

## Stereoselectivity in Norbornene Metathesis with Group 6 Metal-Based Catalysts. Comparative Behavior of Cyclic vs. Acyclic Olefins

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The ring-opening metathesis of bicyclo[2.2.1]heptene (norbornene) has been carried out with group 6 metal-based catalysts associated with various cocatalysts. The percentage of cis double bonds in the polymer has been determined by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR with the precursor complexes  $\text{W}(\text{CO})_5\text{L}$  [ $\text{L} = \text{CO}$ ,  $\text{PPh}_3$ ,  $\text{C}(\text{OC}_2\text{H}_5)(\text{C}_6\text{H}_5)$ ,  $\text{C}(\text{C}_6\text{H}_5)_2$ ],  $\text{M}(\text{CO})_3(\text{Mes})$  (Mes = mesitylene;  $\text{M} = \text{Cr}$ ,  $\text{Mo}$ ,  $\text{W}$ ),  $\text{M}(\text{NO})_2\text{Cl}_2(\text{PPh}_3)_2$  ( $\text{M} = \text{Mo}$ ,  $\text{W}$ ),  $\text{WX}_3$  ( $\text{X} = \text{Cl}$ ,  $\text{OPh}$ ), and  $\text{WOCl}_4$ . With all the catalysts studied the percentage of cis double bonds was found to be equal to  $50 \pm 5\%$ , a value corresponding to a random coordination and (or) reaction of the exo double bond of the norbornene to the metallocarbene. The results contrast sharply with those obtained with acyclic olefins on using the same catalysts. A general explanation is given for the origin of the stereoselectivity in metathesis of acyclic and cyclic olefins. If the coordinated olefin has an energy which is smaller than that of the two possible metallacyclobutanes leading to the cis or the trans isomers, the resulting stereoselectivity will be governed by the energy levels of these two metallacyclobutanes. If the coordinated olefin has an energy which is higher than that of the cis- and trans-directing metallacyclobutanes, the system will lose its stereoselectivity and have a trans/cis ratio of unity. Most acyclic olefins belong to the first category. Highly strained olefins belong to the second category due to the exothermic strain release which is already partially carried out in the metallacyclobutane intermediate. The ligands do not govern the stereoselectivity by their own steric requirements but rather by their electronic effect. Lewis acids decrease the energy levels of the metallacyclobutane by their ability to coordinate to the metal and/or its ligands. The increase of stereoselectivity observed between W and Cr in the metathesis of acyclic olefins, which parallels the decrease of activity, would be due to the high energy level of the chromiacyclobutane.

The stereochemistry of the olefin metathesis reaction has been the subject of recent publications which tried to rationalize the behavior of group 6 transition metals in metathesis of acyclic olefins.<sup>1-9</sup> With acyclic olefins most tungsten-based catalysts exhibit a rather weak stereoselectivity corresponding to a quasi-"random" coordination and (or) a reaction of the olefin to (with) the metallocarbene.<sup>1,4,5</sup> However, in general,<sup>10</sup> tungsten catalysts exhibit a degree of stereoselectivity corresponding to a moderate retention of configuration of the starting olefin.<sup>5,7</sup> Such a retention of configuration is much higher for molybdenum- or chromium-based catalysts<sup>8,11</sup> than for tungsten-based catalysts.

The retention of configuration has been interpreted by an asymmetric ligand arrangement around the metallo-

carbene,<sup>5,15</sup> but recent results seem to confirm the validity of the minimized energy of the substituted metallacyclobutane intermediate.<sup>1,2,8,12,13</sup>

The problem of the stereochemistry with cyclic olefins seems to be, a priori, more simple than with acyclic olefins since the structure of the polymer is a fingerprint of the stereochemistry of the elementary steps occurring on the metallocarbene. In fact, due to possible side reactions, the situation is rather complex,<sup>16-41</sup> and the number of works

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dealing exclusively with the mechanistic origin of the stereochemistry of the ring-opening metathesis is limited.<sup>2,19,20,23,30,39,41</sup> Recent works by Calderon<sup>41</sup> have tried to rationalize the cis stereochemistry observed with some particular catalysts by a cage-like complex in which a double bond of the polymer would always be coordinated to the metallocarbene; but the authors do not explain why such a structure would favor a cis stereoselectivity. Ivin and Rooney<sup>30</sup> consider that the cis stereoselectivity would be due to steric crowding at the metal center by ligands other than the olefin which would favor the orientation of the complexed olefin, which leads to cis double bond formation. In fact, only a few authors tried to correlate the stereoselectivities observed between an acyclic and a cyclic olefin with the same catalysts derived from group 6 transition-metal complexes.

The stereochemistry of metathesis of cis cyclic olefins could be considered as a particular case of cis acyclic olefins (with the exception of the strain release of the cycle by ring opening), and the origin of the stereoselectivity, when it exists, should be the same. It was therefore logical to study the stereoselectivity of metathesis of a cyclic olefin with the same catalysts as those used with acyclic olefins and try to compare the results on a similar basis.

In this paper we report a series of experiments related to the stereochemistry of the ring-opening metathesis of norbornene with group 6 metal complexes exhibiting a wide range of ligands and (or) oxidation states. Those precursor complexes have been studied in detail in the stereochemistry of metathesis of acyclic olefins.<sup>1,8,44</sup>

## Results

**(1) Determination of the Stereochemistry in Metathesis of Norbornene.** The determination of the true stereoselectivity of the propagation step in norbornene polymerization requires a careful approach. In fact, the cyclic double bonds of the monomer become acyclic after opening of the ring, and the latter may retro-coordinate to the metallocarbene center<sup>1,21,29</sup> and lead to cis-trans isomerization, chain breakage with formation of polymers of lower molecular weight,<sup>29,35-38</sup> or chain transfer. A priori, all these possible side reactions may modify the true stereoselectivity of the initially formed polymer backbone. In order to get valid conclusions with regards to the stereochemistry of the propagation step, we found it necessary to check whether or not the stereochemistry of the polymer could depend on experimental conditions such as the olefin/W ratio, the concentration of catalyst, the temperature, the composition of the catalytic system, etc. All these kinetic parameters were selected because they

Table I. Influence of the Olefin/W Ratio on the Stereoselectivity for a Given Concentration of Olefin<sup>a</sup>

[W], mol L <sup>-1</sup>	olefin/W ratio	% cis	yield, %
4 × 10 <sup>-3</sup>	10 <sup>2</sup>	43 ± 5	85
4 × 10 <sup>-4</sup>	10 <sup>3</sup>	52 ± 5	13
4 × 10 <sup>-5</sup>	10 <sup>4</sup>	46 ± 5	28

<sup>a</sup> The catalyst was 1/4/6 W(CO)<sub>3</sub>(Mes)/EtAlCl<sub>2</sub>/O<sub>2</sub>; [olefin] = 0.4 mol L<sup>-1</sup>.

Table II. Influence of the Concentration of the Catalytic System<sup>a</sup>

precursor complex	[olefin], mol L <sup>-1</sup>	[W], mol L <sup>-1</sup>	% cis	yield, %
W(CO) <sub>3</sub> (arene)	0.1	10 <sup>-3</sup>	51 ± 5	10.6
W(CO) <sub>3</sub> (arene)	0.2	2 × 10 <sup>-3</sup>	50 ± 5	28.2
W(CO) <sub>3</sub> (arene)	0.3	3 × 10 <sup>-3</sup>	43 ± 5	66.7
W(OPh) <sub>6</sub>	0.4	4 × 10 <sup>-3</sup>	50 ± 5	37
W(OPh) <sub>6</sub>	0.04	4 × 10 <sup>-4</sup>	44 ± 5	65

<sup>a</sup> Ratios: W/Al, 1/4; W/O<sub>2</sub>, 1/6; olefin/W, 100.

Table III. Influence of Temperature on the Stereochemistry of the Polymer

temp, °C	% cis	yield, %
0	43 ± 5	80
25	43 ± 5	85
75	40 ± 5	79

<sup>a</sup> Catalyst, 1/4/6 W(CO)<sub>3</sub>(Mes)/EtAlCl<sub>2</sub>/O<sub>2</sub>; [W] = 2 × 10<sup>-3</sup> mol L<sup>-1</sup>; [olefin] = 0.2 mol L<sup>-1</sup>.

could, a priori, influence the competition of complexation of the cyclic and the acyclic double bond to the metallocarbene. Such studies were carried out with the precursor complexes W(CO)<sub>3</sub>(Mes) (Mes = mesitylene) or W(OPh)<sub>6</sub> associated with organoaluminum complexes.

With all the catalysts that we have tried in this study, the norbornene polymerization is an extremely fast reaction at room temperature, and the resulting polymer is insoluble in the reaction medium. After separation of the polymer and elimination of the oligomers in methanol, the polymer was dissolved in refluxing deuterated chloroform.

All the stereoselectivities have been determined by <sup>1</sup>H NMR spectroscopy; the cis and trans ethylenic protons give peaks at 5.21 and 5.36 ppm (Me<sub>4</sub>Si).<sup>75</sup> With the catalyst W(CO)<sub>5</sub>C(OC<sub>2</sub>H<sub>5</sub>)(C<sub>6</sub>H<sub>5</sub>), this attribution has been confirmed by <sup>13</sup>C(H) decoupled spectra; the cis and trans ethylenic carbons give multiplets centered respectively at 133.83 and 132.96 ppm (Me<sub>4</sub>Si). All these values are in good agreement with various literature data<sup>31,40</sup> related to polynorbornene (Figures 1 and 2).

As indicated in Table I, the stereochemistry of the polynorbornene does not depend on the olefin/tungsten ratio for a given concentration of olefin. For example, when the olefin/W ratio varies from 10<sup>2</sup> to 10<sup>4</sup>, the percentage of cis double bonds remains constant within experimental error. Simultaneously, the overall yield of polymer which can vary from 13% to 85% does not induce a meaningful variation of stereoselectivity (Table I).

For a constant olefin/W ratio, the cis content of double bond in the polynorbornene does not vary with the concentration of the catalytic system<sup>43</sup> (Table II), and this phenomenon is observed with W(CO)<sub>3</sub>(arene) or W(OPh)<sub>6</sub> as precursor complexes.

It should also be noted that no detectable change of stereoselectivity can be observed when, in three independent experiments, the polymerization was carried out at 0, 25, or 75 °C (Table III).

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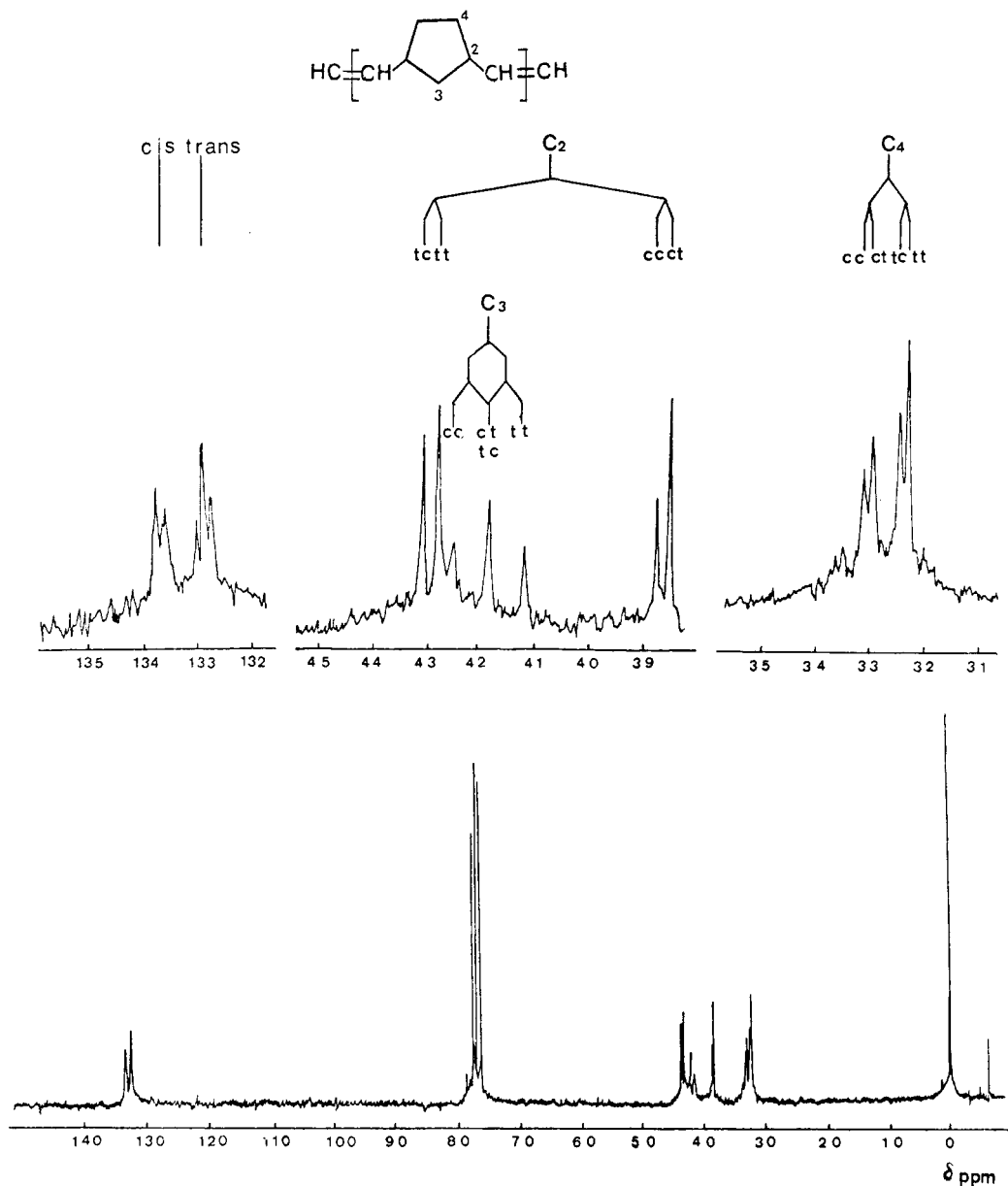
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**Figure 1.**  $^{13}\text{C}$  NMR spectrum of the polynorbornenamer in  $\text{CDCl}_3$  (frequency 62.86 MHz). The catalyst used for polymerization was **3** associated with  $\text{TiCl}_4 + h\nu$ . (Expansion of the  $\text{C}_2$ ,  $\text{C}_3$ , and  $\text{C}_4$  carbons are given above.)

**Table IV.** Influence of the Al/W Ratio on the Stereochemistry of the Reaction<sup>a</sup>

precursor complex	$10^2[\text{EtAlCl}_2]$ , mol $\text{L}^{-1}$	[olefin], mol $\text{L}^{-1}$	$\text{EtAlCl}_2/\text{W}$ ratio	% cis	yield, %
$\text{W}(\text{CO})_3(\text{Mes})$	0.2	0.2	1	49.1	37
$\text{W}(\text{CO})_3(\text{Mes})$	0.8	0.2	4	50	28
$\text{W}(\text{CO})_3(\text{Mes})$	1.2	0.2	6	39	72
$\text{W}(\text{CO})_3(\text{Mes})$	2	0.2	10	14	100
$\text{W}(\text{CO})_3(\text{Mes})$	2	0.2	10	50 <sup>b</sup>	74.5
$\text{W}(\text{CO})_5(\text{CPh}_2)$	0.8	0.4	2	46.2	6
$\text{W}(\text{CO})_5(\text{CPh}_2)$	1.2	0.2	6	27	100

<sup>a</sup>  $\text{W}(\text{CO})_3(\text{Mes})/\text{EtAlCl}_2/\text{O}_2$ , 1/X/1.2X;  $\text{W}(\text{CO})_5(\text{CPh}_2)/\text{EtAlCl}_2$ , 1/X. <sup>b</sup> The reaction has been quenched after a few seconds by methanol.

The most important parameter with respect to stereoselectivity seems to be the Al/W ratio when the catalytic components contain an organoaluminum cocatalyst. In such case it was observed that the solubility of the polymer was varying with time for an Al/W ratio higher than 4. In a typical experiment, with the catalyst  $\text{W}(\text{CO})_3(\text{Mes})$ ,  $\text{C}_2\text{H}_5\text{AlCl}_2$ , and  $\text{O}_2$  for an Al/W ratio of 10, the polymer which was formed in 20 s was insoluble; when recovered after quenching by methanol it contained 50% of cis double bonds. In another experiment with identical cat-

alytic conditions, the reaction was not quenched, and the insoluble polymer initially formed became progressively soluble with time; after 2 h the percentage of trans double bonds was 86%<sup>47</sup> (Table IV). Consequently, at high Al/W

(47) Such an effect of the Al/W ratio was also observed by Günther et al. (see ref 16) in cyclopentene metathesis with the catalyst  $\text{Al}_2(\text{C}_2\text{H}_5)_3\text{Cl}_3$  in toluene at  $-30^\circ\text{C}$ . For Al/W ratios lower than unity the polypentenamer contains 84% of cis double bonds. For Al/W ratios higher than ca. 4 the polypentenamer contains ca. 90% of trans double bonds.

Table V. Effect of the Ligands, Cocatalysts, and Transition Metal on the Stereoselectivity of the Propagation Step with Norbornene<sup>a</sup>

precursor complex	cocatalyst	% of cis double bonds	% yield
W(CO) <sub>5</sub> L			
L = CO (1)	C <sub>2</sub> H <sub>5</sub> AlCl <sub>2</sub>	43 ± 5	2.6
L = CO (1)	CCl <sub>4</sub> + hν	50 ± 5	6.9
L = PPh <sub>3</sub> (2)	C <sub>2</sub> H <sub>5</sub> AlCl <sub>2</sub> + O <sub>2</sub>	50 ± 5	48
L = C(OC <sub>2</sub> H <sub>5</sub> )(C <sub>6</sub> H <sub>5</sub> ) (3)	C <sub>2</sub> H <sub>5</sub> AlCl <sub>2</sub>	52 ± 5	50
L = C(OC <sub>2</sub> H <sub>5</sub> )(C <sub>6</sub> H <sub>5</sub> )	TiCl <sub>4</sub> + hν	44 ± 5	50
L = C(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (12)	C <sub>2</sub> H <sub>5</sub> AlCl <sub>2</sub>	46 ± 5	6
W(OPh) <sub>6</sub> (10)	C <sub>2</sub> H <sub>5</sub> AlCl <sub>2</sub>	50 ± 5	37
WOCl <sub>4</sub> (11)	C <sub>2</sub> H <sub>5</sub> AlCl <sub>2</sub>	53 ± 5	32
WCl <sub>6</sub> (9)	C <sub>2</sub> H <sub>5</sub> AlCl <sub>2</sub> + O <sub>2</sub>	46 ± 5	61
WCl <sub>5</sub> (9)	SnMe <sub>4</sub> + Et <sub>2</sub> O	45 ± 5	2.1
WCl <sub>6</sub> (9)	SnPh <sub>4</sub> + Et <sub>2</sub> O	47 ± 5	1.1
W(NO) <sub>2</sub> Cl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (8)	C <sub>2</sub> H <sub>5</sub> AlCl <sub>2</sub>	50 ± 5	13.1
Mo(NO) <sub>2</sub> Cl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (7)	C <sub>2</sub> H <sub>5</sub> AlCl <sub>2</sub>	50 ± 5	10.6
W(CO) <sub>3</sub> (Mes) (6)	C <sub>2</sub> H <sub>5</sub> AlCl <sub>2</sub>	44 ± 5	85
Mo(CO) <sub>3</sub> (Mes) (5)	C <sub>2</sub> H <sub>5</sub> AlCl <sub>2</sub>	44 ± 5	38
Cr(CO) <sub>3</sub> (Mes) (4)	C <sub>2</sub> H <sub>5</sub> AlCl <sub>2</sub>	41 ± 5	2.6
W(CO) <sub>6</sub> (1)	C <sub>2</sub> H <sub>5</sub> AlCl <sub>2</sub>	43 ± 5	2.6
Mo(CO) <sub>6</sub> (13)	C <sub>2</sub> H <sub>5</sub> AlCl <sub>2</sub>	41 ± 5	2.1

<sup>a</sup> All the experiments are carried out at 25 °C; the solvent is chlorobenzene; the ratios Al/W or Al/Mo or Al/Cr are equal to 4; the ratios Sn/W are equal to 2; the ratio Ti/W is equal to 150. See the Experimental Section part and the supplementary material.

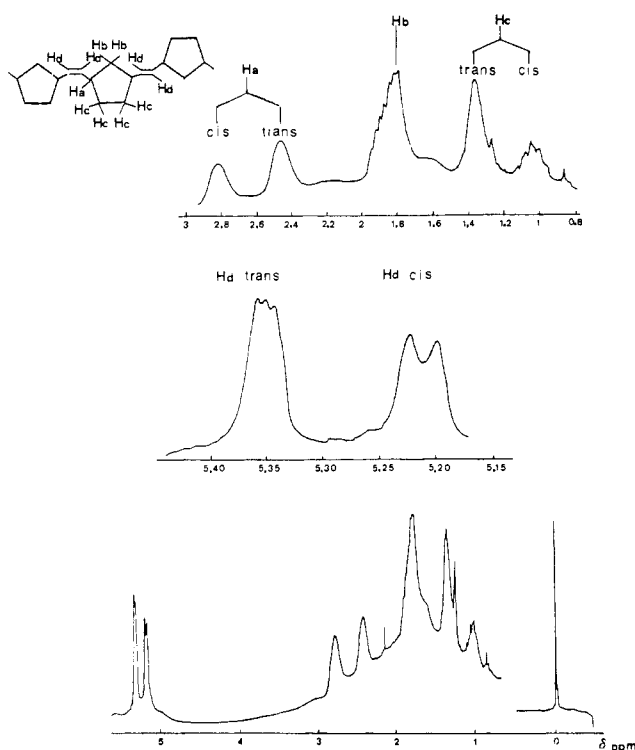


Figure 2. <sup>1</sup>H NMR spectrum of the polynorbornenamer (frequency 250 MHz). (Expansion of H(a), H(b), and H(c) as well as vinylic protons are given above.)

ratios, secondary reactions are occurring which increase the trans content of the polymer toward thermodynamic values.

As a consequence of the above measurements, any meaningful determination of the stereoselectivity of the propagation step in metathesis of norbornene should be carried at very short reaction times and (or) with low Al/W ratios when a Lewis acid cocatalyst is used. When no Lewis acid is present, such procedures are not necessary.<sup>19</sup> In the remainder of this paper we have mainly used the second procedure which gives reliable and reproducible stereoselectivities (within 5%).

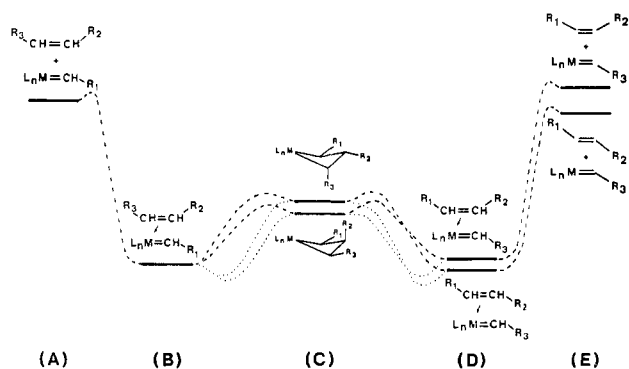
**(2) Effect of Ligands on the Stereoselectivity of the Propagation Step in Metathesis of Norbornene.** If one excepts the precursor complexes W(CO)<sub>5</sub>CPh<sub>2</sub>,<sup>2</sup> W(CO)<sub>5</sub>-

(C(OC<sub>2</sub>H<sub>5</sub>)(C<sub>6</sub>H<sub>5</sub>)),<sup>19</sup> and W(NO)<sub>2</sub>X<sub>2</sub>L<sub>2</sub> (X = Cl, Br; L = PPh<sub>3</sub>, Py), most tungsten-based catalysts exhibit the same stereoselectivity with acyclic olefins such as *cis*-2-pentene regardless of the ligands coordinated to the precursor complexes.<sup>1,44</sup> With norbornene the same trend is observed since all the precursor complexes that have been tried, even W(NO)<sub>2</sub>Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, led to the same percentage of *cis* double bonds within experimental error (Table V).

This value corresponds to a random coordination of the norbornene to the metallocarbene. With the zerovalent complexes of tungsten of the type W(CO)<sub>6-x</sub>L<sub>x</sub> in which L<sub>x</sub> can be the carbonyl ligand, the triphenylphosphine, the phenylethoxycarbene, the diphenylcarbene, or mesitylene, the nature or number of the 2e<sup>-</sup> ligands, their steric hindrance, and (or) their electronic properties have no effect on the resulting stereoselectivity. With the hexavalent precursor complexes of tungsten of the type WX<sub>6</sub> or WOX<sub>4</sub>, in which X may be a chloride or a phenoxy ligand, the nature of this ligand does not affect the stereoselectivity.

**(3) Effect of Cocatalyst on the Stereoselectivity of the Propagation Step.** The role of the Lewis acid cocatalyst in metathesis is not clear yet. Recent results suggest that the Lewis acid may stabilize the metallocarbene as shown in the model compound Cp<sub>2</sub>Ti(CH<sub>2</sub>)-(AlMe<sub>3</sub>).<sup>45,46</sup> Katz<sup>19</sup> has also observed that when no Lewis acid was present, there was considerable stereoselectivity. According to him, the Lewis acid cocatalyst in metathesis could facilitate the breakage of the metallacyclobutane intermediate, forming a substituted metallopropyl cation in which the remaining bonds would rotate; such rotation would decrease the stereoselectivity of the reaction.

Table V reports the effect of some cocatalysts, for a given precursor complex, on the stereoselectivity. With 3, the stereoselectivity does not vary with the nature of the cocatalyst at least when a Lewis acid cocatalyst is used (TiCl<sub>4</sub> + hν or C<sub>2</sub>H<sub>5</sub>AlCl<sub>2</sub> + O<sub>2</sub>). With 9, the stereoselectivity does not vary when the cocatalyst is C<sub>2</sub>H<sub>5</sub>AlCl<sub>2</sub> + O<sub>2</sub>, SnMe<sub>4</sub>, or SnPh<sub>4</sub>. With 1, the stereoselectivity does not vary when the cocatalyst is C<sub>2</sub>H<sub>5</sub>AlCl<sub>2</sub> or CCl<sub>4</sub> + hν, but the latter system is not a relevant example since it is strongly suspected that the cocatalyst oxidizes the tungsten. It should be pointed out here that the same complex (3 or 12) when used without any Lewis acid cocatalyst exhibits with norbornene a very high *cis* stereoselectivity<sup>2,19</sup> and when



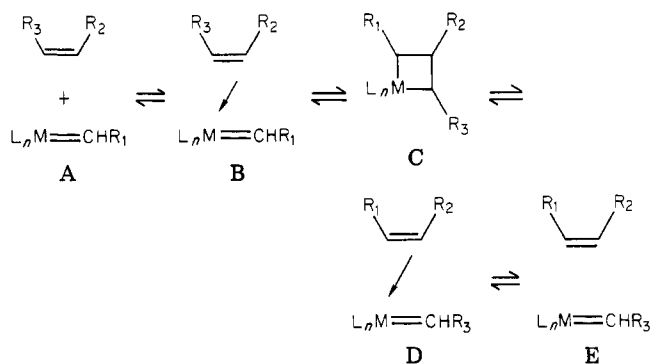
**Figure 3.** Schematic energy levels for the various intermediates involved in metathesis of a cis acyclic olefin.

used with a Lewis acid cocatalysts does not exhibit any stereoselectivity. This suggests that the Lewis acid cocatalysts lead to a loss of stereoselectivity.

**(4) Effect of the Transition Metal on the Stereoselectivity of the Propagation Step.** With norbornene, no detectable change of stereoselectivity was found with the catalysts  $M(\text{CO})_3(\text{Mes})$  ( $M = \text{Cr}, \text{Mo}, \text{W}$ ),  $M(\text{NO})_2\text{Cl}_2(\text{PPh}_3)_2$  ( $M = \text{Mo}, \text{W}$ ), or  $M(\text{CO})_6$  ( $M = \text{Mo}, \text{W}$ ). This result is in sharp contrast with that observed with acyclic olefins where the following order of stereoselectivity was observed:  $\text{Cr} > \text{Mo} > \text{W}$ .<sup>8</sup> Let us mention that the chromium complex  $\text{Cr}(\text{CO})_3(\text{Mes})$  exhibits a poor activity with norbornene as well as with acyclic olefins (Table V).

## Discussion

**(1) Proposal Concerning the Stereochemistry of Metathesis of Acyclic and Cyclic Olefins.** The following elementary steps can be considered in olefin metathesis:

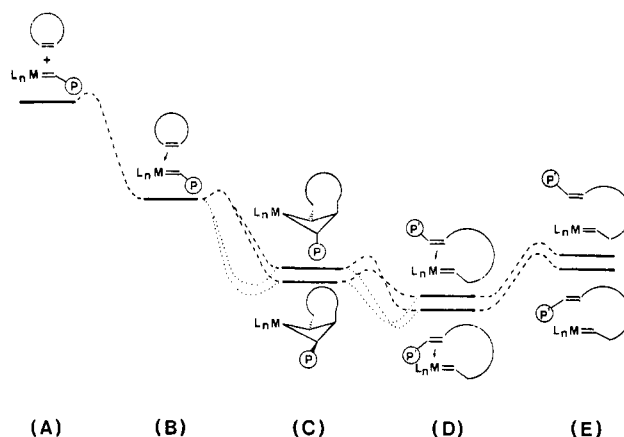


In this scheme  $R_2$  and  $R_3$  represent one cyclic moiety or two different alkyl groups of an acyclic olefin. The first intermediate is the olefin coordinated to the metalcarbene (B), and the second intermediate is the metallacyclobutane (C), giving rise to the new coordinated olefin (D). The final state is the free metalcarbene and the free olefin (E).

In this scheme we will assume that the stereoselectivity is exclusively determined in the intermediate state (C) by the relative stabilities of the substituted metallacyclobutanes: the most stable metallacycles will be those for which the interactions between  $R_1$  and  $R_3$  will be minimized.<sup>2,3,5,8,12,41,42,48</sup>

The cyclic olefins will be considered here as a particular case of a cis acyclic olefin (differences will be considered later on).

(48) T. J. Katz and J. McGinnis, *J. Am. Chem. Soc.*, **97**, 1592 (1975).



**Figure 4.** Schematic energy levels for the various intermediates involved in metathesis of a cis cyclic olefin.

Let us consider in Figures 3 and 4 the energy profiles of the various steps for metathesis of acyclic and cyclic olefins.<sup>49</sup>

If the stereoselectivity is determined exclusively by the various possible configurations of the metallacyclobutane intermediates, it will depend on the respective energy levels of the coordinated olefin (B) and of the metallacyclobutanes (C).<sup>50</sup> If the coordinated olefin (B) has an energy which is smaller than that of the two possible metallacyclobutanes leading, respectively, to cis and trans isomers, the resulting stereoselectivity will be governed by the energy levels of these two metallacycles. If the coordinated olefin has an energy which is higher than that of the cis- or trans-directing metallacyclobutanes, the stereoselectivity will not be governed by the levels of energy of the metallacycles, and the system will lose its stereoselectivity and have a trans/cis ratio of unity. As a consequence of the proposal, the catalysts which are the most active in the propagation step should be the less stereoselective and vice versa.

A priori the parameters which will govern the respective levels of energy of the metallacyclobutanes (C) and of the coordinated olefin (B) will be the cyclic or acyclic character of the olefin, the nature of the transition metal, the nature of the ligands, and the nature of the cocatalysts.

The levels of energy of the metallacyclobutanes are lower with cyclic olefins than with acyclic olefins: the strain release of the cyclic olefin is already partially carried out in the metallacyclobutane intermediate due to an increase of the C-C bond distance.<sup>51</sup>

(49) For an acyclic olefin, the free energy of the final state is almost identical with that of the original state. For a cyclic olefin, the final state is lower than that of the original state due to the release of the strained cycle by opening of the ring. For the thermodynamics aspects of ring-opening polymerization of cyclic olefin see, for example, ref 21, 38, or 55. Equilibrium conversion data for cyclopentene polymerization has provided estimates of the enthalpy (-4.4 kcal/mol) and entropy (-14.9 cal/mol deg) of polymerization.

(50) We assume that the activation energy for the elementary step  $B \rightarrow C$  is not much higher than the free-energy variation for the elementary step  $B \rightarrow C$  when the latter is endothermic (dashed lines in Figures 3 and 4). We assume also that the activation energy for the same elementary step is negligible when the elementary step  $B \rightarrow C$  is exothermic. Activation energies in metathesis are usually small in the range of 5-8 kcal/mol (see ref 11c and 38). It is also possible that the transition state between the coordinated olefin and the metallacyclobutane is lower in energy (dotted lines in Figures 3 and 4). This situation seems to be confirmed by recent extended Hückel calculations by O. Eisenstein and R. Hoffmann *J. Am. Chem. Soc.*, **103**, 5582 (1981). With complexes of the type  $L_nM(\text{CH}_2)(\text{C}_2\text{H}_4)$  ( $M = \text{Fe}, \text{Mo}, \text{W}$ ;  $L = \text{Cl}, \text{CO}, \text{H}$ ) or  $\text{Cp}_2\text{Ti}(\text{CH}_2)(\text{C}_2\text{H}_4)$ , neither the metal (carbene)-olefin complex nor a metallacyclobutane will be the stable geometry but instead an intermediate nonclassical structure partway between the two. Such a conclusion would be even much more in agreement with our results.

Concerning the role of the transition metal, Goddard and co-workers<sup>52</sup> have studied, inter alia, the various energetic paths for ethylene metathesis with the two catalysts  $\text{Cl}_2\text{M}(\text{O})=\text{CH}_2$  ( $\text{M} = \text{Mo}, \text{Cr}$ ).<sup>53</sup> According to their ab initio calculations, for the molybdenum complex the energy of the coordinated olefin is approximately equal to that of the metallacyclobutane, but for the chromium complex, the metallacyclobutane has a much higher energy (10 kcal/mol) than that of the coordinated olefin.

Finally, concerning the ligands, it is implicitly assumed here that they do not govern the stereoselectivity by their own steric requirements but rather by their electronic effect on the energy levels of the metallacycle intermediates. Lewis acid cocatalysts, by their ability to coordinate to the ligands (e.g., via  $\text{M}-\text{Cl} \rightarrow \text{Al}$ ,  $\text{M}-\text{C}=\text{O} \rightarrow \text{Al}$ ,  $\text{M}=\text{O} \rightarrow \text{Al}$ ), will only modify the electronic effect of these ligands.

## (2) Interpretation of the Stereochemical Results.

In the following we will interpret the experimental data with acyclic and cyclic olefins in the light of the previous proposal.

### (2.1) Stereochemistry with Acyclic Olefins.

The results obtained with acyclic olefins suggest that the energy level of the metallacyclobutane is, in general, higher or close to that of the coordinated olefin: the stereochemistry will be governed by the various energy levels of the cis- and trans-directing metallacyclobutanes.

For a given type of ligands the increase of stereoselectivity observed from tungsten to molybdenum and to chromium would parallel the increase of the levels of energy from the tungstacyclobutane to chromiacyclobutane in agreement with ab initio calculations.<sup>52</sup>

The small effect of many ligands coordinated to tungsten on the stereochemistry<sup>1,44</sup> regardless of their own bulkiness, may be associated with the small differences of energy between the tungsta-cyclobutane and the coordinated olefin. With molybdenum the effect of ligands on the stereoselectivity seems to be more pronounced than with tungsten<sup>8,44,71</sup> in agreement with the higher energy of the molybdenacyclobutane.

It should be pointed out here that there are some particular cases of highly stereoselective tungsten based catalysts such as  $\text{W}(\text{CO})_5(\text{CPh}_2)$  which exhibits, in the absence of any Lewis acid co-catalyst, a very small activity in metathesis of acyclic olefins.<sup>2</sup> One may assume that the weak activity associated with the high stereoselectivity is due to the high level of energy of the tungstacyclobutane with these particular ligands. It is quite tempting to generalize the correlation between small activity and high stereoselectivity in metathesis, but this is difficult to prove without a distinction being made between slow rates reflecting high-energy intermediates in the propagation, slow initiation, and fast termination.<sup>72</sup>

### (2.2) Stereochemistry with Cyclic Olefins. (2.2.1) Case of Norbornene.

If one disregards the strain of the cyclopentene ring of norbornene which may decrease, but

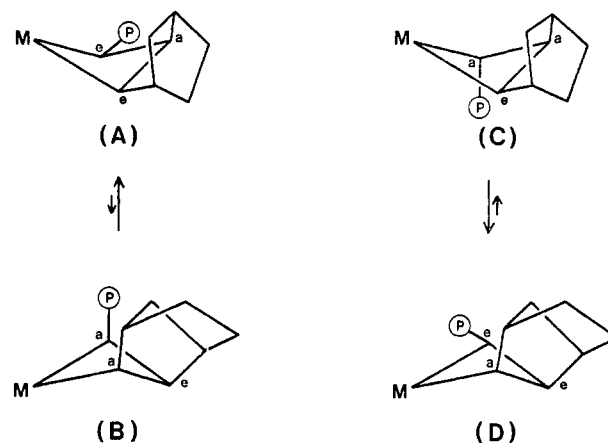


Figure 5. Cis coordination (left) and trans coordination (right) of norbornene by the exo side.<sup>54</sup>

does not prevent<sup>54</sup> the puckering of the metallacyclobutane intermediate (see Figure 5), this cis cycloolefin should lead to a cis polymer. This cis stereoselectivity is effectively observed with  $\text{W}(\text{CO})_5\text{CPh}_2$  when used without any cocatalyst.<sup>2</sup> However, with the catalysts used in the present study, such cis stereoselectivity was not observed with norbornene: regardless of the group 6 transition metals, ligands, or cocatalysts, the polynorbornene obtained has a trans/cis ratio close to unity within experimental error, and this result is in agreement with those published by Ivins and Rooney.<sup>30,39</sup> In our case the lack of stereoselectivity observed has been obtained with those very catalysts which are stereoselective with acyclic olefins.<sup>8</sup> In particular, metals such as Cr or Mo or ligands such nitrosyls, which lead to high stereoselectivity with acyclic olefins,<sup>8,11,44</sup> have no effect on the stereochemistry of polynorbornene.

It is therefore logical to conclude, on the basis of the proposal reported above, that, with the catalysts used here, a strained olefin such as norbornene will give rise to a metallacyclobutane having a level of energy lower than that of the coordinated olefin: the differences of energy between the cis- and trans-directing metallacyclobutanes will not be a discriminating factor of stereoselectivity. It will be impossible to detect with these catalysts the cis stereoselectivity that should appear if the energy level of the metallacyclobutane is higher than that of the coordinated olefin. It is only with some catalytic systems which have no Lewis acid cocatalysts (such as  $\text{W}(\text{CO})_5\text{CPh}_2$ ) or which have some additives such ethyl acrylate<sup>39</sup> which may complex to the catalyst that a cis stereoselectivity may be observed as with acyclic olefins.<sup>73</sup>

### (2.2.2) Interpretation of the Literature Data.

Before any detailed interpretation, one must be careful before using literature results for mechanistic purposes. In fact,

(51) When the coordinated norbornene reaches the metallacyclobutane intermediate, one may consider that the  $\text{C}=\text{C}$  double bond is transformed into a  $\text{C}-\text{C}$  single bond with an increased bond distance of ca. 0.2 Å.

(52) A. K. Rappé and W. A. Goddard III, *J. Am. Chem. Soc.*, **102**, 5114 (1980).

(53) This choice of ligands is most opportune due to the known role of oxygen or oxo ligands in metathesis. See, for example: M. T. Mocella, R. Rovner, and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 4689 (1976); J. M. Kress, M. J. M. Russell, M. G. Wesolek, and J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, 431 (1980). J. H. Wengrovius, R. R. Schrock, M. R. Churchill, I. R. Missert, and W. J. Youngs, *J. Am. Chem. Soc.*, **102**, 4515 (1980). J. M. Basset, G. Coudurier, R. Mutin, H. Pralaud, and Y. Trambouze, *J. Catal.*, **34**, 196 (1974). E. L. Muetterties and E. Band, *J. Am. Chem. Soc.*, **102**, 6574 (1980).

(54) Minimization of the 1-3 and 1-2 interactions of the metallacyclobutane is possible by puckering of the cycle. A certain degree of puckering of the metallacyclobutane can be the result of the two skew boat conformers of norbornane (in Figure 5 we assume that only the exo face of the double bond of norbornene has reacted). Among the four possible metallacycles leading to cis (A  $\rightleftharpoons$  B) or trans (C  $\rightleftharpoons$  D) polynorbornene, the conformers A and D, with the polymeric chain in an equatorial position will be the most favored. Besides, the conformer A will be favored with respect to the conformer D due to the minimized 1-3 interaction (two substituents in pseudoequatorial positions). Regarding the 1-2 interaction, the metallacycle D should be slightly favored with respect to the metallacycle A (e-e vs. e-a interactions), and consequently this effect should lessen the 1-3 effect. Nevertheless, one may consider that an  $\alpha$  substituent in an axial position is more destabilizing than a  $\beta$  substituent in an axial position. In conclusion, the overall stereochemistry with norbornene should be a cis stereochemistry corresponding to the metallacycle A. This result is effectively observed with 3 or 12 in the absence of any cocatalyst<sup>2</sup> or with  $\text{ReCl}_5$ .<sup>39</sup>

it has been demonstrated by Pampus,<sup>28</sup> Höcker,<sup>38</sup> and Teyssié<sup>55</sup> that the microstructure of the polymers (e.g., polypentenamer, polyoctenamer, polydodecenamer, poly-pentadecenamer) can vary during the course of polymerization.<sup>74</sup>

Qualitatively, and in the light of our previous proposal, the group 6 catalysts described in the literature for metathesis of cis cyclic olefins can be divided in two classes already considered by Calderon:<sup>41</sup> the stereoselective catalysts and the nonstereoselective catalysts.

The stereoselective group 6 catalysts<sup>57</sup> such as  $W(CO)_5(CPh_2)$ ,<sup>19</sup>  $WF_6/C_2H_5AlCl_2$ ,<sup>41</sup>  $MoCl_5/Al(i-Bu)_3$ ,<sup>58</sup> exhibit a weak or moderate degree of activity for cis cyclic olefins such as cyclopentene or norbornene, and they give rise to a cis polymer (e.g., polypentenamer<sup>19,41</sup> or polynorbornene<sup>19,57,58</sup>) of rather high molecular weight. Besides, it is almost impossible to regulate the molecular weight of such polymers (e.g., polypentenamer) during the course of the polymerization by adding small amount of  $\alpha$ -olefins<sup>41</sup> as it occurs with nonstereoselective catalysts.<sup>16,59,60</sup> This result is in agreement with the fact that the cis acyclic double bonds of the polymer chain cannot react with the propagating metalcarbene center to give rise inter alia to cis-trans isomerization, intramolecular, or intermolecular chain-transfer processes.

It is therefore logical to observe that the polymer remains cis during the overall polymerization process. Those catalysts exhibit a weak activity in metathesis of acyclic olefins,<sup>61</sup> which is in agreement with the previous observations.

We can consider that, for these catalysts, the energy level of the metallacyclobutanes, due to an electronic effect of the ligands, is very high: the system will be stereoselective with cyclic and acyclic olefins. Thus,  $W(CO)_5(CPh_2)$ , which is the only reported stereoselective catalyst used both with an acyclic and a cyclic olefin, exhibits a very high degree of stereoselectivity with norbornene (cis stereoselectivity), *cis*-2-pentene (cis stereoselectivity), *trans*-2-pentene<sup>2</sup> (trans stereoselectivity<sup>62</sup>), and 1-methyl-*trans*-cyclooctene<sup>27</sup> (trans

stereoselectivity).

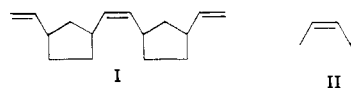
The nonstereoselective catalysts are usually active in metathesis of acyclic olefins. They exhibit a high activity, and probably, with cyclic olefins, due to an electronic effect of ligands, the energy level of the metallacyclobutanes is lower than that of the coordinated olefins. Most of the tungsten- or molybdenum-based catalysts reported so far belong to such a class. Since they are able to carry out metathesis of acyclic and cyclic olefins, it is logical that the trans/cis composition of the polymer varies during polymerization, from a 1:1 to a high trans/cis ratio close to that of thermodynamics.

## Experimental Section

Organometallic reactions and catalytic reactions were carried out under argon by using standard anaerobic techniques. The apparatus used for metathesis experiments included a glass batch reactor with valves allowing argon purges, evacuation, and introduction of the various reagents under a controlled atmosphere. Various gas syringes as well as burets allowed given amounts of  $O_2$ , alkylaluminum, alkyltin,  $TiCl_4$  (etc.), or solvent to be introduced into the reactor.

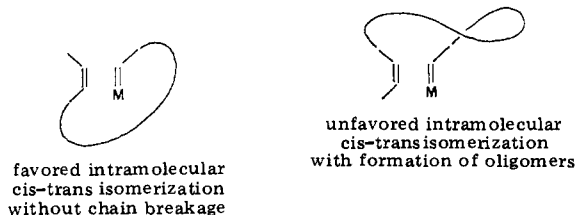
**Materials. (a) Catalysts.**  $M(CO)_5PPh_3$  complexes were obtained by mixing stoichiometric amounts of  $M(CO)_6$  ( $M = Mo, W$ ) and triphenylphosphine according to a procedure described by Poilblanc et al.<sup>64</sup> and Angelici et al.<sup>65</sup>  $M(CO)_3(Mes)$  ( $M = Mo, W$ ) catalysts were purchased respectively from Strem Chemicals Inc. and from Research Organic Inorganic Chemical Corp.  $M(NO)_2Cl_2(PPh_3)_2$  catalysts were synthesized according to a procedure described by Johnson.<sup>66,67</sup>  $WCl_6$  was obtained from Fluka. It was purified by heating under vacuum at ca. 150 °C to remove volatile tungsten oxychlorides.  $W(OPh)_6$  was purchased from ROC/RIC and used as such without further purification.  $W(CO)_5(C(OC_2H_5)(C_6H_5))$  and  $W(CO)_5(C(C_6H_5)_2)$  were prepared according to the procedure described by Casey et al.<sup>68</sup>  $W(CO)_6$

(63) The fact that secondary reaction does not seem to occur to a large extent with norbornene may be due to the bulkiness of the substituent of the acyclic double bond in polynorbornene (I). We have previously observed with the same catalysts as those used here that the bulkiness of the olefin (II) decreases the rate of formal metathesis, and the trans isomer is about 10 times less reactive than the cis isomer.<sup>8</sup>



(55) L. Hocks, D. Berck, A. J. Hubert, and P. Teyssié, *J. Polym. Sci., Polym. Lett. Ed.*, **13**, 391 (1975).

(56) Intramolecular coordination of the first double bond after the metalcarbene explains easily why the monomer-polymer equilibrium is observed with polypentenamer.<sup>29</sup> It is not unreasonable to assume that cis-trans isomerization can be achieved without formation of cyclic oligomers if the first double bonds formed at the beginning of the polymerization will retrocoordinate to the metalcarbene in the less strained manner as depicted here:



(57) Out of group 6 there are a few highly stereoselective catalysts with norbornene such as  $RuCl_3$  (see ref 30) or  $ReCl_5$ : T. Oshika, H. Tabuchi, *Bull. Chem. Soc. Jpn.*, **41**, 211 (1968).

(58) G. Sartori, F. Ciampelli, and N. Camelli, *Chim. Ind. (Milan)*, **45**, 478 (1963).

(59) K. Nützel, F. Haas, and G. Marwede, German Patent 1 919 047.7.

(60) Montecatini Edison, Italian Patent 6 617 575.

(61) As mentioned in ref 2,  $W(CO)_5(CPh_2)$  is able to carry out metathesis of *cis*-2-pentene in octane with a molar ratio of olefin/W of ca. 100. The percentage of conversion is 87% in 40 h. With the catalyst  $W(CO)_3(Mes)/EtAlCl_2/O_2$  under similar experimental conditions equilibrium is reached in 15 min.<sup>8</sup>

(62) The results of ref 2 are somehow difficult to interpret concerning *trans*-2-pentene metathesis. The trans/cis ratios of 2-butene and 3-hexene at low conversion are equal, respectively, to 2.68 and 5.02 which are very close to thermodynamic values.

(64) R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. Fr.*, 1301 (1962).

(65) R. J. Angelici and M. Malone, *Inorg. Chem.*, **6**, 1731 (1967).

(66) B. F. G. Johnson, *J. Chem. Soc. A*, 475 (1967).

(67) F. A. Cotton and B. F. G. Johnson, *Inorg. Chem.*, **3**, 1609 (1964).

(68) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **96**, 7808 (1974).

(69) P. Krausz, F. Garnier, and J. E. Dubois, *J. Am. Chem. Soc.*, **97**, 437 (1975); P. Krausz, F. Garnier, and J. E. Dubois, *J. Organomet. Chem.*, **108**, 197 (1976); P. Krausz, F. Garnier, and J. E. Dubois, *ibid.*, **146**, 125 (1978); A. Agapiou and E. McNelis, *J. Chem. Soc., Chem. Commun.*, 187 (1975); A. Agapiou and E. McNelis, *J. Organomet. Chem.*, **99**, C47 (1975).

(70) Y. Chauvin, D. Commereuc, and D. Crupelinck, *Makromol. Chem.*, **177**, 2637 (1976).

(71) For example, in *cis*-2-pentene metathesis, the variation of stereoselectivity, when going from carbonyl to nitrosyl ligands, is more pronounced with molybdenum than with tungsten based catalysts.<sup>8,44</sup>

(72) It is only with metalcarbene complexes that this general approach would be valid because the initiation step corresponding to the formation of the metalcarbene is avoided. Usually metalcarbenes of tungsten or tantalum exhibit a poor metathesis activity with acyclic olefins and a high stereoselectivity. It is only when a Lewis acid cocatalyst is used that their activity increases and their stereoselectivity decreases. One may reasonably assume that the Lewis acid cocatalyst does not participate in the initiation process but in the propagation step as a complexing agent toward the ligands of the metalcarbene complex.

(73) Ivin, Rooney, et al.<sup>30,39</sup> have studied a great variety of group 6 catalysts in norbornene metathesis. Most of the catalysts they have used exhibit a nonstereoselective behavior: 49% of cis double bonds in polynorbornene with tungsten and 43% with molybdenum. It is only when they use additives such as ethyl acrylate or diethylfumarate in excess that they can increase the cis stereoselectivity. One may speculate on the possibility of such additive to coordinate to the metalcarbene center or to the Lewis acid cocatalyst and thus increase the energy level of the metallacyclobutane.



and  $\text{Mo}(\text{CO})_6$  were obtained from Fluka.

(b) **Cocatalysts.**  $\text{C}_2\text{H}_5\text{AlCl}_2$  was supplied by the Ethyl Corp. It was purified by vacuum distillation, diluted in anhydrous chlorobenzene, and stored under argon.  $(\text{CH}_3)_4\text{Sn}$ ,  $(\text{C}_6\text{H}_5)_4\text{Sn}$ , and  $\text{TiCl}_4$  were supplied by Fluka and used after storage under Ar.

(c) **Solvent.** Chlorobenzene was a commercial Merck product; it was distilled twice from  $\text{P}_2\text{O}_5$  under argon. It was stored under argon over 5-Å molecular sieves.

(d) **Gases.** All the gases used (argon and oxygen) were dried over 5-Å molecular sieves.

(e) **Olefin.** The norbornene was obtained from Aldrich. It was purified by sublimation.

**Procedure for Running the Catalytic Reactions.** A typical procedure was as follows: 0.94 g ( $10^{-2}$  mol) of norbornene were dissolved in 50 mL of chlorobenzene containing  $39 \times 10^{-3}$  g ( $10^{-4}$  mol) of  $\text{W}(\text{CO})_3(\text{Mes})$ . Then 14.4 mL of  $\text{O}_2$  ( $6 \times 10^{-4}$  mol) was introduced into the reactor, and finally the reaction was started at 25 °C by the addition of  $4 \times 10^{-4}$  mol of  $\text{C}_2\text{H}_5\text{AlCl}_2$ . After a suitable time (varying from a few minutes to a few hours) the reaction was quenched by the addition of 5 mL of ethanol, and the polymer was recovered and dried under vacuum at 50 °C. It was then dissolved in refluxing deuterated chloroform. Those samples which could not completely dissolve in refluxing chloroform (presumably cross-linked or having a very high molecular weight) were filtrated so as to give a clear and limpid solution for NMR studies. In one case (catalyst 3) the microstructure of the solid-state polymer was also checked by solid-state  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy (magic angle). Although the spectra were not as well resolved as those for the liquid phase, the cis/trans ratio of the double bonds was approximately equal to that observed in solution, which rules out the possibility of a wrong analysis due to filtration.

**$^{13}\text{C}$  and  $^1\text{H}$  NMR Spectra.** These were obtained on a CAMECA 250 FT spectrometer operating at 250 ( $^1\text{H}$ ) and 62.86

(74) For example, with the catalyst  $\text{WCl}_4(\text{OCH}(\text{CH}_2\text{Cl})_2)_2/\text{AlEt}_2\text{Cl}$  it was found<sup>28</sup> that the proportion of cis double bonds in the polymer decreases with time, and this decay parallels the decrease of molecular weight. This result is in good agreement with the hypothesis that cis-trans isomerization of the double bonds in the polymeric chain may occur during the formation of oligomers or during the intramolecular or intermolecular chain transfer processes. (Let us mention that the intramolecular chain-transfer process can result in cis-trans isomerization without decreasing the molecular weight; see ref 56.) As mentioned by Pampus,<sup>28</sup> the highest drop of cis double bonds content of the poly-pentenamer and the highest drop of molecular weight corresponds to a very short reaction time where the rate of polymerization is the highest. Therefore, with these systems where cis-trans isomerization occurs during propagation, it is very difficult to obtain reliable data on the stereochemistry of the propagation. This secondary cis-trans isomerization does not seem to occur to a significant extent with norbornene (see ref 63).

(75) F. W. Michelotti and W. P. Keaveney, *J. Polym. Sci., Part A*, 3, 895 (1965).

MHz ( $^{13}\text{C}$ ).  $\text{CDCl}_3$  solvent provided the deuterium lock frequency, and protons were decoupled from  $^{13}\text{C}$  nuclei by broad-band irradiation.  $\text{Me}_4\text{Si}$  was used as an internal reference.

**For  $^1\text{H}$  NMR spectra** the following conditions were used: spectral window, 3012 Hz; pulse duration time, 5  $\mu\text{s}$ ; repetition time, 2.71 s; number of pulses, 200–1000, depending on the concentration. The resolution was equal to 0.36 Hz.

**For  $^1\text{H}$ -decoupled  $^{13}\text{C}$  spectra** the following conditions were used: spectral window, 15 151 Hz; pulse duration time, 10  $\mu\text{s}$ ; repetition time, 3.5 s; the number of points to store the FID, 8192; the number of pulses, 20 000–35 000, depending on the concentration. The resolution was equal to 1.8495 Hz/point. We have used the procedure described by Ivin<sup>30</sup> to calculate the trans/cis ratio from the  $^{13}\text{C}$  spectra. We have also carried out the  $^1\text{H}$  NMR spectrum at 250 MHz of the same sample. The *Z* and *E* ethylenic protons are well separated, and it is possible by integration to calculate the respective percentage of cis and trans protons by assuming the same relaxation time for both types of protons. In any case the repetition time was large enough.

The results obtained by  $^{13}\text{C}$  and  $^1\text{H}$  NMR on the same sample gave the same value for the percent of cis double bonds. This was checked with the catalyst 3 associated with  $\text{TiCl}_4 + h\nu$  (percent cis double bonds:  $^1\text{H}$ , 44;  $^{13}\text{C}$ , 46), with the catalyst 6 associated with  $\text{C}_2\text{H}_5\text{AlCl}_2$  (Al/W ratio of 10) (percent cis double bonds:  $^1\text{H}$ , 14;  $^{13}\text{C}$ , 10), and with the catalyst 12 associated with  $\text{C}_2\text{H}_5\text{AlCl}_2$  (Al/W ratio of 6) (percent cis double bonds:  $^1\text{H}$ , 27;  $^{13}\text{C}$ , 25). In all cases the values of stereoselectivities obtained by  $^{13}\text{C}$  NMR were within the range of  $^1\text{H}$  NMR errors. The values reported in the Tables I–V are systematic errors deduced from the various integration methods that we have used (manual graphic, weight of the peaks, and computer method). The maximum error between these was always less than 10%. For a given method of integration, the observed experimental error for the same sample was less than 5%.

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**Registry No.** 1, 14040-11-0; 2, 15444-65-2; 3, 36834-98-7; 4, 12129-67-8; 5, 12089-15-5; 6, 12129-69-0; 7, 14730-11-1; 8, 14871-08-0; 9, 13283-01-7; 10, 4503-97-3; 11, 13520-78-0; 12, 50276-12-5; 13, 13939-06-5; norbornene, 498-66-8.

**Supplementary Material Available:** All detailed experimental conditions such as concentrations of the various reagents for each experiments, temperatures, yields, etc. are available in a table (1 page). Ordering information is given on any current masthead page.