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by

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Abstract

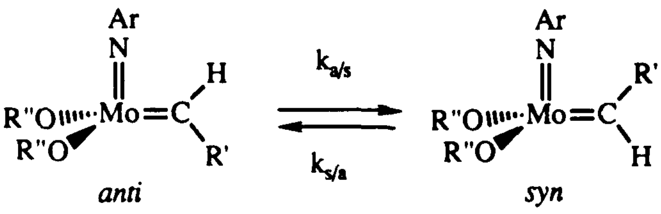
Low temperature (-85 °C) photolysis of complexes of the type *syn*-M(NR)(CHR')(OR")$_2$ (where M = Mo (usually) or W; R = 2,6-*i*-Pr$_2$C$_6$H$_3$, 4-Br-2,6-*i*-Pr$_2$C$_6$H$_2$, 2,6-Me$_2$C$_6$H$_3$, 2-*t*-BuC$_6$H$_4$, 2-*i*-PrC$_6$H$_4$, 1-adamantyl; R' = CMe$_3$, CMe$_2$Ph; OR" = OCMe$_3$, OCMe$_2$(CF$_3$), OCMe(CF$_3$)$_2$, OC(CF$_3$)$_3$, OC(CF$_3$)$_2$(CF$_2$CF$_2$CF$_3$), O-2,6-*i*-Pr$_2$C$_6$H$_3$) in thf-*d*$_8$, toluene-*d*$_8$, or methylcyclohexane-*d*$_{14}$ generated significant quantities of the anti rotamer. Anti to syn isomerization rate constants ($k_{a/s}$) were determined by NMR methods and correlated with the nature of R, R', R", and the solvent. Activation parameters were calculated in toluene-*d*$_8$ and thf-*d*$_8$ for the series Mo(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OR")$_2$ (where OR" = OCMe$_2$(CF$_3$), OCMe(CF$_3$)$_2$, OC(CF$_3$)$_3$, or OC(CF$_3$)$_2$(CF$_2$CF$_2$CF$_3$)). An estimate of $k_{a/s}$ for Mo(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe$_3$)$_2$ at 25 °C was obtained using activation parameters. Values for $k_{a/s}$ were found to vary by up to seven orders of magnitude (at 298K), the smallest values for $k_{a/s}$ being found in complexes that contain the most electron-withdrawing alkoxides in thf as a

solvent. Equilibrium constants ($K_{eq} = k_{a/s}/k_{s/a}$) at 25 °C were obtained from 500 MHz ^1H NMR spectra and found to vary by up to approximately two orders of magnitude. Values for $k_{s/a}$ at 298K were calculated and found to vary by up to six orders of magnitude in the same direction as $k_{a/s}$. 2,3-Bis(trifluoromethyl)norbornadiene (NBDF6) was added to photolyzed initiators of the type $Mo(NR)(CHR')(OR'')_2$ (where R = 2,6-*i*-$Pr_2C_6H_3$, 2-*t*-BuC_6H_4, 1-adamantyl; R' = CMe_3, CMe_2Ph; OR" = $OCMe_2(CF_3)$, $OCMe(CF_3)_2$, $OC(CF_3)_2(CF_2CF_2CF_3)$) in toluene-d_8 and thf-d_8 at temperatures where the rate of isomerization of anti rotamers to syn rotamers was negligible. The anti rotamer of Mo(N-2,6-*i*-$Pr_2C_6H_3$)($CHCMe_2Ph$)$[OCMe(CF_3)_2]_2$ was found to be at least two orders of magnitude more reactive than the syn rotamer in thf-d_8 and in toluene-d_8. Results were similar for other complexes containing an arylimido ligand. The anti rotamer of every complex containing an arylimido ligand reacted with NBDF6 to yield a syn first insertion product that contained a trans C=C bond (anti→syn,trans) and the syn rotamer produced a syn first insertion product that contained a cis C=C bond (syn→syn,cis). For Mo(N-1-adamantyl)-($CHCMe_2Ph$)$[OCMe(CF_3)_2]_2$ both anti and syn isomers reacted at approximately the *same* rate with NBDF6; anti yielded a syn,trans first insertion product (anti→syn,trans); but syn yielded an anti,trans first insertion product (syn→anti,trans). The result of bulk polymerizations (*40-100* equiv of NBDF6) at 25 °C suggest a relationship between alkylidene rotamer isomerization rates and polymer cis/trans content when the initiator contains an arylimido ligand; high-cis polymers are formed when rotamer isomerization rates are negligible on the time scale of polymerization, while high-trans polymers are obtained when rotamer isomerization rates are fast on the time scale of polymerization. A mechanism is proposed for formation of cis polymers that consists of olefin attack (through the exo face) on the CNO face of the syn rotamer of the catalyst with C_7 of the monomer extending over the arylimido ring. Two plausible mechanisms for forming trans polymers are (i) a similar monomer approach to the CNO face of anti rotamers, or (ii) monomer approach to the COO face of the catalyst in which the alkylidene ligand has rotated by up to 90°. Bulk polymerizations with the 1-adamantylimido initiator containing $OCMe(CF_3)_2$ ligands do not yield trans or cis polymer selectively.

INTRODUCTION

In the last few years well-defined metathesis catalysts of the general type $M(NR)(CHR')(OR'')_2$ (M = Mo or W)[1] have proven useful in a variety of olefin metathesis studies, in part because the activity of the catalysts can be varied systematically by altering the electron-withdrawing ability of the alkoxides. Complexes containing *t*-butoxides ($OCMe_3$ and $OCMe(CF_3)_2$ in particular), an arylimido ligand (often NAr, where Ar = 2,6-*i*-$Pr_2C_6H_3$), and molybdenum[2-4] have been the most versatile. In the area of ring-opening metathesis polymerization (ROMP)[5-7] molybdenum complexes have been employed most often to prepare polymers from a variety of norbornenes and norbornadienes.[8-13] Molybdenum complexes appear to tolerate a wide range of functionalities, are stable and active in a variety of solvents, and have been shown to produce polymers that are virtually all trans and highly tactic[10] or all cis with a tactic bias of ~75%.[12] Since polymer properties should vary dramatically with the degree of regularity of the primary polymer structure, the latter findings suggest that we may be able to learn how to control the primary structure of ROMP polymers in a systematic fashion and therefore how to control polymer properties.

Alkylidene rotational isomers or rotamers (eq 1) are found for many high-oxidation state alkylidene complexes.[1,14-18] Rotamers result from a limitation in the number of accessible π orbitals for forming more than one metal-alkylidene π bond in the presence of strong π bonding ligands, especially an imido ligand. Rotamer interconversion rates have been measured for several members of the class of $M(NAr)(CHR')(OR'')_2$ complexes. The most extensive study involved molybdenum complexes in which OR" is a phenoxide.[14] Such studies were possible



$$K_{eq} = k_{a/s} / k_{s/a} \qquad (1)$$

because both rotamers could be observed, and therefore standard ^{1}H NMR techniques could be employed in order to determine rate constants and activation parameters. Rotamer interconversion was found to be first order in metal and did not appear to proceed through a highly polar transition state.[14] Alkylidene rotation in rhenium complexes of the type $Re(CR')(CHR')(OR'')_2$ (where R' = CMe_3 or CMe_2Ph and OR" = $OCMe_x(CF_3)_{3-x}$; x = 0,1,2) also was found to be well-behaved, although the barrier to rotamer interconversion was significantly higher in the rhenium system (25-30 kcal mol^{-1}) than in the molybdenum system.[17]

It has been recognized that rotamers could play a significant role in determining the primary polymer structure in classical ROMP catalyst systems.[19] However, since very little is known even at this stage about the nature of classical ROMP catalysts, and classical catalysts normally cannot be observed by spectroscopic techniques (with one exception[20]), it has not been possible to determine whether rotamers do, in fact, play an important role. Since the cis/trans ratio in certain ROMP polymers depends upon the nature of the molybdenum catalyst,[9,10,12] it is imperative that alkylidene rotation rates and, if possible, relative reactivities of syn and anti rotamers be determined. Unfortunately, lineshape techniques cannot be used because the amount of the minor (anti) rotamer is insignificant (under normal NMR conditions) in the *t*-butoxide and hexafluoro-*t*-butoxide complexes that are employed as initiators. A key finding in the $Re(CR')(CHR')(OR'')_2$ system was that the ratio of rotamers could be altered significantly by photolyzing the rotamer mixture. Rate constants then could be obtained by following the return of the mixture to equilibrium at various temperatures.[17] Photolysis at low temperature was found to generate a significant amount of anti rotamer in the family of *t*-butoxide (including $OCMe_2(CF_3)$ and $OCMe(CF_3)_2$) molybdenum catalysts also and the rate of conversion of the normally unobservable minor rotamer to the major rotamer therefore could be determined.[21] Once the H_α resonance for the minor rotamer was located it became possible to measure K_{eq} ($k_{a/s}/k_{s/a}$), and therefore to calculate $k_{s/a}$. In this paper we report the results of such studies for a variety of Mo complexes, explore the relative reactivity of such rotamers with 2,3-bis(trifluoromethyl)norbornadiene (NBDF6), and attempt to correlate these results with the cis/trans structure of poly(NBDF6). Initial results have appeared in a preliminary communication.[21]

RESULTS

UV/Visible Spectra and Qualitative Photolysis Studies.

UV/Vis spectra of three complexes of the type *syn*-Mo(NAr)(CH-t-Bu)$(OR")_2$ (OR" = $OCMe_3$ (**1'**), $OCMe_2(CF_3)$ (**2'**), or $OCMe(CF_3)_2$ (**3'**)) are shown in Figure 1. (See Table II for the abbreviations used and numbering scheme. Syn refers to the rotamer in which the alkylidene substituent points toward the imido nitrogen atom; equation 1.) Extinction coefficients and λ_{max} values for these neopentylidene complexes and two neophylidene complexes (unprimed compound numbers) are listed in Table I. A weak shoulder that extends into the visible region (between 400 and 500 nm) accounts for the light yellow color of the syn form of all complexes shown in Table I in solution.

Emission lines at 366 and 405 nm from a medium pressure mercury lamp[22] were employed in photochemical experiments. Photolysis of a solution containing the syn rotamer in a sealed NMR tube at -85 °C with either 366 or 405 nm light yielded a mixture of anti and syn rotamers. Samples usually were photolyzed at -85 °C in order to prevent thermal back reaction and to minimize possible sample decomposition. In general photolyses at 366 nm in non-coordinating solvents yielded a higher percentage of anti rotamer in the mixture than photolyses at 405 nm. For example, photolysis of **3'** in toluene-d_8 at -85 °C for 13 h at 405 nm yielded a mixture containing 7% of the anti rotamer, while photolysis at 366 nm for just 4 h yielded a mixture containing 24% of the anti rotamer. Photolysis of Mo(NAr)($CHCMe_2Ph$)-$[OCMe_2(CF_3)]_2$ (**2**) in thf-d_8 at 366 nm yielded a photostationary state that contained about 30% of the anti rotamer. Photolyses in which the entire spectrum from the medium pressure lamp was utilized produced a mixture that contained a minimum of 22% of the anti rotamer. For this reason, 366 nm light was usually employed in photochemical experiments. A photostationary state consisting of approximately a 1:2 mixture of anti and syn rotamers was reached after about

8 h at 366 nm for all complexes in all solvents. All samples in toluene-d_8 turned light red as photolysis proceeded and anti rotamer was formed. In contrast photolyses in thf-d_8 did not produce any significant color change as the anti rotamer was generated.

In all cases, the H_α resonance of the photochemically-generated anti rotamer was found ~1 ppm downfield of the H_α resonance for the syn rotamer. (A list of ^{1}H NMR H_α resonances and $J_{CH\alpha}$ values can be found in Table II.) There are two primary reasons why we ascribe the photochemically-generated alkylidene H_α resonance to the anti rotamer. First, the chemical shift difference between the anti and syn H_α resonances is similar to that in previously studied $Mo(NAr)(CHCMe_3)(OR'')_2$ complexes where OR" = various phenoxides.[2,14] Second, $J_{CH\alpha}$ values between 145 and 155 Hz were found for the downfield rotamer, and between 115 and 125 Hz for the upfield rotamer, analogous to $J_{CH\alpha}$ values found for anti and syn rotamers, respectively, in other complexes of this general type.[1,2,14] When a sample containing the mixture of anti and syn rotamers was allowed to return to equilibrium, the area of the syn H_α resonance returned to what it was (relative to an internal standard) before photolysis, and the spectrum was identical to the spectrum of the sample before photolysis. In NMR spectra of the majority of complexes discussed here that are obtained with routine spectromer settings and acquisition times the anti H_α resonance is not readily observed.

Determination of Anti to Syn Conversion Rates.

Rates of conversion of the anti to the syn rotamer were determined in deuterated toluene, methylcyclohexane, or thf at various temperatures by following the decrease in the intensity of the H_α resonance for the anti rotamer. (Both toluene and thf are commonly employed solvents for ROMP with these initiators.[5,7]) Since K_{eq} is usually large (see below), conversion of the anti to the syn rotamer could be assumed to be irreversible and $k_{a/s}$ could be obtained from a first-order log plot. In a few cases K_{eq} was small enough to lend a slight curvature to the log plot; in these circumstances $k_{a/s}$ was determined by plotting a first-order approach to the known equilibrium. Rate constants for complexes of the type $Mo(NAr)(CHCMe_2Ph)(OR'')_2$ (OR" =

family of *t*-butoxides) at various temperatures are listed in Table III; rate constants for all other complexes are listed in Table IV.

Many rate constants for anti to syn conversion for complexes **2**, **3**, **4**, and **5** in toluene-d_8 and **2** and **3** in thf-d_8 in Table III could be collected over a 20 °C range of temperatures, which is sufficient to allow activation parameters to be determined with some reliable degree of accuracy. The plots shown in Figure 2a (toluene-d_8 solvent) and in Figure 2b (thf-d_8 solvent) illustrate two important findings. First, $k_{a/s}$ decreases dramatically as the electron-withdrawing ability of the alkoxides increases. Even the rate for $\mathbf{4}_{tol}$ (containing $OC(CF_3)_2(CF_2CF_2CF_3) = OR_{F13}$) at a given temperature is slightly faster than the rate for $\mathbf{5}_{tol}$ (containing $OC(CF_3)_3 = OR_{F9}$) at that temperature, a fact that is consistent with the lower electron-withdrawing ability of OR_{F13} (eight fluorines β to oxygen) than OR_{F9} (nine fluorines β to oxygen). Only one value for $k_{a/s}$ could be obtained for the *t*-butoxide complex (**1**), and the experiment had to be done in methylcyclohexane-d_{14} (mch-d_{14}). The sample was photolyzed in a mch-d_{14} glass at 77K, inserted into the NMR probe while still frozen, and thawed in the pre-cooled (-120 °C) probe. Although a color change from orange to orange-red was noted during photolysis in toluene-d_8 at -85 °C, the rate of conversion of anti rotamer to syn rotamer was too fast to follow conveniently even at this temperature. Photolysis of **2** in both toluene-d_8 and in mch-d_{14} revealed less than a factor of two difference in rate, the rate being slower in methylcyclohexane (see Table III). The second important point is that the rate of conversion of anti rotamer to syn rotamer of **2** and **3** is significantly slower in thf-d_8 than in toluene-d_8 (Figure 2b). A rate constant for $\mathbf{1}_{thf}$ could not be obtained, even though a small anti resonance could be observed in some photolyzed samples briefly before the anti form reverted to the syn form, depending on experimental circumstances. These results suggest that rotamer rotation is inhibited by thf to a significant extent only when the metal center is sufficiently electrophilic to bind thf. There is no evidence that thf-d_8 binds well to **1** or slows down rotamer rotation (see also below). Further evidence for binding of thf-d_8 to **2** and **3** consists of the downfield shift of the anti and syn H_α resonances at 25 °C by 0.36 to 0.64 ppm in **2** and **3** relative to their chemical shifts in toluene-d_8; the chemical shifts for anti and syn H_α in **1** at 25 °C are actually slightly upfield in thf-d_8 from where they are in toluene-d_8 (Table II). A downfield shift of the H_α resonance is a characteristic consequence of a base binding to the metal in complexes of this type.[1]

Activation parameters for the six examples shown in Figure 2 are listed in Table V. Unfortunately, $k_{a/s}$ data could be obtained over a maximum range of ~20 °C in the most favorable cases. Nevertheless, the activation data are sufficiently accurate to support several conclusions. A value of ~0 for $\Delta S^\ddagger$ in toluene-d_8 is consistent with a unimolecular process, while the relatively large and positive value for $\Delta S^\ddagger$ in thf-d_8 (+20 to 25 e.u.) is consistent with a process that requires loss of thf from the metal. These values imply that rotation of the alkylidene in five-coordinate base-adducts is slower than in four-coordinate species. This result is consistent with previous findings that rotamer rotation in **3** in the presence of PMe_3 is negligible.[14] $\Delta G^\ddagger$'s are in the same range as those found for Mo phenoxide complexes,[14] but are significantly smaller than $\Delta G^\ddagger$'s for rhenium complexes of the type Re(CR')(CHR')(OR")$_2$ (OR" = $OCMe_3$, OR_{F3}, and OR_{F6}).[17] A redetermination of $k_{a/s}$ for **7** in toluene (Table IV, 7_{tol} at -42 °C) agreed with the value calculated from activation parameters obtained previously for this initiator[14] (found $k_{a/s} = 1.35 \times 10^{-4}\ s^{-1}$; calculated $1.15 \times 10^{-4}\ s^{-1}$ at -42 °C).

Calculated $k_{a/s}$ values for **2**, **3**, **4** and **5** at 298 K are listed in Table VI and a plot of ln $k_{a/s}$ versus the number of fluorines in the alkoxide is shown in Figure 3. (The OR_{F13} alkoxide contains only 8 fluorines β to oxygen and therefore is plotted as "F8".) If we assume that $k_{a/s}$ values for the *t*-butoxide complex fall on these lines, then from the intercept we find that $k_{a/s}$ should be ~500 s^{-1} for **1** in toluene and ~360 s^{-1} for **1** in thf. The fact that the values of $k_{a/s}$ for **1** are similar in thf and toluene is further evidence that thf binds to the metal to a negligible extent in *t*-butoxide complexes at 25 °C. The difference between $k_{a/s}$ for **1** in thf (~360 s^{-1}) and **3** in thf (~4 x $10^{-5}\ s^{-1}$) is impressive (~7 orders of magnitude), and is additional evidence for attenuation of the rate of alkylidene ligand rotation by binding of thf to an electrophilic metal center. The difference between $k_{a/s}$ for **1** in toluene and for **3** in toluene is less significant, but still more than three orders of magnitude and again consistent with thf binding to a relatively electrophilic metal center.

Rate constants obtained for **1-5** (Table III) should be compared with those obtained for variations (Table IV). For example, we find that a neophylidene ligand rotates only slightly more slowly than a neopentylidene ligand (for $\mathbf{2'}_{tol}$ at -56 °C $k_{a/s} = 6.0 \times 10^{-4}$ s^{-1}; calculated for $\mathbf{2}_{tol}$ at -56 °C $k_{a/s} = 2.7 \times 10^{-4}$ s^{-1}). Interestingly, $k_{a/s}$ is two orders of magnitude larger in a tungsten complex than in a closely related molybdenum complex (for $\mathbf{16'}_{tol}$ at -49 °C $k_{a/s} = 2.1 \times 10^{-4}$ s^{-1}; calculated for $\mathbf{3}_{tol}$ at -49 °C $k_{a/s} = 2.6 \times 10^{-6}$ s^{-1}). If the diisopropylphenyl imido ligand is substituted in the para position with bromide, $k_{a/s}$ increases only slightly (for $\mathbf{6}_{tol}$ at -20.8 °C $k_{a/s} = 6.5 \times 10^{-4}$ s^{-1}; for $\mathbf{3}_{tol}$ at -20.8 °C $k_{a/s} = 3.4 \times 10^{-4}$ s^{-1}). In complexes in which methyl groups are present in the ortho positions of the arylimido ligand instead of isopropyl groups the alkylidene rotates only slightly more readily (for $\mathbf{9}_{thf}$ at 22.0 °C $k_{a/s} = 4.5 \times 10^{-5}$ s^{-1}; calculated for $\mathbf{3}_{thf}$ at 22.0 °C $k_{a/s} = 2.6 \times 10^{-5}$ s^{-1}: for $\mathbf{10}_{tol}$ at 0 °C $k_{a/s} = 4.2 \times 10^{-4}$ s^{-1}; calculated for $\mathbf{4}_{tol}$ at 0 °C $k_{a/s} = 1.3 \times 10^{-4}$ s^{-1}). Changing the imido substituent from an aryl to an adamantyl group results in an order of magnitude increase in $k_{a/s}$ (for $\mathbf{15}_{tol}$ at -31.4 °C $k_{a/s} = 5.8 \times 10^{-4}$ s^{-1}; for $\mathbf{3}_{tol}$ at -31.2 °C $k_{a/s} = 5.9 \times 10^{-5}$ s^{-1}). In an ortho-*t*-butyl phenylimido complex containing OR_{F6} ligands $k_{a/s}$ was a factor of ~1400 larger than what it was in the diisopropylphenylimido analog (for $\mathbf{12}_{tol}$ at -67.2 °C $k_{a/s} = 8.4 \times 10^{-5}$ s^{-1}; calculated for $\mathbf{3}_{tol}$ at -67.2 °C $k_{a/s} = 6 \times 10^{-8}$ s^{-1}), while in OR_{F9} complexes $k_{a/s}$ is larger by a factor of ~700 in the ortho-*t*-butylphenylimido complex (for $\mathbf{13}_{tol}$ at -26.6 °C $k_{a/s} = 6.0 \times 10^{-4}$ s^{-1}; calculated for $\mathbf{5}_{tol}$ at -26.6 °C $k_{a/s} = 8.0 \times 10^{-7}$). The effect is less dramatic but still significant (a factor of ~250) when the solvent is thf-d_8 instead of toluene-d_8 (for $\mathbf{12'}_{thf}$ at -2.0 °C $k_{a/s} = 6.6 \times 10^{-5}$ s^{-1}; calculated for $\mathbf{3}_{thf}$ at -2.0 °C $k_{a/s} = 2.7 \times 10^{-7}$). Interestingly, changing an ortho-*t*-butyl to an ortho-isopropyl group in the phenylimido ligand has little effect on the rotation rate (for $\mathbf{14}_{tol}$ at -66.0 °C $k_{a/s} = 4.4 \times 10^{-5}$ s^{-1}; for $\mathbf{12}_{tol}$ at -67.2 °C $k_{a/s} = 8.4 \times 10^{-5}$ s^{-1}).

The complex $Mo(NAr)(CDCMe_3)[OCMe(CF_3)_2]_2$ was synthesized in order to determine the magnitude of any isotope effect; k_H/k_D for anti to syn conversion was found to be 2.0 at -27.4 °C (Table IV). (The sharp and clearly visible isopropyl methine proton resonances in the anti and syn rotamers were followed by ^{1}H NMR in order to determine the rate.) A value of 2 would qualify as a relatively small primary isotope effect or a relatively large secondary isotope effect.

Measurement of K_{eq} and Calculation of $k_{s/a}$.

We noted earlier that in a typical ^{1}H NMR spectrum of an alkylidene complex of the type discussed here the anti H_α resonance is not readily visible. Once H_α resonances for anti rotamers had been observed in photolyzed samples, we could entertain the possibility of observing a tiny amount of the anti rotamer, measuring the syn/anti equilibrium, and thereby determining $k_{s/a}$. In practice a 500 MHz ^{1}H NMR instrument proved adequate. Acquisition times of several hours were required in some cases in which K_{eq} was especially large in order to observe the H_{anti} resonance. In a few cases (**3**$_{thf}$, **7**$_{tol}$, **12'**$_{thf}$, **15**$_{tol}$) the mixture contained 5-10% of the anti rotamer at 298K. As an example of a case in which K_{eq} is large, the alkylidene region of the ^{1}H NMR spectrum of initiator **14**$_{tol}$ is shown in Figure 4. The equilibrium constant was obtained by integrating the anti H_α resonance relative to the downfield ^{13}C satellite of the syn H_α resonance. Values for K_{eq} are listed in Table II. When K_{eq} is large multiple runs were impractical because of the amount of time required to acquire the data.

Several factors dramatically affect K_{eq}. First, K_{eq} decreases in the series $3_{tol} \rightarrow 3_{dme} \rightarrow 3_{thf}$. We propose that one thf binds most effectively to the anti rotamer when the metal is electron deficient and thereby stabilizes the anti rotamer to a significant degree relative to the syn rotamer. The low relative reactivity of the syn rotamer might be ascribed to the steric hindrance between an isopropyl group and the alkylidene subsituent in the adduct formed upon adding a base to the CNO face, as suggested by an X-ray structure of trigonal bipyramidal *syn*-Mo(CH-*t*-Bu)(NAr)$(OR_{F6})_2(PMe_3)$.[14]

The nature of the alkoxide also influences K_{eq}. In the series **1-5**, K_{eq} generally decreases with increasing electron-withdrawing ability of alkoxide (Table II; Figure 5). All complexes in the series **1-5**$_{tol}$ are *neophylidene* complexes. Although the *neopentylidene* series is incomplete, the data that are available suggest that K_{eq} actually *increases* with increasing electron-withdrawing ability of the alkoxides (Table II; Figure 5). (The value of 5000 listed for **5'**$_{tol}$ is a minimum value since the anti resonance was never located even after several hours of data collection.) The greater stability of the syn *neopentylidene* rotamer as the alkoxide is varied in the series **1** to **5** could be ascribed to the step-wise increase in the size of the more electron-withdrawing alkoxides, and might be the "normal" trend. An explanation that would account for more anti *neophylidene* rotamer being present as the alkoxide becomes more electron withdrawing is that a C-H_{ortho} bond interacts with an empty metal orbital on the COO face of the complex, although no NMR data that we have obtained at this point supports this proposal. However, a related interaction of the C-H_{ortho} bond in the tolyl group in $W(NAr)(CHCMe_3)[OC(CF_3)_2(p\text{-}Me\text{-}C_6H_4)]_2$ is a plausible first step leading to $W[OC(CF_3)_2(p\text{-}MeC_6H_3)](NAr)(CH_2CMe_3)[OC(CF_3)_2(p\text{-}MeC_6H_4)]$, in which the tolyl ring in one alkoxide has been orthometalated and the ortho proton transferred to the alkylidene α carbon atom.[23] Other examples in the literature are known in which an anti rotamer is stabilized by binding a functionality in the alkylidene ligand to the metal.[4,24,25]

Finally, K_{eq} changes upon altering the nature of the imido ligand. K_{eq} is larger by approximately a factor of 3 in a complex that contains a diisopropylphenylimido ligand than in one that contains a dimethylphenylimido ligand. Interestingly, the presence of a single ortho *t*-butyl substituent does not alter K_{eq} to a significant degree (compare **5**$_{tol}$ to **13**$_{tol}$, or **3** to **12'**). Perhaps the most dramatic change in K_{eq} (a decrease of two orders of magnitude) is observed upon changing a diisopropylphenylimido to an adamantylimido ligand (compare **3**$_{tol}$ to **15**$_{tol}$). It is tempting to propose that the relatively isotropic adamantyl group is 'larger' than an aryl group (the relatively flat aryl group is oriented 90° to the C/Mo/N plane in order to avoid adverse steric interactions in the syn rotamer[14]), and that the syn rotamer therefore is destabilized in the adamantyl complex. (Other evidence that supports this proposal is presented later.) Steric interactions between alkoxides, the imido ligand, and the alkylidene substituent will counteract one another in many cases, so that predicting the magnitude of K_{eq} *a priori* is not a simple task. However, so far the syn rotamer has always been favored, the exception being when a donor functionality in the alkylidene substituent can coordinate to the metal in the anti rotamer.[1] The only tungsten complex examined had a larger K_{eq} (by approximately a factor of 2) than the analogous molybdenum complex (compare $\mathbf{3'}_{tol}$ to $\mathbf{16'}_{tol}$).

A plot of *ln*(K_{eq}) vs *1/T* for $\mathbf{3}_{tol}$ *at four temperatures is shown in Figure 6.* The difference in enthalpy for the two rotamers ($\Delta H°$) is -5.4 kcal/mol, while the difference in entropy ($\Delta S°$) is -2.4 e.u. In contrast, K_{eq} for $\mathbf{3}_{thf}$ is relatively independent of temperature over approximately the same temperature range (-20° to +50 °C).

Values for $k_{s/a}$ at 298 K can be calculated from the measured values for K_{eq}; they are listed in Table VI. An examination of the $k_{s/a}$ data in Table VI reveals some trends related to those noted for $k_{a/s}$. The virtually identical values of $k_{s/a}$ for $\mathbf{1}_{tol}$ and $\mathbf{1}_{thf}$ are consistent with little or no binding of thf to the relatively electron-rich *t*-butoxide complex. $k_{s/a}$ values for $\mathbf{3}_{tol}$ and $\mathbf{3}_{thf}$ differ by a factor of only ~35 compared to a difference of ~2500 in $k_{a/s}$ values. The most important general conclusion is that $k_{s/a}$ for **1** is larger by five to six orders of magnitude than $k_{s/a}$ for **3**, **4**, or **5**.

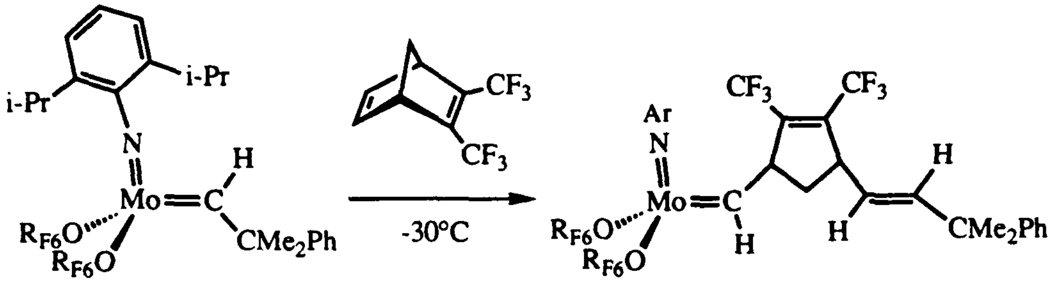
In the process of examining many NMR spectra at low temperature, it was noted that rotation of the arylimido group was also restricted. Consequently, rate constants were measured for aryl group rotation in order to see to what extent aryl group is coupled to alkylidene ligand rotation. Studies of arylimido group rotation in the syn rotamer were straightforward, but anti rotamers could be studied only at temperatures where anti to syn conversion was slow. Since a maximum of only 33% of the anti rotamer could be generated, measurement of rate constants for aryl group rotation in anti rotamers also was complicated by the presence of aryl resonances for the syn rotamer. Data obtained for aryl group rotation in **2** and **3** are listed in Table VII. The main conclusion that is relevant to the processes under discussion here is that aryl groups in all complexes rotate much faster than the alkylidene ligands, and the two processes therefore are not strongly coupled. It is interesting to note that an aryl group rotates more slowly in a syn rotamer than in an anti rotamer, consistent with a greater degree of steric interaction between the phenylimido ligand's ortho substituents and the alkylidene substituent in the syn rotamer. For example, the aryl group rotates nearly five times more rapidly in *anti*-$\mathbf{3}_{thf}$ than in *syn*-$\mathbf{3}_{thf}$. As expected, the effect of a coordinating solvent such as thf-d_8 is dramatic; $\Delta\Delta G^{\ddagger}_{298}$ for aryl group rotation in *syn*-3_{tol} versus *syn*-3_{thf} is 1.6 kcal/mol. Entropies of activation are consistent with a unimolecular process in a non-coordinating solvent, and a dissociative process in thf-d_8, i.e., the aryl group rotates much more readily in the less crowded four-coordinate complex, as one would expect on steric grounds.

In the process of studying aryl group rotation we noted that thf-d_8 binds to the anti rotamer of 2 and 3 to generate an unsymmetric adduct that contains inequivalent imido methine protons and inequivalent methyl protons at the slow exchange limit. This result is consistent with thf binding to one of the CNO faces. Inequivalent methine and methyl resonances coalesce when coordinated thf begins to exchange rapidly with free thf. In contrast, syn rotamers of 2 and 3 are symmetric on the NMR time scale, indicating either that thf-d_8 that is bound to the CNO face exchanges rapidly on the NMR time scale in syn rotamers, or that thf binds preferentially to the COO or NOO face in syn rotamers to give adducts that contain a mirror plane.

Reaction of $Mo(NAr)(CHCMe_2Ph)(OR_{F6})_2$ Rotamers with 2,3-$(CF_3)_2$Norbornadiene.

Because a mixture of syn and anti rotamers of OR_{F6} species can be generated at low temperature and because they do not readily interconvert, it was possible to explore the relative reactivity of the two rotamers toward olefins. Studies of this type reported here involved 2,3-bis(trifluoromethyl)norbornadiene (NBDF6), since poly-NBDF6 with different regular structures[10,12,26] has been prepared with several of the initiators discussed here.[10,12]

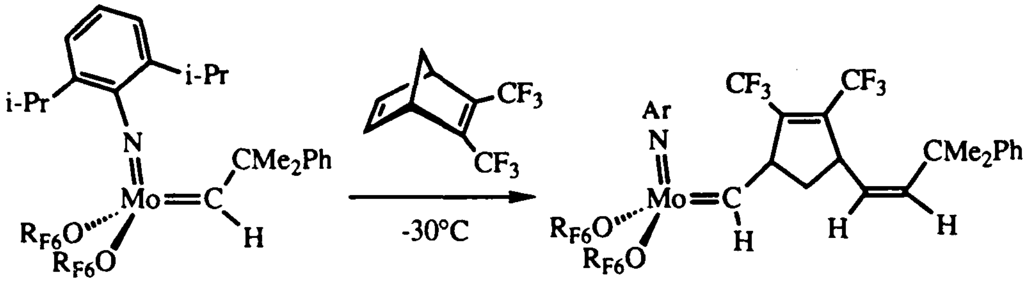
Five equivalents of NBDF6 were added to a thf-d_8 sample that contained 33% *anti*-3 at 77 K, and the sample was thawed and transferred to an NMR probe that had been cooled to -30 °C. *Anti*-3_{thf} was consumed within a few minutes at -30 °C. H_α for a syn first-insertion product (*syn*-3_{thf}+1) was observed at 12.89 ppm ($^3J_{H\alpha H\beta}$ = 7.0 Hz, where H_α is the alkylidene α proton) and the C=C bond is trans according to the value of the olefinic HH coupling ($^3J_{HH}$ = 16 Hz). The syn orientation was assigned to this rotamer on the basis of the value for $J_{CH\alpha}$ (127 Hz). The mixture that then contained *syn*-3_{thf} and *syn*-3_{thf}+1_t (t implies a trans C=C bond in the first insertion product) *did not react* with the excess NBDF6 that was present until the temperature was raised to 0 °C (see below). (The H$_\alpha$ resonances for *syn*-**3** and *syn*-**3**+**1**$_t$ can be seen as part of another spectrum shown in Figure 7a.) When only 0.33 equiv of NBDF6 was added to the 1:2 mixture of *anti*-**3**$_{thf}$ and *syn*-**3**$_{thf}$ at -30 °C, 0.33 equiv of *syn*-**3**$_{thf}$+**1**$_t$ was formed from addition of all NBDF6 to *anti*-**3**$_{thf}$. Within experimental error no *syn*-**3**$_{thf}$ reacted with NBDF6. We conclude that *anti*-**3**$_{thf}$ is much more reactive than *syn*-**3**$_{thf}$, and *syn*-**3**$_{thf}$+**1**$_t$ is the sole product of the reaction between NBDF6 and *anti*-**3**$_{thf}$ (equation 2). We can only guess that *anti*-**3** is approximately two orders of magnitude more reactive than *syn*-**3** (or more) at -30 °C. Photolysis of this mixture of *syn*-**3**$_{thf}$ and *syn*-**3**$_{thf}$+**1**$_t$ (with no NBDF6 now present) generates a mixture of *anti*-**3**$_{thf}$, *anti*-**3**$_{thf}$+**1**$_t$, *syn*-**3**$_{thf}$+**1**$_t$, and *syn*-**3**$_{thf}$ (Figure 7a). The anti assignment for *anti*-**3**$_{thf}$+**1**$_t$ was confirmed by ^{13}C NMR ($J_{CH\alpha}$ = 152 Hz) and ^{1}H NMR ($^3J_{H\alpha H\beta}$ = 10.0 Hz) and the trans C=C bond by the magnitude of the olefinic HH coupling ($^3J_{HH}$ = 16 Hz). The rate of conversion of *anti*-**3**$_{thf}$+**1**$_t$ to *syn*-**3**$_{thf}$+**1**$_t$ could then be determined and was found to be approximately 5 times slower at 35 °C than the rate of conversion of *anti*-**3**$_{thf}$ to *syn*-**3**$_{thf}$ (Table VIII). This result establishes that $k_{a/s}$ for *anti*-**3**$_{thf}$+**1**$_t$ is not orders of magnitude different from $k_{a/s}$ for *anti*-**3**$_{thf}$ and therefore that the trends in $k_{a/s}$ that have been determined for neopentylidene and neophylidene complexes probably also apply roughly to the alkylidene complexes formed upon ring-opening NBDF6. Since the CF$_3$ groups are so strongly electron-withdrawing, we hesitate to ascribe the slower conversion of *anti*-**3**$_{thf}$+**1**$_t$ to *syn*-**3**$_{thf}$+**1**$_t$ to steric factors alone.



(2)

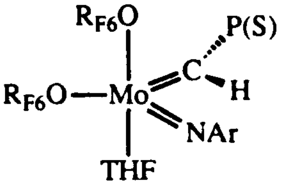
anti-**3** (in thf-d$_8$ or toluene-d$_8$) *syn*-**3**+**1**$_t$

2,3-Bis(trifluoromethyl)norbornadiene reacts with *syn*-**3**$_{thf}$ above approximately 0° to yield a new first insertion product that has an H$_\alpha$ resonance at 12.81 ppm ($^3J_{H\alpha H\beta}$ = 6.5 Hz) and a *cis* double bond ($^3J_{HH}$ = 11.2 Hz), i.e., *syn*-3_{thf}+1_c (equation 3). The NMR spectrum of *syn*-3_{thf}+1_c should be compared to that for *syn*-3_{thf}+1_t (δH_α = 12.89 ppm, $^3J_{H\alpha H\beta}$ = 7.0 Hz, and $^3J_{HH}$ = 16 Hz). As more NBDF6 is consumed new alkylidene resonances for syn insertion products appear in the region between 12.79 and 12.95 ppm and the olefinic region becomes too complex to assign C=C geometries. It is important to note that no anti insertion products are observed.

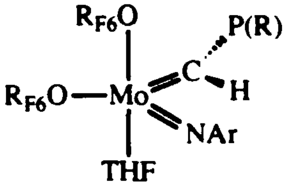


syn-**3** *syn*-**3**+1_c (3)

Low temperature ^{1}H NMR spectra were obtained for the mixture shown in Figure 7a (in thf-d_8). At -80 °C, *two* doublets in a 1:4 ratio are observed for alkylidene H_α protons in two isomers of *anti*-3+1_t. The chemical shift of the downfield (minor) resonance is close (~13.7 ppm) to that for *anti*-**3** while the upfield (major) resonance (~12.9 ppm) is partially obscured by the H_α resonance for *syn*-3+1_t. At -60 °C both doublets are visible and $^3J_{H\alpha H\beta}$ coupling constants can be measured; in the minor resonance $^3J_{H\alpha H\beta}$ = 9.0 Hz, while in the major isomer $^3J_{H\alpha H\beta}$ = 11.1 Hz. As the temperature is raised, the two H_α resonances broaden, coalesce (at ~0 °C), and sharpen to give the doublet at 13.17 ppm in which the coupling constant ($^3J_{H\alpha H\beta}$ = 10 Hz) is approximately an average of the coupling constants in the two isomers of *anti*-3+1_t found at low temperature. This type of behavior is not observed for *syn*-**3**, *anti*-**3**, or *syn*-3+1_t, even though *anti*-**3** in thf at low temperature does show evidence of adding thf to one of the CNO faces, as noted above. We speculate that the two isomers of *anti*-3+1_t observed at low temperatures are thf adducts in which thf binds in an axial position and the imido and alkylidene ligands lie in the equatorial plane. This is the type of structure found for several adducts,[1] e.g., *syn*-Mo(NAr)(CHCMe$_3$)[OCMe(CF$_3$)$_2$]$_2$(PMe$_3$),[14] one that results from adding a base to the CNO face of the catalyst. However, two diastereomers can form in the case of an adduct of *anti*-**3**+**1**$_t$ (see A and B below where R or S is the configuration of C$_\beta$) since C$_\beta$ in the alkylidene formed by addition of NBDF6 is chiral. Only one adduct of *anti*-**3** forms at low temperature because no chiral center is present in the alkylidene ligand. Since thf does not bind strongly to *any* syn rotamer, only one H$_\alpha$ resonance is observed for *syn*-**3** and *syn*-**3**+**1**$_t$ (an expected doublet in each case) at temperatures down to -90 °C.



diastereomer A



diastereomer B

A similar set of experiments was carried out in toluene-d_8 instead of thf-d_8. Five equiv of NBDF6 were added to a toluene-d_8 sample containing 33% *anti*-**3**$_{tol}$ and the sample was thawed (-95 °C) and rapidly transferred to a -80 °C NMR probe. The H$_\alpha$ resonance for the anti isomer already had been replaced by an H$_\alpha$ resonance for *syn*-**3**$_{tol}$+**1**$_t$ ($^3J_{H\alpha H\beta}$ = 8.1 Hz) 0.4 ppm downfield from the H$_\alpha$ resonance for unreacted *syn*-**3**$_{tol}$. Reaction of *anti*-**3**$_{tol}$ at the melting point of toluene-d_8 can be confirmed visually because the red color associated with *anti*-**3**$_{tol}$ disappears immediately upon thawing and mixing of the reactants. (The rate of isomerization of *anti*-**3**$_{tol}$ to *syn*-**3**$_{tol}$ at these temperatures is negligible.) The C=C double bond in *syn*-**3**$_{tol}$+**1**$_t$ was assigned as trans on the basis of $^3J_{HH}$ (15.4 Hz). Neither *syn*-**3**$_{tol}$ nor *syn*-**3**$_{tol}$+**1**$_t$ reacted with NBDF6 at -80 °C. However, after 1 hour at -40 °C all remaining NBDF6 was consumed by *syn*-**3**$_{tol}$ and *syn*-**3**$_{tol}$+**1**$_t$ to give multiple insertion products that appear to be syn on the basis of H$_\alpha$ chemical shifts. We conclude from these results that both syn and anti rotamers are much more reactive in toluene than they are in thf (i.e., thf behaves as a competitive inhibitor) and that *anti*-**3**$_{tol}$ is again much more reactive than *syn*-**3**$_{tol}$. We can speculate that since thf binds readily to *anti*-3_{thf}+1_t, as noted above, but not to *syn*-3_{thf}+1_t, the reactivity of an anti rotamer might be attenuated more strongly in thf than the reactivity of a syn rotamer in thf relative to their reactivities in toluene.

As expected, addition of only 0.33 equiv of NBDF6 to a 1:2 mixture of *anti*-3_{tol} and *syn*-3_{tol} resulted in complete consumption of *anti*-3_{tol} to give *syn*-3_{tol}+1_t. The mixture of 0.33 equiv of *syn*-3_{tol}+1_t and 0.67 equiv of *syn*-3_{tol} could then be photolyzed to give a mixture of *anti*-3_{tol}, *anti*-3_{tol}+1_t, *syn*-3_{tol}+1_t, and *syn*-3_{tol} analogous to that shown in Figure 7a. The rate of conversion of *anti*-3_{tol}+1_t to *syn*-3_{tol}+1_t in this mixture at 0 °C was found to be 15 times slower than the rate of conversion of *anti*-3_{tol} to *syn*-3_{tol} at 0 °C (Table VIII). Note that the rate of conversion of *anti*-3_{thf}+1_t to *syn*-3_{thf}+1_t is significantly slower than the rate of conversion of *anti*-3_{tol}+1_t to *syn*-3_{tol}+1_t (Table VIII), consistent again with thf binding to anti forms. Since the conversion of *anti*-3_{tol}+1_t to *syn*-3_{tol}+1_t was strictly first-order through at least three half-lives, the equilibrium constant ($k_{a/s}/k_{s/a}$) could be estimated to be >100.

Reaction of *syn*-Mo(NAr)(CHCMe$_2$Ph)(OR$_{F3}$)$_2$ with NBDF6 in Toluene.

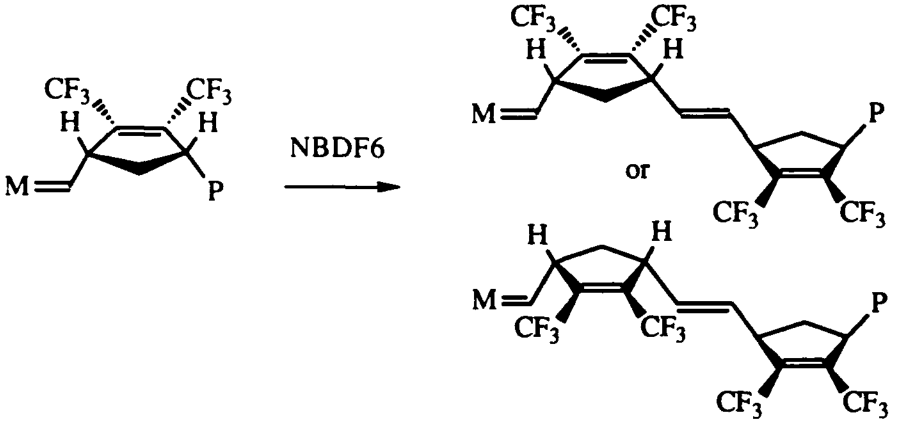
One equivalent of NBDF6 *reacted with* *syn*-2_{tol} (~0.01 M *in toluene*-d_8) at an appreciable rate only at temperatures above -25 °C. A new doublet ($^3J_{H\alpha H\beta}$ = 7.6 Hz) appeared for H_α in *syn*-2_{tol}+1_c about 0.1 ppm downfield of the H_α resonance for *syn*-2_{tol}; note that the C=C bond is cis ($^3J_{HH}$ = 11.3 Hz). Another doublet ($^3J_{H\alpha H\beta}$ = 8.3 Hz) appeared more slowly in the alkylidene region 0.1 ppm downfield of that for *syn*-2_{tol}+1_c that can be assigned to H_α in *syn*-2_{tol}+1_t ($^3J_{HH}$ = 15.1 Hz). The ratio of *syn*-2_{tol}+1_c to *syn*-2_{tol}+1_t is typically 4:1. It is interesting to note that the $^3J_{H\alpha H\beta}$ values for *syn*-2_{tol}+1_c and *syn*-2_{tol}+1_t are slightly different, indicating that the geometry of the C=C bond directly influences the orientation (on the average) of the cyclopentene ring, and therefore $^3J_{H\alpha H\beta}$.

An important question is whether *syn*-2_{tol}+1_t is formed by addition of NBDF6 to *syn*-2_{tol} or whether *anti*-2_{tol} can be generated by isomerization of *syn*-2_{tol} at -26 °C at a rate great enough to be the source of *syn*-2_{tol}+1_t. By extrapolation we find that $k_{a/s}$ = 2.4 x 10^{-2} s^{-1} at -26 °C. *If* the temperature dependence of K_{eq} is roughly the same for 2_{tol} as for 3_{tol}, then K_{eq} can be estimated as 1.1 x 10^{-5} at -26 °C for $\mathbf{2}_{tol}$ and $k_{s/a}$ then can be calculated to be 2.2 x 10^{-6} s^{-1}. If we assume that *anti*-$\mathbf{2}_{tol}$ is so reactive that conversion of syn to anti is rate-limiting, then a value of $k_{s/a}$ = 2.2 x 10^{-6} s^{-1} would imply that ~20% of *syn*-$\mathbf{2}_{tol}$+1_t could form via *anti*-$\mathbf{2}_{tol}$ in 3 hours. Since about 10% of *syn*-$\mathbf{2}_{tol}$ is converted to *syn*-$\mathbf{2}_{tol}$+1_t in a period of approximately three hours at -26 °C, it is possible that *syn*-$\mathbf{2}_{tol}$+1_t forms by addition of NBDF6 to *anti*-$\mathbf{2}_{tol}$, and that *syn*-$\mathbf{2}_{tol}$+1_c forms by addition of NBDF6 to *syn*-$\mathbf{2}_{tol}$ (equation 4).

$$syn\text{-}\mathbf{2}_{tol}+1_t \xleftarrow[\text{NBDF6}]{-26°C} anti\text{-}\mathbf{2}_{tol} \underset{k_{s/a}}{\overset{k_{a/s}}{\rightleftharpoons}} syn\text{-}\mathbf{2}_{tol} \xrightarrow[\text{NBDF6}]{-26°C} syn\text{-}\mathbf{2}_{tol}+1_c \qquad (4)$$

Reaction of Mo(NAr)(CH-t-Bu)(O-t-Bu)$_2$ with NBDF6.

The reaction between **1** and NBDF6 has already been reported, although at that time relatively little was known about syn and anti rotamers and their rates of interconversion.[10] Unfortunately, as we have noted here, it is not possible to study the relative reactivities of *anti*-**1** and *syn*-**1** directly since isomerization of *anti*-**1** to *syn*-**1** is too fast. Nevertheless, the previous results can now be reinterpreted in light of the findings described so far here for reactions involving **3** and **2**. It was observed that addition of 10 or more equivalents of NBDF6 to **1** in C_6D_6 yields two H_α doublets in the alkylidene region for the living alkylidenes (multiple insertion products) that are separated by only ~3 Hz (at 500 MHz). The major species (~86%) and the minor species have identical values for $^3J_{H\alpha H\beta}$ (7 Hz). In the original study these two alkylidene resonances were tentatively attributed to syn (major) and anti rotamers, respectively.[10] However, it now seems unlikely that this is the case for several reasons. First, this interpretation would require that anti and syn rotamers not interconvert rapidly on the NMR time scale, i.e., that k_{sum} (= $k_{a/s}$ + $k_{s/a}$) be very much less than 3 Hz. However, we have found that k_{sum} is ~500 Hz for $\mathbf{1}_{tol}$ (Table VI). Second, it seems unlikely that H_α resonances for anti and syn resonances would be nearly coincident. Third, $^3J_{H\alpha H\beta}$ is the same for the two isomers, whereas in all cases discussed so far $^3J_{H\alpha H\beta}$ for the anti rotamer was found to be larger than $^3J_{H\alpha H\beta}$ for the syn rotamer. Fourth, K_{eq} would be ~6 for the syn and anti multiple insertion products, a value that is inconsistent with K_{eq} data for a *t*-butoxide initiator or first insertion product in toluene (Tables II and VIII). For these cumulative reasons, it seems unlikely that the two H_α resonances observed for multiple insertion products are actually due to syn and anti rotamers. The possibility that the two H_α resonances correspond to the trans or cis configuration of the C=C bond next to the M=C bond also can be ruled out on the basis of the fact that the polymer that is generated from **1** contains ~98% trans C=C bonds. Therefore, the only alternative seems to be that the two H_α resonances arise from the two possible relative orientations of the first two cyclopentene rings in the polymer chain (tacticities; equation 5; P = polymer). Although the tacticity of the particular polymer sample that was prepared in the previously reported NMR studies is not known, the tacticity of such polymers is often in the range 90 to 95 %,[10] a figure that would be consistent with the relative intensities of the two H_α resonances. The near coincidence of the two syn H_α resonances in insertion products having different tacticities would be expected.



(5)

Reaction of Mo(N-2-*t*-BuC$_6$H$_4$)(CHCMe$_3$)[OCMe(CF$_3$)$_2$]$_2$ (12') with NBDF6 in thf.

It is important to establish how complexes that contain imido ligands other than the 2,6-diisopropylphenyl imido ligand behave. Initiator **12'** was a convenient one to study. Experiments similar to those described so far showed that NBDF6 adds to *anti*-**12'**$_{thf}$ far faster than it adds to *syn*-**12'**$_{thf}$. At -37 °C *anti*-**12'**$_{thf}$ begins to react selectively with monomer to yield *syn*-**12'**$_{thf}$+**1**$_t$ (δH_α = 12.69 ppm, $J_{CH\alpha}$ = 126.4 Hz at 20 °C by ^{1}H NMR, $^3J_{H\alpha H\beta}$ = 7.3 Hz, olefinic $^3J_{HH}$ = 15.5 Hz). If only enough monomer is added (0.33 equiv) to consume *anti*-**12'**$_{\text{thf}}$, and the mixture of *syn*-**12'**$_{\text{thf}}$+1_t and *syn*-**12'**$_{\text{thf}}$ photolyzed again, then the mixture of *anti*-**12'**$_{\text{thf}}$+1_t, *anti*-**12'**$_{\text{thf}}$, *syn*-**12'**$_{\text{thf}}$+1_t, and *syn*-**12'**$_{\text{thf}}$ shown in Figure 7b is generated. The H_α doublet resonance for *anti*-**12'**$_{\text{thf}}$+1_t was partially obscured by the H_α resonance for *anti*-**12'**$_{\text{thf}}$ ($^3J_{H\alpha H\beta} \geq$ 7.6 Hz after resolution enhancement). The isomerization of *anti*-**12'**$_{\text{thf}}$+1_t to *syn*-**12'**$_{\text{thf}}$+1_t was determined by reversible first order kinetics to be 1.8×10^{-4} s^{-1}at 20 °C; K_{eq} at this temperature was found to be approximately 13 (Table VIII). Therefore in all important respects, addition of NBDF6 to **12'** is similar to addition of NBDF6 to **3**.

If more NBDF6 is added than is necessary to consume *anti*-**12'**$_{\text{thf}}$ in a photolyzed sample, then at -4.0 °C *syn*-**12'**$_{\text{thf}}$ begins to react with monomer to yield a new alkylidene complex with an H_α resonance at 12.71 ppm that partially overlaps the H_α resonance for *syn*-**12'**$_{\text{thf}}$+1_t at 12.69 ppm. Resolution enhancement allowed $^3J_{H\alpha H\beta}$ = 8.0 Hz to be determined as well as $^3J_{HH}$ = 11.7 Hz for the olefinic protons, consistent with formation of a cis double bond, i.e., *syn*-**12'**$_{\text{thf}}$ → *syn*-**12'**$_{\text{thf}}$+1_c. These results (summarized in equation 6) are analogous to those found for the 2,6-diisopropylphenyl imido complexes. The several small H_α resonances that begin to appear ~0.2 ppm downfield of the H_α resonances for *syn*-**12'**$_{\text{thf}}$+1_c and *syn*-**12'**$_{\text{thf}}$+1_t probably result from further addition of NBDF6 to *syn*-**12'**$_{\text{thf}}$+1 complexes. No anti multiple insertion products are observed.

$$\textit{syn-}\mathbf{12'}_{\text{thf}}+1_t \xleftarrow[\text{NBDF6}]{-37\ ^\circ\text{C}} \textit{anti-}\mathbf{12'}_{\text{thf}} \underset{\text{slow}}{\overset{\text{slow}}{\rightleftharpoons}} \textit{syn-}\mathbf{12'}_{\text{thf}} \xrightarrow[\text{NBDF6}]{-4\ ^\circ\text{C}} \textit{syn-}\mathbf{12'}_{\text{thf}}+1_c \qquad (6)$$

Reactions Between Mo(N-1-Adamantyl)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (15) and NBDF6 in Toluene.

Studies of the reaction of **15**$_{\text{tol}}$ with NBDF6 revealed some significant differences between an adamantylimido and an arylimido complex that reveal the degree to which the imido ligand is likely to be involved at a fundamental level in determining polymer structure. Addition of about 3 equiv of NBDF6 to a mixture of *anti*-**15**$_{\text{tol}}$ and *syn*-**15**$_{\text{tol}}$ results in the immediate formation of a dark gray color as the sample is thawed at -95 °C. At -95 °C, *both syn*-**15**$_{\text{tol}}$ (H_α at 11.70 ppm) and *anti*-**15**$_{\text{tol}}$ (H_α at 12.95 ppm, Figure 8), which essentially do not interconvert at this temperature, are consumed, and *three* new resonances appear. One of these (at 12.15 ppm) can be assigned to H_α in *syn*-**15**$_{\text{tol}}$+1$_{\text{t}}$ (olefinic $^3J_{HH}$ ~14.5 Hz). (Note that the H_α resonance is not a well-resolved doublet under these circumstances, although it is a well-resolved doublet at room temperature; see later.) The H_α resonance at 13.39 ppm can be assigned to *anti*-**15**$_{\text{tol}}$+1$_{\text{t}}$ ($^3J_{H\alpha H\beta}$ = 9.1 Hz; $^3J_{HH}$ = 15.4 Hz). The third resonance (at 12.00 ppm) does not appear to be an H_α resonance for a monoinsertion product because no olefinic proton resonances could be found that go with it. Furthermore, this unknown intermediate is transformed into *anti*-**15**$_{\text{tol}}$+1$_{\text{t}}$ as the temperature is raised to -83 °C. We speculate that *anti*-**15**$_{\text{tol}}$ reacts rapidly with NBDF6 to give *syn*-**15**$_{\text{tol}}$+1$_{\text{t}}$, a type of behavior that is analogous to the behavior of other complexes discussed so far here, but *syn*-**15**$_{\text{tol}}$ reacts unexpectedly rapidly with NBDF6 to give an intermediate that disappears as *anti*-**15**$_{\text{tol}}$+1$_{\text{t}}$ is formed. The latter behavior (equation 7) is completely different from any we have observed so far in this study.

$$\textit{syn}\text{-}\mathbf{15}_{\text{tol}} + \text{NBDF6} \longrightarrow \text{intermediate} \longrightarrow \textit{anti}\text{-}\mathbf{15}_{\text{tol}} + 1_{\text{t}} \qquad (7)$$

In Figure 9 is shown the result of further reactions of *anti*-**15**$_{\text{tol}}$+1$_{\text{t}}$ and *syn*-**15**$_{\text{tol}}$+1$_{\text{t}}$ with NBDF6. As more NBDF6 is consumed syn insertion products begin to dominate, a result that is consistent with the only slightly greater reactivity of anti insertion products. It is interesting to note that a tiny amount of *syn*-**15**$_{\text{tol}}$ reappeared as the temperature was raised from -95 °C, a result that suggests that formation of the unknown intermediate *may be reversible*.

Further studies were carried out in an attempt to identify the unknown intermediate. Addition of one equiv of monomer to *syn*-**15** in pentane at -95 °C slowly yielded (over a period of days) a purple-gray solution and an off-white flocculant precipitate. Upon warming the sample to room temperature the precipitate dissolved and a yellow solution was obtained. Yellow crystals formed upon cooling this solution slowly to -95 °C. A 500 MHz ^{1}H NMR spectrum of these crystals in toluene-d_8 at 25° showed them to consist largely of *syn*-$\mathbf{15}_{tol}$+1_t (Figure 10; δH_α = 11.96 ppm, $J_{CH\alpha}$ = 128.3 Hz, $^3J_{H\alpha H\beta}$ = 8.1 Hz) and a small amount of *anti*-$\mathbf{15}_{tol}$+1_t. We propose that *anti*-$\mathbf{15}_{tol}$+1_t is the initial product of the reaction between *syn*-$\mathbf{15}_{tol}$ and NBDF6 and that *syn*-$\mathbf{15}_{tol}$+1_t forms by isomerization of *anti*-$\mathbf{15}_{tol}$+1_t at 25 °C (K_{eq} = 23). The chemical shift of H_α in *anti*-$\mathbf{15}_{tol}$+1_t (12.47 ppm, 25 °C) and the coupling constant ($^3J_{H\alpha H\beta}$ = 11.5 Hz) are considerably different from the values obtained at -89 °C (13.39 ppm, $^3J_{H\alpha H\beta}$ = 9.1 Hz), although δH_α and $^3J_{H\alpha H\beta}$ for *syn*-$\mathbf{15}_{tol}$+1_t do not change significantly with temperature in the same range. Interestingly, at 25°C the H_α resonance for *syn*-15_{tol}+1_t is a well-resolved doublet, not the broad, poorly resolved resonance found at low temperatures (Figure 8).

There is no evidence that the unknown intermediate formed from NBDF6 and *syn*-$\mathbf{15}_{tol}$ is an insertion product. Therefore it must be either an olefin adduct or a metallacycle of a type not previously seen; in either case olefin could be lost to regenerate *syn*-$\mathbf{15}_{tol}$. There is now evidence in the literature that an olefin adduct of a d^0 tungsten alkylidene complex can be observed at low temperatures.[27] If the unknown species in our system is formed reversibly, it need not be on the pathway to formation of an insertion product. However, whether this unknown species is a true intermediate in the reaction of *syn*-$\mathbf{15}_{tol}$ with NBDF6 to give *anti*-$\mathbf{15}_{tol}$+1, or not, the fact that *syn*-$\mathbf{15}_{tol}$ reacts with NBDF6 at a rate that is of the same order as the rate at which *anti*-$\mathbf{15}_{tol}$ reacts with NBDF6 at low temperatures is still an important finding, one that differs markedly from the results involving arylimido complexes, and one that has a significant impact in determining the structure of the resulting poly-NBDF6 (see below).

Polymerization of NBDF6 and Correlation of Cis/Trans Structure with the Nature of the Alkoxide.

2,3-Bis(trifluoromethyl)norbornadiene was polymerized employing many of the complexes examined here as initiators and the polydispersity and percent cis content determined by techniques that have been employed previously.[10,28] The tacticity of such polymers is discussed elsewhere.[29] The results are listed in Table IX. All polydispersities are low (<1.17) and the yields are high, consistent with a 'living' polymerization process,[5,6] except in the case of the polymer prepared employing $\mathbf{15}_{tol}$ as the initiator. In many cases, a small amount of a doubled molecular weight polymer is observed by GPC which we ascribe to reactions involving traces of oxygen.[30] The molecular weights that are listed are based on calibration with polystyrene standards. Variations in molecular weights may be real (i.e., the result of experimental error in initiator concentration), but also could result from different GPC behavior of polymers with different cis/trans structures and tacticities. It is important to emphasize that low polydispersity polymer is obtained even when catalysts that are relatively active for the metathesis of ordinary olefins, such as **3** in toluene, are employed as initiators. Therefore the polymer structure is the result of only primary metathesis reactions (insertions of monomer). The living nature of these particular systems can be ascribed to the deactivated nature of the monomer, of the disubstituted double bonds that are formed in the polymer backbone, and of the intermediate alkylidene complexes, all by the powerful electron-withdrawing trifluoromethyl groups. It should not be assumed that other monomers necessarily will be polymerized in a living manner with a relatively active species such as **3** in toluene. The solubility of poly-NBDF6 decreases dramatically as the cis content and tacticity increase. For example, poly-NBDF6 made employing $\mathbf{4}_{tol}$ as the initiator (77% syndiotactic) is significantly less soluble than polymers made from $\mathbf{3}_{tol}$ (62% isotactic) or $\mathbf{5}_{tol}$ (40% isotactic). (Tacticities of such polymers will be discussed elsewhere.[29])

The double bonds formed in poly-NBDF6 prepared employing **3** as the initiator in thf are ~98% cis.[12] NMR studies presented above indicated that a cis double bond is formed upon addition of the first equivalent of NBDF6 to *syn*-$\mathbf{3}_{thf}$ and that a syn first-insertion product is generated. The all cis structure can be explained if we assume that a syn rotamer containing a cis double bond is generated upon addition of NBDF6 to *syn*-$\mathbf{3}_{thf}+1_{c}$ and each succeeding insertion product, since virtually no anti rotamer can be generated at any stage of the polymerization process by isomerization of a syn rotamer ($k_{s/a} = 3.1 \times 10^{-6}\ s^{-1}$ at 0 °C for $\mathbf{3}_{tol}$; $k_{s/a} < 2.9 \times 10^{-6}\ s^{-1}$ for $\mathbf{3}_{tol}+1$ at 0 °C; Table VIII). We also know that NDBF6 adds to *anti*-$\mathbf{3}_{thf}$ to yield only a syn insertion product. Therefore, only syn propagating alkylidenes are kinetically relevant, there is only a single propagation rate (assuming that k_p is independent of chain length), polymers having a narrow molecular weight distribution are formed, and only cis double bonds are generated. At this stage it is not known whether the trans double bonds that are present are formed when monomer adds to a small amount of anti alkylidene that is generated by isomerization of a syn alkylidene, or when a monomer adds "incorrectly" to a syn alkylidene to give a trans metallacycle instead of a cis metallacycle.

Similar results were obtained employing **3'** in toluene (Table VIII). The rate of polymerization was qualitatively faster in toluene than in thf, but both $k_{a/s}$ and $k_{s/a}$ are larger in toluene than in thf and $k_{a/s}$ for the first-insertion products also is larger in toluene than in thf (Table VIII). Therefore, the anti rotamer must still be inaccessible during the polymerization reaction. On the basis of these findings we propose that the polymerization proceeds by the same mechanism in both toluene and thf, i.e., NDBF6 adds to the four-coordinate complex, not the five-coordinate base adduct, and in the same manner in each solvent. High cis poly(NBDF6) precipitates from toluene during the polymerization reaction. Nevertheless, the monomer is consumed completely and low or relatively low polydispersities are obtained.

Polymerizations employing $\mathbf{4}_{tol}$ as the initiator required more time than those employing $\mathbf{3}_{tol}$. These findings are consistent with the relative olefin metathesis rates of *cis*-2-pentene by analogous tungsten complexes ($OCMe_3 < OR_{F13} < OR_{F3} < OR_{F6}$[31]). The slightly lower cis content of the polymer (95%) obtained employing **4** could be attributed to some chain growth via anti alkylidenes, but a competing, "incorrect" mode of addition of monomer to the syn rotamer to give a trans metallacycle cannot be ruled out.

Polymers prepared with $\mathbf{2'}_{tol}$ (containing OR_{F3} alkoxides) contain only 22% cis double bonds. This result is consistent with the reactivity studies discussed above since we know that both cis and trans double bonds are generated when NBDF6 is added to *syn*-$\mathbf{2}_{tol}$ at low temperatures, the trans double bonds probably arising via the reaction between NBDF6 and *anti*-$\mathbf{2}_{tol}$. The same is likely to be the case for **2'**. In short, in a bulk polymerization more anti alkylidene is kinetically accessible during polymerization, and trans double bonds therefore are formed via reaction of NDBF6 with anti intermediates.

The high trans content of polymers prepared employing **1** or **1'** as the initiator provides further evidence for a correlation between trans content and accessibility of the anti rotamer. If the syn rotamer of **1** and subsequent insertion products is much less reactive than the anti rotamer, but the anti rotamer is still reactive enough to form polymer and syn to anti conversion is fast, a polymer having only trans double bonds should be generated. An alternative explanation of the selective formation of trans polymer by **1** (or largely trans polymer by **2'**) is that the mechanism of polymerization that gives trans polymer is different from the mechanism that gives cis polymer (see discussion later). The trans content of poly-NBDF6 prepared employing **1** was virtually the same in samples prepared at 0° or 52 °C, at catalyst concentrations between 2 and 10 mM, and in mixtures of toluene and thf. The cis content in the poly-NBDF6 formed employing **11** as the initiator is virtually identical to that prepared employing **1** as the initiator, as might be expected on the basis of similar alkylidene isomerization rates in **1** and **11** and similar steric and electronic properties of *t*-butoxide and adamantoxide ligands.

Polymers synthesized with initiators that contain the 2,6-dimethylphenylimido ligand were virtually identical to those prepared with initiators that contain the 2,6-diisopropylphenylimido ligand. A polymer formed employing $\mathbf{10}_{tol}$ was found to contain 99% cis olefins, a minor improvement over the cis content (95%) in poly-NBDF6 prepared from $\mathbf{4}_{tol}$ as the initiator. The higher cis content could be ascribed to a significantly faster propagation rate for *syn*-**10** in toluene than for *syn*-**4** in toluene, since little difference in $k_{a/s}$ between $\mathbf{10}_{tol}$ and $\mathbf{4}_{tol}$ was found. Such a rate difference could be traced to the less crowded coordination sphere in $\mathbf{10}_{tol}$, rather than to a change in the electronic nature of the initiators. It should be noted that a dramatic difference in structure of polyNBDF6 prepared with diisopropylphenylimido and dimethylphenylimido binaphtholate catalysts has been noted recently.[26]

Polymerizations employing complexes that contain unsymmetrically substituted imido groups, such as 2-*t*-butylphenyl imido, again can be explained in terms of anti and syn rotamer accessibility. The polymer synthesized employing $\mathbf{12'}_{thf}$ as the initiator contained only 72% cis bonds compared to ~98% cis bonds in polymers prepared with $\mathbf{3}^{12}$ or **3'**, even though both initiators contain F6 alkoxides. The fact that alkylidene isomerization rates are ~250 times faster for $\mathbf{12'}_{thf}$ than for $\mathbf{3}_{thf}$ is believed to be the primary reason; a significant amount of anti rotamer is accessible on the time scale of the polymerization and therefore some trans C=C bonds (28%) can form. Poly-NBDF6 obtained employing **12'** in toluene was identical to that obtained employing **12'** in thf, in spite of the fact that K_{eq} is much smaller in thf than in toluene (Table II).

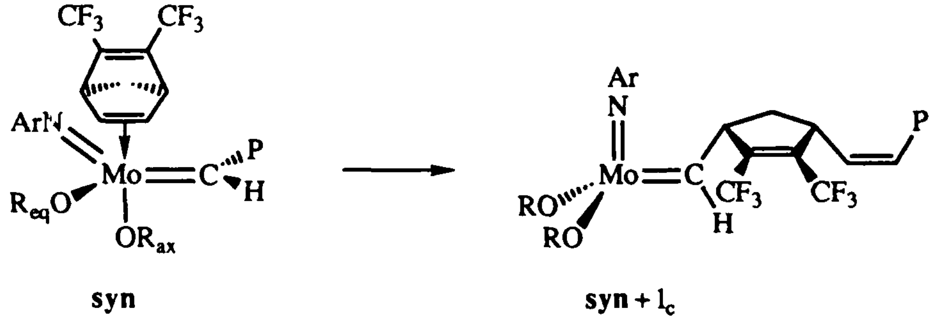
The rapid alkylidene isomerization process in **12'** that we propose gives rise to trans C=C bonds can be counteracted to some degree by replacing OR_{F6} alkoxides with OR_{F9} alkoxides, (cf. $k_{a/s}$ for $\mathbf{13}_{tol}$ and $\mathbf{12}_{tol}$; Table IV). The anticipated result was that poly-NBDF6 made from **13** has a much higher cis content; poly-NBDF6 made from $\mathbf{13}_{tol}$ contains 99% cis double bonds (versus 72% for $\mathbf{12'}_{tol}$). We propose that the anti rotamer cannot compete with the syn rotamer when OR_{F9} alkoxides are employed, so all cis polymer is formed.

The strong correlation between anti rotamer reactivity and trans content and between syn rotamer reactivity and cis content breaks down when **15** is the initiator. Isomerization rate studies found that $k_{a/s}$ values for $\mathbf{15}_{tol}$ were intermediate between those for $\mathbf{2}_{tol}$ and $\mathbf{3}_{tol}$ (Table IV), while reactivity studies showed not only that anti and syn rotamers are about equally reactive, but both produce trans C=C bonds. Therefore one might have expected all-*trans* polymer to be formed. In fact, poly-NBDF6 prepared using **15** as the initiator contained ~20% cis double bonds.[32] Cis C=C bonds must result from propagation reactions that are less trans selective than reactions involving the initiator (*syn*-**15**→*anti*-**15**+1_t; *anti*-**15**→*syn*-**15**+1_t).

DISCUSSION

One of the important questions when we began this work was what is the role of a coordinating ligand such as thf? On the basis of what we have described here we conclude that thf most likely behaves as a competitive inhibitor, but only when the metal is relatively electrophilic, and that except for bulk solvent effects, all polymerization steps (and alkylidene "rotations") proceed via four-coordinate imido alkylidene complexes. The results presented here should be compared with those described in a thorough study of cyclobutene ring-opening by $W(NAr)(CH\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2$ in the presence of trimethylphosphine, which emphasizes (*inter alia*) the importance of decreasing the ratio of the rate of chain propagation relative to chain initiation, a technique that also was employed to polymerize acetylene in a living manner.[33] Both anti and syn rotamers (~1:1) were observed at equilibrium in the operating W catalyst system, the binding constant of PMe_3 to W was large, and the cis content of the resulting polycyclobutene (1,4-polybutadiene) was ~80%.

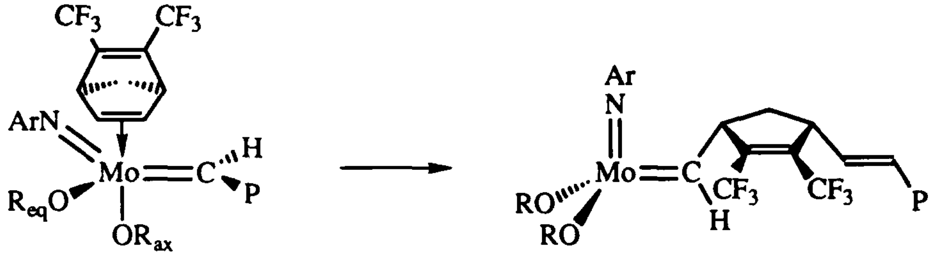
The main result of the study described here is that the high cis content of poly-NBDF6 formed when $Mo(NAr)(CHR')(OR")_2$ initiators are employed that contain very electrophilic OR" groups[12] can be ascribed to chain growth via syn rotamers as a consequence of (i) the inaccessibility of an anti rotamer via rotation about the Mo=C bond on the time scale of the polymerization, and (ii) addition of NBDF6 to a syn rotamer to yield another syn rotamer and a cis C=C bond. Since there is evidence in the literature that a base will add to the CNO face of catalysts of this type when the alkoxide is OR_{F6} and that the aryl ring rotates into the equatorial plane of the resulting trigonal bipyramidal base adduct that contains the imido and alkylidene ligands,[14] we postulate that NBDF6 approaches the CNO face of the catalyst so that the methylene group in the 7 position lies approximately over the "flattened" arylimido ring (the "7-syn" position) and that the C=C and Mo=C vectors are approximately parallel (equation 8). Formation of an "all cis" metallacycle and subsequent ring-opening would then yield a cis double bond and a syn insertion product. (We will be concerned here only with the most basic features of the proposed mechanism, not subtleties such as rearrangement of the metal core of five-



(8)

coordinate metallacyclobutane intermediates, the degree to which the intermediate metallacycle is "bent" in various core geometries, etc.[1]) If the monomer adds to the other CNO face of the initiator then a **syn+1$_c$** product would be obtained that has the opposite configuration at C_β in the alkylidene ligand that is shown in equation 8. The cyclopentene ring and polymer chain will then adopt the most favorable (as yet unknown) orientation that (we will assume) does *not* involve coordination of any double bond in the polymer chain to the metal. (Coordination of a double bond in the polymer chain to the metal has been proposed as an important feature of polymer growth, although no direct evidence of coordination of a C=C bond in a growing polymer chain has been uncovered.[19,34]) The two faces of the Mo=C bond are now inequivalent, so the orientation of the cyclopentene ring that is adopted will determine to what extent the next equivalent of NBDF6 will add to the same side of the Mo=C bond (in the same way) to yield an isotactic polymer, or to the opposite side of the Mo=C bond to yield a syndiotactic polymer.[29] The "7-syn" orientation of the monomer is preferred in arylimido complexes because the relatively flat aryl ring must lie approximately in the trigonal plane in the transition state shown in equation 8 and because steric interaction between the incoming NBDF6 and the R group of the equatorial alkoxide (OR_{eq}) is thereby minimized. Steric interaction between the incoming monomer and the alkylidene's substituent must be of relatively little importance. Steric interaction between the two *alkoxide* ligands prevents the equatorial alkoxide R group from simply turning toward the axial alkoxide and thereby creating enough space for the monomer to approach the CNO face in the "7-anti" orientation (180° to the orientation shown). The dramatically lower reactivity of the syn $Mo(NAr)(CHP)(OR_{F6})_2$ rotamer (P = polymer) relative to the anti rotamer might be ascribed to steric interaction between the growing polymer and the ortho substituents in the NAr ring in the pseudo trigonal bipyramidal transition state shown, as suggested by the structure of *syn*-$Mo(NAr)(CH\text{-}t\text{-}Bu)(OR_{F6})_2(PMe_3)$.[14]

Evidence in the literature suggests that bases also will add to the CNO face of a pseudotetrahedral catalyst containing an anti alkylidene ligand and an OR_{F6} alkoxide.[14] If steric interaction between the incoming NBDF6 and the equatorial alkoxide forces the NBDF6 to add in roughly the same manner (the "7-syn" orientation), then the anti rotamer will give rise to a *syn* insertion product that has one or the other possible configuration at C$_\beta$ and that contains a *trans* C=C bond (e.g., equation 9). The anti rotamer is more reactive than the syn rotamer since there is relatively little steric interaction between the alkylidene ligand's H$_\alpha$ (which points toward the arylimido ring) and the arylimido ligand's ortho substituents in the pseudo TBP transition state (eq. 9). There is also less interaction between the incoming monomer and the polymer chain in an anti rotamer than in a syn rotamer. If the anti rotamer is several orders of magnitude more reactive than the syn rotamer, then the small amount of trans polymer that forms in systems in which the alkoxide is very electron-withdrawing could arise via addition of NBDF6 to the anti rotamer. Reactivity studies involving **2** in toluene were fully consistent with this proposal.

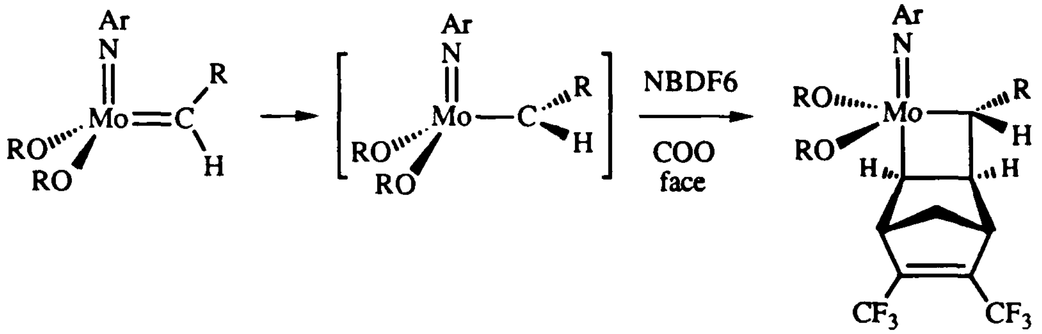


anti **syn + 1$_t$** (9)

An important question is whether the trend toward higher trans content (up to 98% trans) as the alkoxide becomes less electron-withdrawing and alkylidenes rotate rapidly on the time scale of polymerization can be ascribed to chain propagation solely via the anti rotamer (equation 10). Since K$_{eq}$ is ~10^3 and only ~2% cis polymer is formed, an anti rotamer that gives rise to

$$\text{anti} \xrightarrow{\text{NBDF}_6} \text{syn}+1_t \overset{\text{fast}}{\rightleftharpoons} \text{anti}+1_t \xrightarrow{\text{NBDF}_6} \text{syn}+2_{t,t} \xrightarrow{\text{etc.}} \text{all trans} \qquad (10)$$

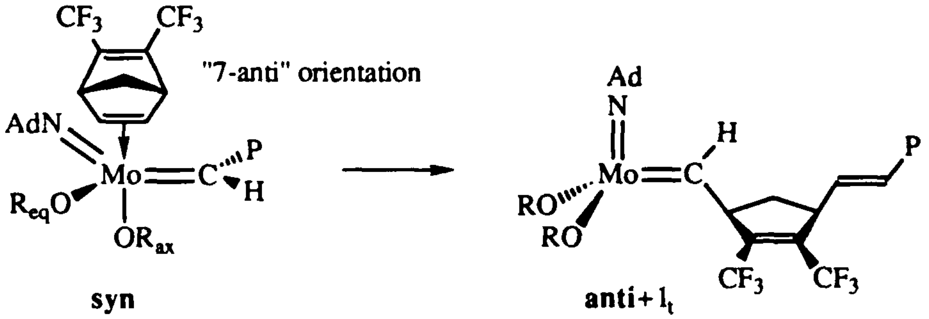
polymer that contains essentially only trans C=C bonds would have to be approximately five orders of magnitude more reactive than a syn rotamer toward NBDF6. Although this large reactivity difference does not exclude the possibility that chain growth to give trans polymer takes place solely via anti intermediates, it is large enough to require that serious consideration be given to the possibility that chain growth occurs via a mechanism other than NBDF6 attack on the CNO face of the catalyst as the alkoxide becomes less electron-withdrawing. The only other plausible way of forming a metallacycle intermediate is via NBDF6 attack on the COO face, but only if the alkylidene rotates (in *either* the syn or anti rotamer) by up to 90° in the process (e.g., equation 11).[35] In this case the direction of addition to the Mo=C bond might be determined by steric interactions between NBDF6 and the *alkylidene* substituent, since steric interaction between NBDF6 and each alkoxide would be approximately the same in the two possible approaches of the monomer to the COO face. Considering alkylidene rotation as part of the process of adding an olefin to the metal is possible only because alkylidene rotation is fast on the time scale of polymerization, and because the Mo=C bond in a "rotated" alkylidene probably would be inherently much more reactive than the Mo=C bond in a "normal" alkylidene that lies in the N/Mo/C plane. (In the "rotated" alkylidene three π bonding LCAO's constructed from the nitrogen p_x, carbon p_y, and Mo d_{xy} orbitals contain 4 electrons; one electron pair would be in what is approximately a non-bonding orbital.) Therefore at this stage we must leave open the question as to how all trans polymers are formed.



(11)

If cis double bonds are formed selectively by CNO face attack in a syn rotamer and trans double bonds are formed selectively by CNO face attack in an anti rotamer, then the catalytic reaction can be said to involve two kinetically distinct pathways related by an equilibrium between two low energy species (anti and syn rotamers in this case). The best documented and perhaps best known catalytic reaction in this category is the asymmetric hydrogenation reaction catalyzed by chiral rhodium phosphine complexes.[36] If cis double bonds are formed selectively by CNO face attack in a syn rotamer and trans double bonds are formed selectively by COO face attack in either rotamer with concomitant alkylidene rotation by 90°, the two reactions still could be related via some equilibrium between two intermediates, one in each manifold. It is interesting to compare a competitive CNO and COO face attack with a similar proposed "face selectivity" in rhenium imido alkylidyne bisalkoxide complexes that are catalysts for the metathesis of bulky disubstituted acetylenes.[37] It was proposed that only bulky disubstituted acetylenes were metathesized because they were forced to add to the less favorable COO face for steric reasons, and in so doing were denied access to a stable, catalytically inactive type of rhenacyclobutadiene complex.

The results of reactivity studies of NBDF6 with **15** and the results of bulk polymerizations strongly suggest that the steric properties of the imido ligand are of fundamental importance in determining polymer cis/trans structure. The approximately equal reactivity of anti and syn rotamers and formation of a trans C=C bond when the syn rotamer reacts with NBDF6 are characteristic of reactions involving **15**. An attractive possibility is that NBDF6 does not add selectively in the "7-syn" orientation, but primarily in the "7-anti" orientation in order to avoid steric interaction with the roughly spherical adamantyl group (equation 12). The "7-anti" approach of NBDF6 to the syn rotamer would explain the *syn*-**15**→*anti*-**15**+1_t finding. The anti insertion product has approximately the same reactivity as a syn insertion product and so would also react with NBDF6. NBDF6 adds to *anti*-**15** in the "7-syn" position again, perhaps



(12)

because of a reduced steric interaction between the monomer and the alkylidene's substituent in the anti rotamer, even though steric interaction with the adamantylimido group is still significant. Evidently "mistakes" beyond the first insertion of monomer yield cis C=C bonds and therefore formation of some cis double bonds in the polymer. However, why an intermediate is formed rapidly from the syn rotamer, and exactly what that intermediate is, is still a mystery.

We hope to compare the findings reported here with those obtained in systems that employ other alkoxide (or phenoxide) or imido ligands, e.g., the recent variations of the complexes studied here that contain binaphtholate or tartrate derivatives,[26] and other monomers. An example of the extent to which mechanism can depend on identity of the monomer is illustrated by some recent results to be reported by Feast, Ivin, and Gibson, et al., which also provide an independent check of one of the rate constants reported here. They found that 1,7,7-trimethylnorbornene is polymerized very slowly by **3** in dichloromethane to give an all trans polymer at a rate that is independent of monomer concentration and with a rate constant that is essentially the same as $k_{s/a}$ at 298K for $\mathbf{3}_{tol}$ (7×10^{-5} s^{-1}; Table VI), consistent with a rate-limiting conversion of syn to anti rotamer followed by relatively rapid reaction of the anti rotamer with monomer to give a syn insertion product that contains a trans C=C bond.[38] (Evidently the rate of reaction of 1,7,7-trimethylnorbornene with syn rotamers is negligibly small.) We are at a stage where each well-defined catalyst system will have to be evaluated carefully and objectively, but it now seems possible that an understanding of how to control cis/trans selectivity and tacticity at a fundamental level is in the offing. Finally, it is important to point out that the principles elucidated here are also likely to operate in many classical catalyst systems, since few are likely to contain symmetric catalysts in which syn and anti rotamers cannot exist or have identical reactivities.

EXPERIMENTAL

All manipulations were performed in a Vacuum Atmospheres Glove Box or using standard high-vacuum line techniques. Toluene-d_8, thf-d_8, C_6D_6, and methylcyclohexane-d_{14} were purified by vacuum transfer from sodium benzophenone ketyl or by passing through activated alumina. CD_2Cl_2 and glyme-d_{10} was vacuum transferred from CaH_2. NMR spectra were collected on a Varian VXR 500 MHz spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane and coupling constants are reported in Hz. Actual temperatures during variable temperature experiments were determined by monitoring peak separation in neat MeOH below room temperature and ethylene glycol above room temperature. All temperature data are reported to ±1 °C. UV/Vis spectra were collected on a Hewlett-Packard 8452A diode array spectrophotometer using a 1 cm pathlength septum-capped quartz cell.

$Mo(NAr)(CHCMe_2Ph)(OCMe_3)_2$,[2] $Mo(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$,[4] $Mo(NAr)(CHCMe_2Ph)(OAr)_2$,[2] $Mo(NAr)(CHCMe_3)[OCMe(CF_3)_2]_2$,[2] $Mo(NAr)(CDCMe_3)[OCMe(CF_3)_2]_2$ (employing Me_3CCD_2MgCl),[2] and $W(NAr)(CHCMe_3)[OCMe(CF_3)_2]_2$[31] were prepared according to literature methods. The synthesis of all other initiators has been reported recently elsewhere.[39]

Photolyses.

Photolyses were performed on solutions of the initiators in sealed high resolution NMR tubes. Typical concentrations for NMR studies varied between 7.5 x 10^{-2} M up to 0.15 M (for some equilibrium constant measurements). The apparatus employed for photolysis consisted of the NMR sample tube supported in a quartz dewar containing pentane, hexane or heptane as a coolant, a cold finger of a low temperature refrigeration unit, and a thermocouple for temperature control. The dewar was further supported in a sodium borosilicate glass jar. The temperature typically employed was -85 °C. **1** was photolyzed in a methylcyclohexane-d_{14} glass at 77K.

A medium-pressure mercury vapor lamp (Hanovia 673A[22]) was employed. It was supported in a box with a small rectangular opening at one end. Two 2" x 2" filters were attached to the sodium borosilicate glass jar that surrounded the quartz dewar.

Kinetics of Rotational Isomer Interconversion.

After photolysis for up to 8 hours at -85 °C, the cold samples were placed directly into a preequilibrated 500 MHz ^1H NMR probe for rate constant analysis. (In the case of photolysis of **1** in mch-d_{14} at 77K the NMR probe was held at a temperature of -120 °C.) Samples were equilibrated 10 min prior to data collection. Raw data were collected over two to three half-lives by observing the disappearance of the anti resonance with respect to an internal standard (mesitylene). For all initiators other than $\mathbf{3}_{\mathrm{thf}}$, $\mathbf{7}_{\mathrm{tol}}$, $\mathbf{12'}_{\mathrm{thf}}$, and $\mathbf{15}_{\mathrm{tol}}$, the disappearance of the anti rotamer followed simple, irreversible first-order kinetics.[40] The rate of disappearance of these four initiators was obtained employing reversible first-order kinetics owing to the small value for K_{eq}.

In many cases, trace quantities of diethyl ether from the glove box atmosphere (up to 1% relative to catalyst) contaminated the initiator solutions. Diethyl ether is basic enough to bind only to the anti alkylidene of the most electrophilic initiators at low temperatures. However, it was never bound to a significant extent at the temperatures where anti converted back to syn and therefore the measured rates were not affected by its presence.

Measurements of Equilibrium Constants.

In all cases, equilibrium measurements were preceded by T_1 measurements on the syn alkylidenes and, where possible, on the anti alkylidene. If T_1 values could not be obtained at room temperature for the anti rotamers, values of T_1 were obtained at low temperatures in the absence of interconversion, where it was found that T_1 for the anti rotamer was always equal to or less than the value of the syn rotamer. The largest value obtained for T_1 at any temperature was 4.1 sec, and generally all initiator T_1 values were <1 sec at low temperatures. Recommended Ernst pulse widths were employed under the assumption that T_1 for the anti H_α resonance was less than or equal to that of the syn H_α resonance. Integrated areas were obtained by comparison of the anti resonance with the downfield ^{13}C satellite (0.55 %) of the syn resonance.

Reactivity Studies.

The following is a typical procedure: 60 mg (0.078 mmol) of *syn*-**3** was dissolved in 600 μL of toluene-d_8 or thf-d_8 in a thin-walled NMR tube equipped with a stopcock adapter. The solution was photolyzed at -85 °C until the photostationary state was reached (~33% anti rotamer). From 0.33 to 5 equiv of 2,3-bis(trifluoromethyl)norbornadiene were vacuum transferred either neat (5 equiv) or as a stock solution in the appropriate solvent onto the frozen solution. The frozen solution in the tube was not previously degassed, therefore upon thawing N_2 bubbles evolved which served to mix the monomer and initiator. Care was taken to maintain a temperature at which the anti to syn isomerization rate was negligible. The cold solution was then placed into a precooled NMR probe for observation. In the case of the addition of 0.33 equiv of NBDF6 the tubes were subsequently sealed and photolyzed again at -85 °C. The cold tubes were transferred to the preequilibrated NMR probe for determining the rate of conversion of anti to syn first-insertion product.

Synthesis of the first-insertion product of 15.

A pentane (1.2 mL) solution of **15** (49 mg, 0.066 mmol) was transferred to a glass tube (fitted with a Teflon stopcock) that could be attached to the high vacuum line. A stock pentane solution of NBDF6 (1.54 mL 0.069 mmol) was syringed into another tube (also fitted with a Teflon stopcock) that was similarly attached to the high vacuum line. The monomer solution was vacuum transferred onto the frozen catalyst solution. The solutions mixed rapidly upon thawing, but **15** precipitated anyway. Reaction commenced when the temperature reached ~-95 °C. At this temperature and with continued mixing the color changed from yellow to gray-purple as **15** was consumed. When the sample was allowed to warm to room temperature the precipitate dissolved and the color returned to the original yellow. The solution was cooled slowly down to -90 °C over several days during which time yellow crystals formed on the sides of the tube. Pentane was removed *in vacuo* and the tube was sealed and the crystals isolated in the dry box (yield about 40%).

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References

(1) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1.

(2) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

(3) Fox, H. H.; Yap, K. B.; Robbins, J.; Cai, S.; Schrock, R. R. *Inorg. Chem.* **1992**, *31*, 2287.

(4) Fox, H. H.; Lee, J.-K.; Park, L. Y.; Schrock, R. R. *Organometallics* **1993**, *12*, 759.

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

(6) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907.

(7) Schrock, R. R. in "Ring-Opening Polymerization"; D. J. Brunelle, Ed.; Hanser: Munich, 1993; pp 129.

(8) Bazan, G. C.; Schrock, R. R.; Cho, H.; Gibson, V. C. *Macromolecules* **1991**, *24*, 4495.

(9) Bazan, G.; Schrock, R. R.; Khosravi, E.; Feast, W. J.; Gibson, V. C. *Polymer Commun.* **1989**, *30*, 258.

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

(11) Bazan, G. C.; Oskam, J. H.; Cho, H.-N.; Park, L. Y.; Schrock, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 6899.

(12) Feast, W. J.; Gibson, V. C.; Marshall, E. L. *J. Chem. Soc., Chem. Commun.* **1992**, 1157.

(13) Feast, W. J.; Gibson, V. C.; Ivin, K. J.; Khosravi, E.; Kenwright, A. M.; Marshall, E. L.; Mitchell, J. P. *Makromol. Chem. - Macromol. Chem. Phys.* **1992**, *193*, 2103.

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

(15) Kress, J.; Osborn, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 3953.

(16) Schrock, R. R.; Messerle, L. W.; Wood, C. D.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 3793.

(17) Toreki, R.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 3367.

(18) Schrock, R. R. in "Reactions of Coordinated Ligands"; P. S. Braterman, Ed.; Plenum:

New York, 1986; Vol. 1.

(19) Ivin, K. J. "Olefin Metathesis"; Academic Press: New York, 1983.

(20) Ivin, K. J.; Milligan, B. D. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 269.

(21) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 7588.

(22) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, NY, 1973.

(23) 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.

(24) Johnson, L. K.; Virgil, S. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 5384.

(25) Toreki, R.; Vaughan, G. A.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1993**, *115*, 127.

(26) McConville, D. H.; Wolf, J. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 4413.

(27) Kress, J.; Osborn, J. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1585.

(28) bin Alimuniar, A.; Blackmore, P. M.; Edwards, J. H.; Feast, W. J.; Wilson, B. *Polymer* **1982**, *27*, 1281.

(29) Oskam, J. H.; O'Dell, R.; Schrock, R. R., in preparation.

(30) Feast, W. J.; Gibson, V. C.; Khosravi, E.; Marshall, E. L.; Mitchell, J. P. *Polymer* **1992**, *33*, 872.

(31) Schrock, R. R.; DePue, R.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423.

(32) Unpublished results by Harold H. Fox. We thank him for permission to quote them here.

(33) Schlund, R.; Schrock, R. R.; Crowe, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 8004.

(34) Patton, P. A.; McCarthy, T. J. *Macromolecules* **1987**, *20*, 778.

(35) A referee felt that we should also allow for the possibility that no metallacyclobutane intermediates actually form. Of course that possibility cannot be excluded, although there is considerable evidence at this stage of research that metallacycles that have some degree of stability and well-defined structures are intermediates in metathesis reactions.

(36) Landis, C. R.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 1746.

(37) Weinstock, I. A.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1991**, *112*, 135.

(38) Feast, W. J. ; Ivin, K. J.; Gibson, V. C., personal communication.

(39) Oskam, J. H.; Fox, H. H.; Yap, K. B.; McConville, D. H.; O'Dell, R.; Lichenstein, B. J.; Schrock, R. R. *J. Organomet. Chem.* in press.

(40) Espenson, J. H. "Chemical Kinetics and Reaction Mechanisms"; McGraw-Hill: New York, NY, 1981.

Table I. UV/Vis spectral data for **1**, **1'**, **2**, **2'**, and **3'** (syn rotamers) at 25°C.[a]

initiator		solvent	λ (nm)	ε (L mol^{-1} cm^{-1})
$\mathrm{Mo(NAr)(CHCMe_2Ph)(OCMe_3)_2}$	**1**	$\mathrm{CH_2Cl_2}$	244	20,500
			305	10,300
$\mathrm{Mo(NAr)(CHCMe_3)(OCMe_3)_2}$	**1'**	$\mathrm{CH_2Cl_2}$	244	17,400
			305	8,700
$\mathrm{Mo(NAr)(CHCMe_2Ph)(OR_{F3})_2}$	**2**	$\mathrm{CH_2Cl_2}$	244	20,100
			305[b]	9,600
		toluene	288	7,100
			338	4,800
		THF	221	18,700
			250	20,600
			305	10,000
$\mathrm{Mo(NAr)(CHCMe_3)(OR_{F3})_2}$	**2'**	$\mathrm{CH_2Cl_2}$	244	17,500
			305[b]	10,300
$\mathrm{Mo(NAr)(CHCMe_3)(OR_{F6})_2}$	**3'**	$\mathrm{CH_2Cl_2}$	244	27,300
			305[b]	17,000

[a] A prime indicates a neopentylidene complex; no prime indicates a neophylidene complex; see Table II for other nomenclature and abbreviations. [b] Two maxima (see Figure 1) are present at ~295 and 325 nm. λ_{max} and absorbance values listed here are the average of the two.

Table II. Alkylidene H_α chemical shifts and coupling constants, and equilibrium constants in $Mo(NR)(CHR')(OR'')_2$ complexes.[a]

initiator[a]		solv	δ (anti)	$^1J_{CH}$ (anti)	δ (syn)	$^1J_{CH}$ (syn)	K_{eq} (298K)
$Mo(NAr)(CHCMe_2Ph)(OCMe_3)_2$	**1**	tol	12.22		11.34	119.2	1200
		thf	12.03		11.27	119.5	730
$Mo(NAr)(CHCMe_2Ph)(OR_{F3})_2$	**2**	tol	12.79	148.2	11.65	119.9	1800
		thf	13.24	142.8	12.17	118.7	1400
$Mo(NAr)(CHCMe_2Ph)(OR_{F6})_2$	**3**	tol	13.30	153.3	12.11	120.3	1400
		thf	13.66	144.9	12.75	119.8	23
		dme	13.72		12.63	120.5	550
$Mo(NAr)(CHCMe_2Ph)(OR_{F13})_2$	**4**	tol	14.00	154.9	12.92	122.0	600
$Mo(NAr)(CHCMe_2Ph)(OR_{F9})_2$	**5**	tol	13.86	155.7	12.87	122.5	190
$Mo(NAr)(CHCMe_3)(OR_{F3})_2$	**2'**	tol	12.50		11.60	118.3	2100
$Mo(NAr)(CHCMe_3)(OR_{F6})_2$	**3'**	tol		151.7		119.1	2100
$Mo(NAr)(CHCMe_3)(OR_{F9})_2$	**5'**	tol					>5000
$Mo(N\text{-}4\text{-}Br\text{-}2,6\text{-}i\text{-}Pr_2C_6H_2)(CHCMe_2Ph)(OR_{F6})_2$	**6**	tol	13.22	153.2	12.01	120.6	1100
$Mo(NAr)(CHCMe_2Ph)(OAr)_2$	**7**	tol	12.69	152.5	11.72	120.0	9.6
$Mo(N\text{-}2,6\text{-}Me_2C_6H_4)(CHCMe_2Ph)(OR_{F3})_2$	**8**	C_6D_6			11.72		
$Mo(N\text{-}2,6\text{-}Me_2C_6H_4)(CHCMe_2Ph)(OR_{F6})_2$	**9**	thf	13.74	145.8	12.72	120.8	
$Mo(N\text{-}2,6\text{-}Me_2C_6H_4)(CHCMe_2Ph)(OR_{F13})_2$	**10**	tol	13.93		12.84	121.6	1800
$Mo(N\text{-}2\text{-}t\text{-}BuC_6H_4)(CHCMe_2Ph)(OAd)_2$	**11**	C_6D_6			11.06		
$Mo(N\text{-}2\text{-}t\text{-}BuC_6H_4)(CHCMe_2Ph)(OR_{F6})_2$	**12**	tol		151.8	11.79		
$Mo(N\text{-}2\text{-}t\text{-}BuC_6H_4)(CHCMe_3)(OR_{F6})_2$	**12'**	tol	12.78	151.6	11.71	118.3	2000
		thf	13.48	142.1	12.49	117.6	15
$Mo(N\text{-}2\text{-}t\text{-}BuC_6H_4)(CHCMe_2Ph)(OR_{F9})_2$	**13**	tol	13.71		12.47	121.3	450
$Mo(N\text{-}2\text{-}i\text{-}PrC_6H_4)(CHCMe_2Ph)(OR_{F6})_2$	**14**	tol	13.06	154.6	11.95	118.8	360
$Mo(NAd)(CHCMe_2Ph)(OR_{F6})_2$	**15**	tol	13.09	155.7	11.82	119.4	12
$W(NAr)(CHCMe_3)(OR_{F6})_2$	**16'**	tol	10.55		8.85	114.0	5000

[a] Ar = $2,6\text{-}i\text{-}Pr_2C_6H_3$, $OR_{F3} = OCMe_2(CF_3)$, $OR_{F6} = OCMe(CF_3)_2$, $OR_{F9} = OC(CF_3)_3$, $OR_{F13} = OC(CF_3)_2(CF_2CF_2CF_3)$, Ad = 1-adamantyl, tol = toluene-d_8, thf = thf-d_8, dme = 1,2-dimethyoxyethane.

Table III. Rate Constant Data for Complexes of the Type Mo(NAr)(CHCMe$_2$Ph)(OR")$_2$.[a]

		T (±1°C)[b]	$k_{a/s}$(x10^{-4}s^{-1})
Mo(NAr)(CHCMe$_2$Ph)(OCMe$_3$)$_2$	**1**$_{mch}$	-83.0	1.96
Mo(NAr)(CHCMe$_2$Ph)(OR$_{F3}$)$_2$	**2**$_{tol}$	-62.1	0.902
		-57.3	2.11
		-52.6	5.44
		-47.6	9.96
		-47.6	10.8
		-44.5	17.8
Mo(NAr)(CHCMe$_2$Ph)(OR$_{F3}$)$_2$	**2**$_{thf}$	-20.2	0.409
		-16.9	0.762
		-12.5	2.07
		-7.8	5.41
		-2.0	14.5
		0.1	19.4
Mo(NAr)(CHCMe$_2$Ph)(OR$_{F3}$)$_2$	**2**$_{mch}$	-44.5	11.7
Mo(NAr)(CHCMe$_2$Ph)(OR$_{F6}$)$_2$	**3**$_{tol}$	-31.2	0.589
		-26.1	1.30
		-24.1	1.74
		-20.8	3.40
		-14.9	6.21
		-10.6	14.8
		-9.4	13.6
Mo(NAr)(CHCMe$_2$Ph)(OR$_{F6}$)$_2$	**3**$_{thf}$	23.3	0.327
		28.3	0.863
		33.0	1.79
		33.0	1.59
		38.0	3.73
		39.2	4.59
		46.1	13.7
Mo(NAr)(CHCMe$_2$Ph)(OR$_{F13}$)$_2$	**4**$_{tol}$	-5.5	0.757
		0.5	1.17
		5.3	2.15
		6.0	2.93
		9.6	3.99
		15.0	11.3
		16.9	13.4
Mo(NAr)(CHCMe$_2$Ph)(OR$_{F9}$)$_2$	**5**$_{tol}$	4.4	1.08
		13.7	3.40
		25.0	15.5

[a] mch = methylcyclohexane. Other abbreviations as in Table II. [b] Temperature calibrated with neat methanol below 25°C and neat ethylene glycol above 25°C.

Table IV. Rate constants for all other initiators of molybdenum and tungsten.[a]

		T (±1°C)[b]	k_a/s(x10^{-4}s^{-1})
Mo(NAr)(CHCMe$_3$)(OR$_{F3}$)$_2$	**2'**$_{tol}$	-66.0	1.08
		-56.0	6.01
Mo(NAr)(CHCMe$_3$)(OR$_{F6}$)$_2$	**3'**$_{tol}$	-27.4	2.26
Mo(NAr)(CDCMe$_3$)(OR$_{F6}$)$_2$	**3'**$_{tol}$-d$_1$	-27.4	1.10
Mo(N-4-Br-2,6-*i*-Pr$_2$C$_6$H$_2$)(CHCMe$_2$Ph)(OR$_{F6}$)$_2$	**6**$_{tol}$	-29.6	1.90
		-26.1	3.52
		-24.4	3.55
		-20.8	6.51
		-19.6	7.20
Mo(NAr)(CHCMe$_2$Ph)(OAr)$_2$	**7**$_{tol}$	-42.0	1.35
Mo(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OR$_{F6}$)$_2$	**9**$_{thf}$	22.0	0.451
Mo(N-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OR$_{F13}$)$_2$	**10**$_{tol}$	0	4.22
Mo(N-2-*t*-BuC$_6$H$_4$)(CHCMe$_2$Ph)(OR$_{F6}$)$_2$	**12**$_{tol}$	-67.2	0.835
Mo(N-2-*t*-BuC$_6$H$_4$)(CHCMe$_3$)(OR$_{F6}$)$_2$	**12'**$_{tol}$	-70.0	2.02
Mo(N-2-*t*-BuC$_6$H$_4$)(CHCMe$_3$)(OR$_{F6}$)$_2$	**12'**$_{thf}$	-2.0	0.655
Mo(N-2-*t*-BuC$_6$H$_4$)(CHCMe$_2$Ph)(OR$_{F9}$)$_2$	**13**$_{tol}$	-26.6	5.99
Mo(N-2-*i*-PrC$_6$H$_4$)(CHCMe$_2$Ph)(OR$_{F6}$)$_2$	**14**$_{tol}$	-66.0	0.44
		-60.0	1.64
Mo(N-1-adamantyl)(CHCMe$_2$Ph)(OR$_{F6}$)$_2$	**15**$_{tol}$	-38.5	2.26
		-31.4	5.75
W(NAr)(CHCMe$_3$)(OR$_{F6}$)$_2$	**16'**$_{tol}$	-53.0	1.32
		-51.8	2.10
		-49.0	2.14
		-43.0	6.61
		-38.5	23.9

[a] See Table II for abbreviations. [b] Temperature calibrated with neat methanol below 25°C and neat ethylene glycol above 25°C.

Table V. Calculated activation parameters for anti to syn conversions.

Initiator		$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)	$\Delta G^{\ddagger}_{298}$ (kcal mol^{-1})
Mo(NAr)(CHCMe$_2$Ph)(OR$_{F3}$)$_2$	**2**$_{tol}$	15.6 (0.5)	-2 (2)	16.3 (0.8)
	2$_{thf}$	26.1 (0.5)	25 (2)	18.7 (0.8)
Mo(NAr)(CHCMe$_2$Ph)(OR$_{F6}$)$_2$	**3**$_{tol}$	18.3 (0.7)	-2 (3)	18.8 (1.1)
	3$_{thf}$	29.8 (0.6)	21 (2)	23.4 (0.8)
Mo(NAr)(CHCMe$_2$Ph)(OR$_{F13}$)$_2$	**4**$_{tol}$	20.4 (1.6)	-2 (6)	20.8 (2.4)
Mo(NAr)(CHCMe$_2$Ph)(OR$_{F9}$)$_2$	**5**$_{tol}$	20.7 (0.9)	-2 (3)	21.3 (1.4)

Table VI. Calculated $k_{a/s}$ values (using $\Delta G^{\ddagger}_{298}$ values in Table V), K_{eq}, and $k_{s/a}$ values at 298K.

Initiator		$k_{a/s}$ (s^{-1})	K_{eq}	$k_{s/a}$ (s^{-1})
Mo(NAr)(CHCMe$_2$Ph)(OCMe$_3$)$_2$	1_{tol}	~500[a]	1200	~0.4
	1_{thf}	~360[a]	730	~0.5
Mo(NAr)(CHCMe$_2$Ph)(OR$_{F3}$)$_2$	2_{tol}	6.8	1800	0.004
	2_{thf}	0.12	1400	0.00009
Mo(NAr)(CHCMe$_2$Ph)(OR$_{F6}$)$_2$	3_{tol}	0.10	1400	0.00007
	3_{thf}	0.000042	23	0.000002
Mo(NAr)(CHCMe$_2$Ph)(OR$_{F13}$)$_2$	4_{tol}	0.0034	600	0.000006
Mo(NAr)(CHCMe$_2$Ph)(OR$_{F9}$)$_2$	5_{tol}	0.0015	190	0.000008

[a] Calculated from the intercepts in Figure 3.

Table VII. Aryl group rotation for **2** and **3** in several solvents.

Initiator	T_c (°C)	$\Delta\nu$ (Hz)	k_{rot} at T_c (s^{-1})[b]	$\Delta S^{\ddagger}$ (e.u.)	$\Delta G^{\ddagger}_{298}$ (kcal mol^{-1})	*i*-Pr resonances employed
syn-$\mathbf{2}_{tol}$	-80	~32[a]	70			methyls
anti-$\mathbf{2}_{tol}$	-90	-	fast			-
syn-$\mathbf{2}_{thf}$	-40	88	195			methyls
anti-$\mathbf{2}_{thf}$	-50	-	fast			-
syn-$\mathbf{3}_{CD2Cl2}$	~-60	108	240[c]	-0.9	10	methyls
anti-$\mathbf{3}_{CD2Cl2}$	-90	-	fast			-
syn-$\mathbf{3}_{tol}$	-61.5	59	130[d]	-1.8	10.3	methyls
syn-$\mathbf{3}_{thf}$	~-10	116	245	17	11.9	methyls
anti-$\mathbf{3}_{thf}$	~-10	506	1100	27	11	methines

[a] Estimated at -90°C. [b] $k = \pi(\Delta\nu)/2^{1/2}$. [c] Additional k's were obtained at -50° (700 s^{-1}), -40° (1900 s^{-1}), and -30° (6000 s^{-1}) on the basis of linewidth at half-height ($w_{1/2}$ = 3.1 Hz) at -20° after subtracting $^3J_{HH}$ = 6.7 Hz and calculated using $k = \pi(\Delta\nu)^2/(2\Delta w)$ where $\Delta w = w - w_f$. Activation data were generated from a plot of ln(k) versus 1/T (R = 0.994); $\Delta S^{\ddagger}$ = -0.9 e.u., $\Delta H^{\ddagger}$ = 9.8 kcal/mol, $\Delta G^{\ddagger}_{298}$ = 10 kcal/mol. [d] Ten rate constants were obtained. Activation parameters were generated from a plot of ln(k) versus 1/T (R = 0.997); $\Delta S^{\ddagger}$ = -1.8 e.u., $\Delta H^{\ddagger}$ = 9.8 kcal/mol, $\Delta G^{\ddagger}_{298}$ = 10.3 kcal/mol.

Table VIII. Comparison of $k_{a/s}$, K_{eq}, and $k_{s/a}$ for initiators and first-insertion products.

Complex	Temp(°C)	$k_{a/s}$ ($x10^{-4}s^{-1}$)	$k_{a/s}$ ratio	K_{eq}[a]	$k_{s/a}$ ($x10^{-6}s^{-1}$)
$\mathbf{3}_{\mathrm{tol}}$	0	43[b]	15	1400	3.1
$\mathbf{3}_{\mathrm{tol}}$+1	0	2.9		>100	<2.9
$\mathbf{3}_{\mathrm{thf}}$	35	2.4[b]	5.3	23	10
$\mathbf{3}_{\mathrm{thf}}$+1	35	0.45		~13[c]	~35
$\mathbf{12'}_{\mathrm{thf}}$	-2	0.66	13[d]	15	4.4
$\mathbf{12'}_{\mathrm{thf}}$+1	20	1.8		13	14

[a] $K_{eq} = k_{a/s}/k_{s/a}$. [b] Calculated from activation parameters. [c] Value estimated from a measurement of 14.6 at 60°C with a temperature dependence similar to that of $\mathbf{3}_{\mathrm{thf}}$. [d] Calculated $k_{a/s} = 2.35 \times 10^{-3}\ s^{-1}$ for $\mathbf{12'}_{\mathrm{thf}}$ at 20 °C assuming $\Delta G^{\ddagger}_{298} = 20.5$ kcal mol^{-1}, $\Delta H^{\ddagger} = 27.4$ kcal mol^{-1}, and $\Delta S^{\ddagger} = 23$ e.u. (based on $\mathbf{2}_{\mathrm{thf}}$ and $\mathbf{3}_{\mathrm{thf}}$).

Table IX. Polymerizations of 2,3-bis(trifluoromethyl)norbornadiene.[a]

Initiator	solv	equiv	time(h)	M_n(calcd)	M_n(found)	PDI	cis(%)
1	tol	100	3.5	22814	16600	1.06	3
1'	tol	102	4.5	23220	15060[c]	1.05	2[b]
1	thf	100	3.5	22814	20600	1.09	2
11	tol	108	20	24639	27100	1.14	4
2'	tol	50	5	11407	11800	1.10	22
3'	tol	100	1.2	22814	19500	1.05	98[d]
4	tol	40	4	9126	6300	1.08	95
5	tol	100	2	22814			99[e]
10	tol	39	1	8897	5400	1.11	99
12'	tol	100	0.4	22814	12500	1.12	72
12'	thf	100	20	22814	22300	1.17	72
13	tol	100	0.4	22814	18300	1.10	99
15	tol	100	20	22814	28000	1.31	19[f]

[a] All polymerizations yield >90% polymer in the time period listed. [b] This polymer was reported elsewhere (Bazan et al., *J. Am. Chem. Soc.* **1990**, *112*, 8378). [c] GPC was obtained in CH_2Cl_2 instead of thf. [d] Poly-NBDF6 prepared in the presence of 10 equivalents of acetonitrile had M_n = 15800, PDI = 1.06, and % cis = 98. The polymer prepared in thf was virtually identical (Feast et al., *J. Chem. Soc., Chem. Commun.* **1992**, 1157). [e] Contribution by R. O'Dell. [f] Contribution by H. H. Fox.