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77 Massachusetts Avenue
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John H. Oskam and Richard R. Schrock*

Contribution from

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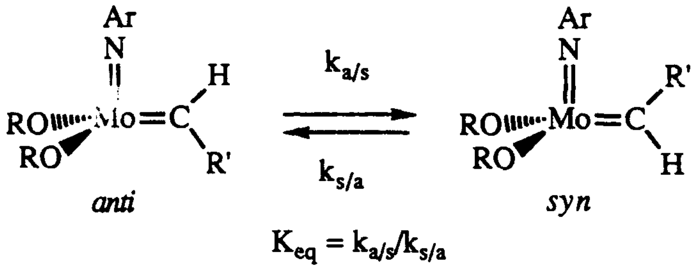
Abstract

Anti rotamers of $Mo(CHCMe_2Ph)(NAr)(OR)_2$ complexes (Ar = 2,6-C_6H_3-i-Pr_2; OR = $OCMe_2(CF_3)$, $OCMe(CF_3)_2$, and $OC(CF_3)_2(CF_2CF_2CF_3)$) can be generated at -80° in toluene by photolysis at 366 nm and the rate of conversion of anti to syn rotamers determined by NMR methods. At equilibrium the anti rotamers can be observed by high field proton NMR at 25° after many transients and values for K_{eq}(syn/anti) thereby determined. K_{eq} can be determined at 0° when OR = $OCMe_3$ and $k_{anti/syn}$ estimated. The rate of conversion of the anti to the syn rotamer in toluene is found to vary by at least five orders of magnitude as the alkoxide is changed from t-butoxide to $OC(CF_3)_2(CF_2CF_2CF_3)$. The results in THF are analogous, although the rates of rotamer interconversion are much slower for any given alkoxide. Addition of 2,3-bis(trifluoromethyl)norbornadiene to mixtures containing both anti and syn $Mo(CHCMe_2Ph)(NAr)[OCMe(CF_3)_2]_2$ showed that in both toluene and THF the anti rotamer was orders of magnitude more reactive than the syn rotamer.

Alkylidene complexes of the type $M(CHR')(NAr)(OR)_2$ (M = Mo or W; R' = alkyl, aryl, etc.; Ar = 2,6-C_6H_3-i-Pr_2) are useful initiators for the polymerization of cyclic olefins,[1-5] in some cases in a living manner[1] and stereoselectively.[6] Syn and anti rotamers of such species have been observed in solution when OR is a phenoxide ligand, and they have been shown to interconvert with $\Delta G^{\ddagger} = 16\text{-}18$ kcal mol^{-1} (equation 1).[7] The rate of syn/anti interconversion, the size of K_{eq}, and the relative reactivity of syn and anti rotamers could all play important roles in determining the stereoselectivity of ring-opening of norbornenes and norbornadienes if these quantities vary significantly with the nature of the alkoxide. We now have been able to acquire such data for molybdenum compounds that contain OR = $OCMe_3$ (OR_{F0}), $OCMe_2(CF_3)$ (OR_{F3}), $OCMe(CF_3)_2$ (OR_{F6}), and $OC(CF_3)_2(CF_2CF_2CF_3)$ (OR_{F13}) ligands. We find that the rate of interconversion of rotamers and their reactivities can vary by many orders of magnitude, and that under at least some circumstances the rotamer that is present in vanishingly small quantities is the most reactive towards 2,3-bis(trifluoromethyl)norbornadiene.



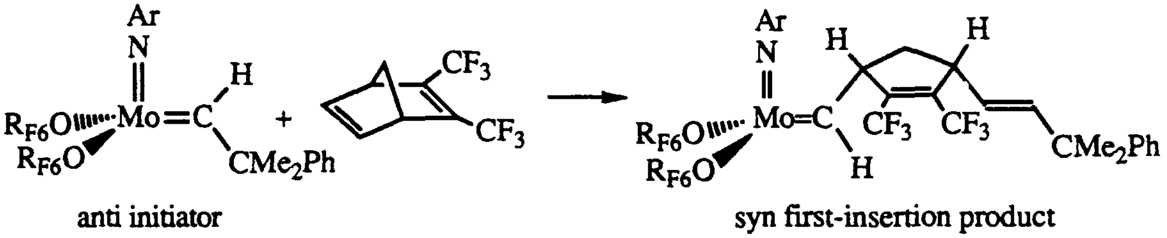
(1)

An alkylidene H_α resonance for the anti rotamer cannot be observed routinely in any $Mo(CHCMe_2Ph)(NAr)(OR)_2$ compound (OR = OR_{F0}, OR_{F3}, OR_{F6}, or OR_{F13}). However, photolysis of solutions of compounds in which OR = OR_{F3}, OR_{F6}, or OR_{F13} at 366 nm in toluene or THF at -80°C for several hours yields mixtures that contain up to 35% of the anti rotamer as determined by appearance of a resonance downfield of that for H_α in the syn rotamer which has a characteristic[7,8] relatively large value for $J_{CH\alpha}$ (140-155 Hz; see supplementary material). The syn/anti photostationary state typically is reached after approximately 8 h of photolysis. The first order rate of conversion of the anti rotamer to the syn rotamer was determined by ^1H NMR versus an internal standard such as mesitylene. Although most rate constants so far have been determined only over a range of ca. 20°C, some trends are clear (Table I). We find that in toluene the rate of rotamer isomerization is dramatically slowed as alkoxide ligands become more electron-withdrawing, decreasing by approximately three orders of magnitude in the series **2** to **4**. Since anti **1** could not be observed upon photolysis of syn **1** at -80°C, we estimate that the rate of conversion of anti **1** to syn **1** is probably at least two orders of magnitude faster than anti **2** to syn **2**. Therefore the decrease in the rate of conversion of anti to syn rotamer (**1** to **4**) is approximately five orders of magnitude.

Once the H_α resonance in the anti rotamer was located, we could find it at room temperature (only at 0°C for OR = $OCMe_3$) at 500 MHz (up to 12,000 transients were required in some cases) and integrate it versus the downfield ^{13}C satellite of the syn H_α resonance. Therefore we could determine K_{eq}, $\Delta G°$, and $k_{syn/anti}$ (Table I). K_{eq} is relatively constant in the series **1** to **4**, the difference in standard free energy between anti and syn rotamers being approximately 4 kcal mol^{-1}. Since K_{eq} is relatively constant $k_{s/a}$ also varies approximately five orders of magnitude in the series **1** to **4**.

Similar experiments were carried out in THF-d_8 for two complexes (**5** and **6** in Table I). (The nature of the THF adducts that are likely to be present under such circumstances has not been established.) Both $k_{a/s}$ and $k_{s/a}$ decrease approximately an order of magnitude for **5** versus **2**, but the decrease for **6** versus **3** is approximately three orders of magnitude, consistent with the expected stronger binding of THF to a more electrophilic metal, and the fact that loss of a coordinating ligand from a five-coordinate species is likely to be required in order for rotamers to interconvert.[7]

The relative reactivities of syn and anti rotamers with 2,3-bis(trifluoromethyl)norbornadiene have been determined qualitatively when OR = $OCMe(CF_3)_2$ by adding monomer to the mixture of syn and anti rotamers generated by photolysis at -80°C. A toluene sample containing 33% anti **3** was frozen at 77K, five equiv of 2,3-bis(trifluoromethyl)norbornadiene was added, and the sample was thawed and rapidly transferred to a -80°C NMR probe. The H_α resonance for the anti rotamer had been replaced by an H_α resonance for the syn "first insertion product" ($J_{H\alpha H\beta}$ = 8.1 Hz) downfield from the H_α resonance for the unreacted syn initiator (equation 2; see also below and Figure 1).



(2)

The C=C double bond in this "first insertion product" was found to be trans on the basis of the value for J_{HH} (15.4 Hz). After 1 hour at -40°C all monomer was consumed to give other "living alkylidenes," but some syn initiator remained. Addition of only 0.33 equiv of 2,3-bis(trifluoromethyl)norbornadiene to a similar photolyzed mixture of syn and anti $Mo(CHCMe_2Ph)(NAr)(OR_{F6})_2$ resulted in complete consumption of the anti initiator. We conclude that the reactivity of the anti initiator is very much greater than that of the syn initiator in toluene, and estimate that difference to be at least two orders of magnitude. We also can conclude that only a trans C=C bond is formed from the anti rotamer. Finally, the mixture of 0.67 equiv of syn initiator and 0.33 equiv of syn first insertion product was photolyzed to give a mixture that contains the anti initiator and anti first insertion product ($J_{H\alpha H\beta}$ = 12.4 Hz; see also Figure 1). The rate of conversion of anti to syn first insertion product at 0°C could then be determined and was found to be 15 times slower than the rate of conversion of anti **3** to syn **3** at 0°.

Analogous experiments in THF-d_8 showed that both anti **6** and syn **6** react significantly more slowly with 2,3-bis(trifluoromethyl)norbornadiene than anti **5** and syn **5**, as one would expect if THF binds to the metal, but the difference in reactivity between anti **6** and syn **6** is still marked. Anti **6** was consumed in a few minutes at -30°C to again produce a syn first insertion product (J_{CH} = 127 Hz; $J_{H\alpha H\beta}$ = 7.0 Hz) whose C=C bond is trans (J_{HH} = 16 Hz). Syn **6** reacted only very slowly at 0°C. Addition of 0.33 equiv of monomer to the mixture containing 0.33 equiv of anti **6** generated 0.33 equiv of the syn first-insertion product. Subsequent photolysis of this mixture then yielded a mixture of anti and syn initiator and anti (J_{CH} = 152 Hz; $J_{H\alpha H\beta}$ = 10.0 Hz) and syn first-insertion product (Figure 1). The rate of conversion of the anti first-insertion product to the syn first-insertion product at 35°C was found to be approximately 5 times slower than the rate of conversion of anti **6** to syn **6** at 35°C.

Many careful studies will be required before we can determine the full implications of observations of the type outlined here. However, even at this stage it is clear that the polymerization pathway could depend dramatically upon conditions, the nature of the alkoxide, and the inherent reactivity of the monomer, and that reactions could proceed entirely via the minor, virtually unobservable anti rotamer if syn/anti interconversion is fast relative to the rate of polymerization, or entirely via the major syn rotamer if syn/anti interconversion is slow relative to the rate of polymerization. For example, the high trans content of poly(2,3-bis(trifluoromethyl)norbornadiene) prepared from anti-$Mo(CHCMe_2Ph)(NAr)(O\text{-}t\text{-}Bu)_2$[6] is likely to arise solely from reactions involving anti rotamers of chain propagating intermediates. Studies designed to correlate observations of the type outlined here with the cis/trans ratio and tacticity in polymers prepared using these Mo catalysts are under way, as are experiments designed to test whether the selectivities observed here extend to reactions involving acyclic internal olefins.

Acknowledgements. RRS thanks the Office of Naval Research for supporting this research, Prof. James Feast and Dr. Vernon Gibson for communication of unpublished results, and Dr. R. Toreki for suggesting photolysis as a means of converting syn to anti, a techniques that was first employed for interconverting syn and anti rhenium alkylidene complexes.[9]

Supplementary Material Available. NMR data, details of the kinetic studies, and values for $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ for various interconversions.

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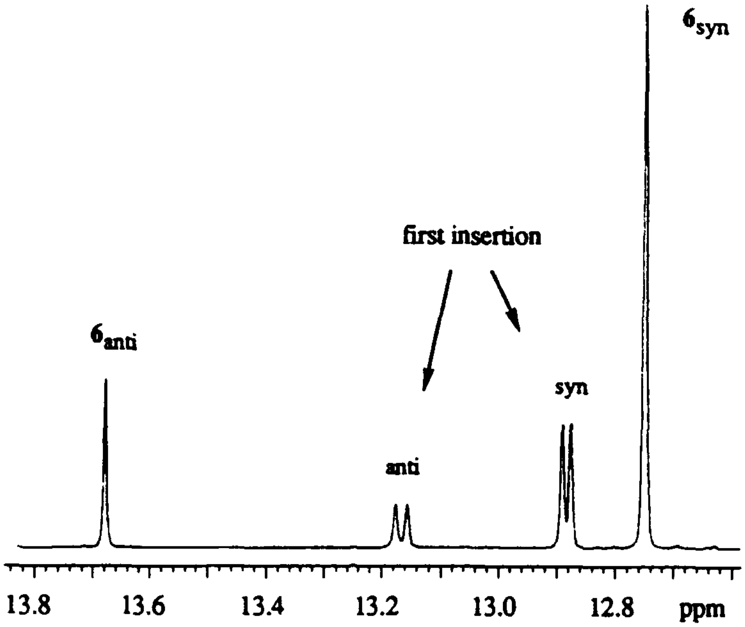
Figure Captions.

Figure 1. 500 MHz ^{1}H NMR spectrum at 35°C showing the alkylidene region after the addition of 0.33 equiv 2,3-bis(trifluoromethyl)norbornadiene to photolyzed **6** in d_8-thf, followed by further photolysis at low temperature.



6_{syn}
first insertion
6_{anti}
syn
anti
13.8
13.6
13.4
13.2
13.0
12.8
ppm

Table 1. Rates of interconversion and equilibrium constants at 25°C for syn and anti rotameric forms of complexes of the type $Mo(CHCMe_2Ph)(NAr)(OR)_2$.[a]

	OR	solv	$k_{a/s}(s^{-1})$	$K_{eq}(298)$	$k_{s/a}(s^{-1})$	$\Delta G°_{298}$
1	OR_{F0}	tol	~1000[b]	1200[c]	~1	-3.8
2[d]	OR_{F3}	tol	6.6	1850	$4x10^{-3}$	-4.5
3	OR_{F6}	tol	0.07	1450	$5x10^{-5}$	-4.3
4	OR_{F13}	tol	$4.2x10^{-3}$	620	$7x10^{-6}$	-3.8
5	OR_{F3}	thf	0.39	1400	$3x10^{-4}$	-4.3
6	OR_{F6}	thf	$3.2x10^{-5}$	23	$1x10^{-6}$	-1.9

[a] See supplementaly material for activation parameters from which $k_{a/s}$ values are calculated.

[b] Estimated assuming that T_c is 25°C and that $\upsilon_{anti} - \upsilon_{syn}$ = ~400Hz.

[c] K_{eq} was measured at 0°C, since the anti rotamer interconverted rapidly with the syn rotamer at 25°C.

[d] For the analogous $CHCMe_3$ complex $k_{a/s} = 10.5$, $K_{eq} = 2200$, $k_{s/a} = 5x10^{-3}$, and $\Delta G°_{298} = -4.6$.

Supplementary Material

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by

John H. Oskam and Richard R. Schrock*

Experimental Section.

All reagents were handled in the dry box or using standard high vacuum line techniques. Deuterated solvents were purified as follows: d$_8$-toluene was dried by passage through activated alumina immediately prior to use, d$_8$ -thf was purified by vacuum transfer from sodium benzophenone ketyl prior to use. In all rate constant measurements sealed thin-walled NMR tubes were employed. Photolysis was performed at -85°C using a Hanovia medium pressure mercury lamp (No. 673A) with a band-pass filter which allows maximum transmission of the 366nm emission line. ^{1}H NMR data was collected on a Varian VXR-500 MHz spectrometer.

Rate constant measurements. Typical concentrations for rate constant measurements are 7.5E-2 M in either thf-d$_8$ or toluene-d$_8$. After photolysis for up to 8 hours at -85°C the cold samples were placed directly into a preequilibrated probe for rate constant analysis. Samples were equilibrated 10 minutes prior to data collection. Raw data was collected over at least two half-lives by observation of the disappearance of the anti resonance with respect to mesitylene. Collection of data beyond two half-lives was hampered by the relatively small amount (33 %) of anti starting material initially present. Collection of data over temperature ranges larger than ~15°C was limited by spectrometer instability over long periods of time at low temperatures. In all cases except for **6** the disappearance of anti followed first order kinetics. The disappearance of anti **6** and of the first insertion product formed by addition of 2,3-bis(trifluoromethyl)norbornadiene to **6** followed reversible first order kinetics. Therefore $k_{a/s}$ values were derived from $k_{obs} = k_{a/s} + k_{s/a}$ and from K_{eq}.

Equilibrium constant measurements. Equilibrium constants were obtained using either the same sealed NMR tubes as for rate constant measurements or solutions were made at higher concentrations, typically up to 0.15 M. In all cases equilibrium measurements were preceeded by t_1 measurements of the syn alkylidenes and, where possible, on the anti alkylidene. Recommended ernst pulse widths were employed assuming that t_1 for the anti resonance was less than or equal to that of the syn rotamer. Integral areas were obtained by comparison of the anti resonance with the downfield ^{13}C satellite (0.55 %) of the syn resonance.

Rotamer reactivites. Typical reactivity studies employed the following procedure: 60 mg (0.078 mmoles) of syn-$Mo(CHCMe_2Ph)(NAr)(OCMe(CF_3)_2)_2$ was dissolved in 600µL d_8-toluene or d_8-thf in a thin-walled NMR tube with a stopcock adapter. The solution was photolysed at low temperatures as previously described until the solution was 33% anti. From 0.33 to 5 equiv of 2,3-bis(trifluoromethyl)norbornadiene were vacuum transferred either neat (5 equiv) or as a stock solution of the appropriate solvent onto the frozen initiator solution. The frozen solution was not previously degassed, therefore upon thawing N_2 bubbles evolved which served to mix the monomer and initiators. Care was taken to maintain temperatures at which isomerization rates of the rotamers were near zero. The cold solution was then placed into a precooled NMR probe for observation. In the case of the addition of 0.33 equiv monomer the tubes were subsequently sealed and photolysed at -85°C. The cold tubes were again transferred to the preequilibrated NMR probe for collection of the rate constants for interconversion of the first insertion product.

Table 2. Activation Parameters. Values for $\Delta G^{\ddagger}$ calculated at 298°K.

	M	CHCR'	OR	solv	$\Delta H^{\ddagger}$(kcals/mole)	$\Delta S^{\ddagger}$(e.u.)	$\Delta G^{\ddagger}$(kcals/mole)
1	Mo	$CHCMe_2Ph$	OR_{F0}	tol	NA	NA	NA
2	Mo	$CHCMe_2Ph$	OR_{F3}	tol	16	-2.6	16.3
	Mo	$CHCMe_3$	OR_{F3}	tol	15	-3.8	16.1
3	Mo	$CHCMe_2Ph$	OR_{F6}	tol	17	-5.5	19.0
4	Mo	$CHCMe_2Ph$	OR_{F13}	tol	24	11	20.7
5	Mo	$CHCMe_2Ph$	OR_{F3}	thf	29	36	18.0
6	Mo	$CHCMe_2Ph$	OR_{F6}	thf	29	20	23.4

Table 3. δ(ppm) and J_{CH} (Hz) for syn and anti alkylidenes at 25°C.

	M	CHCR'	OR	solvent	δ(anti)	J_{CH} (anti)	δ(syn)	J_{CH} (syn)
1	Mo	$CHCMe_2Ph$	OR_{F0}	tol	NA	NA	11.34	119.2
2	Mo	$CHCMe_2Ph$	OR_{F3}	tol	12.79	148.2	11.65	119.9
	Mo	$CHCMe_3$	OR_{F3}	tol	12.50	NA	11.60	118.3
3	Mo	$CHCMe_2Ph$	OR_{F6}	tol	13.30	153.3	12.11	120.3
4	Mo	$CHCMe_2Ph$	OR_{F13}	tol	14.00	154.9	12.92	122.0
5	Mo	$CHCMe_2Ph$	OR_{F3}	thf	13.24	142.8	12.17	118.7
6	Mo	$CHCMe_2Ph$	OR_{F6}	thf	13.66	144.9	12.75	119.8

Table 4. Rate data (s^{-1}) for rotamer conversion of first insertion products of the addition of 2,3-bis(trifluoromethyl)norbornadiene to $Mo(CHCMe_2Ph)(NAr)(OCMe_2(CF_3)_2)_2$ compared to the initiators.

	M	CHR'	OR	solvent	$k_{a/s}$ (°C)	$k_{a/s}$-init (°C)	k_{init}/k_{insert}
3	Mo	1st insertion	OR_{F6}	tol	2.9E-4 (0)	4.3E-3 (0)	15
6	Mo	1st insertion	OR_{F6}	thf	4.5E-5 (35)	3.1E-4 (35)	6.9

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