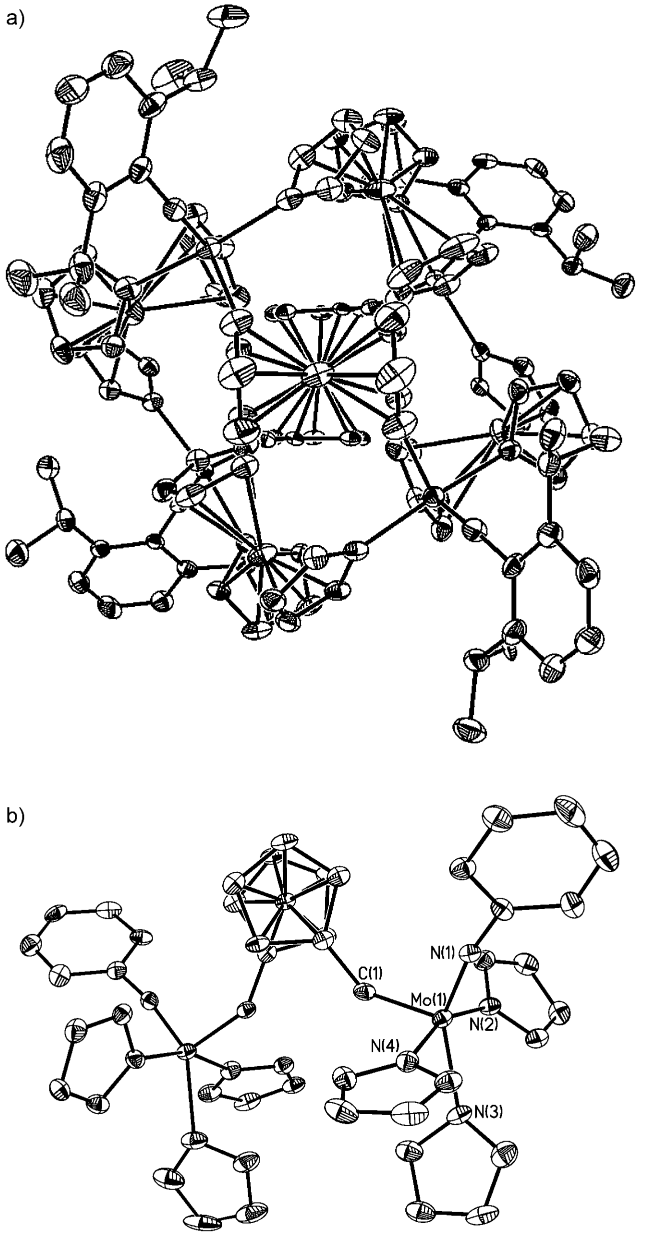


Figure 2. a) Thermal ellipsoid drawing of the full asymmetric unit of **3**. Solvent molecules and hydrogen atoms have been removed for clarity. b) Thermal ellipsoid drawing of one molecule of **3** within the unit cell. Solvent molecules, hydrogen atoms, isopropyl groups, and lithium atoms have also been removed for clarity.

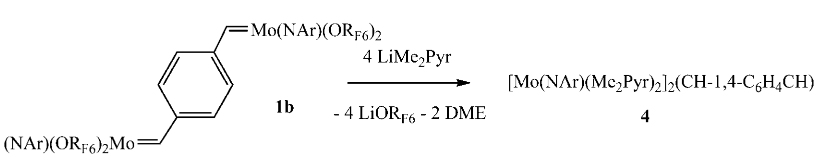
groups (1.46–0.55 ppm) and two methine (3.85 and 2.81 ppm) protons are inequivalent as a consequence of the imido rings being locked on the NMR timescale. Four ferrocene resonances are observed (4.93, 4.58, 4.44 and 3.79 ppm). The pyrrolide resonances (7.69–5.82 ppm) are sharp and resolved at low temperatures. Complex fluxionality leads to broadening of all resonances at room temperature.

Addition of four to six equivalents of lithium pyrrolide to a cooled solution of **1** in dichloromethane led to a product having two major alkylidene resonances (14.10 and 13.72 ppm) and two minor alkylidene resonances (14.49 and 14.17 ppm) in the ^{1}H NMR spectrum, in addition to the resonance for **3** at 14.01 ppm. We postulate that the product with two major alkylidene resonances in ^{1}H NMR spectra (14.10 and 13.72 ppm) contains only one extra equivalent of lithium pyrrolide per dimer, that is to say that one equivalent of lithium pyrrolide is bound to only one molybdenum atom. The major alkylidene resonances are characteristic of *syn* species. The minor alkylidene resonances are most likely *anti* isomers (vide infra). All species in these product mixtures react with 4–10 equivalents of H_2[Biphen] (H_2[Biphen] = 3,3'-di-*tert*-butyl-5,5′,6,6′-tetramethylbiphenyl-2,2′-diol) to yield [Mo(NAr)(Biphen)(CHC_5H_4)]$_2$Fe, as described in the next section.

Reaction of four equivalents of lithium 2,5-dimethylpyrrolide with [Mo(NAr)(OR_{F6})$_2$]$_2$(DME)$_2$(CH-1,4-C_6H_4CH) (**1b**) in cold DME produced [Mo(NAr)(Me_2Pyr)$_2$]$_2$(CH-1,4-C_6H_4CH) (**4**) in good yield [Eq. (3)]. The alkylidene resonance is observed at 13.5 ppm in the ^{1}H NMR spectrum with $J_{CH} = 134$ Hz. Variable temperature ^{1}H NMR spectroscopic studies suggests that the arylimido groups rotate freely and pyrrolide ligands interconvert at 50 °C, while at −30 °C to −70 °C, two diastereomers (*meso* and *rac*) are observed in a ratio of approximately 1:0.6. Satisfactory elemental analyses also could not be obtained for **4**.

Reactivity of Molybdenum Pyrrolide Complexes with Enantiomerically Pure Diols

We were especially interested in the synthesis of compounds of the type [Mo(NAr)(diolate)(CHC_5H_4)]$_2$Fe, which would allow the structure of any polymers prepared with these species to be controlled efficiently through enantiomorphic site control. If the growing polymer chain remains bound to the metal center, a polymer's structure can be controlled even though the diolate is racemic. However, in order to simplify the analysis of reactions between chiral diols and bifunctional pyrrolide catalyst precursors, enantiomerically pure diols were employed. The complexity that arises when using a racemic diol will be illustrated below in one case. Three enantiomerically pure diols were investigated, namely, (*R*)- and (*S*)-H_2[Biphen],[10–12] (*R*)-H_2[Benz$_2$Bitet] ((*R*)-3,3′-dibenzhydryl-5,5′,6,6′,7,7′,8,8′-octahydro-1,1'-binaphthyl-2,2′-diol),[10,13] and (*R*)-H_2[Mes$_2$Bitet] ((*R*)-3,3′-dimesityl-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diol)[10] (Figure 3). These diols were chosen because monofunctional molybdenum-based metathesis catalysts that contain them



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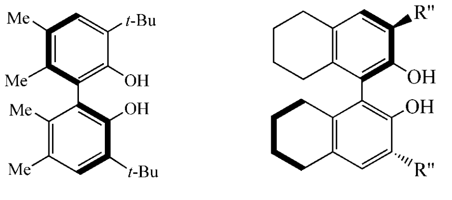


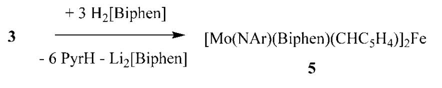
(S)-H_2[Biphen]

(R)-H_2[$Benz_2$Bitet], R'' = $CHPh_2$
(R)-H_2[Mes_2Bitet], R'' = 2,4,6-$Me_3C_6H_2$

Figure 3. Chiral diols selected for evaluation in syntheses of bimetallic catalysts.

have been explored previously.[6] The $[Biphen]^{2-}$ ligand is the most sterically demanding of the three as a consequence of the *tert*-butyl groups in the 3 and 3' positions.

Three equivalents of (*S*)-H_2[Biphen] are required for a clean reaction of it with **3** to form [Mo(NAr)(Biphen)-$(CHC_5H_4)]_2Fe$ (**5**) [Eq. (4)]. The third equivalent of H_2[Biphen] reacts with the two equivalents of lithium pyrrolide in **3** to form Li_2[Biphen] and two equivalents of pyrrole.



$$\mathbf{3}\ \xrightarrow[\text{- 6 PyrH - Li}_2\text{[Biphen]}]{\text{+ 3 H}_2\text{[Biphen]}}\ \underset{\mathbf{5}}{[\text{Mo(NAr)(Biphen)(CHC}_5\text{H}_4)]_2\text{Fe}} \qquad (4)$$

^1H NMR spectroscopy of (*S*,*S*)-**5** reveals four resonances in the alkylidene region at 12.71 ppm (70 %, $J_{CH}=152$ Hz), 12.55 ppm (14 %, $J_{CH}=152$ Hz), 11.31 ppm (14 %, $J_{CH}=125$ Hz) and 11.13 ppm (2 %, $J_{CH}=125$ Hz; Figure 4a). We assign these four alkylidene resonances (respectively) to the *anti/anti* isomer, the *anti* peak of the *anti/syn* isomer, the *syn* peak of the *anti/syn* isomer, and the *syn/syn* isomer on the basis of the J_{CH} values in each case. Four alkylidene carbon resonances are observed in the ^{13}C NMR spectra (at 265.23, 264.87, 260.47, 260.05 ppm), consistent with this proposal. If the synthesis is repeated with (rac)-H_2[Biphen], eight resonances are observed (Figure 4b) as a consequence of the formation of (*S*,*R*)-**5** in addition to (*R*,*R*)-**5** and (*S*,*S*)-**5**; four of these resonances are found at the same chemical shifts observed when (*S*)-H_2[Biphen] is employed. All of these observations are consistent with the proposed bifunctional nature of the compounds being prepared. The added complexity of the spectrum associated with the use of racemic diols demonstrates why it is desirable to use enantiomerically pure diols when evaluating reactions of them with bifunctional precursors.

There are no significant changes in the variable temperature ^1H NMR spectra of (*S*,*S*)-**5** in the range −60 °C to 60 °C, except for the typical locked rotation of the isopropyl resonances on the NMR timescale at low temperatures and rapid rotation of the diisopropylphenyl ring at high temperatures. X-ray quality crystals of (*S*,*S*)-**5** have remained elusive arising from its high solubility in most organic solvents. X-ray quality crystals also could not be obtained from a racemic mixture.

The in situ reaction between two equivalents of H_2[$Benz_2$Bitet] and **3** produced a species whose ^1H NMR spectrum revealed an alkylidene proton at 13.37 ppm (86 %, *syn/syn* isomer) and two minor resonances at 13.90 ppm and 13.29 ppm (7 % each, the *anti* and *syn* resonances of the *anti/syn* isomer, respectively). This product was not isolated.

Compound **3** apparently does not react cleanly with two equivalents of H_2[Mes_2Bitet], and no pure compounds could be isolated. Multiple resonances were observed in the alkylidene region of the ^1H NMR spectra.

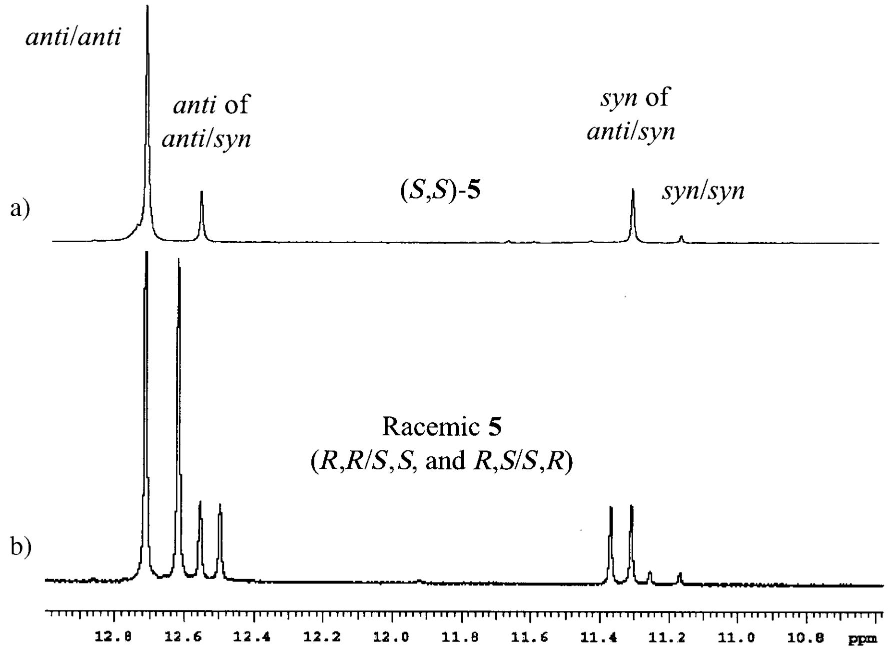


Figure 4. Alkylidene region of ^1H NMR spectra for (a) (*S*,*S*)-5 and (b) *rac*-5.

No reaction between **2** and H_2[Biphen] was observed, while reactions between **2** and H_2[$Benz_2$Bitet] or H_2[Mes_2Bitet] were slow and produced mixtures with multiple alkylidene resonances. Heating reaction mixtures to 50 °C for several hours did not produce any one product at the expense of the others initially present.

Reactions between **4** and the three diols are the best-behaved. Compound **4** reacts cleanly with H_2[$Benz_2$Bitet] and H_2[Mes_2Bitet] to yield isolable complexes [Mo-(NAr)($Benz_2$Bitet)$]_2$(CH-1,4-C_6H_4CH) (**6**) and [Mo-(NAr)(Mes_2Bitet)$]_2$(CH-1,4-C_6H_4CH) (**7**), respectively. Brown **6** can be isolated and recrystallized in moderate yield. The alkylidene proton in the ^1H NMR spectrum is observed at 11.25 ppm and has a J_{CH} value of 125 Hz, consistent with an alkylidene oriented *syn* with respect to the imido group. Compound **7** also can be isolated in moderate yield. Its alkylidene peak is observed in its ^1H NMR spectrum at 11.23 ppm with $J_{CH} = 125$ Hz, which is indicative of a *syn* orientation of the alkylidene with respect to the imido group. Pure **4** does not react readily with H_2[Biphen].

Polymerization of 2,3-Dicarbomethoxynorbornadiene (DCMNBD) and 2,3-Bis(trifluoromethyl)norbornadiene (NBDF6) with In Situ Generated and Isolated Bifunctional Initiators Containing Chiral Diolates

2,3-Dicarbomethoxynorbornadiene (DCMNBD) and 2,3-bis(trifluoromethyl)norbornadiene (NBDF6) were the two monomers chosen for polymerization experiments. They were chosen because polymerizations with monofunctional molybdenum imido alkylidene initiators containing chiral diolates have been explored previously.[14] The *cis*/*trans* ratio as well as the percent tacticity of the polymers can be determined by examining the ^{13}C NMR spectra. Initiators **5**, **6**, and **7** were employed, both as isolated and purified compounds, or as generated in situ.

The synthesis of the polymers prepared with the isolated initiators is straightforward. A solution of either DCMNBD or NBDF6 was added in one portion to a stirred solution of either **5**, **6**, or **7** in toluene. To prepare the corresponding in situ initiators, 3.2 equivalents of H_2[Biphen], H_2[Benz$_2$Bitet], or H_2[Mes$_2$Bitet] were added to a solution of **3**, or 2.2 equivalents of H_2[Benz$_2$Bitet] or H_2[Mes$_2$Bitet] were added to **4**. The solution containing the diol and pyrrolide complex was stirred at room temperature for fifteen minutes, at which time a solution of either DCMNBD or NBDF6 (approximately 100 equivalents) was added. After four hours, the polymerization was quenched with excess benzaldehyde (see Experimental Section for details). Poly(DCMNBD) was precipitated from methanol while poly(NBDF6) was precipitated from pentane.

The *cis*/*trans* ratio and the percent tacticity of the polymers were determined by ^{13}C NMR spectroscopy; the values are given in Table 3. Polymers prepared using initiator **5** show varied *cis*/*trans* ratios, and the observed tacticities are modest. The presence of isomers of **5** (which is a mixture of 70 % *anti/anti*, 28 % *anti/syn*, and 2 % *syn*/*syn*) helps explain the formation of both *cis* and *trans* double bonds in the polymer since the *syn* and *anti* isomers play a major role in determining whether polymers prepared from norbornenes or norbornadienes contain *cis* or *trans* double bonds.[14] It is interesting to note that the poly(NBDF6) prepared with isolated **5**, or **5** that is generated in situ, gave identical results. Poly(DCMNBD) prepared with **5** gave different results depending on whether the initiator is isolated or prepared in situ. In both cases however, the tacticity was relatively low. The lower tacticity of poly(DCMNBD) prepared with initiator **5** is likely to be the reason why these were the only polymers that were soluble in THF, and therefore, the only polymers that could be analyzed by gel permeation chromatography (GPC) in THF. Poly(DCMNBD) prepared with in situ generated and isolated initiator **5** gave M_n values of 1.3×10^4 and 1.8×10^4 (vs polystyrene standards) and PDI values of 1.22 and 1.25, respectively.

Table 3. Data for poly(DCMNBD) and poly(NBDF6) prepared using initiators **5**, **6**, and **7**.

Initiator	Form	Monomer	*Trans/ Cis*	% Tacticity	Yield of isolated product [%]
5	isolated	NBDF6	84:16	79	>95
5	in situ	NBDF6	83:17	79	>95
5	isolated	DCMNBD	42:58	45	90
5	in situ	DCMNBD	29:71	65	75
6	isolated	NBDF6	0:100	>95	>95
6	in situ	NBDF6	0:100	>95	>95
6	isolated	DCMNBD	0:100	>95	>95
6	in situ	DCMNBD	0:100	>95	>95
7	isolated	NBDF6	16:84	74	84
7	in situ	NBDF6	16:84	74	>95
7	isolated	DCMNBD	14:86	82	>95
7	in situ	DCMNBD	0:100	>95	>95

The polymers prepared using initiator **6**, either isolated or prepared in situ, gave identical results for both poly(DCBNBD) and poly(NBDF6). The polymers contain 100 % *cis* double bonds and are greater than 95 % tactic. The same result was observed when the catalyst employed was prepared from monomeric Mo(NAr)(Pyr)$_2$(CHCMe$_2$Ph) and H_2[Benz$_2$Bitet], confirming that the bifunctional nature of initiator **6** was irrelevant.

Poly(NBDF6) samples prepared with isolated or in situ generated **7** contained approximately 85 % *cis* double bonds, and are ~75 % tactic. Different results were observed in the preparation of poly(DCMNBD) depending on the method of catalyst preparation. The isolated initiator produced samples of poly(DCMNBD) with *trans/cis* ratios similar to those observed for poly(NBDF6), while in situ generated **7** gave all *cis*, highly tactic poly(DCMNBD). All *cis*, highly tactic poly(DCMNBD) was formed when the initiator was prepared in situ from monomeric Mo(NAr)(Pyr)$_2$(CHCMe$_2$Ph) and H_2[Mes$_2$Bitet].

Conclusions

A series of pyrrolide bifunctional molybdenum complexes linked by alkylidenes derived from divinylferrocene or divinylbenzene were prepared. The reactivities of the bifunctional complexes, [Mo(NAr)(X)$_2$]$_2$(linker) (where X = pyrrolide or 2,5-dimethylpyrrolide, linker = divinylbenzene or divinylferrocene) with various diols were explored and three new bifunctional initiators (**5**, **6**, and **7**) were isolated. Compounds **5**, **6**, and **7** were employed as initiators for polymerization of DCMNBD and NBDF6 to give polymers whose percent tacticity and *cis*/*trans* ratios usually were similar to those found for polymers prepared with monomeric initiators.

We have demonstrated that initiators can be prepared in situ and used for ROMP polymerization of DCMNBD and NBDF6. However, the synthesis of bifunctional initiators through addition of a chiral diol to a pyrrolide precursor should not be viewed as a general one. It is important to first screen reactions between the diol and the pyrrolide precursor in order to determine whether the reaction is facile, complete, and well-behaved. Initiators that form completely and cleanly can be used for the synthesis of polymers employing initiators that are prepared in situ.

Experimental Section

General

All manipulations were performed in oven-dried (200 °C) glassware under an atmosphere of nitrogen in a Vacuum Atmospheres glovebox or using standard Schlenk techniques. HPLC-grade solvents were purified by passage through an alumina column and stored over 4 Å Linde-type molecular sieves prior to use. Deuterated solvents were degassed and distilled from CaH_2 or sodium benzophenone ketyl. Commercial reagents were used without further purification unless stated otherwise. $[Mo(NAr)(OR_{F6})_2(CHC_5H_4)]_2Fe$,[4] $[Mo(NAr)(OR_{F6})_2]_2(DME)(CH\text{-}1,4\text{-}C_6H_4CH)$,[4] $Mo(NAr)(Pyr)_2(CHCMe_2Ph)$,[7] (*R*)-$H_2$[Biphen] and (*S*)-$H_2$[Biphen],[12] (*R*)-$H_2$[Benz$_2$Bitet],[10] (*R*)-$H_2$[Mes$_2$Bitet],[10] NBDF6,[15] and DCMNBD[16] were prepared according to literature procedures.

NMR spectra were recorded on a Varian INOVA 500 spectrometer. ^{1}H NMR chemical shifts are given in ppm versus residual protons in the deuterated solvents as follows: $\delta = 7.27$ ppm ($CDCl_3$), $\delta = 7.16$ ppm (C_6D_6), $\delta = 2.09$ ppm ($C_6D_5CD_3$), $\delta = 2.05$ (($(CD_3)_2CO$). GPC analyses (solvent = tetrahydrofuran, 1 mL min^{-1}) were carried out using a Waters GPC system equipped with 1 Styragel HT3 column (500–30000 MW range), 1 Styragel HT4 column (5000–600000 MW range), 1 Styragel HT5 column (50000–4×10^6 MW range), a refractive index detector, and a UV detector (254 nm) was used for molecular weight measurement relative to polystyrene standards.

Synthesis

2: $[Mo(NAr)(Me_2Pyr)_2(CHC_5H_4)]_2Fe$: Solid $Li(NC_4H_2Me_2)$ (0.14 g, 1.4 mmol) was added to a −30 °C solution of $[Mo(NAr)(OR_{F6})_2(CHC_5H_4)]_2Fe$ (0.50 g, 0.34 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for two hours and then placed in a −35 °C freezer for twelve hours. The precipitate of $LiOR_{F6}$ was removed by filtration. The volatile components of the red filtrate were removed in vacuo. The resulting solid was redissolved in ether (5 mL), and the solution was placed in a −35 °C freezer. The burgundy crystals that formed were isolated by filtration and dried in vacuo; yield 0.25 g (65 %): ^{1}H NMR (C_6D_6): $\delta = 13.1$ (s, 1 H, MoC*H*R, $J_{CH} = 136$ Hz), 7.00 (m, 3 H, Ar-C*H*), 5.98 (br s, 2 H, $NC_4H_2(CH_3)_2$), 4.17 (br s, 2 H, FeC_4H_5), 3.84 (br s, 2 H, FeC_4H_5), 3.39 (sept, 2 H, $CH(CH_3)_2$), 2.08 (br s, 12 H, $NC_4H_2(CH_3)_2$), 1.04 ppm (br s, 6 H, $CH(CH_3)_2$); Arising from the poor solubility of this compound ^{13}C NMR data could not be readily collected. No resonances for $LiOR_{F6}$ were found in ^{19}F NMR spectra. Apparent decomposition of **2** over a period of days prevented satisfactory elemental analyses.

3: $[Mo(NAr)(Pyr)_3(CHC_5H_4)]_2FeLi_2$: Solid $Li(NC_4H_4)$ (0.51 g, 6.9 mmol) was added to a −30 °C solution of $[Mo(NAr)(OR_{F6})_2(CHC_5H_4)]_2Fe$ (1.7 g, 1.2 mmol) in CH_2Cl_2 (10 mL). The solution was stirred at room temperature for two hours during which time a bright red precipitate formed. The precipitate was isolated by filtration and dried in vacuo; yield 1.3 g (97 %): ^{1}H NMR (C_6D_6): $\delta = 14.01$ (s, 1 H, MoC*H*R, $J_{CH} = 124$ Hz), 7.49 (m, 1 H, py-C*H*), 7.31 (m, 2 H, py-C*H*), 7.12 (m, 3 H, Ar-C*H*), 6.76 (br s, 1 H, py-C*H*), 6.37 (br s, 2 H, py-C*H*), 6.03 (br s, 4 H, py-C*H*), 5.92 (br s, 2 H, py-C*H*), 4.82 (br s, 2 H, FeC_4H_5), 4.52 (br s, 1 H, FeC_4H_5), 3.94 (br s, 1 H, FeC_4H_5), 3.48 (sept, 2 H, $CH(CH_3)_2$), 1.91 (br s, 6 H, $CH(CH_3)_2$), 0.79 ppm (br s, 6 H, $CH(CH_3)_2$); ^{13}C NMR ($C_6D_5CD_3$): $\delta = 283.07$, 151.73, 126.89, 109.11, 108.81, 106.45, 94.45, 73.63, 71.78, 70.27, 30.72, 28.42, 23.19, 22.31 ppm. No resonances for $LiOR_{F6}$ were found in ^{19}F NMR spectra. Apparent decomposition of **3** over a period of days prevented satisfactory elemental analyses.

4: $[Mo(NAr)(Me_2Pyr)_2]_2(CH\text{-}1,4\text{-}C_6H_4CH)$: Solid $Li(NC_4H_2Me_2)$ (0.16 g, 1.6 mmol) was added to a −30 °C solution of $[Mo(NAr)(OR_{F6})_2]_2(DME)(CH\text{-}1,4\text{-}C_6H_4CH)$ (0.59 g, 0.39 mmol) in DME (10 mL). The solution was stirred at room temperature for one hour and the volatile components were removed in vacuo. The solid was triturated with diethyl ether multiple times until a bright orange powder was obtained. The powder was isolated by filtration and dried in vacuo; yield 0.40 g (88 %): ^{1}H NMR (C_6D_6): $\delta = 13.51$ (s, 1 H, MoC*H*R, $J_{CH} = 134$ Hz), 7.12 (m, 3 H, Ar-C*H*), 7.00 (m, 2 H, Ar-C*H*), 5.96 (br s, 4 H, $NC_4H_2(CH_3)_2$), 3.44 (sept, 2 H, $CH(CH_3)_2$), 2.11 (br s, 12 H, $NC_4H_2(CH_3)_2$), 0.96 ppm (br s, 6 H, $CH(CH_3)_2$); ^{13}C NMR ($C_6D_5CD_3$): $\delta = 291.99$, 157.72, 148.03, 123.99, 106.99, 28.23, 24.06, 21.75, 18.53 ppm. No resonances for $LiOR_{F6}$ were found in ^{19}F NMR spectra. Apparent decomposition of **4** over a period of days prevented satisfactory elemental analyses.

5: $[Mo(NAr)(Biphen)(CHC_5H_4)]_2Fe$: 2.9 equivalents of (*R*)- or (*S*)-H_2[Biphen] (441 mg, 1.25 mmol) were added to a stirred solution of **3** (500 mg, 0.43 mmol) in toluene (5 mL). The solution was stirred at room temperature for three hours and the volatile components were removed in vacuo. The remaining solid was dissolved in pentane and passed through a glass filter tip pipette to remove the byproduct in the reaction (LiPyr). The volatile components were again removed in vacuo, the solid redissolved in pentane (2 mL), and the solution was placed in a −35 °C freezer overnight. A burgundy solid formed which was isolated by filtration and dried in vacuo; yield 400 mg (65 %): ^{1}H NMR (C_6D_6): $\delta = 12.71$ (s, MoC*H*R, 70 %, *anti/anti* isomer, $J_{CH} = 152$ Hz), 12.55 (s, MoC*H*R, *anti* peak of *anti/syn* isomer, 14 %, $J_{CH} = 152$ Hz), 11.31 (s, MoC*H*R, 14 %, *syn* peak of *anti/syn* isomer, $J_{CH} = 125$ Hz) and 11.13 ppm (s, MoC*H*R, 2 %, *syn/syn* isomer, $J_{CH} = 125$ Hz). The following resonances are reported for the major isomer only: $\delta = 7.32$, 7.29, 7.16, 7.09 (m, 5 H, Ar-C*H*), 4.60 (s, 1 H, FeC_4H_5), 4.56 (s, 1 H, FeC_4H_5), 3.95 (s, 1 H, FeC_4H_5), 3.87 (s, 1 H, FeC_4H_5), 3.82 (sept, 2 H, $CH(CH_3)_2$), 2.26 (s, 3 H, Me-Biphen), 2.20 (s, 3 H, Me-Biphen), 1.87 (s, 3 H, Me-Biphen), 1.77 (s, 3 H, Me-Biphen), 1.63 (s, 9 H, *t*Bu-Biphen), 1.52 (s, 9 H, *t*Bu-Biphen), 1.36 (d, 6 H, $CH(CH_3)_2$), 1.29 ppm (d, 6 H, $CH(CH_3)_2$); ^{13}C NMR ($C_6D_5CD_3$): $\delta = 265.23$ (*anti/anti* isomer), 264.87 (*anti* peak of *anti/syn* isomer), 260.47 (*syn* peak of *anti/syn* isomer), 260.05 ppm (*syn/syn* isomer); The following resonances are reported for the major isomer (*anti/anti*) only: $\delta = 155.66$, 152.27, 148.17, 147.36, 144.88, 142.04, 140.98, 136.65, 135.27, 132.18, 131.54, 131.14, 131.07, 130.97, 129.27, 128.89, 127.33, 123.23, 89.52, 73.26, 72.87, 69.71, 69.14, 35.86, 35.70, 30.17, 29.92, 24.82, 23.58, 20.84, 20.78, 16.89, 16.84 ppm; elemental analysis: calcd (%) for $C_{82}H_{104}Mo_2N_2O_4Fe$: C 68.90; H 7.33, N 1.96. Found: C 69.08; H 7.30; N 1.88.

6: $[Mo(NAr)(Benz_2Bitet)]_2(CH\text{-}1,4\text{-}C_6H_4CH)$: H_2[Benz$_2$Bitet] (86 mg, 0.14 mmol) was added to a stirred solution of **4** (70 mg, 0.069 mmol) in toluene (3 mL). The reaction was stirred at room temperature for three hours, at which time the volatile components were removed in vacuo. The resulting dark orange solid was washed with pentane to remove residual H_2[Benz$_2$Bitet]. The solid was dissolved in ether (2 mL). A powder formed by slowly diffusing pentane into the solution. The powder was isolated by filtration and dried in vacuo; yield 50 mg (39 %): ^{1}H NMR (C_6D_6): $\delta = 11.24$ (s, 1 H, MoC*H*R, $J_{CH} = 125$ Hz), 7.55 (d, 2 H, Ar-C*H*), 7.43 (d, 2 H, Ar-C*H*), 7.27 (t, 2 H, Ar-C*H*), 7.22–6.79 (m, 5 H, Ar-C*H*), 6.49 (s, 1 H, Ar-C*H*), 5.89 (s, 1 H, Ar-C*H*), 3.98 (sept, 2 H, $CH(CH_3)_2$), 2.55–2.11 (br m, 8 H, CH_2-Bitet), 1.50–1.02 (br m, 8 H, CH_2-Bitet), 1.24 (d, 6 H, $CH(CH_3)_2$), 0.92 ppm (d, 6 H, $CH(CH_3)_2$); ^{13}C NMR ($C_6D_5CD_3$): $\delta = 258.38$, 154.79, 151.20, 149.08, 145.82, 145.77, 143.95, 143.85, 138.21, 137.55, 136.89, 136.10, 135.72, 135.17, 134.20, 133.77, 133.51, 130.76, 130.34, 130.27, 130.22, 130.16, 129.86, 129.66, 129.32, 129.14, 129.06, 128.91, 128.80, 127.70, 127.04, 126.74, 126.63, 126.55, 126.04, 126.83, 52.22, 50.06, 30.42, 30.27, 29.89, 28.82, 28.45, 24.05, 23.96, 23.63, 23.40, 23.30, 22.94, 21.77 ppm.

7: $[Mo(NAr)(Mes_2Bitet)]_2(CH\text{-}1,4\text{-}C_6H_4CH)$: H_2[Mes$_2$Bitet] (104 mg, 0.20 mmol) was added to a stirred solution of **4** (100 mg, 0.010 mmol) in toluene (3 mL). The reaction was stirred at room temperature for three hours, at which time the volatile components were removed in vacuo. The resulting dark orange solid was washed with pentane to remove residual H_2[Mes_2Bitet] and then dried in vacuo; yield 100 mg (60%): ^{1}H NMR (C_6D_6): $\delta = 11.23$ (s, 1H, MoC*H*R, $J_{CH} = 125$ Hz), 7.20 (s, 1H, Ar-C*H*), 6.97 (s, 1H, Ar-C*H*), 6.92 (s, 1H, Ar-C*H*), 6.88 (m, 3H, Ar-C*H*), 6.64 (s, 1H, Ar-C*H*), 6.08 (s, 2H, Ar-C*H*), 3.23 (br s, 2H, C*H*(CH_3)$_2$), 2.8–2.4 (br m, 8H, C*H*$_2$-Bitet), 2.57, 2.50, 2.42, 2.26, 2.03, 1.83 (all s, each 3H, C*H*$_3$Mes), 1.7–1.4 (br m, 8H, C*H*$_2$-Bitet), 0.80 ppm (br s, 12H, CH-(C*H*$_3$)$_2$); ^{13}C NMR ($C_6D_5CD_3$): $\delta = 260.50$, 154.77, 153.18, 151.90, 145.20, 138.17, 137.76, 137.71, 137.35, 136.79, 136.56, 136.17, 136.08, 136.01, 135.85, 135.83, 135.14, 134.18, 133.8, 132.4, 132.4, 132.42, 129.73, 129.67, 129.56, 128.87, 128.73, 128.63, 128.37, 128.31, 126.81, 126.03, 123.42, 30.51, 30.24, 29.43, 28.84, 24.15, 24.09, 23.99, 23.89, 23.79, 23.56, 23.11, 21.75, 21.67, 21.59, 21.54, 21.41, 21.25 ppm; elemental analysis: calcd (%) for $C_{108}H_{120}Mo_2N_2O_4$: C 76.21; H 7.11; N 1.65. Found: C 75.88; H 6.98; N 1.61.

Observation of reaction between 3 and H_2[$Benz_2$Bitet]. H_2[$Benz_2$Bitet] (2.1 equiv, 113 mg, 0.18 mmol) in toluene (1 mL) was added to a stirred solution of **3** (100 mg, 0.86 mmol) in toluene (3 mL). The solution was stirred at room temperature for three hours, at which time the volatile components were removed in vacuo. The solid was dissolved in toluene. The resulting solution was diluted with pentane and placed in a −35 °C freezer. The brown solid that formed was isolated by filtration and dried in vacuo: ^{1}H NMR (C_6D_6) (reported for the alkylidene region only) $\delta =$ 13.9 (7%), 13.37 (86%), 13.3 ppm (7%).

Example of Polymerization of DCMNBD with Isolated Initiator. DCMNBD (58 mg, 100 equiv, 0.28 mmol) in 2 mL of toluene was added to a stirred solution of **4** (5.2 mg, 0.0028 mmol) in 4 mL toluene. The mixture was stirred for four hours at which time two drops (~20 mg) of benzaldehyde were added. The solution was stirred for an additional hour, at which time the polymer was precipitated from methanol. The precipitate was collected and dried in vacuo before analysis by ^{1}H and ^{13}C NMR; yield 55 mg (98%).

Example of Polymerization of DCMNBD with Initiator Prepared In Situ. H_2[$Benz_2$Bitet] (12.4 mg, 2.2 equiv, 0.021 mmol) in 1 mL of toluene was added to a stirred solution of **4** (10 mg, 0.0098 mmol) in 4 mL of toluene. The solution was stirred at room temperature for fifteen minutes. At that time, a solution of DCMNBD (223 mg, 110 equiv, 0.107 mmol) in 2 mL of toluene was added all at once. The mixture was stirred for four hours at which time two drops (~20 mg) of benzaldehyde were added. The solution was stirred for an additional hour, at which time the polymer was precipitated from pentane. The precipitate was collected and dried in vacuo before analysis by ^{1}H and ^{13}C NMR; yield 218 mg (98%).

Polymerization of NBDF6. The procedure for polymerization of NBDF6 is analogous to those given for polymerization of DCMNBD except the polymers were precipitated from pentane instead of methanol.

X-ray Crystallography

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 K_α radiation ($\lambda = 0.71073$ Å), performing ϕ-and ω-scans. The structures were solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[17] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms (except hydrogen atoms on the carbon atoms that bind directly to molybdenum, which have been taken from the difference Fourier synthesis and refined semi-freely with the help of distance restraints) 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 1.

Compound **2** crystallizes in the monoclinic space group $P2_1/n$ with half a molecule of **2** and half a molecule of diethyl ether in the asymmetric unit. The rest of the main molecule as well as an alternative site for the thus disordered solvent (both sites are mutually exclusive and statistically each is occupied in 50% of all unit cells) are generated by the crystallographic inversion center.

Compound **3** crystallizes in the triclinic space group $P\bar{1}$, with one complete dimer-of-dimers in the asymmetric unit. The structure contains one disordered imido ligand. The pyrrole rings of N(7) and N(107) probably are also disordered (elongated thermal ellipsoids), however it was not possible to resolve this disorder. The same is true for the ferrocene subunit around Fe(2), which seems to be disordered slightly along the Cp-Cp axis.

Both structures contain solvent molecules. One half molecule of diethyl ether is located near the crystallographic inversion center in the asymmetric unit of the structure of **2** and the asymmetric unit of the structure of **3** contains 9.5 benzene molecules, at least four of which are disordered. The second half of the half molecule of benzene is generated by the crystallographic inversion center; this molecule is actually well-behaved. All disorders that could be resolved were refined with the help of similarity restraints on 1–2 and 1–3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. The ratios between the two components of each disorder were refined freely, while constraining the sum of occupancies to unity.

CCDC -691322 and -691323 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif

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