CH_2SiMe_3), 7.88 (CH_2Si), 4.60 ($Si(CH_3)_3$), 3.77 (*cis*-$CH_2Si(CH_3)_3$), −0.03 ($Si(CH_3)_3$). MS (EI, 70 eV) $M^+ - CH_3$ 637, $M^+ - CH_2SiMe_3$ 565, $M^+ - C(CMe_3)CH_2SiMe_3$ 482; MS (EI, eV) $M^+ - CH_2SiMe_3$ 565, ($M^+ - C(NCMe_3)CH_2SiMe_3$) 482, $(C(NCMe_3)(CH_2SiMe_3)_2)^+$ 257, $(C(NCMe_3)CH_2SiMe_3)^+$ 170, $(NCH(CH_2SiMe_3)^+$/114. Anal. Calcd for $C_{21}H_{56}N_2OsSi_4$: C, 40.58; H, 8.67; N, 4.30. Found: C, 38.26; H, 7.94; N, 4.06.

Reaction of $Os(NCH_3)(CH_2SiMe_3)_4$ with HCl. A solution of $Os(NMe)(CH_2SiMe_3)_4$ (4 mg, 0.007 mmol) in C_6D_6 (0.6 mL) was prepared and placed in a NMR tube. One equivalent of HCl gas (0.17 mL, 0.007 mmol) was injected. Proton NMR spectra were taken periodically as reaction proceeded. By NMR 1 equiv of $SiMe_4$ was observed for every equivalent of $Os(NMe)(CH_2SiMe_3)_3Cl$ produced. $Os(NMe)(CH_2SiMe_3)_3Cl$: ^1H NMR (200 MHz, C_6D_6, 16.5 °C) δ 4.527 (d, J = 5.6, 2 H, *cis*-$OsCH_2$), 4.489 (s, 2 H, $OsCH_2$), 4.178 (d, J = 5.6, 2 H, *cis*-$OsCH_2$), 1.260 (s, 3 H, $OsNCH_3$) 0.175 (s, 18 H, *cis*-$Si(CH_3)_3$), 0.045 (s, 9 H, $Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6, 20.0 °C) δ 52.10 (*cis*-$OsCH_2$), 50.96 ($OsNCH_3$), 28.31 ($OsCH_2$), 2.96 ($CH_2Si(CH_3)_3$), 2.37 (*cis*-$CH_2Si(CH_3)_3$). $SiMe_4$: ^1H NMR (200 MHz, C_6D_6, 16.5 °C) δ −0.010 (s). The assignment of the $SiMe_4$ peak was verified by injecting small amounts of $SiMe_4$ into the sample.

Reaction of $Os(O)(CH_2SiMe_3)_4$ with Electrophiles, General Procedure. A solution of $Os(O)(CH_2SiMe_3)_4$ (11 mg, 0.020 mmol) in C_6D_6 (0.6 mL) was prepared and placed in an NMR tube. One equivalent of reactant was added, and an NMR was taken. The sample was allowed to sit for 4–5 h and then heated at 70 °C for 2–3 h, and the NMR study was repeated. Alternately a larger amount of electrophile would be added, and the above procedure was repeated. The following electrophiles were tested: $BF_3{\cdot}O(CH_3)_2$, $CH_3OSO_2CF_3$, $(CH_3)_3SiOSO_2CF_3$, HCl(g), $[(CH_3)_3O][BF_4]$, and CH_3I.

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Living Ring-Opening Metathesis Polymerization of 2,3-Difunctionalized Norbornadienes by $Mo(CH\text{-}t\text{-}Bu)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(O\text{-}t\text{-}Bu)_2$

G. C. Bazan,[†] E. Khosravi,[‡] R. R. Schrock,*[,†] W. J. Feast,*[,‡] V. C. Gibson,[‡] M. B. O'Regan,[†] J. K. Thomas,[†] and W. M. Davis[†]

Contribution from the Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, UK. Received February 28, 1990

Abstract: Benzonorbornadiene (**1**), 2,3-dicarbomethoxynorbornadiene (**2**), and 2,3-bis(trifluoromethyl)norbornadiene (**5**) can be polymerized by $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ (Mo(CH-*t*-Bu)) in a well-behaved living manner to give essentially monodisperse homopolymers. Poly-**2** and (especially) poly-**5** are highly trans and are believed to be tactic. The rate of polymerization of **2** is approximately 30 times faster than that of **5** at room temperature, a factor of approximately 10 of which can be ascribed to the lower reactivity of **5** relative to **2**, and the remainder to the lower reactivity of living poly-**5** relative to living poly-**2**. 7-Isopropylidene-2,3-dicarbomethoxynorbornadiene is not polymerized at all by Mo(CH-*t*-Bu), although it does react with Mo(CH-*t*-Bu) to give an isolable "first insertion product" (**4**) about 500 times more slowly than **2** reacts with Mo(CH-*t*-Bu). An X-ray structure of **4** shows it to be a pseudo-tetrahedral species containing a syn alkylidene ligand (substituent pointing toward the imido nitrogen atom), one face of which is blocked by the isopropylidene group and the other face of which is blocked by a carbomethoxy group. (Crystal data for **4** are a = 13.64 (1) Å, b = 17.414 (5) Å, c = 17.64 (1) Å, V = 4130 (5) Å^3, β = 99.84 (6)°, space group = $P2_1/n$, Z = 4, M_r = 735.85, ρ = 1.183 g/cm^3, μ = 3.48 cm^{-1}, R_1 = 0.047, and R_2 = 0.064.) **5** reacts with W(CH-*t*-Bu) to give an isolable square-pyramidal metallacycle at a rate that is second order overall and for which $\Delta S^\ddagger = -40$ eu. (Crystal data for **6** are a = 12.268 (8) Å, b = 18.436 (3) Å, c = 16.08 (1) Å, β = 94.63 (3)°, V = 3624 (5) Å^3, space group = $P2_1/n$, Z = 4, M_r = 803.62, ρ = 1.473 g/cm^3, μ = 33.12 cm^{-1}, R_1 = 0.067, and R_2 = 0.074.) The imido group is in an apical position in this metallacycle with the *tert*-butyl group in the WC_3 ring pointing toward the imido nitrogen atom and the monomer away from it (a trans metallacyclic ring). This metallacycle rearranges to give the "first insertion product" in a first-order manner for which $\Delta S^\ddagger = -3$ eu.

Introduction

Complexes of the type $M(CHR)(NAr)(O\text{-}t\text{-}Bu)_2$ (M = W[1] or Mo;[2] NAr = $N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$) are relatively inactive for metathesis of ordinary internal olefins, but will effect living ring-opening metathesis polymerization (living ROMP[3]) of mono- and polycyclic olefins.[4] Both Mo and W initiators (and related more active species containing more electron-withdrawing alkoxide ligands[1]) are now available via relatively direct high yield syntheses of versatile precursors of the type $M(CHR)(NAr)(triflate)_2(dme)$ (R = CMe_3 or CMe_2Ph; M = W[1b] or Mo[2b]). *tert*-Butoxide initiators that contain molybdenum are potentially the most in-

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[‡] Durham University.

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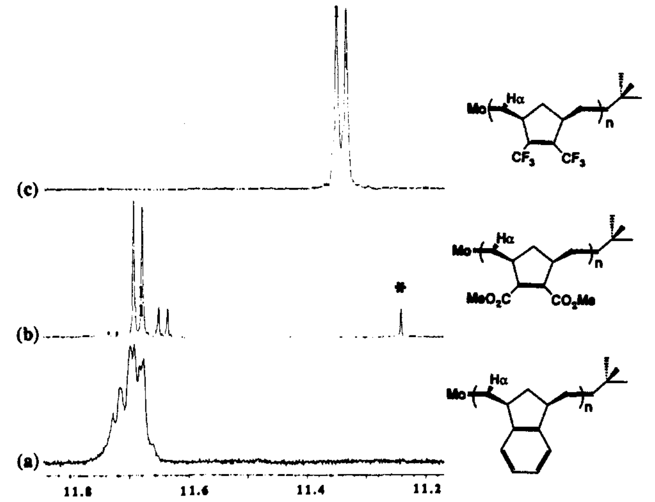
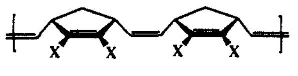


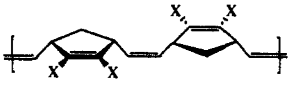
Figure 1. Proton NMR (alkylidene region) of (a) polybenzonorbornadiene (20 equiv); (b) poly-**2** (20 equiv); (c) poly-**5** (20 equiv). Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ is indicated with an asterisk.

teresting since molybdenum appears to tolerate functionalities more than tungsten.[4c,5]

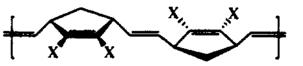
2,3-Disubstituted norbornadienes are convenient monomers for a detailed study of ring opening for several reasons. First, the only stereochemistry possible in the polymer is either a cis or a trans configuration about the double bond formed upon ring opening, or meso or racemic dyads depending upon whether the chiral allylic carbons on either side of chain vinylenes have the same configuration (racemic dyads, syndiotactic polymer) or opposite configuration (meso dyads, isotactic polymer). Head/tail, tail/tail, and head/head regiochemistries are encountered if the monomer is not symmetrically substituted. Therefore only four possible primary structures for polymers made from such symmetric norbornadiene monomers are possible and are illustrated below. (Analogous relatively simple primary structures can be



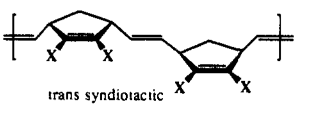
cis isotactic



cis syndiotactic



trans isotactic



trans syndiotactic

obtained by using pure cis-exo- or cis-endo-disubstituted norbornenes, although purification of all endo or all exo monomers can be tedious.) Second, several 2,3-disubstituted norbornadienes can be prepared readily and steric and electronic properties thereby varied to a significant degree in a family of closely related polymers. Third, the substituted double bond should not be attacked for steric reasons. What we will present here is the first of a series of studies aimed at elucidating the reactions of norbornene-like monomers with catalysts that are relatively inactive for the metathesis of ordinary internal olefins. Part of this work has appeared in a preliminary communication.[5]

Table I. GPC Characterization of Polymers Prepared by Using Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ as the Catalyst at 22 °C[a]

monomer	equiv	time, h	M_n calcd	M_n found	PDI
1	100	0.5	14360	23267	1.04
	200	0.5	28560	44690	1.05
	500	0.5	71160	132176	1.09[b]
2	100	0.5	20980	12430	1.04
	200	0.5	41800	19250	1.07
5	51	4.5	11700	7740	1.07
	102	4.5	23220	15060	1.05
	202	4.5	46090	27130	1.05
	153	18	34880	32900	1.05
	257	24	58660	56350	1.04
	723	24	164900	152150	1.04

[a] Capped with pivaldehyde. M_n values versus polystyrene. [b] High MW shoulder present.

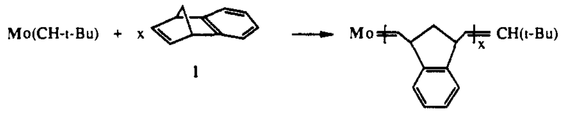
Table II. Rate Constants for Polymerization at 22 °C

monomer	k_p/k_i	k_p, M^{-1} s^{-1}	k_i, M^{-1} s^{-1}
1	7.0 (5)		
2	30 (3)	2 (1)	0.7 (3)
3	~0	~0	0.0013 (1)
5	0.72 (5)	0.057 ± 0.007	0.08 (1)[a]

[a] Rate of tungstacycle (**6**) formation = 0.20 (1).

Results

Benzonorbornadiene. Benzonorbornadiene (**1**) reacts smoothly and very rapidly with Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ to yield the living oligomers shown in eq 1 (Mo(CH-*t*-Bu) = Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$). For relatively small x (e.g. $x < 30$) the



(1)

reaction can be followed conveniently by proton NMR. The alkylidene resonance at 11.23 ppm in Mo(CH-*t*-Bu) is replaced by a relatively complex set of alkylidene resonances further downfield for the living oligomers (Figure 1). It was not possible to distinguish the resonance(s) for the oligomers in which x has a specific value, as is the case for other monomers to be discussed below. The fact that the resonance is complex even when x is large is also peculiar in view of the relative simplicity of the resonance(s) for large oligomers described below. A plausible explanation is that when a flat ring is present H$_\alpha$ is sensitive to the cis or trans configuration of at least the next double bond in the chain, and two different alkylidene rotamers (see below) are present.

A value for the ratio of the propagation rate constant to the initiation rate constant, k_p/k_i (r; Table II) can be obtained by measuring how much neopentylidene initiator remains upon addition of a few equivalents of monomer[6] (see Experimental Section for details); r was found to be 7 ± 0.5 (Table II). A significant error arises from the fact that the reaction is rapid and mixing is not instantaneous. The value for k_p/k_i is expected to be >1 because a complex containing the neopentylidene ligand should be less reactive than that containing the alkylidene ligand formed upon opening the C(5)/C(6) double bond in benzonorbornadiene. The percentage trans double bonds is 76% judging from the ratio of the resonances for trans and cis olefinic protons (at 5.64 and 5.57 ppm in CDCl$_3$) or methine protons adjacent to trans and cis double bonds (at 5.10 and 5.05 ppm). The reaction is too fast to measure either k_p or k_i directly at 25 °C by routine techniques.

The polymers or oligomers can be cleaved off the metal with benzaldehyde or pivaldehyde in a smooth and quantitative Wittig-like reaction (eq 2). Mo(O)(NAr)(O-*t*-Bu)$_2$ can be observed in solution, but it decomposes upon attempted isolation. It is not possible to determine the degree to which the terminal double bond

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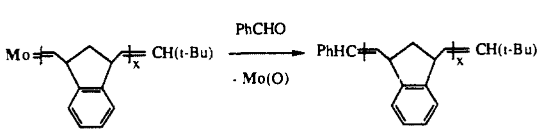


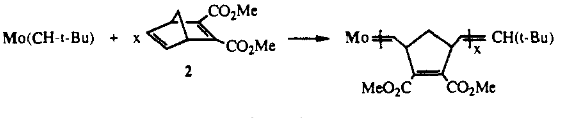
(2)

is all trans in this case for experimental reasons, although it is usually highly trans, and sometimes all trans, as in the case of *exo,exo*-2,3-dicarbomethoxynorbornene, for example.[7] GPC analysis of the polymers prepared in which x is as large as 500 showed them to have polydispersities of ~1.05 (Table I). Such narrow polydispersities are not inconsistent with a value of $k_p/k_i = 7$. Polydispersities for polymers containing several hundred monomer units can be as low as 1.05 even when k_p/k_i is as high as 100.[6]

Carbon NMR studies reveal a complex set of overlapping olefinic carbon resonances near 134 ppm, consistent with the presence of carbons in cis and trans vinylene units with chemical shifts further affected by the geometry of neighboring double bonds, and possibly also racemic and meso dyads. These data convincingly show that ring opening of **1** is not stereoselective, as already can be concluded on the basis of proton NMR data.

Polybenzonorbornadiene, with a degree of polymerization of up to 500, is soluble in toluene or dichloromethane, and except for its expected sensitivity to oxygen,[8] it is well-behaved. (Polybenzonorbornadiene prepared with use of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$[9] is similar to that reported here, except that it is only 70% trans, consistent with what in general seems to be a lower stereoselectivity and higher reactivity of a well-defined W catalyst versus an analogous Mo catalyst.) These properties contrast with those reported by Grubbs[10] for polybenzonorbornadiene prepared with a titanium catalyst, where insolubility became a limiting factor when fewer than 10 equiv of benzonorbornadiene had been polymerized. Benzonorbornadiene also has been polymerized by classical catalysts (e.g., $WCl_6/SnMe_4$).[8] However, broad molecular weight distributions and partial solubilities were ascribed (in part) to oxidation of the polymer in air. In contrast, the polybenzonorbornadiene made here has a low polydispersity and contains ≥99% carbon and hydrogen. Therefore, it would appear that polymerization of **1** by Mo(CH-*t*-Bu) (and W(CH-*t*-Bu)[9]) is the most successful synthesis of polybenzonorbornadiene. In general complications may arise in part from the fact that the tertiary proton in the polymer is both allylic and benzylic. Use of Mo(CH-*t*-Bu), a relatively mild reagent, may minimize such complications.

Dicarbomethoxynorbornadiene. The simplicity of the alkylidene proton NMR resonances observed in a reaction between 2,3-dicarbomethoxynorbornadiene[11] (**2**) and Mo(CH-*t*-Bu) in C_6D_6 contrasts markedly with the complex pattern observed in the reaction involving **1**. Only two new alkylidene proton resonances ultimately are observed at a field strength of 500 MHz, two doublets in a ratio of approximately 5:1 at 11.694 and 11.652 ppm (Figure 1b). Another 5:1 set of alkylidene proton doublets appears first when 1 equiv of **2** is added and disappears as more monomer is added. They can be ascribed to the first insertion product ($x = 1$ in eq 3). From data like those shown in Figure 1b it can be determined that $k_p/k_i \approx 3$ for this monomer. The main question is why *two* resonances are associated with the living oligomer. W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$[1b] and W(CHPh)(NAr)[OCMe(CF$_3$)$_2$]$_2$[1a] have been shown to be pseudo-tetrahedral species in which the alkylidene substituent points toward the imido nitrogen atom (the syn isomer below), but formation of an anti rotamer would also seem to be possible. (Formation of a pseudo-triple metal–imido bond is known to force the alkylidene's β-carbon atom and α-hydrogen atom to lie in the N–M–C$_\alpha$ plane.[12]) In fact, there is evidence for syn and anti rotamers in several systems, especially as the size of R (or the alkoxide) becomes smaller than a *tert*-butyl group.[1b,2b] Therefore we ascribe one resonance in the spectra of the living oligomers to the syn rotamer of the living oligomer and the other resonance to the anti rotamer. Unfortunately NOE experiments have not been conclusive, and we therefore cannot tell which is which. The ^{13}C NMR spectrum of living poly-**2** shows that $J_{CH} = 130$ Hz for the alkylidene resonance of the major rotamer and $J_{CH} = 123$ Hz for the minor rotamer. Data for other alkylidene complexes suggest that J_{CH} for the syn rotamer is lower than that for the anti rotamer, although again the data are not extensive. If this rule holds true then the major rotamer in this case is anti.



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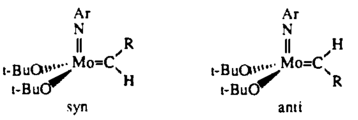

Other explanations of the NMR results were considered. One alternative explanation is that the minor resonance is ascribable to a living oligomer in which the configuration about the first C=C bond in the chain (after the Mo=C bond) is cis instead of trans. However, carbon NMR spectra (see below) suggest that double bonds in the polymer are between 90 and 95% trans. Also, formation of exclusively a trans *tert*-butyl-substituted double bond as a result of the first insertion reaction is a feature of all known ring-opening reactions with catalysts of this type,[4f] so two alkylidene resonances should not be observed in the first insertion product ($x = 1$). Another alternative explanation is that a double bond somewhere in the polymer chain is coordinated to the metal and thereby leads to formation of two isomers. Although interactions of that nature have been proposed for classical ROMP initiators,[13a] there is no hard evidence that supports such proposals, and in any case such interactions seem unlikely in a well-defined "deactivated" catalyst of the type discussed here in which the metal center is sterically congested. The possibility that binding of the carbonyl group of the ester gives rise to isomers also does not seem likely for two reasons. The first is that propagation is fast (see below). One would expect intramolecular coordination via the carbonyl oxygen to block propagation to a significant degree. Secondly, IR spectra of the living oligomers in the ν_{CO} region show no evidence of any shifted C=O absorption, and in fact are identical with those of a structurally characterized monoinsertion product (see below) in which no carbonyl group is bound to the metal.

The ^{13}C NMR spectrum of poly-**2** can be fully assigned (Figure 2; see experimental section). The major resonances for poly-**2** are analogous to those observed for all trans poly-**5** (see below; Figure 4b), while other resonances are analogous to those observed for atactic poly-**5** (Figure 4a). Therefore poly-**2** is largely (estimated 90–95%) trans.

We have determined k_p for the polymerization of **2**, although that cannot be done very accurately because the reaction is so fast. Several determinations by NMR (two) and gas chromatography (three) indicate that $k_p = 2 \pm 1$ M^{-1} s^{-1} at 22 °C. Since $k_p/k_i = 3 \pm 0.3$, $k_i \approx 0.7 \pm 0.3$ M^{-1} s^{-1} for **2** when the initiator is Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (Table II).

Addition of excess benzaldehyde to the living polymer of **2** (x_{avg} up to 200) gives virtually monodisperse poly-**2** (Table I).

7-Isopropylidene-2,3-dicarbomethoxynorbornadiene. 7-Isopropylidene-2,3-dicarbomethoxynorbornadiene[14] (**3**) was employed in order to explore the influence of a substituent at the 7-position.

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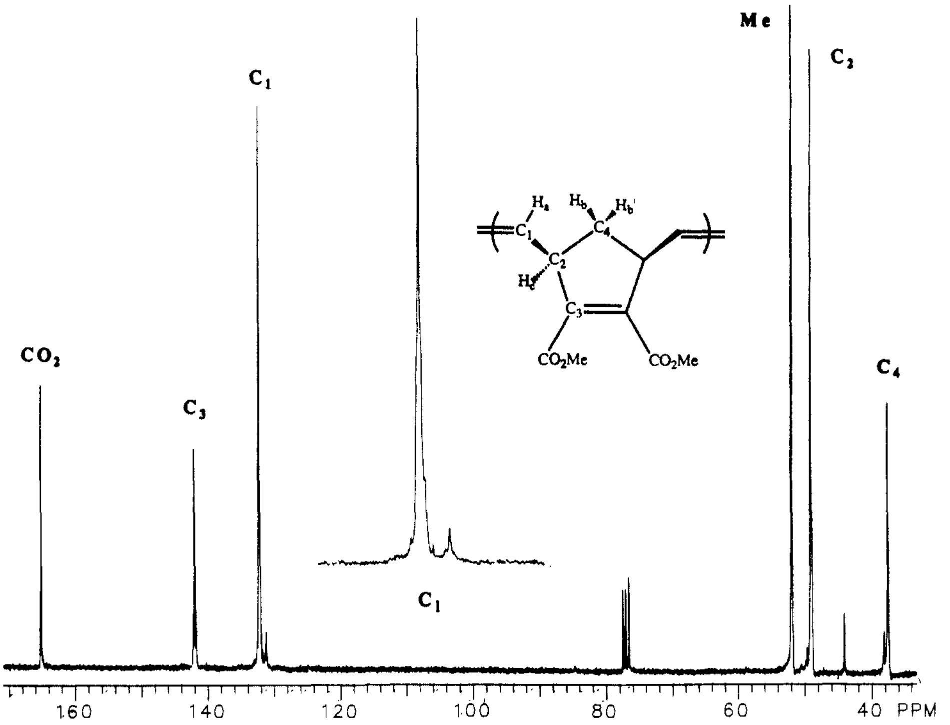
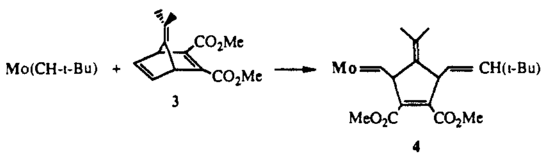


Figure 2. Carbon NMR spectrum of poly-2.

3 reacts very slowly with Mo(CH-*t*-Bu) at 25 °C. In fact the reaction must be heated to 45–55 °C in order that all of the initiator is consumed in a few hours. Only *one* new alkylidene resonance is observed that can be assigned to the alkylidene resonance in one rotamer of the first insertion product (4, eq 4).



(4)

Since only 1 equiv of monomer is consumed, even at 55° over a period of several hours, $k_p \approx 0$. Therefore the "initiation" can be studied directly. The reaction shown in eq 4 was found to be first order in Mo(CH-*t*-Bu) and 3 with $\Delta H^{\ddagger} = 15.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -18$ eu and k_{calc} (22 °C) = 1.3×10^{-3} M^{-1} s^{-1} (Table II; see Experimental Section for details). Therefore 3 reacts ~500 times more slowly than 2 at 22 °C, a difference that must be ascribed to steric factors. The "new" alkylidene ligand in 4 must be significantly larger than a neopentylidene ligand in order that 3 virtually does not react with 4. It should be noted that 4 *will* react with norbornene to give polynorbornene, but k_p/k_i was found to be ~270 by the NMR method mentioned earlier; one might expect living polynorbornene to be much more reactive than 4.

The "first insertion product" (4) can be isolated and completely characterized. Proton and carbon NMR details can be found in the Experimental Section. According to proton and carbon NMR spectra only one rotamer is present (>98%).

An X-ray study of 4 reveals it to have the structure shown in Figure 3. (Relevant bond distances and angles can be found in Table III.) Its basic structure is pseudo-tetrahedral in which the alkylidene ligand adopts the syn conformation. Bond lengths and angles are similar to those found for W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$[1b] and W(CHPh)(NAr)[OCMe(CF$_3$)$_2$]$_2$[1a] and therefore will not be discussed in detail. The plane of the phenyl ring of the virtually linear imido ligand contains the Mo–O(1) bond and approximately bisects the O(2)–Mo–C(1) angle. The *tert*-butyl group containing C(3) therefore is forced down and away from the isopropyl group containing C(261) that points toward it. The isopropyl group containing C(221) occupies the space between and above O(2) and C(1). Therefore the *tert*-butyl group containing C(4), and C(11) of the alkylidene ligand, can turn up around it. The very bulky substituted C$_5$ ring in the alkylidene ligand turns away from the imido ligand. Consequently the isopropylidene group more or less occupies the region on one side of the Mo=C(1) bond, while a carbomethoxy group occupies the region on the other side of the Mo=C(1) bond. The configuration about the C(131)–C(132) bond is trans, as expected.

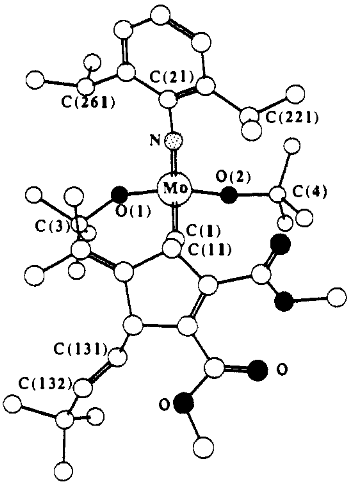
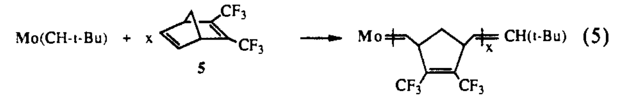


Figure 3. View of the product of the reaction between Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and 7-isopropylidene-2,3-dicarbomethoxynorbornadiene.

Table III. Selected Intramolecular Distances (Å) and Angles (deg) Involving the Non-hydrogen Atoms in 4

Mo–N	1.731 (4)	N–Mo–O(2)	116.8 (2)
Mo–O(2)	1.873 (3)	N–Mo–O(1)	114.6 (2)
Mo–O(1)	1.873 (3)	N–Mo–C(1)	100.2 (2)
Mo–C(1)	1.880 (4)	O(2)–Mo–O(1)	107.0 (1)
C(1)–C(11)	1.522 (5)	O(2)–Mo–C(1)	108.5 (2)
C(12)–C(121)	1.326 (6)	O(1)–Mo–C(1)	109.4 (1)
C(131)–C(132)	1.291 (6)	Mo–O(1)–C(3)	147.9 (3)
C(14)–C(15)	1.336 (6)	Mo–O(2)–C(4)	154.8 (4)
		Mo–N–C(21)	171.7 (3)
		Mo–C(1)–C(11)	140.0 (3)

2,3-Bis(trifluoromethyl)norbornadiene. 2,3-Bis(trifluoromethyl)norbornadiene[15] (5) reacts smoothly with Mo(CH-*t*-Bu) to give living oligomers (eq 5; Figure 1c; see also ref 5). Only one alkylidene resonance is observed for the first insertion product, although another might be hidden among the complex set of resonances in that region for the α-proton in each living alkylidene complex up to $x = 4$.[5] For $x > 4$ all alkylidene resonances overlap



(5)

to give a typical broadened doublet alkylidene resonance (Figure 1c). A shoulder can be observed in the 500-MHz ^{1}H spectrum on the doublet for $x \geq 10$ that does not disappear upon addition of more monomer. Resolution enhancement[5] shows that the ratio of the two resonances is ~1:6. These resonances can be ascribed to the syn and anti rotamers of the living alkylidene complexes, although again we cannot say with certainty which is which. The proton-decoupled carbon NMR spectrum of the living oligomer where $x = 10$ is consistent with this proposal in that two carbon resonances in a ratio of ~1:6 are observed at 253.1 and 252.6 ppm, respectively. The relatively low solubility of poly-**5** prevented a determination of J_{CH} for the minor isomer in a gated experiment, so J_{CH} values could not be correlated with the resonances observed.

The ratio of k_p to k_i for polymerization of **5** was shown to be 0.72, i.e., **5** reacts *more* slowly with the new alkylidene complex than it does with the neopentylidene initiator. The rate of polymerization of **5** ($k_p = 0.057 \pm 0.007$ M^{-1} s^{-1}) also is between 15 and 50 times slower than that of **2**. From these data we conclude that $k_i = 0.08 \pm 0.01$ M^{-1} s^{-1}, i.e., **5** is about an order of magnitude less reactive than **2** (k_i for **2** = 0.7 M^{-1} s^{-1}) toward Mo(CH-*t*-Bu). If the lower reactivity of **5** can be ascribed to an electronic deactivation of the unsubstituted double bond in **5**, then the living alkylidene made from **5** is also likely to be deactivated as a nucleophile. The difference in the reactivity of the living alkylidenes made from **2** and **5** toward norbornene can be assessed by measuring k_p/k_i for each, where $k_{i(2)}$ is the rate of reaction of living **2** with norbornene, and $k_{i(5)}$ is the rate of reaction of living poly-**5** with norbornene; note that k_p should be the same for both since this represents the reactivity of living polynorbornene with norbornene. We find that $k_p/k_{i(2)} = 4.8$ and $k_p/k_{i(5)} = 10.2$ so that $k_{i(2)}/k_{i(5)} \approx 2$, i.e., living poly-**2** reacts approximately twice as fast with norbornene as living poly-**5** at 22 °C. The CF$_3$ group is somewhat more electron withdrawing than the CO$_2$Me group and therefore deactivates the nucleophilic alkylidene carbon atom to a slightly greater extent. The difference would probably be accentuated in a reaction involving monomers larger than norbornene (i.e., **2** and **5**), so a difference in the rate of polymerization of **2** and **5** of greater than 20 might be expected (15–50 is found). These findings are also consistent with the fact that $k_p/k_i = 0.75$ for polymerization of **5**; living poly-**5** is deactivated toward further reaction with **5** for (two) electronic reasons, but Mo(CH-*t*-Bu) is relatively unreactive for steric reasons. The two effects are approximately equivalent so a k_p/k_i of ca. 1 is observed.

Virtually monodisperse poly-**5** (see Table I) is produced upon adding pivaldehyde (or benzaldehyde) to living poly-**5**. Carbon NMR spectra of poly-**5** (~1:1 cis:trans) obtained by using WCl$_6$/SnMe$_4$ show two vinylene carbon resonances, two methine carbons, and a partially resolved multiplet for the methylene carbon. In the original spectra[15] each vinylene resonance is resolved into two resonances, the methylene resonance is resolved into at least five components, and the methine carbon line widths are broad. In contrast the carbon NMR spectrum of poly-**5** prepared by using Mo(CH-*t*-Bu) (Figure 4b) contains only sharp resonances that can be assigned to an all trans form (~98%), which is consistent with the tendency for this catalyst to form predominantly trans polynorbornene. The resonances for residual cis poly-**5** (~2%) can barely be observed. The origin of the multiple resonances observed in the spectra described earlier cannot be defined unambiguously, but it is certain that multiple resonances arise as a consequence of cis/trans and/or meso/racemic dyad sequence effects. It is our opinion that the five resonances observed for the methylene carbon atom in poly-**5** prepared by using WCl$_6$/SnMe$_4$ are best explained in terms of meso/racemic splittings of the three resonances (cc, ct, and tt) expected as a result of adjacent vinylene effects, rather than as an effect due to the next nearest vinylenes. The influence of CF$_3$ units four bonds distant from the methylene in question is likely to be greater than the effect of a vinylene six bonds away; the CF$_3$ units also are much closer in space to the methylene in question. On this basis we assigned an atactic microstructure to the material prepared previously and, by analogy, the simple spectrum and narrow line widths observed for poly-**5** produced in this work are consistent with it being a highly tactic polymer. At this stage we are unable to say whether it is trans,syndiotactic or trans,isotactic, but the remarkably high value for the dielectric constant above T_g (see later) would appear favor a trans,syndiotactic microstructure.

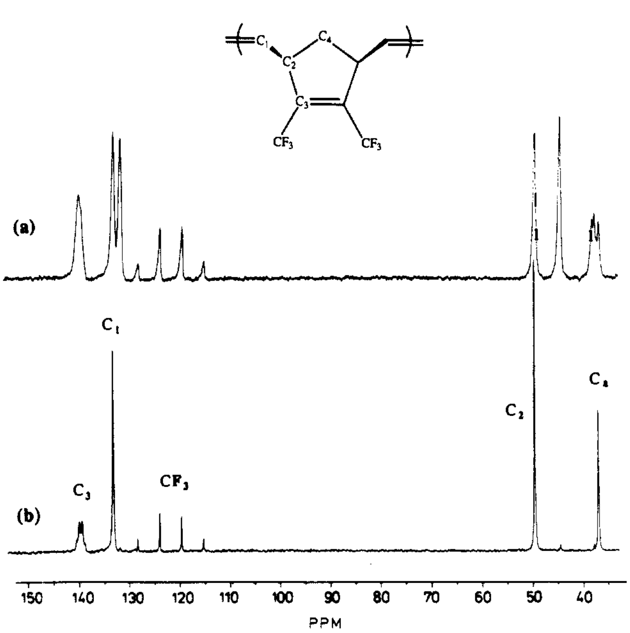
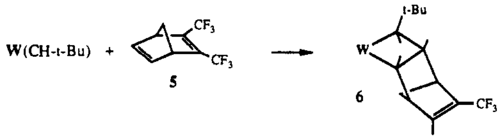


Figure 4. Carbon NMR spectrum of poly-**5** prepared with use of (a) WCl$_6$/SnMe$_4$; (b) Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$.

The Formation, X-ray Structure, and Decomposition of a Tungstacyclobutane Complex Containing 5. It was noted in the preliminary communication[5] that W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ would not polymerize **5** to give homopolymers with low PDIs. Therefore this reaction was examined in detail in an attempt to determine why this is the case.

Addition of **5** to W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ at 0 °C in toluene-d_8 yields a new species quantitatively whose proton and carbon NMR data are consistent with it being a square-pyramidal tungstacyclobutane complex (**6**, eq 6). Resonances for one H$_\alpha$ proton can be observed at 2.23 ppm and the H$_\beta$ proton at 2.77 ppm, while a COSY experiment located the other H$_\alpha$ proton resonance at 1.17 ppm. Square-pyramidal metallacycles such as W[CH$_2$CH(*t*-Bu)CH$_2$](NAr)[OCMe$_2$(CF$_3$)]$_2$ have been observed;[16] its ring proton resonances are found at 1.12 (H$_\alpha$) and 2.36 ppm (H$_\alpha$) and 2.62 ppm (H$_\beta$). A structural study showed that H$_\beta$ points toward the axial imido ligand, i.e., the *tert*-butyl group is located in a pseudo-equatorial position. In another structurally characterized square-pyramidal tungstacyclobutane complex, W[CH(*t*-Bu)CH$_2$CH(CO$_2$Me)](NAr)[OCMe$_2$(CF$_3$)]$_2$, prepared by adding methyl acrylate to W(CH-*t*-Bu)(NAr)-



(6)

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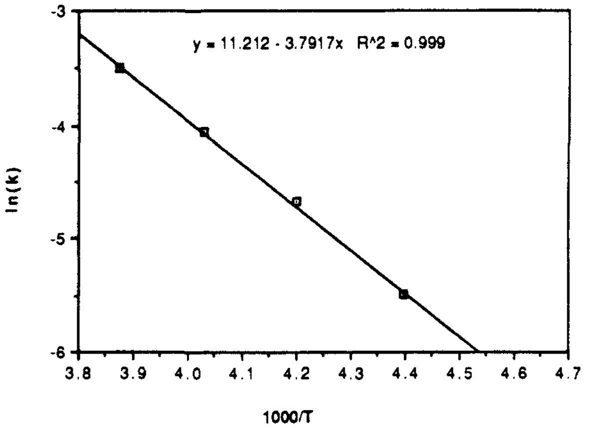


Figure 5. Arrhenius plot for formation of **6**.

$[OCMe_2(CF_3)]_2$, the α-*tert*-butyl group is in a pseudo-equatorial position and the α-carbomethoxy group is in a pseudo-axial position.[17] The resonance for the α-proton near the *tert*-butyl group is found at 1.98 ppm, that for the axial β-proton is found at 2.71 ppm, and that for the equatorial α-proton is found at 2.39 ppm. Therefore the proton NMR data for **6** are consistent with the structure shown in eq 6 in which the imido ligand is on the same side of the WC_3 ring as the *tert*-butyl group. Resonances for the ring carbon atoms in the carbon NMR spectrum of **6** would have to be assigned by using 2D techniques since five doublets are found in the region where one would expect to find resonances for the ring carbon atoms (20–50 ppm[17]). Metallacycles containing norbornene have been observed in other systems.[3,18,19]

The formation of **6** was found to be second order with $\Delta H^\ddagger = 6.6$ kcal mol^{-1} and $\Delta S^\ddagger = -40$ eu over a temperature range of 40 °C (see Experimental Section and Figure 5). At 22 °C the rate constant for formation of **6** is calculated to be 0.20 M^{-1} s^{-1}. This value should be compared to $k_i = 0.08$ M^{-1} s^{-1} for the reaction between Mo(CH-*t*-Bu) and **5**. We can conclude that **5** reacts with W(CH-*t*-Bu) approximately 2.5 times faster than it reacts with Mo(CH-*t*-Bu). This is the relative reactivity of W[1] versus Mo[2] complexes that has been suspected on the basis of qualitative observations, although we were somewhat surprised that the difference in rates was not larger. The slower rate of formation of the Mo analogue of **6** must be at least part of the explanation why it cannot be observed.

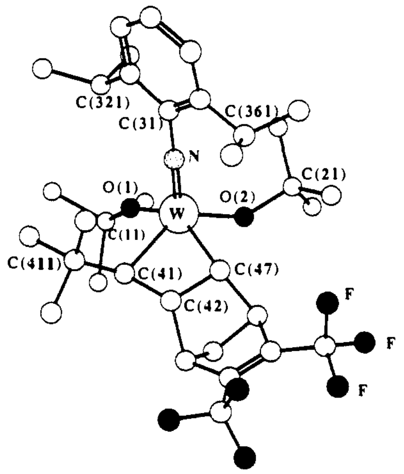


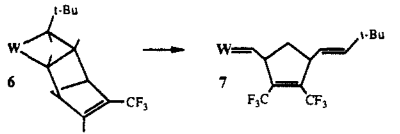
Figure 6. View of the tungstacycle (**6**) made by treating W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ with **5**.

Table IV. Important Bond Distances (Å) and Angles (deg) in **6** (left) Compared with Those in $W(CH_2CH(t\text{-}Bu)CH_2)(NAr)[OCMe_2(CF_3)]_2$ (right)

W–N	1.72 (1)	W–N	1.736 (7)
W–O(1)	1.862 (9)	W–O(1)	1.869 (7)
W–O(2)	1.91 (1)	W–O(2)	1.886 (6)
W–C(41)	2.25 (1)	W–C(21)	2.17 (1)
W–C(47)	2.19 (1)	W–C(23)	2.14 (1)
C(41)–C(42)	1.52 (2)	C(21)–C(22)	1.57 (1)
C(42)–C(47)	1.50 (2)	C(22)–C(23)	1.55 (1)
O(1)–W–O(2)	98.4 (5)	O(1)–W–O(2)	99.6 (3)
C(41)–W–C(47)	64.6 (5)	C(21)–W–C(23)	63 (1)
W–C(41)–C(42)	94.1 (8)	W–C(21)–C(22)	95 (1)
W–C(47)–C(42)	97.5 (9)	W–C(23)–C(22)	97 (1)
C(41)–C(42)–C(47)	104 (1)	C(21)–C(22)–C(23)	93 (1)
W–O(1)–C(11)	157 (1)	W–O(1)–C(3)	164.4 (7)
W–O(2)–C(21)	141 (1)	W–O(2)–C(4)	158.6 (7)
W–N–C(31)	168.5 (9)	W–N–C(11)	167.9 (7)
N–W–O(1)	111.5 (4)	N–W–O(2)	111.7 (3)
N–W–O(2)	115.5 (5)	N–W–O(1)	113.9 (3)
N–W–C(41)	100.3 (5)	N–W–C(21)	99.4 (4)
N–W–C(47)	98.6 (5)	N–W–C(23)	98.4 (3)
C(47)–W–O(2)	84.7 (5)	O(2)–W–C(21)	87.4 (3)
C(41)–W–O(1)	90.9 (4)	O(1)–W–C(23)	89.2 (3)
W–C(41)–C(411)	126 (1)		
W–C(47)–C(46)	118 (1)		
C(47)–W–O(1)	144.4 (5)		
C(41)–W–O(2)	136.1 (4)		

An X-ray study of **6** was carried out at low temperature (Figure 6). It is approximately a square pyramid in which the imido ligand occupies an apical position. Bond distances and angles are very similar to those found in $W[CH_2CH(t\text{-}Bu)CH_2](NAr)[OCMe_2(CF_3)]_2$ (see Table IV). Metal–ligand bond lengths and angles around the metal are not unusual, and the virtually identical long C–C bond lengths in the tungstacyclic ring (1.50 and 1.52 Å) are typical of metallacyclobutane rings that contain other d^0 metals.[20] As expected, **5** has added to the tungsten–neopentylidene bond in the syn rotamer through the more accessible exo face to give the trans tungstacycle. The *tert*-butyl group containing C(411) forces the phenyl ring of the diisopropylphenylimido ligand to turn so that the plane of the phenyl ring contains the W–O(1) bond. The *tert*-butyl group of the *tert*-butoxide ligand containing C(11) is forced down and away from the imido ligand by the isopropyl group containing C(321); the *tert*-butyl group of the other *tert*-butoxide ligand (containing C(21)) can bend up toward the imido ligand. The isopropyl group containing C(361) occupies a significant amount of space above C(47), a fact that virtually eliminates the possibility of forming an analogous cis tungstacyclobutane ring. This structure study provides good evidence that trans metallacycles are formed readily from syn alkylidenes.

The "decomposition" of **6** consists of rearrangement (ring-opening) to give **7** (eq 7). By proton NMR the conversion of **6** to **7** is high if the temperature is kept below ~40 °C (in order to prevent decomposition of **7**). The rate of consumption of **6**



(7)

is cleanly first order with $\Delta H^\ddagger = 22$ kcal mol^{-1} and $\Delta S^\ddagger = -3$ eu, as determined by following the decrease in the resonance for

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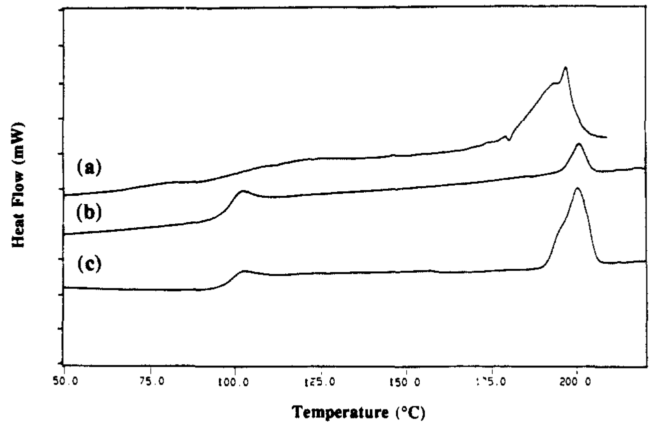

Figure 7. DSC study of stereoregular poly-5 (M_n = 34880 versus polystyrene; PDI = 1.05): (a) as precipitated; (b) melted, quenched, and annealed 2 h at 180°; (c) melted, quenched, and annealed 16 h at 180°.

the β-proton in the WC_3 ring. The fact that 7 is thermally unstable explains the failure of W(CH-*t*-Bu) to smoothly polymerize 5. If the Mo analogue of 6 were to rearrange significantly more rapidly than 6, then since it is formed more slowly than 6, the likelihood of observing it would decrease even further. At this stage there are no data that could be used to support a proposal that molybdacycles rearrange more rapidly than tungstacycles.

In the downfield region of the proton NMR spectrum of 7 an alkylidene H_α resonance first grows in at 8.35 ppm. Another then appears at 9.28 ppm, apparently as a result of conversion of the complex giving rise to the first resonance into the complex giving rise to the second. The two resonances appear to reach an equilibrium ratio for which the upfield (initial) alkylidene resonance dominates (91%). We propose that the two alkylidene resonances can be ascribed to rotamers of 7, and that the rotamer which gives rise to the resonance at 9.28 ppm forms first from 6. If this is true then we would expect the rotamer that forms first to be anti.

Polymer Properties. The contrast between the properties of poly-5 prepared here and those of atactic samples prepared previously[15] is consistent with a highly stereoregular structure. Poly-5 shows behavior that one would expect for a semicrystalline thermoplastic, whereas all earlier atactic samples were amorphous. X-ray diffraction studies on fibers drawn from the melt show evidence of crystalline order and orientation on stretching,[21a] whereas fibers drawn from the melt of atactic poly-5 are weak, cannot be stretched, and show no evidence of order by X-ray diffraction. DSC studies reveal a well-defined T_g at 97 °C and a broad melting endotherm at about 200 °C (Figure 7), the shape and area of which is dependent on sample history. In samples precipitated from solution the T_g transition is not particularly marked and the melting peak shape is consistent with the presence of multiple melting points. In melt-quenched samples the T_g transition is marked and the melting peak area is small. The melting peak area increases on prolonged annealing at 180 °C, a slow ordering process that is consistent with low chain mobility in the solid state. The T_g of poly-5 is a function of the proportion of trans vinylene units (Table V), a fairly typical manifestation of variations in chain microstructure.

Dynamic mechanical thermal analysis of solution-cast films of trans tactic poly-5 and atactic samples prepared by using $WCl_6/SnMe_4$ catalyst confirm the T_g values obtained from DSC. Both tactic and atactic samples show no energy dissipation peaks below T_g, indicating that in the solid state both are relatively stiff polymers with little or no motion below T_g. The plots of loss tangent (tan δ) against temperature are relatively flat with an abrupt change at T_g, consistent with the hypothesis that even in the stereoregular sample the polymer films cast from solution are predominantly amorphous.[22]

Table V. Variation of trans Content with T_g

initiator	trans, %	T_g, °C	T_m, °C
$WCl_6/SnMe_4$	54	125	none
$RuCl_3/SnMe_4$	70	117	none
$MoCl_5/SnMe_4$	87	104	none
Mo(CH-*t*-Bu)	98	97	200

Preliminary dielectric measurements[21b] as a function of temperature and frequency on films of atactic and trans-tactic poly-5 indicate that above T_g the latter has a very much higher dielectric constant (>40) than the former (<14), a fact that appears to require extensive and regular alignment of large dipoles, one that is most consistent with a trans-syndiotactic structure for poly-5 prepared by using Mo(CH-*t*-Bu).

Poly-2 appears to be thermally unstable in air, since the glass transition (~140 °C) does not appear to be reversible. Instability is confirmed by TGA. The polymer begins to decompose at ~200 °C and at 300 °C degrades rapidly.

Discussion

Control over both structure and molecular weight distribution during synthesis is a prerequisite for development of detailed structure–property correlations for any polymer. Classical, multicomponent ROMP initiators have suffered from disadvantages that include limited tolerance of functional groups, lack of molecular weight control, and an element of irreproducibility.[13] Furthermore, these ill-defined catalysts only rarely produce stereoregular polymers.[23] As we have demonstrated here, it is possible to control a polymerization reaction precisely by using a well-defined catalyst that contains bulky alkoxide and imido ligands.

The most important result that requires some discussion is the high stereoselectivity of the polymerization of 2,3-bis(trifluoromethyl)norbornadiene, even though we do not know whether the polymer is isotactic or syndiotactic. In Scheme I is shown one enantiomer of the syn rotamer of the living polymer. (Trifluoromethyl groups and ligand substituents are omitted from much of the scheme for clarity.) The orientation of the cyclopentene ring in the alkylidene ligand in the syn rotamer that is shown is the same as that found in the X-ray structure of 4. It was chosen since it clearly differentiates the two faces of the M=C bond. (Whether this particular orientation is correct or not is not crucial to the argument.) If a molecule of 5 approaches the front face of the M=C bond to give a trans metallacycle, then when the metallacycle opens up the anti alkylidene complex shown must be formed in which the chain has grown in a trans,isotactic fashion. (Note that we have assumed that the core does not rearrange, i.e., the metallacycle does not "flip" relative to the nitrogen atom of the imido ligand, before it opens. That possibility cannot be discounted at this stage.) Rotation about the M=C bond would yield the same enantiomer of the syn isomer that we started with (considering only carbon configurations in the first monomer unit) and the process can be repeated. If a molecule of 5 approaches the back face of the M=C bond to give a trans metallacycle, then an anti alkylidene complex would be formed in which the chain has grown in a trans,syndiotactic fashion. Rotation about the M=C bond would yield the other possible syn isomer and the process can be repeated. Polymerization by the anti rotamer also can lead to either trans,isotactic or trans,syndiotactic polymer, if rotation about the M=C bond is fast relative to the reaction of either rotamer with additional monomer. It seems most plausible that stereoselectivity would arise in a reaction in which rotamers interconvert readily and one rotamer reacts more readily than the other, than in a reaction in which each rotamer must react stereoselectively, and that is the explanation we prefer.

There are two pieces of evidence that suggest that rotation about the M=C bond takes place at a rate that is competitive with the rate of polymerization. Rotation about the M=C bond in com-

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[21] (a) Ward, I. M.; Davies, G. R. Work in progress. (b) Hubbard, H. V. St. A.; Lewis, E. L. V. Work in progress.

[22] We thank Polymer Laboratories, Loughborough for DMTA measurements and I. M. Ward and G. R. Davies for helpful discussions.

[23] Hamilton, J. S.; Ivin, K. J.; Rooney, J. J. *Brit. Pol. J.* **1984**, *16*, 21.

plexes of this type that contain more electron-withdrawing ligands has been found to be in the range of 15–18 kcal mol^{-1}.[1,2] Second, the product of the reaction between Mo(CH-*t*-Bu) and 1 equiv of **2** ($x = 1$; eq 3) consists of both syn and anti rotamers, a result that could be explained in terms of one rotamer being formed initially (presumably the anti rotamer) followed by equilibration of it with the other, at least under the conditions of this particular experiment. If rotation about the M=C bond is fast relative to the rate of reaction of either rotamer with monomer, then the ratio observed by NMR (approximately 6:1 for the living poly-**5**) is a measure of the relative energies of the rotamers. It is interesting to note that if the rate of rotamer interconversion does not vary widely and is of the order of the rate of reaction of monomer with a living alkylidene, then a monomer that reacts very rapidly might not allow enough time for a given rotamer to convert into the other, while a monomer that reacts relatively slowly would allow time for a given rotamer to convert into the other.

A lack of stereoselectivity in a given polymerization reaction could arise in a number of ways. Let's consider first the situation where rotamers interconvert readily: (i) one rotamer reacts faster than the other, but not stereoselectively; (ii) both rotamers react at approximately the same rate, but only one or neither stereoselectively. If rotamers do not interconvert readily relative to the rate of polymerization, then the ratio observed is a measure of their relative reactivities at equilibrium and the reaction involves each rotamer sequentially, the overall rate being determined by the slowest reacting rotamer. In the most complex circumstance where chain growth competes with rotamer interconversion, one might expect stereoselectivity to be sensitive to catalyst and monomer concentration and donor solvent, as well as temperature.

So far we have discussed the polymerization as if a square pyramid is close to the transition state for ring opening. However, that probably is not the case. A square-pyramidal metallacycle simply is the only one that can be observed. It is perhaps more sensible to propose that the first metallacycle is a trigonal bipyramid formed by adding the olefin to a C–N–O face of the pseudo-tetrahedral catalyst. A single Berry-type pseudorotation about equatorial N then yields the observed square pyramid (Scheme II). This square pyramid could then form a new trigonal bipyramidal metallacycle by continuing pseudorotation about N, the one that is required before the ring can open and an anti alkylidene complex formed. This would imply that a square-pyramidal metallacycle could be stabilized if the bulk of the substituents on the ring prevent ready formation of a required TBP species. Conversely, less crowded metallacycles (e.g., those made from benzonorbornadiene) could rearrange readily to alkylidenes largely because the required TBP species could be accessed. Although intermediate TBP and SP metallacyclic species should be significantly distorted from ideality, and pseudorotations therefore not definable as precisely as in ideal cases, it is at least sensible to propose that "square-pyramidal" metallacycles are not those first formed in a reaction between the alkylidene complex and the olefin, and do not open directly to an alkylidene complex. Therefore steric interactions in intermediates closer to the transition state would have to be evaluated in order to draw firm conclusions concerning the precise origin of stereoselectivity.

The situation could be complicated even further since a monomer could approach the C–O–O face to yield a metallacycle if the alkylidene rotates by 90° about the M=C bond. (Approach on the O–O–N face cannot lead to formation of a metallacycle.) It is even possible, although we think not likely, that a given monomer can attack either a C–N–O face *or* the C–O–O face, i.e., that it can be polymerized by two subtly different mechanisms. Such a situation would thwart our attempt to understand and control polymerization reactions in detail. In view of the fact that bulky ligands are present in these catalysts, we favor the hypothesis that only one mechanism is operative (attack on the C–N–O face) and that only one of the two possible rotamers is involved in the stereoselective reaction. Recent studies of acetylene metathesis by a rhenium complex of the type $Re(C\text{-}t\text{-}Bu)(NAr)[OCMe(CF_3)_2]_2$ have suggested that attack on the C–N–O face is preferred.[24]

2,3-Dicarbomethoxynorbornadiene (**2**) is polymerized ~30 times faster than **5**, since **5** is approximately 1 order of magnitude less reactive than **2**, and the alkylidene end of the living polymer made from **5** is several times less reactive than that made from **2**. In the case of 7-isopropylidene-2,3-dicarbomethoxynorbornadiene, steric interactions govern polymerization to such an extent that only the reaction between Mo(CH-*t*-Bu) and monomer takes place at any convenient rate. The isopropylidene and carbomethoxy groups effectively protect both faces of the alkylidene toward reaction with more 7-isopropylidene-2,3-dicarbomethoxynorbornadiene. At the other end of the reactivity range are benzonorbornadiene and norbornene itself.[4a] Both must be too small to give all trans polymer with these particular catalysts.

Evidence is accumulating which suggests that the rate of transforming a metallacyclobutane complex formed in a ROMP reaction into an alkylidene complex is significantly greater when that metallacycle is all cis relative to when that metallacycle is trans. Often the initial metallacycle contains a bulky group (e.g., *tert*-butyl) and therefore is all trans, while subsequent metallacycles are mixtures of cis and trans. That is the case in the reaction between trigonal-bipyramidal *trans*-$Ta[CH_2C_5H_8CH_2CH(t\text{-}Bu)](DIPP)_3$ (DIPP = $2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$) and norbornene;[18] rapid propagation relative to initiation was ascribed to formation of cis metallacycles that opened relatively quickly. Although these metallacycles could not be observed, they take part in formation of more than half the polymer since the cis/trans ratio of double bonds in the resulting polynorbornene is ca. 1. A similar phenomenon was observed in cationic TBP tungstacyclobutane complexes prepared by treating $W(CH\text{-}t\text{-}Bu)(OCH_2\text{-}t\text{-}Bu)_2X_2$ (X = halide) with norbornene in the presence of a halide acceptor; only trans metallacycles could be observed, but propagation was faster than initiation, consistent with the relative instability of all cis metallacycles.[25] Since trans metallacyclobutane complexes are likely to decompose more slowly than cis metallacyclobutane complexes in the case of Mo(CH-*t*-Bu) also, the percentage of trans metallacycle present at any point actually must be much higher than 98%.

To our knowledge, the reaction of W(CH-*t*-Bu) with **5** to give **6** (eq 6) is the first time that the kinetics for formation of a metallacyclobutane complex from a norbornene has been determined. It is interesting also to note that the value for $\Delta S^{\ddagger}$ (−3 eu) for transformation of **6** into **7** (eq 7) is virtually identical with the $\Delta S^{\ddagger}$ value found for loss of olefin from square-pyramidal $W[CH_2CH(t\text{-}Bu)CH_2](NAr)(OAr)_2$ ($\Delta H^{\ddagger} = 19.7\ (4)$ kcal mol^{-1}, $\Delta S^{\ddagger} = -6\ (1)$ eu).[17,26] $\Delta S^{\ddagger}$ values for loss of olefin from three $W[CH_2CH(TMS)CH_2]$ TBP metallacycles have been found to be 11 eu (OR = DIPP), 13 eu (OR = $OCMe(CF_3)_2$), and 23 eu (OR = $OC(CF_3)_2(CF_2CF_2CF_3)$).[26] Therefore $\Delta S^{\ddagger}$ appears to correlate with the geometry of the metallacyclobutane complex. There is one other measurement of the rate of rearrangement of a tungstacyclobutane complex, that made by adding norbornene to $W(CH\text{-}t\text{-}Bu)(OCH_2\text{-}t\text{-}Bu)_2Br_2$ in the presence of $GaBr_3$.[19b] NMR studies suggest that this initial trans tungstacycle has a TBP geometry, but $\Delta S^{\ddagger} = -6$ eu. Therefore any correlation between $\Delta S^{\ddagger}$ and metallacycle geometry may be valid only within a given class of compounds.

Conclusion

We have demonstrated that the initiator $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ allows exceptionally well regulated living ROMP for a series of symmetrically substituted norbornadienes and that substituents in the monomer remote from the site of reaction can have a profound effect on both the rate and stereochemical course of the polymerizations. The Mo initiator tolerates a variety of substituents, and control of polydispersity and tacticity is possible simultaneously. These results suggest that it will be possible to

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(24) Weinstock, I. A.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.*, in press.

(25) Kress, J.; Osborn, J. A.; Ivin, K. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1234.

(26) Feldman, J.; Davis, W. M.; Thomas, J. K.; Schrock, R. R. *Organometallics* **1990**, *9*, 2535.

prepare a variety of homopolymers and block and graft copolymers with well-defined molecular architectures, and since a major objective of polymer synthesis is to control the size and primary structure of a polymer, they represent a significant contribution to available methodology.

Although many questions concerning the mechanism and stereochemistry of ring-opening polymerization in general remain to be answered, we are now in a position of being able to answer some of them. It is interesting to note that although many of those questions now concern what are ostensibly relatively fine mechanistic details, the answers nevertheless may prove crucial to our understanding the factors that control reactivity and stereoselectivity in ROMP reactions.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques. Pentane was washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was distilled from calcium hydride under nitrogen. Tetrahydrofuran was predried over calcium chloride and distilled from sodium benzophenone ketyl under nitrogen. Toluene was distilled from molten sodium and kept over sodium potassium alloy. All deuterated NMR solvents were passed through a column of activated alumina. Benzonorbornadiene,[8] 2,3-dicarbomethoxynorbornadiene,[11] 2,3-bis(trifluoromethyl)norbornadiene,[15] 7-isopropylidene-2,3-dicarbomethoxynorbornadiene,[14] W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$,[1] and Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$[2] were prepared as described in the literature.

NMR data are listed in parts per million downfield from TMS for proton and carbon. Coupling constants are quoted in Hertz. Obvious multiplicities and routine coupling constants usually are not listed. Spectra were obtained in benzene-d_6 at 25 °C unless otherwise noted. Gel permeation chromatographic (GPC) analysis were carried out with use of Shodex KF-802.5, 803, 804, 805, 800P columns, a Knauer differential refractometer, and a Spectroflow 757 absorbance detector on polymer samples 0.1–0.3% w/v in dichloromethane. The GPC columns were calibrated versus commercially available polystyrene standards (Polymer Laboratories Ltd.) ranging from 1206 to 1.03×10^6 MW. Thermal analysis (TGA) was done on a Perkin-Elmer TGS-2 thermogravimetric analyzer. Elemental analysis were performed by using a Perkin-Elmer CHN 2400 Elemental Analyzer.

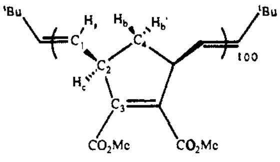
Determination of the Ratio of k_p to k_i. For a reaction in which M is the concentration of monomer, M_0 the initial concentration of monomer, I the concentration of initiator (M(CH-*t*-Bu)), and I_0 the initial concentration of initiator, $M - M_0 = (1 - r)(I - I_0) + rI_0 \ln (I/I_0)$ if $I \neq 0$ and $r = k_p/k_i$.[6] If a given quantity of monomer is added to and polymerized by the initiator then $M \rightarrow 0$ and $M_0/I_0 + r \ln (I/I_0) + (1 - r)(I/I_0 - 1) = 0$. By measuring the amount of remaining initiator (I), r can be determined. Accurate values for k_p/k_i can be determined only when I is significantly less than I_0, but greater than zero. All experiments were done at ~22 °C.

As an example, details of the determination of k_p/k_i for **5** are the following. Approximately 4 mg of **5** (1.9×10^{-5} mol) in C_6D_6 (400 μL) was added at room temperature to a rapidly stirred solution of Mo(CH-*t*-Bu) (10 mg, 2.1×10^{-5} mol) in C_6D_6 (400 μL). After 30 min the number of equivalents of monomer added was determined by integrating the bridgehead methylene proton resonance in the ring-opened monomers (1.8–2.2 ppm) versus the methine proton resonance in the imido ligand (3.8–4.1 ppm). The ratio of I/I_0 was obtained by measuring the ratio of the unreacted neopentylidene to total alkylidene proton resonances. Three determinations gave M_0/I_0 = 1.11, 1.45, 1.07; I/I_0 = 0.283, 0.186, 0.293; and r = 0.72, 0.73, 0.71, respectively.

This method of determining k_p/k_i is not straightforward if the conditions (e.g., a lower temperature) are such that the first, more stable α *tert*-butyl-substituted metallacycle forms as an intermediate. In this circumstance the value of k_p/k_i would depend on the concentration of metal complex in a given experiment.[27]

Polymerization of Benzonorbornadiene (1). A solution of benzonorbornadiene (291 mg, 2.05 mmol) in toluene (3.0 mL) was added dropwise to a rapidly stirred solution of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (10 mg, 0.0205 mmol) in toluene (3.0 mL) and the solution was stirred for 20 min. The polymerization was quenched by addition of 25 μL of pivaldehyde. After 20 min the solution was added to 250 mL of hexane, and the precipitated polymer was isolated by centrifugation, washed with hexane, and placed under vacuum overnight (yield 280 mg, 94% white powder). Anal. Calcd for $C_{1110}H_{1020}$: C, 92.84; H, 7.16. Found: C, 91.42; H, 7.33. Proton and carbon NMR are the same as those reported previously.[8]

Polymerization of 2,3-Dicarbomethoxynorbornadiene (2). A solution of **2** (427 mg, 2.05 mmol) in toluene (5 mL) was added dropwise to a rapidly stirred solution of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (10 mg, 0.0205 mmol) in toluene (5 mL) over a period of 1 min. The color of the solution changed from yellow-orange to red. The living polymer was capped by adding of 25 μL of pivaldehyde and isolated as described above (yield 390 mg; 91%): ^{1}H NMR (CDCl$_3$) δ 5.45 (br, H$_a$), 3.71 (s, CO$_2$C*H*$_3$), 3.52 (br, H$_c$), 2.43 (m, H$_b$ or H$_b$′), 1.47 (m, H$_b$ or H$_b$′), 0.92 (s, CH(C*H*$_3$)$_3$; ^{13}C NMR δ 165.2 (*C*O$_2$CH$_3$), 142.1 (C$_3$), 132.3 (C$_1$, d, J_{CH} = 154), 51.9 (CO$_2$*C*H$_3$, quartet, J_{CH} = 144), 49.0 (C$_2$, d, J_{CH} = 132), 37.6 (C$_4$, t, J_{CH} = 130), 29.5 (C(*C*H$_3$)$_3$); IR (C$_6$D$_6$) cm^{-1} 1722 (s, CO), 1643 (m, CC); see Figure 2.



Polymerization of 2,3-Bis(trifluoromethyl)norbornadiene (5). A solution of **5** (7.71 g, 33.8 mmol) in toluene (10 mL) was added dropwise to a rapidly stirred solution of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (23 mg, 0.047 mmol) in toluene (15 mL) over a period of 50 min. The reaction was stirred for up to 24 h and analyzed by ^{19}F NMR to confirm that no monomer remained. Pivaldehyde (50 μL) was then added. After 30 min the volume of the mixture was reduced to one third of the original and was added dropwise to large volume of vigorous stirred methanol. The polymer precipitated as a white powder which was washed several times with methanol and dried under vacuum for 48 h (yield 7.25 g, 94%): ^{1}H NMR (acetone-d_6, 400 MHz) δ 5.67 and 5.72 (apparent AB quartet, J_{AB} = 14.9), 3.80 (br, allylic H), 2.65 and 2.72 (apparent AB quartet, J_{AB} = 13.6; H$_A$, t, J_{HH} = 9.38; H$_B$, t, J_{HH} = 2.67, methylene protons); ^{13}C NMR (acetone-d_6) δ 140.20 (=*C*CF$_3$), 133.50 (=CH), 122.00 (CF$_3$), 49.80 (CH), 37.20 (CH$_2$); see Figure 4b.

Determination of k_p for 2. The monomer (0.430 g, 100 equiv) in 3.30 mL of C$_6$D$_6$ was added to a rapidly stirred solution of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (10 mg) in 3.30 mL of C$_6$D$_6$. Aliquots (400 μL) were taken at regular intervals, quenched with benzaldehyde (25 μL), and examined by proton NMR; the resonances at 2.18 and 2.02 ppm were monitored. Alternatively the monomer (0.105 g, 25 equiv), toluene (50 μL as a reference), and Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (10 mg) were added to 25 mL of benzene. Aliquots were withdrawn, quenched with 25 μL of benzaldehyde, and examined by GC. The consumption of **2** was evaluated assuming pseudo-first-order kinetics.

Determination of k_p for 5. The monomer (0.24 g, 1.07 mmol) in toluene (5 mL) was added dropwise over a period of 35 min to a rapidly stirred solution prepared by mixing a solution of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (10 mg, 0.021 mmol) in toluene (3 mL) and trifluorotoluene (as a reference; 308 mg, 2.11 mmol) in toluene (2 mL). Aliquots (100 μL) were taken at intervals and benzaldehyde (25 μL) in toluene was added. The samples were analyzed by fluorine NMR, which displayed a singlet at 59.64 ppm for the polymer, a singlet at 62.50 ppm for the monomer, and a singlet at 63.03 ppm for the reference (external CFCl$_3$). The reaction was followed by monitoring the loss of monomer with time. The data were evaluated by pseudo-first-order kinetics. Four determinations were made: [Mo]$_0$ = 0.0008, 0.0019, 0.0039, 0.0041 M; [monomer]$_0$ = 0.0417, 0.1975, 0.1038, 0.1037 M; k_p = 0.054, 0.065, 0.061, 0.048 M^{-1}, all respectively. Therefore k_p = 0.057 (0.007), and since k_p/k_i = 0.72, k_i = 0.079 (0.010).

Synthesis of 4. A solution of **2** (101 mg, 0.41 mmol) in toluene (3.0 mL) was added to a stirred solution of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (200 mg, 0.41 mmol) in toluene (3.0 mL). After 8 h the toluene was removed in vacuo to yield the product as a dark orange oil (300 mg) which was shown by ^{1}H NMR to be 90–95% **4**. Diffraction quality crystals were obtained by slow crystallization from a minimum amount of toluene at −30 °C over a period of two months: ^{1}H NMR (C$_6$D$_6$) δ 11.03 (d, 1, J = 8, H$_\alpha$), 7.09 (d, 2, H$_m$), 7.05 (t, 1, H$_p$), 6.40 (d, 1, J = 8, H$_\beta$), 5.55 (d, 1, C*H*-*t*-Bu), 5.44 (dd, 1, C*H*CH-*t*-Bu), 4.23 (sept, 2, C*H*(CH$_3$)$_2$), 4.01 (d, 1, C*H*CHCH-*t*-Bu), 3.46 (s, 3, CO$_2$C*H*$_3$), 3.41 (s, 3, CO$_2$C*H*$_3$), 1.40 (d, 6, CH(C*H*$_3$)$_2$), 1.35 (s, 9, OC(C*H*$_3$)$_3$), 1.34 (d, 6, CH(C*H*$_3$)$_2$), 1.33 (s, 9, OC(C*H*$_3$)$_3$, 1.02 (s, 9, CHC(C*H*$_3$)$_3$); ^{13}C NMR δ 250.4 (C$_\alpha$, J_{CH} = 128), 165.4, 165.1, 153.0, 145.1, 144.2, 142.8, 139.6, 135.2, 126.8, 124.3, 123.0, 78.2, 77.7, 66.5, 52.7, 51.6, 51.3, 33.2, 32.5, 32.1, 31.9, 29.8, 28.5, 24.6, 24.1, 21.6, 20.2; IR (C$_6$D$_6$) cm^{-1} 1725, 1720 (s, CO), 1640 (m, CC).

Rate of Formation of 4. Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (10 mg) was dissolved in 700 μL of benzene-d_6, and the solution was transferred to an NMR tube. The solution was frozen at −30 °C and 65 μg (13 equiv)

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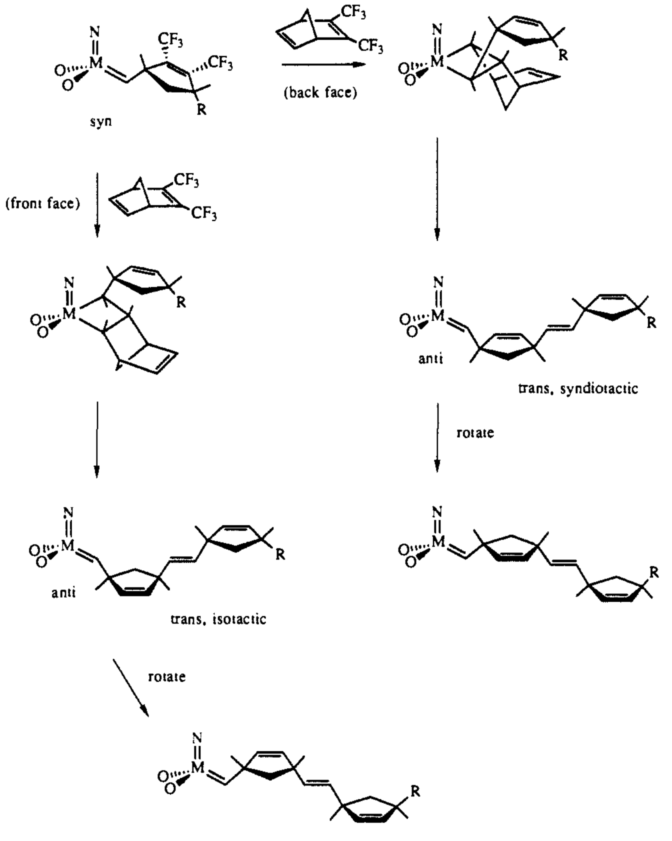
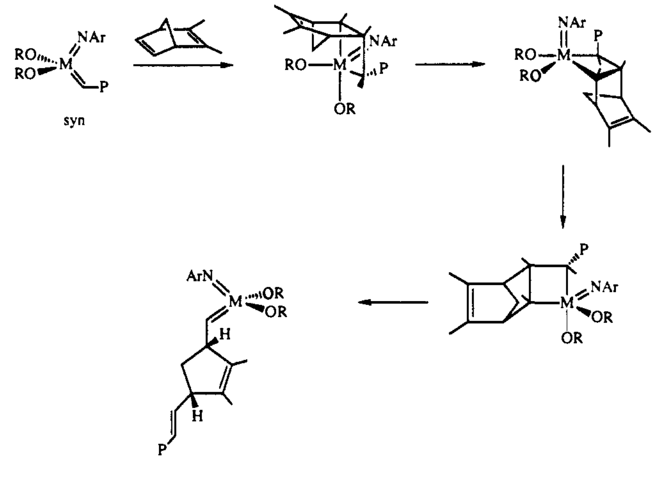
[27] We thank K. Yap for pointing out this potential complication.

Scheme I



Scheme II



of 3 was added as a solid. The sample was thawed and placed in a preset and calibrated NMR probe and allowed to equilibrate for 5 min. Spectra were collected over at least three half-lives at 12.7, 21.7, 22.0, and 27.5 °C. The propagating and initial alkylidene resonances were followed and the data treated assuming pseudo-first-order conditions. At 40.5 °C data were collected on a sample consisting of 6 mg of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and 16 mg of 3 in 600 μL of benzene-d_6. Data were fit to a second-order rate law. Thermodynamic parameters from an Arrhenius plot were found to be $\Delta H^* = 15.6\ (1.0)$ kcal mol^{-1} $\Delta S^* = -18$ (3) eu, and $\Delta G^*(298) = 21.0\ (1.3)$ kcal mol^{-1}.

Synthesis of 6. Solutions of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (100 mg, 0.17 mmol) and **5** (35 mg, 0.15 mmol) were made up with use of a minimum amount of toluene (~500 μL for each) and were cooled to −35 °C. (It is important that the compounds stay in solution.) The solutions were mixed at −35 °C and stored at −35 °C for 4 days. Yellow X-ray quality crystals formed. The solvent was removed and the crystals stored at −78 °C: ^{1}H NMR (toluene-d_8, −25 °C, 500 MHz) δ 7.01 (t, 1, H$_p$), 6.97 (d, 2, H$_m$), 3.98 (septet, 2, C*H*(CH$_3$)$_2$), 3.73 (s, 1, bridgehead H), 2.98 (s, 1, bridgehead H), 2.77 (dd, 1, $J_{H\alpha H\beta} = 9$, H$_\beta$), 2.23 (d, 1, $J_{H\alpha H\beta} = 9$, H$_\alpha$), 1.45 (d, 1, C*H*$_2$ bridgehead), 1.32 (s, 9, OC(C*H*$_3$)$_3$), 1.30 (C*H*$_2$ bridgehead by COSY), 1.27 (s, 9, OC(C*H*$_3$)$_3$), 1.24 (d, 6, C*H*(CH$_3$)$_2$), 1.20 (d, 6, C*H*(CH$_3$)$_2$), 1.17 (H$_\alpha$, by COSY), 1.08 (s, 9. C(C*H*$_3$)$_3$); ^{13}C NMR (toluene-d_8, −25 °C) δ 149.5, 146.5, 145.3, 143.0, 127.6, 123.1, 83.13, 82.69, 72.30, 52.81, 50.22, 48.96, 42.70, 37.94, 32.18, 32.10, 30.95, 28.4, 27.2, 23.6.

Rate of Formation of 6. The reaction was too fast to study by pseudo-first-order kinetics. A solution of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (10 mg in 400 μL of toluene-d_8, 4.38 (0.05) × 10^{-2} M) was placed in a 5-mm NMR tube equipped with a 24/40 ground glass joint and stoppered with a rubber septum. The catalyst solution was frozen at 77 K and a solution of 4 mg of **5** in 400 μL of toluene-d_8 (4.38 (0.05) × 10^{-2} M) was added via syringe. The contents of the NMR tube were frozen and the NMR tube was evacuated and sealed. The two solutions were mixed at −80 °C and kept frozen at 77 K until kinetic measurements were done. The reaction was followed by measuring the disappearance of the H$_\alpha$ resonance in the neopentylidene complex against the appearance of metallacycle resonances at four different temperatures (227.4, 238.2, 248.2, and 258.2 K) with a sample equilibration time in the NMR probe of 5 min. Observed rate constants were 4.14, 9.30, 17.4, and 30.2 × 10^{-3} M^{-1} s^{-1}, respectively. The Arrhenius plot had $\rho = 0.999$. Consistent results were obtained only when stock solutions of the reactants were prepared in volumetric flasks and reaction temperatures were measured carefully.

Ring Opening of 6 To Give 7. The metallacycle was made in situ by allowing W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (63 mg, 0.11 mmol) in toluene-d_8 (1.20 mL) to react with **5** (23 mg, 0.10 mmol) in toluene-d_8 (1.20 mL) at −35 °C for 12 h. In order to monitor the reaction by ^{1}H NMR mesitylene was added as an internal standard (15 mg, 0.12 mmol). The metallacycle solution (800 μL) was placed into 5-mm NMR tubes and quickly frozen until the kinetic measurements. First-order behavior was monitored at three different temperatures (288.5, 298.5, and 308.4 K). Observed rate constants were 0.766, 3.10, and 9.29 × 10^{-4} s^{-1}, respectively. The Arrhenius plot had $\rho = 0.998$: ^{1}H NMR (toluene-d_8, −25 °C) δ 8.35 (d, 1, $J_{H\alpha H\beta} = 9$, H$_\alpha$), 7.09 (t, 1, H$_p$), 7.05 (d, 2, H$_m$), 5.52 (b, 1, H$_\beta$), 5.45 (d, 1, C*H*-*t*-Bu), 5.31 (dd, 1, C*H*CH-*t*-Bu), 3.89 (sept, 2, C*H*(CH$_3$)$_2$), 3.13 (b, 1, C*H*CH-*t*-Bu), 2.31 (m, 1, C*H*H), 1.68 (m, 1, C*H*H), 1.314 (s, 18, OC(C*H*$_3$)$_3$), 1.28 (d, 6, CH(CH$_3$)(C*H*$_3$)), 1.24 (d, 6, CH(CH$_3$(C*H*$_3$)), 0.96 (s, 9, CH(C(C*H*$_3$)$_3$)).

X-ray Study of 4. Data were collected at −65 °C on a Rigaku AFC6 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069) and a 12 KW rotating anode generator. A total of 10212 reflections were collected, 9813 of which were unique. Equivalent reflections were merged. The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection, indicating crystal and electronic stability. No decay correction was applied. The structure was solved by a combination of the Patterson method and direct methods. Refinement was by full-matrix least squares with use of TEXSAN.[28] Hydrogen atoms were included in calculated positions (d_{C-H} = 0.95 Å). Final $R_1 = 0.047$ and $R_2 = 0.064$. Crystal data can be found in the abstract.

X-ray Study of 6. Data were collected at −78 °C on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). A total of 8944 reflections were collected, 8505 of which were unique. Equivalent reflections were merged. The final refinement was based on 4708 reflections ($I > 3\sigma(I)$). The intensities of three representative reflections which were measured after every 60 min of X-ray exposure time remained constant throughout data collection indicating crystal and electronic stability. An empirical absorption correction[29] was applied. The data were corrected for Lorentz and polarization effects and a correction for secondary extinction was applied. The structure was solved by the Patterson method and subsequent difference Fourier maps. The refinement was by full-matrix least squares with use of TEXSAN. Carbon atoms and the nitrogen atom were refined isotropically. All other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions (d_{C-H} = 0.95 Å). Final $R_1 = 0.067$ and $R_2 = 0.074$. Crystal data can be found in the abstract.

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Supplementary Material Available: ORTEP drawings, fully labeled drawings, and tables of final positional parameters and thermal parameters for **4** and **6** (19 pages); listing of observed and calculated structure factors for **4** and **6** (53 pages). Ordering information is given on any current masthead page.

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(28) TEXRAY Structure Analysis Package, Molecular Structures Corporation, 1985.

(29) Walker; Stuart *Acta Cryst.* **1983**, *A39*, 158.