J. Am. Chem. Soc. 1991, 113, 6899-6907

Living Ring-Opening Metathesis Polymerization of 2,3-Difunctionalized 7-Oxanorbornenes and 7-Oxanorbornadienes by $Mo(CHCMe_2R)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(O\text{-}t\text{-}Bu)_2$ and $Mo(CHCMe_2R)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OCMe_2CF_3)_2$

Guillermo C. Bazan, John H. Oskam, Hyun-Nam Cho, Lee Y. Park, and Richard R. Schrock*

Contribution from the Department of Chemistry, 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received February 12, 1991*

Abstract: 7-Oxabenzonorbornadiene (**9**), 2,3-*endo-cis*-diacetoxy-7-oxanorbornene, and 2,3-*endo-cis*-(isopropylidenedioxy)-7-oxanorbornene can be polymerized by $Mo(CHCMe_2R)(NAr)(O\text{-}t\text{-}Bu)_2$ (Ar = 2,6-C_6H_3-*i*-Pr_2; R = CH_3, C_6H_5) ([Mo]($CHCMe_2R$)) to give polymers with narrow molecular weight distributions (PDI < 1.17). However, 2,3-bis(trifluoromethyl)-7-oxanorbornadiene (**1**), 2,3-dicarbomethoxy-7-oxanorbornadiene (**4**), and 2,3-*trans*-dicyano-7-oxanorborn-5-ene (**12**) form stable metallacycles upon addition to [Mo]($CHCMe_2R$). The rate of reaction of **1** with [Mo]($CHCMe_2R$) has been determined qualitatively to be comparable to that of norbornene in competition experiments, a result that implies that the lone pair on the oxygen in the 7-position is accelerating metallacycle formation. The metallacycle that results from addition of **1** to [Mo]($CHCMe_2Ph$) is square pyramidal with the imido ligand in the apical position. (Crystal data for **2b**: $a = 12.420$ (3) Å, $b = 15.466$ (4) Å, $c = 20.856$ (6) Å, $V = 3852$ (2) Å^3, $\beta = 105.97$ (2)°, space group = $P2_1/n$, $Z = 4$, $M_r = 779.76$, $\rho = 1.345$ g/cm^3, $\mu = 3.9$ cm^{-1}, $R_1 = 0.049$, $R_2 = 0.068$.) The MoC_3 ring is planar with the CMe_2Ph group pointed toward the imido ligand and the C_7 frame of the monomer pointed away from it (a trans metallacyclic ring). The oxygen in the 7-position of the norbornene moiety is located 3.332 (4) Å from the metal. Electronic and steric factors that influence first-order breakup of the metallacycle have been studied for monomers **1** and **4**. The more reactive catalyst, $Mo(CHCMe_2Ph)(NAr)(OCMe_2CF_3)_2$, can polymerize **1**, **4**, and **12** to give polymers with narrow molecular weight distributions (PDI < 1.15).

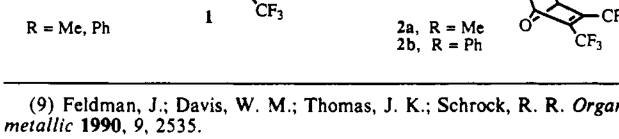
Introduction

Complexes of the type $Mo(CHR)(NAr)(O\text{-}t\text{-}Bu)_2$[1] (Ar = 2,6-$C_6H_3$-*i*-$Pr_2$; R = *t*-Bu, CMe_2Ph) can be used to initiate the living ring-opening metathesis polymerization (ROMP) of functionalized norbornenes,[2] norbornadienes,[3] and 7,8-bis(trifluoromethyl)tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene,[4] to give polymers with narrow molecular weight distributions (polydispersities of 1.05–1.10). In some cases (2,3-bis(trifluoromethyl)norbornadiene and 2,3-bis(carbomethoxy)norbornadiene), the resulting polymer is virtually all-trans and possibly also tactic.[3] $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ also has been used to synthesize Pb-containing block copolymers from which PbS clusters were generated by addition of hydrogen sulfide.[5]

An important class of readily prepared norbornenes and norbornadienes are those that contain oxygen in the 7-position. 7-Oxanorbornenes and 7-oxanorbornadienes have been polymerized by Ru- and Os-based classical catalysts in ethanol[6] and in water,[7] and the resulting polymers have been shown to act as acyclic ionophores.[7] Poly(2,3-dicarbomethoxy-7-oxanorbornadiene) also has been reported to be converted into a polyene upon dehydrogenation with DDQ.[8] An interesting finding is that 7-oxanorbornene and 7-oxanorbornadiene derivatives are necessary to generate especially active and long-lived Ru catalysts in water.[7] If we assume that ruthenium alkylidene complexes are involved in ring opening of norbornenes and norbornadienes in water, it is important to determine how 7-oxa derivatives behave in a relatively well-understood and well-behaved ring-opening catalyst system. The mechanistic understanding gained thereby we hope to be of use in understanding less well-defined catalyst systems. Fortunately, 7-oxa monomers are readily available in wide variety, so that mechanistic details can be explored through systematic variations of the monomer. Initial findings concerning reactions of 7-oxa derivatives with well-characterized $Mo(CHR)(NAr)(OR')_2$ complexes are reported here.

Results

Reactions Involving 7-Oxanorbornadienes. Addition of up to 100 equiv of 2,3-bis(trifluoromethyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene (**1**) to $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ ([Mo](CH-*t*-Bu)) or $Mo(CHCMe_2Ph)(NAr)(O\text{-}t\text{-}Bu)_2$ ([Mo]($CHCMe_2Ph$)) in a variety of solvents under a variety of conditions yields a red solution but no polymer. NMR studies reveal that only 1 equiv of **1** reacts with [Mo](CH-*t*-Bu). The resulting species can be isolated and have proton and carbon NMR spectra (Figure 1) that are similar to those of previously characterized square-pyramidal tungstacyclobutane complexes[9] and, in particular, that which is formed by adding 2,3-bis(trifluoromethyl)norbornadiene to $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ ([W](CH-*t*-Bu)).[3] Therefore the products are proposed to be the square-pyramidal metallacycles shown in eq 1.



(1)

---

[1] Schrock, R. R.; Murdzek, J. S.; Bazan, G. S.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

[2] Bazan, G. C.; Schrock, R. R.; Cho, H.-N.; Gibson, V. C. *Macromolecules*, in press.

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

[4] (a) Krouse, S. A.; Schrock, R. R. *Macromolecules* **1988**, *21*, 1885. (b) Park, L. Y.; Stieglitz, S. G.; Crowe, W. M.; Schrock, R. R. *Macromolecules*, in press. (c) For the synthesis of polyenes employing the analogous tungsten catalyst, see: Knoll, K.; Schrock, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 7989.

[5] Sankaran, V.; Cummins, C. C.; Schrock, R. R.; Cohen, R. E.; Silbey, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 6858.

[6] Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983.

[7] (a) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 960. (b) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542.

[8] Hamilton, G. H.; Marquess, D. G.; O'Neill, T. J.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* **1990**, 119.

[9] Feldman, J.; Davis, W. M.; Thomas, J. K.; Schrock, R. R. *Organometallic* **1990**, *9*, 2535.

0002-7863/91/1513-6899$02.50/0

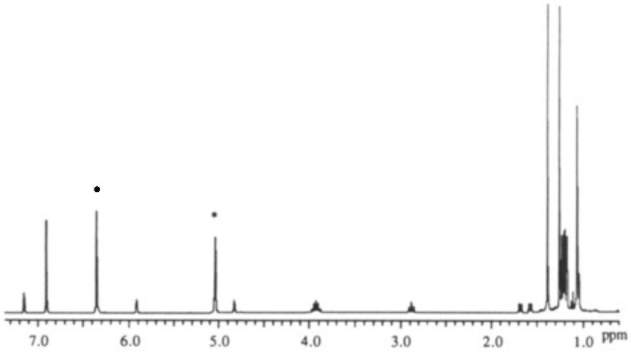


Figure 1. ^{1}H NMR spectrum of a sample of 5 equiv of **1** added to [Mo](CH-*t*-Bu). ⁕ = unreacted **1**.

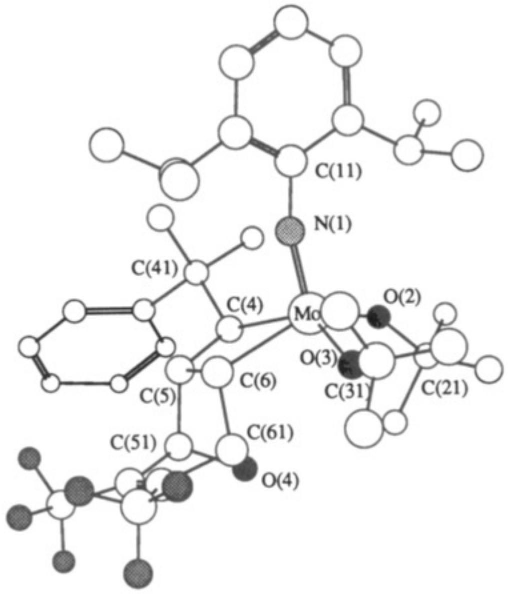


Figure 2. View of the molybdacycle **2b** formed by adding **1** to [Mo](CHCMe$_2$Ph).

An X-ray study of **2b** (Figure 2, Table I) confirmed the proposal. The metallacycle is identical in all important respects to the tungstacycle formed by adding 2,3-bis(trifluoromethyl)norbornadiene to [W](CH-*t*-Bu).[3] Note that the MC$_3$ ring in both complexes is flat, unlike the case of other characterized tungstacyclobutanes such as W[CH$_2$CH(*t*-Bu)CH$_2$](NAr)[OCMe$_2$(CF$_3$)]$_2$, where the metallacycle is puckered significantly toward the imido ligand (dihedral angle = 33° between the C$_\alpha$–W–C$_\alpha$ and C$_\alpha$–C$_\beta$–C$_\alpha$ planes).[9] Note that C(41) is pushed significantly away from the imido ligand, which explains the equivalent coupling constants between H$_\beta$ and the two H$_\alpha$ protons ($J_{H_\alpha H_\beta}$ = 8 Hz). Note also that the phenyl group of the dimethylphenylmethyl substituent is positioned near the norbornene ring. Therefore the norbornene protons on that side of the C$_7$ cage, particularly those on C(51) and C(5), are shielded to a significant degree versus those on the opposite side of the ring, thus aiding assignment. (See supplementary material.) Perhaps the most important feature of the structure is that the oxygen atom in the 7-position of the norbornadiene system is 3.332 Å from the metal center, too great a distance for a bond to the metal to be considered.

Table I. Important Bond Distances (Å) and Angles (deg) in **2b** (Column 2) Compared with Those in the Trans Metallacycle Prepared by Adding 2,3-Bis(trifluoromethyl)norbornadiene to W(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$ (Column 3)[3]

	Mo	W
M–N(1)	1.722 (4)	1.72 (1)
M–O(2)	1.856 (4)	1.862 (9)
M–O(3)	1.896 (4)	1.91 (1)
M–C(4)	2.227 (5)	2.25 (1)
M–C(6)	2.211 (6)	2.19 (1)
C(4)–C(5)	1.506 (7)	1.52 (2)
C(5)–C(6)	1.516 (7)	1.50 (2)
O(2)–M–O(3)	99.9 (2)	98.4 (5)
C(4)–M–C(6)	63.8 (2)	64.6 (5)
M–C(4)–C(5)	97.0 (3)	94.1 (8)
M–C(6)–C(5)	97.4 (3)	97.5 (9)
C(4)–C(5)–C(6)	101.8 (4)	104 (1)
M–O(2)–C(21)	149.8 (4)	157 (1)
M–O(3)–C(31)	143.2 (3)	141 (1)
M–N(1)–C(11)	165.3 (4)	168.5 (9)
N(1)–M–O(2)	113.4 (2)	111.5 (4)
N(1)–M–O(3)	111.7 (2)	115.5 (5)
N(1)–M–C(4)	100.7 (2)	100.3 (5)
N(1)–M–C(6)	103.0 (2)	98.6 (5)
C(6)–M–O(3)	82.8 (2)	84.7 (5)
C(4)–M–O(2)	90.7 (2)	90.9 (4)
M–C(4)–C(41)	126.5 (3)	126 (1)
M–C(6)–C(61)	112.9 (4)	118 (1)
C(6)–M–O(2)	139.0 (2)	144.4 (5)
C(4)–M–O(3)	137.9 (2)	136.1 (4)

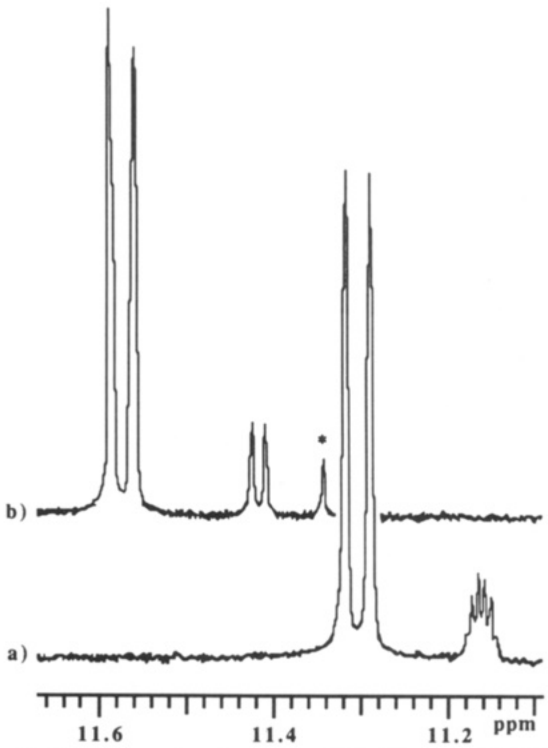
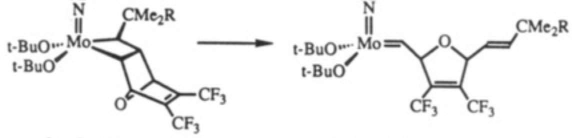


Figure 3. ^{1}H NMR spectra of syn and anti alkylidenes of (a) **3b** formed upon breakup of metallacycle **2b** and (b) **6b** formed upon breakup of metallacycle **5b**. ⁕ = unreacted [Mo](CHCMe$_2$Ph).

Both **2a** and **2b** are remarkably stable. After 24 h in C$_6$D$_6$ at room temperature, ~75% of **2a** is still present. As the metallacycle opens (eq 2), *two* new alkylidene resonances appear at 11.233 ppm (major) and 11.072 ppm (minor) in a 9:1 constant ratio (Table IV). These two resonances are assigned to the two rotameric forms (syn and anti) of the alkylidene ligand, as has been observed in other circumstances,[1,10,11] syn referring to the rotamer in which the alkylidene substituent points toward the imido ni-



(2)

2a, R = Me
2b, R = Ph

3a, R = Me
3b, R = Ph

---

(10) (a) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L. Y.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Krüger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262. (b) Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423.

(11) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158.

Table II. Arrhenius Activation Parameters and Selected Rate Constants for Metallacycle Breakup

metallacycle	k, s^{-1} (T, °C)	ΔS^*, eu	ΔH^*, kcal/mol	ΔG^*, kcal/mol	ρ
2a	4.2×10^{-5} (35)^a	−17 (4)	19 (1)	23.9	0.998
	7.3×10^{-7} (0)^a				
2b	8.6×10^{-6} (35)^a	−6.3 (5)	23.1 (2)	25.0	0.99997
5a	4.5 (1) $\times 10^{-4}$ (35)				
5b	2.67 (1) $\times 10^{-4}$ (35)	−13 (1)	19.0 (3)	22.9	0.9995
7	4.30 (7) $\times 10^{-5}$ (35)	−9 (2)	21.3 (2)	24.1	0.99993
10	(1−3) $\times 10^{-4}$ (0)				

^{a}Calculated from Arrhenius parameters.

trogen atom. Chemical shift alone is not a reliable indicator of whether the alkylidene ligand is syn or anti, but in several X-ray studies the syn rotamer is the one observed.[1,3,10] The resonance for the major (syn) rotamer is a discrete doublet with $J_{H_\alpha H_\beta}$ = 8 Hz, analogous to what has been observed in other circumstances,[11] but the resonance for the minor rotamer is significantly more complex, approximately a 1:3:4:4:3:1 sextet (Figure 3a). Since the analogous dicarbomethoxy derivative (Figure 3b; see later) shows two resonances that are doublets, with $J_{H_\alpha H_\beta}$ = 4.5 Hz for the minor isomer, H_α in the minor rotamer must be coupled to a CF_3 group by about half the magnitude of $J_{H_\alpha H_\beta}$. We believe the coupling between H_α and CF_3 to be through bonds (five) in a configuration that results from restricted rotation about the C_α–C_β bond. Note that the magnitude of $J_{H_\alpha H_\beta}$, which also is a function of any restricted rotation about the C_α–C_β bond, is small, while $J_{H_\alpha H_\beta}$ is more than twice as large in the major isomer and $^5J_{H_\alpha F}$ is too small to observe. However, it is still possible that a CF_3 group in the minor rotamer is interacting with the metal and that H_α is coupled to CF_3 through the metal. An analogous coupling is being studied in a related system in which the concentration of that isomer is high initially and will be reported elsewhere. In both rotamers, the resulting C=C bond is entirely trans. Therefore the two rotamers arise from the same trans metallacycle. We presume at this stage that a single rotamer is formed from the metallacycle whose structure has been determined, and then the equilibrium syn/anti mixture is established relatively rapidly.

Decomposition of **2** to **3** is quantitative by proton NMR spectroscopy and cleanly first order, as determined by following the decrease in intensity of the resonance H_β in the MoC_3 ring of **2** relative to an internal standard. By comparing activation parameters for ring-opening of **2a** to **3a** (Table II), we can conclude that replacing a methyl group with a phenyl group in the alkylidene substituent decreases the rate of rearrangement of the MoC_3 ring to an alkylidene complex by a factor of ~5 at 35 °C.

Competition experiments were employed in order to determine approximately how fast **1** reacts with the initiator. When a mixture of 3 equiv of **1** and 3 equiv of 2,3-bis(trifluoromethyl)norbornadiene was added to a rapidly stirred solution of [Mo](CH-*t*-Bu) in C_6D_6, only **1** reacted to give **2a**. Therefore **1** reacts more than ~50 times faster than 2,3-bis(trifluoromethyl)norbornadiene, which is a deactivated, slower reacting monomer.[3] Addition of a mixture of 6 equiv of **1** and 6 equiv of norbornene to [Mo]($CHCMe_2Ph$) resulted in polymerization of 98% of the norbornene. **2b** could be observed, but no alkylidene complex was present. Addition of a mixture of 3 equiv of **1** and 15 equiv of norbornene resulted in "termination" of the polymerization of norbornene after 40% of the norbornene had been consumed. Again, **2b** was the only observable metallacycle. Addition of a mixture of 3 equiv of **1** and 25 equiv of norbornene gave similar results, with 52% of the norbornene being consumed. Examination of a 500-MHz ^1H NMR spectrum in this case revealed a resonance assigned to the terminal olefinic proton of polynorbornene that is estimated to be ≤0.20 of a proton in area. Therefore ~20% of the catalyst is consumed in initiating polymerization of norbornene. Note that neither 6 nor 15 equiv of norbornene alone would react with all of the initiator because of the relatively large value for k_p/k_i. (It is often possible to evaluate k_p/k_i readily, where k_p is the rate constant for propagation and k_i the rate constant for initiation, if one assumes that both initiation and propagation are bimolecular reactions and that all propagation steps take place at the same rate.[12,13]) Nevertheless a majority of the initiator (~80%) clearly is reacting with **1** in the presence of 25 equiv of norbornene. We can conclude that **1** reacts significantly faster (perhaps 30 times) than norbornene with [Mo]($CHCMe_2Ph$) but that *norbornene* reacts faster than **1** with the Mo=C bond in living polynorbornene.

The competition experiments reveal some potentially interesting details that are worth discussing. In all cases, 1–2 equiv of **1** is consumed; i.e., **1** also must be consumed in a manner other than to form **2b**. Also the cis:trans ratio in the living polynorbornene is different in different experiments. Homopolymerization of 25 equiv of norbornene yields a living 25-mer that contains 65% trans olefinic linkages, while polymerization of 25 equiv of norbornene in the presence of 3 equiv of **1** yields a polymer that contains 46% trans double bonds. A 15:3 ratio of norbornene to **1** yields a polymer that contains 41% trans double bonds, while a 1:1 ratio (6 equiv each) yields a polymer that contains 32% trans double bonds. In the 25:3 case, since ~20% of the catalyst is initiated by norbornene and about half of the norbornene is consumed, the average chain length is considerably greater than a 25-mer. These data suggest that the stereospecificity of norbornene polymerization is disrupted to a significant extent when **1** is present. One possibility is that **1** occasionally inserts into living polynorbornene and thereby disrupts the stereochemistry for several insertions of norbornene thereafter until the stereospecificity of the homopolymerization is eventually reestablished. If this is the case, it is surprising that such a small amount of incorporated **1** could affect the stereochemistry to the degree that it does. Alternatively, **1** might affect the stereospecificity of norbornene addition by coordinating to the metal through the oxygen atom and thereby directing addition of the next equivalent of norbornene without itself actually adding to the Mo=C bond.

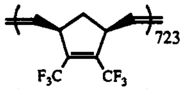
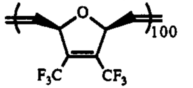
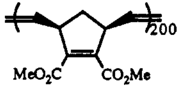
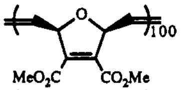
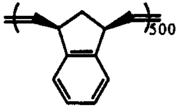
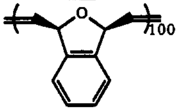
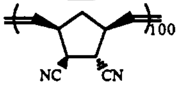
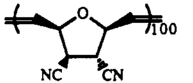
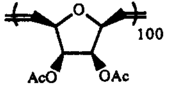
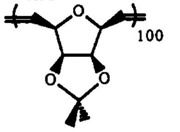
Since alkylidene resonances for living polynorbornene cannot be observed in the competition experiments, we wanted to determine whether a stable metallacyclobutane complex is formed by adding **1** to living polynorbornene but simply cannot be observed in the complex proton NMR spectrum. Not all **1** is consumed when ~2 equiv is added to living polynorbornene (25-mer), but no metallacycle resonances are visible by ^1H NMR spectroscopy. However, deuterium NMR analysis of a mixture obtained by adding 2 equiv of **1**-d_4 to living polynorbornene (25-mer) reveals resonances that can be attributed to a square-pyramidal metallacycle whose chemical shifts are such that in the proton NMR spectrum they would be coincident with resonances for the polymer. Interestingly, resonances in the olefinic and allylic regions (δ = 5–6 ppm) suggest that this observable metallacycle is *not* the first metallacycle formed by adding **1** to living polynorbornene but that formed by adding a second (or perhaps even a third) equivalent of **1**; i.e., the first metallacycle is considerably *less* stable than the second and the second possibly less stable than the third. The observable metallacycle (second or third) is itself considerably less stable than **2b**, since it opens slowly over several hours at room temperature and reacts with more monomer. Once the monomer is consumed, living alkylidene resonances are observed. Therefore incorporation of **1** into living polynorbornene is entirely plausible,

---

[12] For instance, k_p/k_i for norbornene reacting with [Mo]($CHCMe_2Ph$) is ~14. Addition of 6 equiv of norbornene would initiate ~64% of the catalyst, 15 equiv would initiate ~85%, and 25 equiv would initiate ~93%.

[13] (a) Gold, L. *J. Chem. Phys.* **1958**, *28*, 91. (b) Rempp, P.; Merrill, E. W. *Polymer Synthesis*; Huethig and Wepf: New York, 1986.

Table III. T_g Data for the 7-Oxa and Their Corresponding 7-CH_2 Polymers

	% trans	T_g, °C
	98	97[a]
	65	92
	95	140[b]
	30	107
	75	
	50	167
	na[c]	176
	na	193
	40	132
		171

[a] Poly(2,3-bis(trifluoromethyl)norbornadiene) also has a melting transition (T_m) = 200 °C. [b] T_g is estimated and irreversible. [c] Polymerized in 90% THF/10% CH_3CN by Mo(NAr)-($CHCMe_2Ph$)(O-*t*-Bu)$_2$.

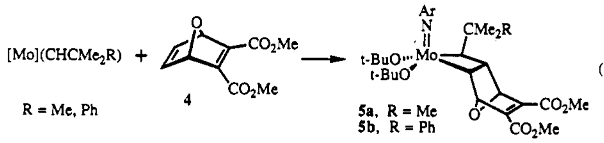
since the resulting metallacycles are not nearly as stable as **2b**. However, since **1** reacts so much more slowly with living polynorbornene than norbornene does, little should be consumed until nearly all of the norbornene has been consumed, as we observe.

Proton NMR experiments revealed that addition of **1** to Mo(CH-*t*-Bu)(NAr)[OCMe(CF_3)$_2$]$_2$ yielded living poly-**1**, but no metallacycles could be observed at room temperature. The ratio k_p/k_i was found to be large (30–50). Some resonances were observed that could be ascribed to propagating alkylidene complexes. In contrast, **1** adds to Mo($CHCMe_2Ph$)(NAr)-($OCMe_2CF_3$)$_2$,with k_p/k_i = 2.4 and thus provides greater potential for the formation of poly-**1** with a narrow molecular weight distribution.

Addition of 100 equiv of **1** to Mo($CHCMe_2Ph$)(NAr)-($OCMe_2CF_3$)$_2$ in toluene produces an initial red color typical of a metallacycle, which quickly changes to the orange color typical of a propagating alkylidene complex. After about 15 min, a second liquid phase appears in the stirred solution as a haze and remains for the duration of the polymerization reaction. The polymer is then cleaved from the metal with benzaldehyde. A 100-mer of poly-**1** cannot be precipitated from pentane or methanol because of its broad solubility range. Poly-**1** can be precipitated by adding an acetone solution to water, but neither molybdenum nor any excess **1** that may be present is thereby removed. Some of the color that arises from residual molybdenum can be removed by passing a solution of poly-**1** in dichloromethane through a column of neutral activated alumina. A sample of poly-**1** that had been precipitated in water was isolated in 93% yield and by GPC was shown to have a PDI = 1.04; no residual monomer was present. This result suggests that secondary metathesis of the double bonds in the polymer chain is slow. More than 100 equiv of **1** can be polymerized to give poly-**1** that has a very low polydispersity, even though the presence of two liquid phases during the polymerization reaction might lead one to predict that the molecular weight distribution would be broader.

Proton and carbon NMR analyses of poly-**1** indicate that double bonds in the polymer chain are ~65% trans. Resonances were assigned by comparison with those for poly(2,3-dicarbomethoxy-7-oxanorbornadiene);[8] the resonance for the doubly allylic ring proton when the adjacent double bond is trans is always downfield of where it is when the adjacent double bond is cis. A glass transition (T_g) has been identified by DSC in poly-**1** at 95 °C. (See Table III for T_g data.)

2,3-Dicarbomethoxy-7-oxanorbornadiene (**4**) (2,3-dicarbomethoxy-7-oxabicyclo[2.2.1]hepta-2,5-diene) reacts with [Mo](CH-*t*-Bu) as shown in eq 3. X-ray-quality crystals of **5a**

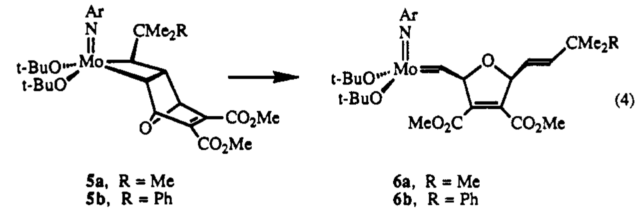


(3)

were obtained by vapor diffusion of pentane into a concentrated solution of **5a** in ether. Unfortunately, the structure could not be refined fully due to disorder in the carbomethoxy groups. However, the overall geometry of the structure that was obtained was virtually identical with that found for **2b**; neither the oxygen in the 7-position nor one in a carbomethoxy group interacted with the metal in any way.

Addition of a mixture of 3 equiv of **4** and 3 equiv of 2,3-dicarbomethoxynorbornadiene to [Mo]($CHCMe_2Ph$) gave **5b** only, and no 2,3-dicarbomethoxynorbornadiene was consumed. A similar competition experiment between **4** and **1** for [Mo]-($CHCMe_2Ph$) showed that **4** and **1** were equally reactive within experimental error. Note that 2,3-dicarbomethoxynorbornadiene reacts with [Mo](CH-*t*-Bu) ~9 times faster than does 2,3-bis(trifluoromethyl)norbornadiene.[3]

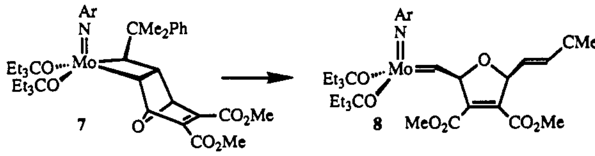
The metallacyclic ring in **5** opens to yield two alkylidene rotamers of **6** in a 9:1 ratio (eq 4). The proton NMR spectra of



(4)

6 can be fully assigned by COSY experiments. In the major rotamer $J_{H_\alpha H_\beta}$ = 7–8 Hz, while in the minor isomer $J_{H_\alpha H_\beta}$ = 4.5 Hz; in each, the alkylidene resonance is a doublet. As discussed earlier, the lower value for $J_{H_\alpha H_\beta}$ in the minor (proposed anti) rotamer is consistent with a different dihedral angle between H_α and H_β in a conformer formed by rotation about the C_α–C_β bond. The two doubly allylic protons also are coupled to each other with a *J* value of 1 Hz. A single rate determination showed that **5a** rearranges cleanly in a first-order fashion and completely to the two rotamers of **6a** (k = 4.5 (1) × 10^{-4} s^{-1} at 35 °C), while rearrangement of **5b** to the two rotamers of **6b** has been observed at several temperatures (Table II and Experimental Section). Note that the metallacycle that contains the neophyl group again rearranges more slowly by a factor of ~2 (k = 2.7 × 10^{-4} s^{-1} at 35 °C). In THF-d_8, the rate of rearrangement of **5b** to **6b** increases by a factor of 2 (k = 5.30 (5) × 10^{-4} s^{-1} at 35 °C) relative to the rate of rearrangement in C_6D_6.

Experiments employing Mo($CHCMe_2Ph$)(NAr)($OCEt_3$)$_2$ demonstrate that increased steric bulk of the alkoxides also significantly slows the rate of rearrangement of a metallacycle. At 35 °C, the rate of rearrangement of **7** to **8** (eq 5) in C_6D_6 was 4.3 × 10^{-5} s^{-1}, ~6 times slower than rearrangement of **5b** and



(5)

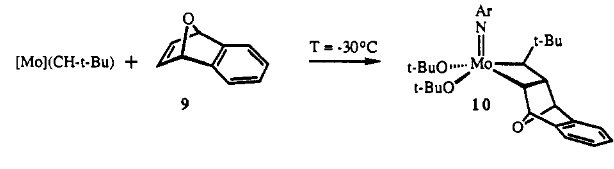
a full order of magnitude slower than rearrangement of **5a** (Table II).

Several attempts were made to polymerize **4** by employing [Mo](CHCMe$_2$Ph) as the initiator. Since **5** (eq 4) was found to rearrange approximately 1 order of magnitude faster than **2** (eq 2), **6** could be obtained quantitatively in a few hours. Five equivalents of **4** was added to **6b** prepared in this manner in C_6D_6. Proton NMR analysis indicated that living alkylidene complexes were all destroyed before all of the monomer was consumed. If less than 5 equiv of **4** is added to **6b**, then all of **4** is consumed. Results were identical in THF-d_8. While dilute samples (~0.01 M) of **6b** in C_6D_6 or THF-d_8 were stable for several hours, a relatively concentrated sample (~0.1 M) in THF-d_8 decomposed rapidly. Attempts to polymerize **4** in dichloromethane also were not successful. Not surprisingly, therefore, addition of a few equivalents of **4** to the living alkylidene prepared by adding 30 equiv of norbornene to [Mo](CHCMe$_2$Ph) also destroyed all alkylidene complexes.

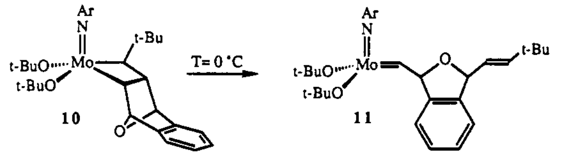
In view of the above results, we were surprised to discover that **4** *can* be polymerized by starting with Mo(CHCMe$_2$Ph)(NAr)(OCMe$_2$CF$_3$)$_2$ in dichloromethane. Addition of 100 equiv of **4** to Mo(CHCMe$_2$Ph)(NAr)(OCMe$_2$CF$_3$)$_2$ produces an initial red color, which rapidly fades to orange, characteristic of a propagating living alkylidene complex, and the reaction mixture remains orange for the duration of the polymerization. The GPC of isolated poly-**4** is unimodal with PDI = 1.15. Interestingly, polymerization of **4** employing Mo(CHCMe$_2$Ph)(NAr)(OCMe$_2$CF$_3$)$_2$ in other solvents such as toluene or THF under the same conditions yields polymers that have bimodal distributions; the reasons are not known. NMR analyses indicate that the double bonds in the polymer are only ~30% trans. DSC studies showed a T_g at ~110 °C (see Table III) along with a strong exotherm beginning at ~160 °C that is consistent with chemical degradation. The glass transition is reversible if the sample is not heated above 160 °C.

Addition of 100 equiv of 7-oxabenzonorbornadiene (1,4-dihydronaphthalene 1,4-*endo*-oxide, **9**) to [Mo](CH-*t*-Bu) yields poly(7-oxabenzonorbornadiene) (poly-**9**). The reaction mixture turns red upon adding **9** and then slowly fades to orange over a period of 45 min. The polymerization was terminated by adding benzaldehyde (or pivaldehyde), and the polymers were isolated by precipitation in hexane or methanol. Polydispersities of isolated polymers depended on both solvent and concentration of the initiator. In polar solvents such as THF, polymers had narrower polydispersities (PDI = 1.34–1.51 for a 100-mer) but GPC traces show tailing toward the lower molecular weight end of the distribution. In benzene, polymers were produced that had an even broader molecular weight distribution (PDI = 1.80 for a 100-mer). Narrower polydispersities were obtained when solutions were more dilute in initiator.

Analysis by ^{1}H NMR spectroscopy at −30 °C in toluene-d_8 of the product of the addition of 1 equiv of **9** to [Mo](CH-*t*-Bu) revealed the formation of a square-pyramidal metallacycle (**10**, eq 6) analogous to **2** to **5**. Qualitatively, **10** is much less stable than **2** or **5**; approximately 60% is converted to syn and anti forms of **11** (eq 7) after 1 h at 0 °C. Two equivalents of **9** was added to [Mo](CH-*t*-Bu) in toluene-d_8 at room temperature, and the solution was frozen immediately at 77 K. The proton NMR spectrum (at −30 °C) of the resulting mixture revealed that no [Mo](CH-*t*-Bu) remained. **10** had formed quantitatively, a small amount had rearranged to syn and anti **11** (~9:1 ratio), and the extra equivalent of monomer had been consumed to give one or more species having an alkylidene resonance at 11.69 ppm ($J_{\mathrm{H}_\alpha\mathrm{H}_\beta}$ = 6.8 Hz). As the rest of **10** rearranged, only the intensities of syn and anti **11** increased until the mixture consisted of **11** and the species that give(s) rise to the alkylidene resonance(s) at 11.69 ppm. These results are consistent with **11** reacting quickly with **9** to yield a metallacyclobutane complex that is relatively unstable and that rearranges to a new alkylidene complex; i.e., **9** would be consumed before the majority of **10** would rearrange.



(6)



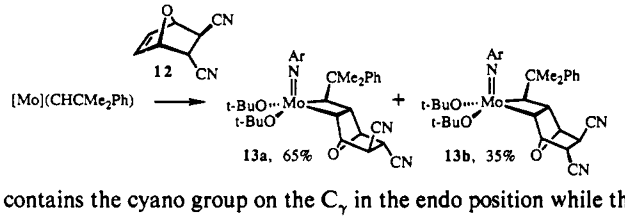
(7)

Figure 4a shows the alkylidene region of the proton NMR spectrum of a sample consisting of 3 equiv of **9** added to [Mo](CH-*t*-Bu) in C_6D_6. Two rotamers of **11** are present along with a small amount of the second and higher insertion products (an ill-defined broad hump centered around 11.66 ppm). If 1 equiv of **9** is added to [Mo](CH-*t*-Bu), followed after 30 min by another 2 equiv, the spectrum shown in Figure 4b is obtained. Alkylidene H$_\alpha$ resonances for the propagating alkylidene complexes now predominate. Note that resonances for both syn and anti rotamers are observed at 11.66 ppm (major) and 11.52 ppm (minor). The complex pattern for each resonance presumably is a composite of doublet resonances for the second, third, fourth, etc. insertion product, rather than due to the cis or trans nature of the first carbon–carbon double bond in the growing chain next to the Mo=C bond, although that possibility cannot be excluded at this stage. (Since the carbon–carbon double bond in the first insertion product is entirely trans, the H$_\alpha$ resonance would be a simple doublet in the first insertion product even if the H$_\alpha$ chemical shift were sensitive to the C=C configuration in general.) Attempts to isolate **11** failed, perhaps in part as a consequence of two rotamers being present.

The above studies suggested that **10** rearranges relatively slowly to **11** and that **11** then acts as an initiator for rapid subsequent polymerization of **9**. Therefore the procedure was changed. Instead of the complete addition of **9**, only 2–3 equiv was added. After 20 min, the initial red color turned back to orange (characteristic of an alkylidene complex) and the rest of **9** (98 equiv) was then added and the polymer was isolated in the usual fashion. For this polymer PDI = 1.06, a value that clearly results from a well-controlled polymerization in which all chains initiate more or less at the same time. We conclude that rapid formation of **10**, followed by a slow rearrangement to **11**, and then rapid propagation are what causes relatively large and variable polydispersities of the polymers prepared when **9** is added to [Mo](CH-*t*-Bu) all at once.

Poly(7-oxabenzonorbornadiene) (poly-**9**) has not been reported before to our knowledge. It is a white powder, it is soluble in a variety of solvents (CHCl$_3$, CH$_2$Cl$_2$, toluene), and it has good thermal properties. It has a T_g of 167 °C (Table III) and is thermally stable up to 320 °C in a nitrogen atmosphere (determined by TGA). It is not stable toward oxidation, however. IR analysis reveals a strong OH absorption around 3420 cm^{-1} that increases upon increased exposure to air.

Reactions Involving 7-Oxanorbornenes. Addition of 1 equiv of 2,3-*trans*-dicyano-7-oxanorborn-5-ene (**12**) to [Mo](CHCMe$_2$Ph) yields two square-pyramidal transoid metallacycles, according to proton NMR studies (eq 8). The major isomer (65%, **13a**) contains the cyano group on the C$_\gamma$ in the endo position while the



(8)

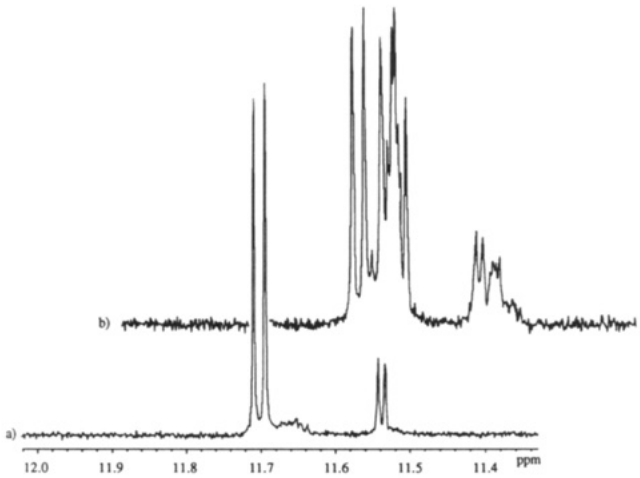


Figure 4. Alkylidene region of the 500-MHz ^{1}H NMR spectra (in C_6D_6) of the product of (a) addition of 3 equiv of **9** to [Mo](CH-*t*-Bu) and (b) addition of 1 equiv of **9** followed after 20 min by 2 equiv of **9**.

minor isomer (35%, **13b**) has this same cyano group on the C_γ in the exo position. A cyano group in the endo position deshields the metallacycle protons nearest to it. Hence, for **13a**, H_α appears as a doublet at 2.36 ppm ($CH_\alpha CMe_2Ph$ appears at 1.80 ppm), while, for **13b**, the H_α resonance appears at 1.66 ppm ($CH_\alpha CMe_2Ph$ appears at 1.80 ppm also for **13b**). Likewise, H_β for **13a** appears as a doublet of doublets at 2.62 ppm, while, for **13b**, which has the adjacent cyano in the endo position on the C_δ, H_β is shifted to 3.49 ppm. Identical values for $J_{H_\alpha H_\beta}$ suggest that the structures are both transoid. We have not succeeded at obtaining crystals of either **13a** or **13b**. Qualitative observations suggest that **13a** and **13b** are at least as stable as **2b**.

Addition of 1 equiv of **12** to $Mo(CHCMe_2Ph)(NAr)(OCEt_3)_2$ yields a 70:30 mixture of metallacycles analogous to those shown in eq 8. Therefore the greater steric bulk of the $OCEt_3$ groups affects the relative proportions of isomers to only a small extent.

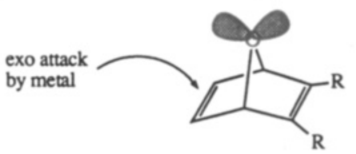
Monomer **12** (100 equiv) can be polymerized quantitatively in 2 h by using the initiator $Mo(CHCMe_2Ph)(NAr)(OCMe_2CF_3)_2$ in THF. Proton and carbon NMR spectra of poly-**12** are extremely complex and as yet not assigned. Poly-**12** has a T_g = 193 °C (by DSC; Table III) and begins to decompose—the white powder turns black—at ~240 °C. The glass transition is reversible when the temperature is kept below 240 °C.

2,3-*endo-cis*-Diacetoxy-7-oxanorbornene reacts with [Mo](CH-*t*-Bu) quantitatively to yield polymers with good polydispersities (1.17 for a 100-mer) and a 40% trans double-bond content. They are soluble in a variety of solvents and can be cast into flexible transparent films. TGA studies show that the polymer decomposes in two stages, although the features are less pronounced than those observed when poly(2,3-*endo-cis*-diacetoxynorbornene) decomposes. The weight loss during the first degradation (300 °C) of 60% suggests that 2 equiv of acetic acid is lost from each monomer unit (theory 57%). At slightly higher temperatures, the polymer degrades further by less obvious pathways. T_g was determined to be 132 °C by DSC (Table III).

2,3-*endo-cis*-(Isopropylidenedioxy)-7-oxanorbornene is polymerized smoothly by [Mo](CH-*t*-Bu) in THF to give polymers with a narrow molecular weight distribution (PDI = 1.09 for a 150-mer). DSC analysis reveals a *Tg* at 171 °C, while TGA reveals the onset of decomposition at ~200 °C.

Discussion

Two primary conclusions can be drawn from the results presented here. The first is that 7-oxa derivatives react much more rapidly than their norbornadiene analogues with $Mo(CHR)(NAr)(OR')_2$ complexes. This is particularly surprising since the unsubstituted C=C bond in the 7-oxa derivatives is likely to be electron poor relative to norbornadiene analogues on the basis of ionization potentials.[14] Therefore, if coordination of the C=C bond to an electrophilic metal center alone were to determine monomer reactivity, the 7-oxa derivatives would be expected to be less reactive. We propose that the rate of reaction of the 7-oxa derivatives is increased by initial coordination to the metal of an oxygen lone pair on the same side as the unsubstituted C=C bond. Reactivity differences ascribable to electronic differences of substituents should be minimal. Therefore, as one would predict, although 2,3-dicarbomethoxynorbornadiene is 10 times more reactive than 2,3-bis(trifluoromethyl)norbornadiene,[3] **1** and **4** are approximately equally reactive. It is not clear whether the oxygen lone pair actually attacks the metal first, or whether attack by the metal on the exo face of the olefin is concurrent with lone pair attack. In any case, reactions involving 7-oxa derivatives are greatly accelerated. The smaller size of O vs CH_2 is also consistent with the observed reactivity differences, but sterics alone would not explain the lack of a significant difference in reactivity between **1** and **4**.



The finding that the 7-oxa monomers react more rapidly than norbornene with $[Mo](CHCMe_2Ph)$ but less rapidly than norbornene with living polynorbornene is initially surprising. There are a couple of possible explanations. For steric reasons, all-trans square-pyramidal metallacycles are believed to form upon addition of norbornene or 7-oxa derivatives to *syn*-$[Mo](CHCMe_2Ph)$. But both syn and anti rotamers of living polynorbornene are present and may react with monomer to give some cis metallacycles. It is also quite possible that the metallacycles that are involved in the most rapid polymerization step may not be square pyramidal at all. Therefore competition between a 7-oxa derivative and norbornene for living polynorbornene could be entirely different from the competition for *syn*-$[Mo](CHCMe_2Ph)$. Another possible explanation is that the way in which a 7-oxa derivative adds to an alkylidene is substantially different from the way norbornene adds and that in crowded circumstances (*syn*-$[Mo](CHCMe_2Ph)$) the 7-oxa derivative competes more effectively. That could be the case if the relatively accessible oxygen lone pair were to coordinate to the metal first followed by addition of the double bond to the metal and subsequently to the Mo=C bond.

There is precedent in the literature that supports a special role for the oxygen in 7-oxanorbornadienes with regard to binding to metals. Irradiation of a solution of $Fe(CO)_5$ and **9** yields Fe(7-oxanorbornadiene)$(CO)_4$, while the same reaction with benzonorbornadiene fails.[15] In general, olefins having strongly electron-withdrawing substituents directly attached to the coordinated double bond form stable $Fe(CO)_4$(olefin) complexes, so one would expect both benzonorbornadiene and 7-oxanorbornadiene to form stable complexes.[16] Assistance by the lone pair on oxygen could be invoked in order to explain this difference in coordinating ability. Participation of the oxygen lone pairs in **9** in controlling stereochemistry of reactions[17] and coordination to metal complexes[18] has been suggested previously but not proven conclusively.

A second conclusion that can be drawn from the results reported here is that metallacyclobutane complexes made from 7-oxa derivatives seem to be stabilized to a significant degree toward rearrangement to an alkylidene complex, but not by any direct interaction between the oxygen in the 7-position and the metal. Therefore the metallacycle must be stabilized inductively, as has been found recently also for 2-oxametallacyclobutane complexes of Mo and W.[19] The complexes reported here are the only

---

(14) Gassman, P. G.; Yamaguchi, R. *Tetrahedron* **1982**, *38*, 1113.

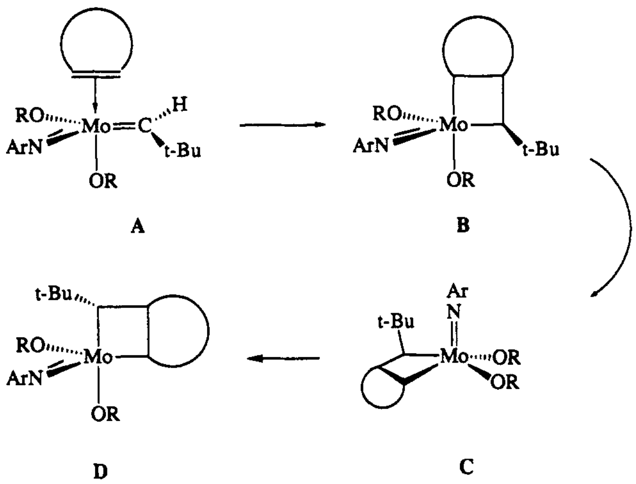
(15) Lombardo, L.; Wege, D.; Wilkinson, S. P. *Aust. J. Chem.* **1974**, *27*, 143.

(16) Weiss, E.; Stark, K.; Lancaster, J. E.; Murdoch, H. D. *Helv. Chim. Acta* **1963**, *46*, 288.

(17) Warrener, R. N. *J. Am. Chem. Soc.* **1971**, *93*, 2346.

(18) Sun, C.-H.; Chow, T. J. *Heterocycles* **1988**, *27*, 217.

Scheme I



examples of stable molybdacyclobutane complexes formed from a reaction between an olefin and a molybdenum alkylidene complex. (Related tungstacycle derivatives are significantly more stable.[20]) A metallacycle is most likely to be observable when it forms rapidly and rearranges slowly. That appears to be the case in the examples reported here.

Comparison of rates of rearrangement of 7-oxanorbornadiene metallacycles supports the proposal that the metallacycles are stabilized inductively. A single measurement of rearrangement of **10** at 0 °C (60% metallacycle consumed in 60 min) suggests that the first-order rate constant is in the range (1–3) $\times 10^{-4}$ s^{-1}. The rate constant for rearrangement of **2a** at 0 °C is calculated to be 7.3×10^{-7} s^{-1}. Therefore, a change from a bis(trifluoromethyl) to a benzo derivative increases the rate of rearrangement of the ring at 0 °C by 2 orders of magnitude. Similarly, the calculated rate constant for the rearrangement of **2a** at 35 °C (4.2×10^{-5} s^{-1}) is 1 order of magnitude smaller than that measured for **5a** (4.5 (1) $\times 10^{-4}$ s^{-1}) at 35 °C. Steric differences between the substituents in these metallacycles (benzo, CO_2Me, and CF_3) are likely to contribute in only a minor way to metallacycle stability.

Large groups *near* the metal center *do* stabilize metallacycles. Changing the substituent on the alkylidene, and therefore on the α-carbon in the metallacycle, from *tert*-butyl to the more bulky dimethylphenylmethyl group decreases the rate of breakup by a factor of approximately 5, while changing the alkoxide from *tert*-butoxide to triethylcarbinoxide decreases the rate of rearrangement by approximately 1 order of magnitude. We assume that electronic differences between the groups compared here would contribute relatively little to metallacycle stability.

Exactly how these electronic and steric effects are involved in stabilization of square-pyramidal metallacycles is not well understood. Entropies of activation for ring opening are consistent with a considerable amount of rearrangement before the transition state is reached. It has been proposed that square-pyramidal metallacycles must rearrange to trigonal-bipyramidal metallacycles before the olefin can be lost[3,9] and that the initial adduct is the one formed when the olefin attacks the CNO face of the catalyst.[21] A plausible scenario for formation and ring opening of a metallacyclobutane complex is shown in Scheme I.

One possible reason that metallacycles formed by adding 7-oxanorbornadienes to [Mo]($CHCMe_2R$) are stable is that the rate of interconversion of C to D is slowed by electron-withdrawing substituents on the metallacycle and/or bulky groups near the metal center. One can imagine that bulky alkoxides and a bulky substituent in a syn alkylidene ligand could slow rearrangement of C to D, but it is less obvious why electron-withdrawing substituents should also. One might argue that the C=C bond that must form from D is more electron poor, and since the metal in high-oxidation-state alkylidene complexes appears to behave as an electrophile (with little π back-bonding from what could be interpreted as a d^0 metal to the olefin), incipient formation of a relatively electron-poor olefin raises the level of the transition state for ring opening. (At this point it is much less clear what effect, if any, electronegative substituents would have on the ground-state energy of the metallacyclobutane complex.) The small steric difference between O and CH_2 would not seem to be significant enough to increase the stability of the metallacycle made from the 7-oxa derivative to the extent that is observed.

Square-pyramidal metallacyles are not observable at 25 °C upon adding 7-oxa derivatives to the trifluoro-*tert*-butoxide complexes. (They can be observed at low temperatures; these studies will be reported elsewhere.) More electron-withdrawing alkoxides allow trigonal-bipyramidal metallacycles having an axial imido ligand to be accessed,[9,22] and accessibility of such metallacycles appears to correlate with their rate of rearrangement.

The choice of $Mo(CHCMe_2Ph)(NAr)(OCMe_2CF_3)_2$ for polymerization of **1** was based on several facts. First, complexes that contain more electron-withdrawing alkoxides lead to less stable metallacycles and a more accessible transition state, as outlined above. Such catalysts are more active and therefore attack ordinary double bonds in the polymer chain. For example, polynorbornene (100-mer) prepared by employing Mo(CH-*t*-Bu)(NAr)($OCMe_2CF_3)_2$ in tetrahydrofuran had PDI = 1.25. But an electron-withdrawing substituent on the alkylidene deactivates what could be viewed as a nucleophilic alkylidene carbon atom, while electron-withdrawing substituents deactivate double bonds in the polymer formed by ring opening of the monomer.[3,11] Therefore, in this particular case, both the living alkylidene and the C=C double bonds in the polymer are deactivated, and secondary metathesis therefore is slow.

Polymerizations of 7-oxa norbornadienes in general proceed less stereoselectively than polymerization of norbornadiene analogues, even when tert-butoxide catalysts are employed (Table III). For example, polybenzonorbornadiene[3] contains 76% trans olefinic bonds, while poly(7-oxabenzonorbornadiene) contains only 50% trans double bonds. One possibility is that the more reactive 7-oxa derivatives attack the metal to give a metallacycle in several different ways. Another is that since two rotamers of the living alkylidene are seen in these polymerizations and since the oxa monomers are much more reactive than previously studied monomers, the relative rates of metallacycle formation versus rotamer isomerization become much more important.[3] (Activation energies for formation of cis metallacycles relative to trans metallacycles should be significantly different for the anti rotamer than for the syn rotamer.)

The polymers obtained from 7-oxanorbornene and 7-oxanorbornadiene derivatives have the highest glass-transition temperatures observed of all the polynorbornene derivatives prepared so far. Of particular note are poly(*trans*-dicyanonorbornene)[23] and poly(*trans*-dicyano-7-oxanorbornene). A drawback that is likely to limit their utility in applications where a high T_g is desirable is their poorer thermal stability above T_g.

Experimental Section

General Details. All polymerizations were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques. Tetrahydrofuran was predried over calcium chloride and distilled from sodium benzophenone ketyl under nitrogen immediately prior to use. Toluene was distilled from molten sodium and stored over sodium–potassium alloy. All deuterated NMR solvents were passed through a column of activated alumina except for deuterated THF, which was vacuum-transferred from benzophenone ketyl. Norbornene was doubly distilled from molten sodium. Commercially available aldehydes were purified by distillation under nitrogen. 2,3-Bis(trifluoromethyl)-7-oxanorbornadiene,[24] 2,3-dicarbomethoxy-7-oxanorbornadiene,[25] 7-oxa-

---

[19] Bazan, G. C.; Schrock, R. R.; O'Regan, M. B. *Organometallics* **1991**, *10*, 1062.

[20] Bazan, G. Ph.D. Thesis, Massachusetts Institute of Technology, 1990.

[21] Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; O'Regan, M. B.; Schofield, M. H. *Organometallics* **1991**, *10*, 1832.

[22] Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.*, in press.

[23] Oskam, J. H. Unpublished results.

Table IV. Selected NMR Data for Molybdacyclobutane and Alkylidene Complexes[a]

	δ				δ		
cmpd	H_α	H_α'	H_β	$J_{H_\alpha H_\beta}$	C_α	C_α'	C_β
2a	1.68	1.57	2.88	8	41.2	38.1	62.3
2b	1.94	1.75	2.71	7.5	40.8	34.6	62.5
5a	1.98	1.73	3.07	8	41.6	37.8	62.4
5b	2.03	1.93	2.75	7.7	41.5	37.5	62.6
7	2.02	1.80	2.79	7.9			
10	1.85	1.85	2.87				
13a	2.36	1.80	2.62	8			57.8
13b	1.66	1.80	3.49	8			57.5
3a	11.233 (90%)			8.5			
	11.072[b]						
3b	11.273 (85%)			8.0			
	11.18[b]						
6a	11.565 (90%)			7.5			
	11.414			4.5			
6b	11.44 (90%)			8.0			
	11.11			4.5			
8	11.31 (87%)			8.1			
	11.52			6.9			
11	11.69 (85%)			7.5			
	11.47			4.0			

[a] All H_α and H_β resonances are primarily doublets unless otherwise noted. $J_{H_\alpha H_\beta}$ is given in hertz. [b] A multiplet.

benzonorbornadiene,[26] and 2,3-*trans*-dicyano-7-oxanorbornene[27] were prepared by literature procedures.

NMR data are listed in parts per million downfield from TMS for both proton and carbon resonances. Coupling constants are quoted in hertz. Obvious multiplicities and routine coupling constants often are not listed. Especially relevant NMR data can be found in Table IV, and the complete set of data can be found in the supplementary material. Gel permeation chromatographic (GPC) analysis was carried out at room temperature by employing a Rheodyne Model 7125 sample injector, a Kratos Spectroflow 400 pump, Shodex KF-802.5, 803, 804, 805, and 800P columns, a Knauer differential refractometer, and a Spectroflow 757 absorbance detector for samples 0.1–0.3% w/v in dichloromethane that were filtered through a Millex-SR 0.5-μm filter in order to remove particulates. The GPC columns were calibrated versus commercially available polystyrene standards (Polymer Laboratories Ltd.) ranging from MW = 1206 to 1.03×10^6. Thermal analysis (TGA) was done on a Perkin-Elmer TGS-2 thermogravimetric analyzer. Differential scanning calorimetry was performed on a Perkin-Elmer DSC-4 instrument at a heating rate of 30 °C/min.

Synthesis of 2a. A solution of 2,3-bis(trifluoromethyl)-7-oxanorbornadiene (47 mg, 0.2 mmol) in diethyl ether (500 μL) was added to a light orange solution of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (100 mg, 0.2 mmol) in ether (1.0 mL), and the mixture was stirred for 20 min. Cooling the resulting deep red solution to −40 °C for 48 h yields the product as red platelike crystals (105 mg, 75%). Anal. Calcd for $MoC_{35}H_{49}NO_3F_6$: C, 55.23; H, 6.88; N, 1.95. Found: C, 55.24; H, 7.10; N, 1.82.

Synthesis of 2b. To a 700-μL pentane solution of Mo(CHCMe$_2$Ph)(NAr)(O-*t*-Bu)$_2$ (55 mg, 0.10 mmol) was added a 700-μL pentane solution of 2,3-bis(trifluoromethyl)-7-oxanorbornadiene (23 mg, 0.10 mmol). The resulting red solution was cooled to −40 °C, and red crystals were collected after 24 h (48 mg, 62%). Anal. Calcd for $MoC_{38}H_{51}NO_3F_6$: C, 58.53; H, 6.59; N, 1.80. Found: C, 58.96; H, 6.71; N, 1.85.

X-ray Study of 2b. Data were collected at −72 °C on a Rigaku AFC6 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) and a 12-kW rotating anode generator. A total of 7499 reflections were collected, 7114 of which were unique. Equivalent reflections were merged. The intensities of three representative reflections measured after every 150 reflections remained constant throughout the data collection, indicating crystal and electronic stability. No decay correction was applied. An empirical absorption correction was applied. The data were corrected for Lorentz and polarization effects. The Mo atom was located by using the Patterson method. All other atoms were located in difference Fourier maps. The final refinement was based on 4691 reflections ($I > 3.00\sigma(I)$); a full-matrix least-squares refinement was done by TEXSAN.[28] All non-hydrogen atoms were refined anisotropically. Crystal data for **2b**: a = 12.420 (3) Å, b = 15.466 (4) Å, c = 20.856 (6) Å, V = 3852 (2) Å^3, β = 105.97 (2)°, space group = $P2_1/n$, Z = 4, M_r = 779.76, ρ = 1.345 g/cm^3, μ = 3.9 cm^{-1}, R_1 = 0.049, R_2 = 0.068.

Rate of Decomposition of 2a. Solutions of **2a** (12 mg, 1.7×10^{-5} mol) and mesitylene (~2 mg, 1.7×10^{-5} mol) in C_6D_6 were prepared from stock solutions, placed in 5-mm NMR tubes, and frozen in liquid N_2 until measurements were made. The metallacycle α or β resonances were monitored versus the internal standard in the ^{1}H NMR spectra. Rates were determined at 40, 50, and 60 °C with a sample equilibration time in the NMR probe of 10–15 min. Observed rate constants were 0.68 (1), 1.95 (1), and 4.37 (3) $\times 10^{-4}$ s^{-1}, respectively. The Arrhenius plot had ρ = 0.998.

Rate of Decomposition of 2b. The method was analogous to that used to study the decomposition of **2a**. Observed rate constants were 0.550 (7) $\times 10^{-4}$ s^{-1} at 50 °C, 1.63 (2) $\times 10^{-4}$ s^{-1} at 60 °C, and 4.70 (5) $\times 10^{-4}$ s^{-1} at 70 °C. The Arrhenius plot had ρ = 0.99997.

Typical Competition Experiment Involving 1 and 2,3-Bis(trifluoromethyl)norbornadiene. 2,3-Bis(trifluoromethyl)-7-oxanorbornadiene (25 mg, 0.054 mmol) in 350 μL of toluene-d_8 was combined with 350 μL of toluene-d_8 solution of 2,3-bis(trifluoromethyl)norbornadiene (25 mg, 0.054 mmol), and the resulting solution was split into two equal parts. The first was diluted to 700 μL and placed in a 5-mm NMR tube. The second was added to a rapidly stirred 350-μL toluene-d_8 solution of [Mo](CHCMe$_2$Ph) (10 mg, 0.018 mmol). The solution turned red immediately. It was placed in a 5-mm NMR tube and examined at −25 °C by ^{1}H NMR spectroscopy. Examination of the starting monomer ratio versus the final monomer ratio revealed that 1 equiv of **1** had reacted prior to addition of any 2,3-bis(trifluoromethyl)norbornadiene. Only metallacycle **2b** was present.

All other competition experiments were performed in toluene-d_8 by using the same concentration of [Mo](CHCMe$_2$Ph). Varying amounts of the competing monomers were premixed in a similar fashion, and the solutions were then divided prior to addition to the catalyst solution.

Synthesis of 5a. A solution of 2,3-dicarbomethoxy-7-oxanorbornadiene (43 mg, 0.2 mmol) in ether (500 μL) was added to a light orange solution of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (100 mg, 0.2 mmol) in ether (1.0 mL). After 15 min, the solution was placed inside an open 5-mL vial and this in turn placed inside a 20-mL vial containing pentane. After 1 week at −40 °C, red crystals of the product were obtained; yield 45 mg (31%). Anal. Calcd for $MoC_{35}H_{55}NO_7$: C, 60.25; H, 7.94; N, 2.01. Found: C, 60.31; H, 7.82; N, 1.68.

Synthesis of 5b. To a 500-μL pentane solution of Mo(CHCMe$_2$Ph)(NAr)(O-*t*-Bu)$_2$ (152 mg, 0.28 mmol) was added a 500-μL pentane solution of 2,3-dicarbomethoxy-7-oxanorbornadiene (58 mg, 0.28 mmol). The resulting red solution was cooled to −40 °C to give a red semicrystalline solid after 1 week.

Rate of Decomposition of 5a. A single rate was determined at 35 °C by ^{1}H NMR spectroscopy by measuring the disappearance of the H_β resonance in **5a** (12 mg in 750 μL C_6D_6) versus an internal standard (mesitylene). First-order behavior was observed with a rate of 4.5 (1) $\times 10^{-4}$ s^{-1}.

Rate of Decomposition of 5b. Metallacycle **5b** was generated in situ by adding a solution of 2,3-dicarbomethoxy-7-oxanorbornadiene (29 mg, 0.14 mmol) in C_6D_6 (1700 μL) to a solution of Mo(CHCMe$_2$Ph)(NAr)(O-*t*-Bu)$_2$ (75 mg, 0.14 mmol) and mesitylene (2.7 mg, 0.023 mmol) as internal standard in C_6D_6 (1800 μL). The solution was divided into 5-mm NMR tubes, each containing ~700 μL. Disappearance of the metallacycle H_β resonance was followed versus the internal standard. Observed rate constants were 0.970 (5) $\times 10^{-4}$ and 0.890 (5) $\times 10^{-4}$ s^{-1} at 25 °C, 2.67 (1) $\times 10^{-4}$ and 2.66 (3) $\times 10^{-4}$ s^{-1} at 35 °C, and 7.46 (7) $\times 10^{-4}$ and 7.32 (2) $\times 10^{-4}$ s^{-1} at 45 °C. The Arrhenius plot had ρ = 0.9995. The observed rate constant at 35 °C in THF-d_8 was 5.30 (5) $\times 10^{-4}$ s^{-1}.

Synthesis of 7 and Decomposition of 7 to 8. A solution of 2,3-dicarbomethoxy-7-oxanorbornadiene (5.0 mg, 0.024 mmol, from a stock solution) in 400 μL of C_6D_6 was added to a 400-μL C_6D_6 solution of Mo(CHCMe$_2$Ph)(NAr)(OCEt$_3$) (15 mg, 0.024 mmol). The solution turned deep red immediately.

Kinetic data were collected by using the in situ generated sample above and mesitylene (2.7 mg, 0.023 mmol) as an internal standard by following the decrease in the H_β resonance. Observed rate constants were 0.425 (7) $\times 10^{-4}$ s^{-1} at 35°, 1.28 (2) $\times 10^{-4}$ s^{-1} at 45°, and 3.77 (4) $\times$

---

(24) Peinzkbach, H.; Bingmann, H.; Markert, J.; Fischer, G.; Knothe, L.; Eberbach, W.; Brokatsky-Geiger, J. *Chem. Ber.* **1986**, *119*, 589.

(25) Stork, G.; van Tamelen, E. E.; Friedman, L. J.; Burgstahler, A. *J. Am. Chem. Soc.* **1953**, *75*, 384.

(26) Stiles, M.; Miller, R. G.; Burkhardt, U. *J. Am. Chem. Soc.* **1963**, *85*, 1792.

(27) Mowry, D. T. *J. Am. Chem. Soc.* **1947**, *69*, 573.

(28) TEXRAY Structure Analysis Package, Molecular Structure Corp., 1985.

10^{-4} s^{-1} at 55°. The Arrhenius plot had $\rho = 0.99993$.

Observation of 10 and Decomposition of 10 to 11. A solution of 7-oxabenzonorbornadiene (6 mg, 40 × 10^{-5} mol) in toluene-d_8 (300 μL) was added to a solution of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (20 mg, 4 × 10^{-5} mol) in toluene-d_8 (350 μL), and the solution was frozen until analyzed by NMR spectroscopy. Warming the solution to 0 °C resulted in 60% consumption of the metallacycle to yield two rotamers of **11**.

Synthesis of the Mixture of 13a and 13b. A 400-μL C_6D_6 solution of Mo(CHCMe$_2$Ph)(NAr)(O-*t*-Bu)$_2$ (15 mg, 0.027 mmol) was added to 2,3-*trans*-dicyano-7-oxanorbornene (4 mg, 0.027 mmol, slightly soluble in C_6D_6). The monomer dissolved quickly as the red metallacycle formed. No crystals could be obtained from pentane at −40 °C.

Polymerization of 2,3-Bis(trifluoromethyl)-7-oxanorborna-2,5-diene. A 7-mL toluene solution of 2,3-bis(trifluoromethyl)-7-oxanorbornadiene (1060 mg, 4.61 mmol) was added rapidly to a 7-mL toluene solution of Mo(CHCMe$_2$Ph)(NAr)(OCMe$_2$CF$_3$)$_2$ (31 mg, 0.047 mmol). The color changed from yellow to red and then gradually to orange. After about 15 min, a second liquid phase appeared. When stirring was stopped, the second phase appeared orange while the rest of the solution was light yellow. Polymerization was terminated after 50 min by adding benzaldehyde (100 μL, reaction time 20 min). The solvent was removed in vacuo, and the solids were then taken up in acetone. The acetone solution was poured into water, and the resulting yellow polymer was collected, washed, and dried; yield 0.987 g (93%). Characterization by GPC yielded a single peak of $M_w = 18\,900$, $M_n = 18\,150$, and polydispersity = 1.04. ^{1}H NMR (CD$_2$Cl$_2$): δ 5.93 (br, 2, cis and trans C*H*=CH), 5.72 (both br, cis C*H*(O)), 5.57 (br, trans C*H*(O)). ^{13}C NMR (CDCl$_3$): δ 135.5 (CF$_3$*C*=*C*CF$_3$), 131.3 (cis and trans *C*H=*C*H), 85.5 (trans *C*H(O)), 81.2 (cis *C*H(O)).

Polymerization of 2,3-Dicarbomethoxy-7-oxanorborna-2,5-diene. A 3-mL CH$_2$Cl$_2$ solution of 2,3-dicarbomethoxy-7-oxanorbornadiene (1060 mg, 2.43 mmol) was added rapidly to a 4-mL CH$_2$Cl$_2$ solution of Mo(CHCMe$_2$Ph)(NAr)(OCMe$_2$CF$_3$)$_2$ (10 mg, 0.0243 mmol). A faint red color dissipated quickly to give an orange reaction mixture. After 60 min, polymerization was terminated by adding benzaldehyde (40 μL, 20 min). The polymerization solution was diluted by a factor of 2, and the polymer was precipitated by pouring the mixture into 150 mL of pentane. The polymer was collected on a frit, washed with pentane, and dried under vacuum for 2 h. The resulting polymer was off-white and powdery; yield 472 mg (92%). Characterization by GPC in CH$_2$Cl$_2$ revealed a single peak of $M_w = 30\,700$, $M_n = 26\,600$, and a polydispersity of 1.15. Proton NMR analysis indicates 30% trans double bonds. ^{1}H NMR (CD$_2$Cl$_2$): δ 5.91 (br, 2, cis and trans C*H*=CH), 5.65, 5.58 (both br, cis C*H*(O)), 5.47 (br, trans C*H*(O)), 3.77 (br, 6, OC*H*$_3$). ^{1}H NMR (CDCl$_3$): δ 5.84 (br, 2, cis and trans C*H*=CH), 5.76, 5.51, 5.49 (br, cis C*H*(O)), 5.41 (br, trans C*H*(O)), 3.74, 3.73 (br, 6, OC*H*$_3$). ^{13}C NMR (CDCl$_3$): δ 162.6–162.1 (C=O), 138.9–137.1 ((CO$_2$Me)*C*=*C*(CO$_2$Me)), 131.4 (*C*H=*C*H), 85.8 (trans *C*H(O)), 81.3 (cis *C*H(O)), 52.4 (O*C*H$_3$).

Polymerization of 7-Oxabenzonorbornadiene. Stock solutions (2000 μL) of both Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$ (10 mg, 2.05 × 10^{-5} mol) and 7-oxabenzonorbornadiene (296 mg, 2.05 mmol) in THF were split into 2 × 1000 μL portions. The first polymerization was carried out by adding the monomer to the catalyst all at once while being stirred vigorously and then waiting 45 min. The second was carried out by first adding 40 μL (4.0 × 10^{-5} mol, ~4 equiv) of the monomer solution to the catalyst. The resulting solution was stirred approximately 20 min until the red solution became orange. The rest of the monomer solution was added dropwise over a period of 5 min, and the mixture was stirred an additional 20 min. Both polymerizations were terminated by adding excess benzaldehyde (15 μL, 30 min). The polymers were isolated by pouring the reaction solution into a large excess of hexane or methanol (200 mL) followed by centrifugation. The polymers were purified by pouring a chloroform solution into hexane. They were dried in vacuo for 24 h. GPC analysis showed that the maxima of both peaks appeared at approximately the same retention time. The polymer prepared by the second method had a polydispersity index of 1.05. ^{1}H NMR (CDCl$_3$): δ 7.29 (br, 4, H$_{ar}$), 6.16 (br, 0.5, cis or trans C*H*=CH), 6.06 (br, 0.5, cis or trans C*H*=CH), 5.76 (br, 0.5, OC*H*), 5.66 (br, 0.5, OC*H*), 0.9 (br, C*Me*$_3$ end group). ^{13}C NMR (CDCl$_3$): δ 141.6 (C$_{ar}$), 133.9 (C$_{ar}$), 130.02 (C$_{ar}$), 128.8 (*C*H=CH), 122.8 (*C*H=CH), 84.3 (*C*H allylic), 79.7 (*C*H, allylic).

Polymerization of 2,3-*trans*-Dicyano-7-oxanorbornene. A 1.5-mL THF solution of Mo(CHCMe$_2$Ph)(NAr)(OCMe$_2$CF$_3$)$_2$ (25 mg, 0.038 mmol) was rapidly added to a rapidly stirred 10-mL THF solution of 2,3-*trans*-dicyano-7-oxanorbornene (556 mg, 3.8 mmol). The solution turned faintly red and then slowly orange. After 2 h, the polymerization was terminated with benzaldehyde (50 μL, 20 min), and the polymer was isolated by precipitation in pentane and dried in vacuo for 2 h; yield 561 mg (100%). Proton NMR spectroscopy revealed that no monomer remained in the polymer. (The monomer is completely insoluble in pentane.) ^{1}H NMR (THF-d_8): δ 6.15, 6.05, 5.97 (C*H*=C*H*), 5.04, 4.97, 4.86, 4.80, 4.64 (C*H*(O)), 3.96, 3.62 (C*H*(CN)). ^{13}C NMR (THF-d_8, resonances not yet fully assigned): 132.6–130.4 (*C*H=*C*H), 118.1–117.3 (*C*N), 82.34, 79.6–79.1, 77.1–77.0, 72.8, 58.9, 40.7–40.1.

Preparation of *endo-cis*-7-Oxabicyclo[2.2.1]hept-5-ene-2,3-diol Diacetate. A solution of 7-oxabicyclo[2.2.1]hept-5-ene-2,3-diol[29] (endo major isomer, 6.4 g, 0.05 mol) in 60 mL of dry pyridine at −78 °C was treated with 25 mL of acetic anhydride. The solution was stirred for 24 h at room temperature and then poured into 200 mL of ice water. After 1 h, the resulting mixture was extracted with dichloromethane three times and the combined extracts were washed successively with cold 2 N HCl, aqueous NaHCO$_3$, and brine. The dried (Na$_2$SO$_4$) solution was concentrated under reduced pressure to obtain a light yellow solid. Two recrystallizations from ethyl ether gave pure white crystalline product (>98% endo; 8.5 g, 80% yield; mp 75–76 °C). ^{1}H NMR (CDCl$_3$): δ 6.47 (m, 2 H, C*H*=C*H*), 5.12–5.13 (m, 2 H), 5.10 (m, 2 H), 2.00 (s, 6 H, C*H*$_3$).

Polymerization of 2,3-*endo-cis*-Diacetoxy-7-oxanorbornene. A solution of the monomer (435 mg, 2.05 mmol) in THF (5 mL) was added dropwise quickly to a rapidly stirred solution of Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$ (10 mg, 2.05 × 10^{-5} mol) in THF (5 mL). After 30 min, the polymerization was quenched with benzaldehyde (15 μL, 30 min). The polymer was isolated by precipitation from methanol followed by three subsequent reprecipitations and finally was placed under vacuum for 24 h; yield 400 mg (92%). ^{1}H NMR (CDCl$_3$): δ 5.73 (br, 0.4, cis or trans CH=CH), 5.65 (br, 0.6, cis or trans C*H*=CH), 5.42 (br, 1, OC*H*), 4.78 (br, 0.6, C*H* allylic), 4.50 (br, 0.4, C*H* allylic), 2.03 (br, 3, OC*Me*), 0.98 (s, C*Me*$_3$ end group).

Preparation of *endo-cis*-(Isopropylidenedioxy)-7-oxabicyclo[2.2.1]hept-5-ene. To a solution of 7-oxabicyclo[2.2.1]hept-5-ene-2,3-diol[29] (endo major isomer, 6.4 g, 0.05 mol) in 150 mL of dry acetone at room temperature was added 50 mL of 2,2-dimethoxypropane and a catalytic amount of *p*-toluenesulfonic acid. The solution was stirred at room temperature for 3 h. After the solvents were evaporated in vacuo, the residue was diluted with 100 mL of chloroform and the resulting mixture was washed with brine and water and dried with MgSO$_4$. The solvents were evaporated in vacuo, and the viscous oil was purified by vacuum distillation at 48–50 °C (0.1 Torr) to give the white solid >98% endo product; yield 6.8 g (81%; mp 38 °C). ^{1}H NMR (CDCl$_3$): δ 6.44 (s, 2 H, C*H*=C*H*), 4.90–4.92 (dd, 2 H, CH=CHC*H*), 4.36–4.84 (m, 2 H, OC*H*C*H*O), 1.32 (s, 3 H, C*H*$_3$), 1.33 (s, 3 H, C*H*$_3$).

Polymerization of 2,3-*endo-cis*-(Isopropylidenedioxy)-7-oxanorbornene. This polymer was prepared by a procedure analogous to those described above. Yields were in the 85–95% range. ^{1}H NMR (CDCl$_3$): δ 6.00 (br multiplet, 2, C*H*=CH), 4.67 (br, 2, OC*H*), 4.32 (br, 1.6, C*H* allylic), 4.01 (br, 0.8, C*H* allylic), 1.48 (s, 3, C*H*$_3$), 1.22 (s, 3, C*H*$_3$), 0.98 (s, C*Me*$_3$ end group). ^{13}C NMR (DMSO-d_6): δ 131.6 (br, *C*H=CH), 130.8 (br, *C*H=CH), 76.8, 75.7, 72.8, 26.0 (*C*H$_3$), 25.2 (*C*H$_3$), 25.1 (*C*H$_3$), 22.2 (*C*(CH$_3$)$_2$).

Acknowledgment. R.R.S. thanks the Office of Naval Research (Grant N00014-89-J1542) for research support, and G.C.B. thanks the NSERCC for a Predoctoral Fellowship. We thank Dr. William M. Davis for collecting the data for **2b** and **5a** and M. B. O'Regan for her efforts to refine the structure of **5a**.

Supplementary Material Available: A complete textual presentation of the NMR data, a labeled ORTEP drawing, and tables of final positional parameters and final thermal parameters (9 pages); a listing of observed and calculated structure factors for **2b** (32 pages). Ordering information can be found on any current masthead page.

---

(29) Newman, M. S.; Addor, W. *J. Am. Chem. Soc.* **1955**, *77*, 3789.