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Characteristics of $RuCl_2(CHPh)(PCy_3)_2$ as a Catalyst for Ring-Opening Metathesis Polymerization

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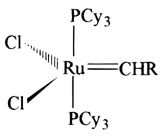
ABSTRACT: Ring-opened metathesis polymers and copolymers have been formed from norbornene, norbornadiene, a range of their derivatives, and cyclopentene using $RuCl_2(CHPh)(PCy_3)_2$, as catalyst. ^{13}C NMR analysis of the polymers illustrate a rather selective propagation reaction. The catalyst is highly regioselective, and the polymers are generally high trans with a strong isotactic bias. However, polymers from diene monomers tend to be less isotactic than those from the corresponding monoenes, and in the case of 7-methylnorbornadiene the polymer has an overall syndiotactic bias. A rate enhancing effect, noted previously, due to an oxygen atom proximate to the monomer double bond, is less pronounced than with other initiators. Catalyst activity, in the case of certain diene monomers, was shown to be monomer dependent and rate enhancements were also achieved using phenol as solvent. The results are interpreted in terms of the steric and electronic properties of both the catalyst and the monomers.

Introduction

The advent of well-defined metallacarbene complexes which may be used as initiators for olefin metathesis reactions has led to a dramatic increase in the level of interest in the field. This is a result, not only of the potential for the stereospecific synthesis of numerous ring systems by ring-closing metathesis (RCM) but also of the preparation of novel, highly functionalized, polymers of predictable molecular weights and low polydispersities by both ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET). Living polymers are frequently formed due to the level of control which may be exercised over initiation and termination reactions possible with these catalysts.[1]

A range of metallacarbene complexes related to **1**[1e] and **2**[2] have been widely used in these studies, but it is the Ru complex **1** and its analogues which have excited most interest because, although less reactive than the Mo complexes, they are much more accessible and exhibit a high tolerance to heteroatom functionality in the substrate as well as to ubiquitous impurities such as oxygen and water.[3] Variants bearing polar phosphine ligands have been prepared which are active in aqueous media,[4] and recently it has been shown that more active forms of **1** may be synthesized where one or both of the PCy_3 ligands may be replaced by other ligands, for example N-heterocyclic carbenes.[5]



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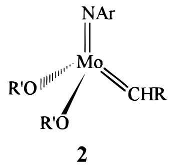

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Most of the studies on **1** and its analogues have concentrated on their use in synthesis, and little is known about the behavior of such catalysts in terms of the microstructure of polymers produced in ROMP reactions, which, as we have shown previously,[6] is a valuable source of information concerning the factors which control activity and selectivity of metathesis catalysts.

Hitherto, we have systematically studied the microstructures of polymers produced by classical, metal−salt type catalyst systems using a portfolio of monomers mostly based on bicyclo[2.2.1]hept-2-ene (norbornene), **3**, and bicyclo[2.2.1]hepta-2,5-diene (norbornadiene), **4**; see Chart 1. These were chosen because the ^{13}C NMR spectra of polymers formed from a number of them allow one to define different characteristics of the catalyst. For example, the ratio of cis and trans double bonds and their distribution in the polymer is easily determined, while polymers formed from **8** have shown wide, catalyst-dependent, variations in regioselectivity.[6b,g] In addition, the spectra of poly(**10**)[6c] and poly(**12**)[6f] show multiple splitting due to tacticity effects, and copolymers formed from **3** and cyclopentene, **9**, allow one to examine relative reactivities as well as mechanistic features.[6h,7]

The polymerization of matched pairs of monomers, for example, **15** and **16** and **18** and **19**, is another fruitful area of interest where the role of the proximate oxygen atom in activating the double bond can be investigated[8] and compared with the similar effect of the oxygen atom in **13** in terms of syn versus anti direction of attack in the [2 + 2] cycloaddition step.[6f]

Each of these monomers has now been polymerized with the commercially available **1**, and the behavior of the catalyst in terms of its stereo and regioselectivity, as well as its behavior in copolymerization reactions, is described and compared with that of the classical catalyst systems.

Results and Discussion

Stereoselectivity. The ratio of cis and trans double bonds (expressed as the fraction of cis double bonds, σ_c) and their distribution is the primary microstructural variant of the products in metathesis polymerizations. Factors which influence σ_c, such as monomer and catalyst reactivity, steric constraints at the catalyst site, the influence of the stereochemistry of the last formed double bond on the next propagation event, and the geometry of the carbene ligand have been the subject of numerous studies.[1c]

The initial observation in our survey of the polymerization characteristics of **1** in this context was that σ_c of the polymers was generally less than 0.3; see Table 1. Significantly, norbornadiene, **4**, was polymerized in

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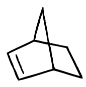
Chart 1



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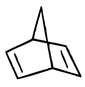

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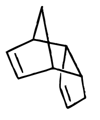

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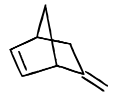

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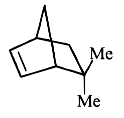

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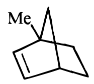

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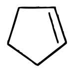

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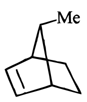

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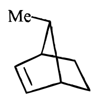

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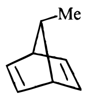

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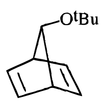

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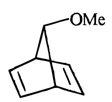

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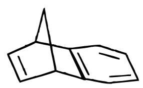

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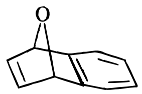

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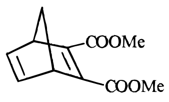

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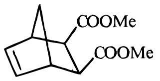

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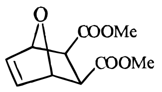

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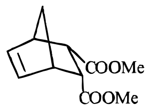

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Table 1. Microstructural Characteristics of Homopolymers Formed Using 1

polymer	σ_c	tacticity[a]	regioselectivity	polymer	σ_c	tacticity[a]	regioselectivity
poly(**3**)	0.17	isotactic[b]		poly(**12**)	0.29	syndiotactic[d]	all anti
poly(**4**)	0.14	isotactic[b]		poly(**13**)	0.29	syndiotactic	all anti
poly(**5**)	0.13		none	poly(**14**)	0.29		all anti
poly(**6**)	0.32		none	poly(**15**)	0.50		
poly(**7**)	0.19		none	poly(**16**)	0.46		
poly(**8**)	0.22		all HT[c]	poly(**17**)	0.11	isotactic	
poly(**9**)	0.10			poly(**18**)	0.26	isotactic	
poly(**10**)	0.20	isotactic[d]		poly(**19**)	0.50		
poly(**11**)				poly(**20**)	0.10		

[a] This column refers to the tacticity bias of the polymer. [b] Tacticity estimated from the hydrogenated polymer. [c] Both cis and trans junctions. [d] Tacticity estimated directly from the ring-opened polymer.

high yield to give a polymer with $\sigma_c = 0.14$, the highest trans polymer yet obtained with this monomer;[9,10] other diene monomers similarly gave high trans polymers. Even when the solvent was changed to dioxan, which substantially increases the cis content in polymers formed from W and Mo halide-based catalysts,[8] the temperature lowered to −40 °C, or the monomer concentration decreased by a factor of 10, σ_c changed very little. These low σ_c values are in complete contrast to those observed with noble metal−salt type catalysts such as $RuCl_3$ and $OsCl_3$, which give high trans content polymers from monoenes, but with dienes give high cis polymers as a result of steric constraints at the site imposed by the diene monomer which also acts as a chelated spectator ligand.[6f,9] Clearly these dienes are not acting in this way with **1** during the propagation reaction. A higher cis content ($\sigma_c \approx 0.50$) was obtained with **15**, **16**, and **19**. Although other factors may be involved here, this lower selectivity seems to be associated with an apparently faster propagation reaction which we have observed with these monomers.[8]

The ^{13}C NMR spectra of all the polymers revealed an essentially random distribution of cis and trans double bonds which is expected for polymers of $\sigma_c < 0.5$, even poly(**19**) had a random distribution with **1** as catalyst despite the fact that the polymer prepared from **19** using $RuCl_3$, with $\sigma_c = 0.5$, was surprisingly highly blocky.

Regioselectivity. If it is assumed that attack on the double bond occurs exclusively at the *exo* face in the ROMP of norbornene, norbornadiene, and their derivatives,[1c] then regioselective behavior falls into three different categories. In the case of diene monomers the double bonds may have different reactivities, due, for example, to their positions in the polycyclic system, as in the case of dicyclopentadiene, **5**.[9b] Alternatively, structurally similar double bonds may show differential reactivity due to steric constraints of substituents, as with 7-methylnorbornadiene **12**,[6f] or special electronic effects, as with the 7-substituted ether derivatives **13** and **14**,[6e] and the diester-substituted norbornadiene derivative **17**. Finally, substituent orientation effects, for example, head-to-tail (HT) bias, may be observed in the case of polymers formed from unsymmetrical monomers, if the substituent is sufficiently close to the double bond. This latter effect is seen in polymers formed from **8**[6b] but not from **6** or **7**.[1c]

Table 2. Ring-Opening Metathesis Copolymerization Using 1

A	B	f_A	F_A	σ_c (A units)	σ_c (B units)
3	**9**	0.50[a]	0.85	0.13	~0
3	**9**	0.50[b]	0.61	0.28	~0.20
3	**4**	0.50	0.50	0.14	0.16
10	**11**	0.49	1.00	0.20	
15	**16**	0.50	0.05		0.46
18	**19**	0.50	0.32	0.25	0.21

[a] Methylene chloride solvent. [b] Chlorophenol solvent.

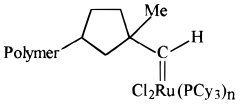
With regard to the first category, **1** behaves much as expected in the polymerization of **5** and **6** with attack occurring exclusively at the more strained double bond. The fact that no tricyclic addition polymer is formed along with poly(**6**), frequently the case when metal–salt type catalysts are employed,[11] highlights the advantage of using Lewis acid free catalyst systems such as **1**. Poly(**4**), poly(**5**), poly(**6**), and poly(**12**), however, still have a strong tendency to become insoluble, presumably through cross-linking.

Second, in dienes, if substituents are closer to one double bond, **1** often behaves with complete regioselectivity, polymerizing **10** exclusively from a mixture of **10** and **11** and attacking **12**–**14** only at the anti face, a fact readily established from ^1H and ^{13}C NMR analysis. This is in stark contrast to the behavior of a number of other catalysts, not necessarily more reactive than **1**, which are capable of polymerizing both **10** and **11**[6c] and can give up to 23% syn attack at **12**[6f] and up to 50% syn attack on the *tert*-butyl ether **13**.[6e] In fact all polymers hitherto formed from **13** using numerous catalyst systems, including $OsCl_3$ and the Schrock Mo complexes,[12] contain substantial proportions of units resulting from syn attack which is believed to be due to oxygen-promoted assistance of the [2 + 2] cyclobutanation step at the syn face of the molecule.[6f] The high regioselectivity observed in the polymerization of **13** and **14** using **1** is therefore remarkable and is attributed to the combined steric effects of monomer and catalyst. Oxygen-promoted assistance may exert its full effect, however, when monomer steric effects are minimized, because when one compares the apparent reactivities of the oxygen and methylene-bridged analogues **15**/**16** and **18**/**19**, in low-yield copolymerization reactions, Table 2, the oxygen-bridged analogues **16** and **19** are now judged to be more reactive by their preferential incorporation into the polymer chain. This is discussed in more detail later.

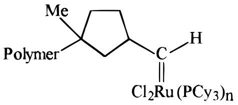
A striking example of regioselectivity is seen in the polymerization of **8** using **1** where a strongly head-to-tail (HT) biased polymer with respect to both cis and trans double bonds is formed, as observed by inspection of the olefinic region of the ^{13}C NMR spectrum, Figure 1a.[13]

Regioselective behavior in ROMP is highly monomer dependent, as recent studies have shown. It is not a feature when **1** is used to initiate the polymerization of 5-substituted cyclooctenes[14] nor when W and Mo carbene initiators are used in the polymerization of 3-methylcyclobutene;[15] however, these latter catalysts are regioselective when used to polymerize 3,3-dimethylcyclobutene. For similar steric reasons the polymerization of **5**, **6**, or **7** is not regioselective using **1**.

The bulk of the monomer substituent and its proximity to the double bond are clearly important for regioselectivity, but so also is the nature of the catalyst. For example, when **8** is polymerized using **1**, Figure 1a, the HT-bias is as strong as that found using $OsCl_3$, Figure 1c, in contrast to the absence of any effect at all in the polymer formed using $RuCl_3$, Figure 1b; significantly, all these polymers are high trans. The difference in regioselective behavior between the classical $OsCl_3$ and $RuCl_3$ catalysts was attributed to differences in the polarity of the π-component of the Mt=C bond.[16] However, in the case of **1**, we believe that the regioselectivity observed in the polymerization of monomer **8** may be due to the strong steric effect exerted by the presence of one or perhaps both bulky PCy_3 ligands[17] on the Ru carbene such that propagation by the tail metallacarbene is strongly preferred, with a corresponding full HT orientational bias in both the cis- and trans-forming cyclobutanation steps.



$\mathbf{P}_{HEAD}$



$\mathbf{P}_{TAIL}$

n = 1,2

It is interesting that the $MoCl_5/Me_4Sn$/dioxan catalyst, high cis directing with a variety of monoenes and dienes,[18] also gives a mainly trans strongly HT-biased polymer from **8**. Again the combined steric effects of the 1-methyl substituent of **8** and the complexed dioxan renders unfavorable the formation of not only cis head-to-head junctions but even cis head-to-tail junctions. This result therefore reinforces the conclusions that steric effects are very important in the polymerization of **8**, even in making trans junctions.

Tacticity. Tacticity in polymers formed in the ROMP of symmetrically substituted norbornene derivatives is defined by the sequence of the configurations of pairs of methine carbon atoms along the polymer chain; thus –RS–RS–RS– represents an isotactic sequence and –RS–SR–RS– a syndiotactic sequence, which may also be referred to respectively as erythrodiisotactic and erythrodisyndiotactic. Viewed as a 3-D structure this translates as different relative orientations of neighboring cyclopentane rings as shown for poly(**3**) in Chart 2.

Although methods for determining the tacticity of ROMP polymers are well developed[19] the detailed mechanistic aspects of the reactions leading to polymers of different tacticities are less well understood than that of the other microstructural features discussed above. A knowledge of the tacticity of polymers formed from various monomers with catalyst systems such as **1**, where the structure of the propagating species is better defined, will become increasingly important.

When polymers are high cis, or high trans as is more usual using **1**, there is the added advantage that derivatives, fully hydrogenated with diimine, can be used to ascertain the tacticity of the precursor materials or in some cases to cross-check the tacticity assignment of different precursor polymers. When the monomer has a plane of symmetry, the only possible ^{13}C NMR line splitting for the hydrogenated material, in the absence of any syn/anti substituent effects, which may be a problem in polymers formed from **12** or **13**, is due to tacticity. The value of this approach is exemplified for high trans poly(**3**) and poly(**4**) prepared using **1**, Figure 2, where the chemically identical hydrogenated forms of the polymers show a triplet ($\delta_{mm} > \delta_{mr/rm} > \delta_{rr}$) for C^7 and a doublet ($\delta_r > \delta_m$) for C.[5,6,20] This line order is assigned on the basis of comparison with the spectra of polymers made using the $ReCl_5$ catalyst which has been

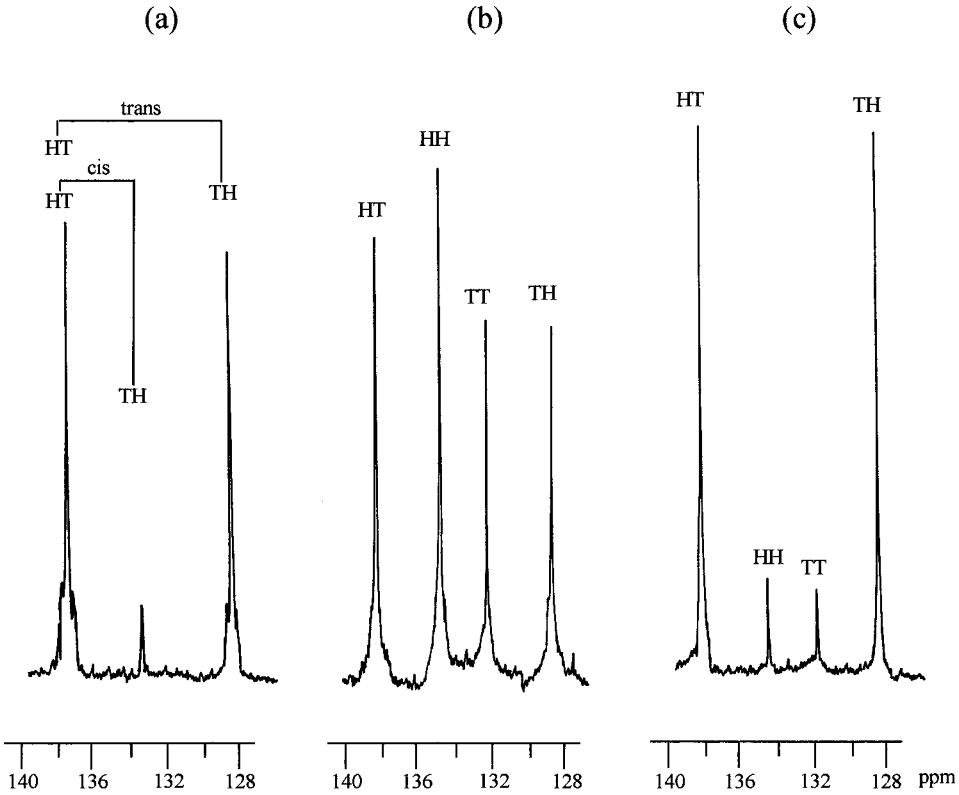
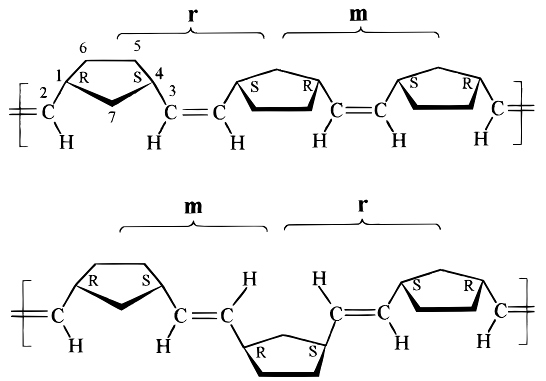


Figure 1. Olefinic region of the ^{13}C NMR spectra of samples of poly(**8**) with varying head-to-tail bias formed using (a) **1**, completely biased, $\sigma_c = 0.22$; (b) RuCl$_3$, no bias, $\sigma_c \approx 0$; and (c) OsCl$_3$, strong bias, $\sigma_c \approx 0$.

Chart 2



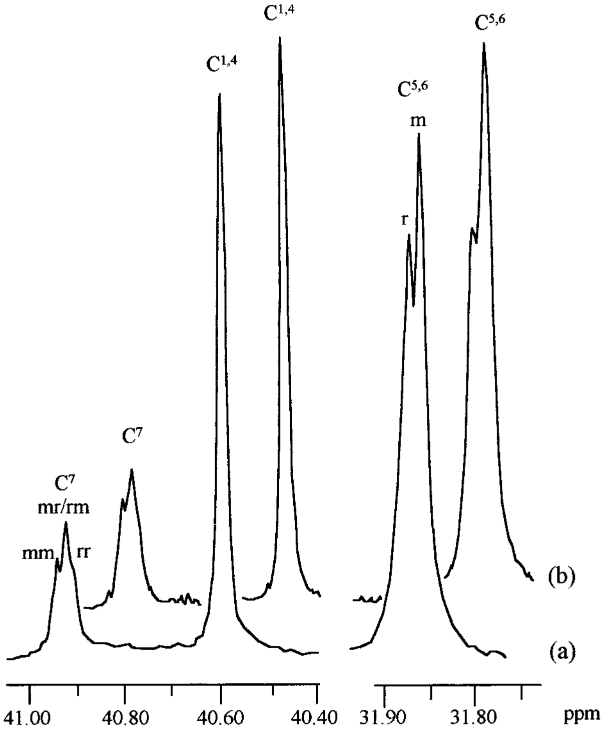


Figure 2. ^{13}C NMR spectra of hydrogenated polymers with different isotactic bias prepared using **1**, derived from (a) poly(**4**), and (b) (offset upfield) poly(**3**). For the sake of clarity the C^{5,6} region is a $\times$2 expansion.

shown to give highly syndiotactic polymers with resolved, alkyl-substituted norbornenes,[16a,21] the position of the r and rr lines is thus defined. The spectra in Figure 2 both show an isotactic bias, although, significantly, the polymer formed from the diene has a higher proportion of syndiotactic junctions, indicating a degree of monomer-dependent tacticity, vide infra.

The introduction of a 7-methyl substituent, as in poly(**10**)[6c] and poly(**12**),[6f] permits the direct observation of tacticity, i.e., before hydrogenation, on the well-separated cis and trans resonances of the spectra, and this allows the tacticity of the dyads embracing each type of double bond to be determined directly.

In the case of poly(**10**), Figure 3, the C^{2,3} olefinic resonance appears as a partially resolved quartet with the cis and trans components being split into isotactic, m, and syndiotactic, r, components, the relative intensities of the t_m, t_r and c_m, c_r lines show clearly a strong bias toward isotactic trans junctions and a partial bias toward isotactic cis junctions. The cis/trans splitting of C^{1,4} is typically large, but tacticity splitting only is of significance on the trans line where again the isotactic component predominates, mirroring the C^{2,3} trans line.

The C^7 resonance is partially tacticity-resolved in numerous spectra of poly(**10**), the cc and ct components both showing tacticity splitting.[6c] In the spectrum of the

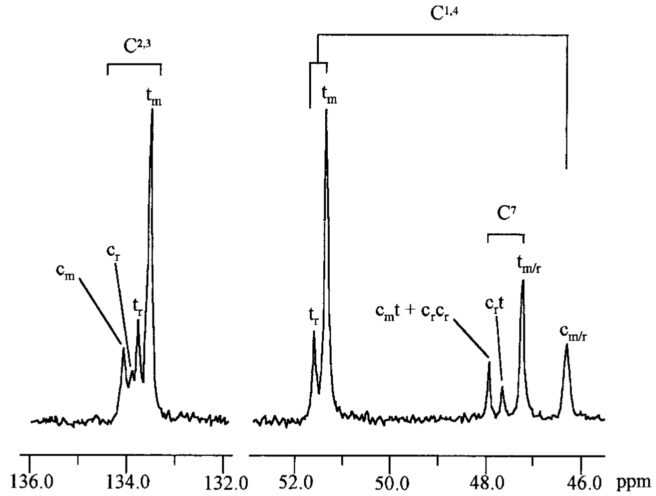


Figure 3. $C,^{1,4}$ $C^{2,3}$, and C^7 signals in the ^{13}C NMR spectrum of poly(**10**) prepared using **1** ($\sigma_c = 0.20$). A strong isotactic bias is evident for both cis and trans junctions.

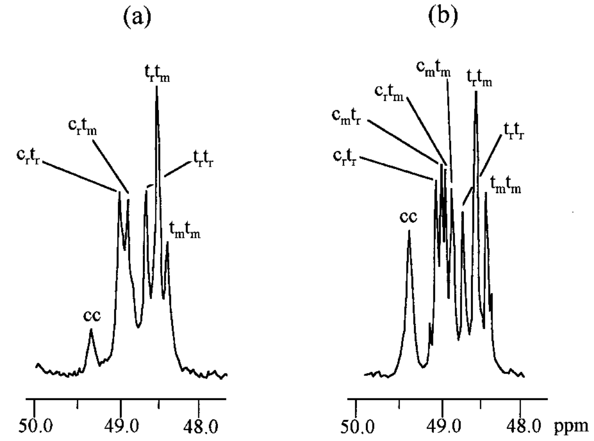


Figure 4. C^7 signals in the ^{13}C NMR spectrum of different samples of poly(**12**) prepared using (a) **1**, where a syndiotactic bias is evident for both cis and trans junctions; (b) for comparison, the C^7 signal in atactic poly(**12**) prepared using the WCl_6/Me_4Sn catalyst.

present high trans polymer, Figure 3, most of the cis signal is present as ct, which is sensitive to tacticity only on the cis side and thus appears as a doublet assigned c_mt and c_rt with the former signal predominating (the small cc component, known from higher cis cases to be split into a triplet,[6c] is obscured by the noise). The intensity ratio of lines within the various signal groups are in qualitative agreement and confirm the overall isotactic bias of the polymer.

Poly(**10**) was hydrogenated, but we were surprised to find that the product would not dissolve or even swell in a number of solvents, including $CDCl_3$, under conditions where numerous samples of syndiotactic and atactic polymer freely enter solution. It is well-known that tacticity can profoundly effect solubility[22] and we therefore attribute this polymer's behavior to a highly isotactic microstructure.

High trans poly(**17**) and poly(**18**) were also made using **1** and then hydrogenated as this had been found previously to give the same saturated structures (the diimine reagent attacks the cyclopentyl ring double bond regiospecifically from the syn side[23]). The ^{13}C NMR spectra then allow a comparison of the tacticity of the two polymers, the only possible line splitting now being due to this effect. Both showed the same tactic bias, presumed isotactic, based again on the assumed C^7 line order and in accord with assignments for the unhydrogenated precursors.[23]

Surprisingly yields of poly(**17**) made using **1** were very small, whereas, as we have found previously[23] $RuCl_3$ is an excellent catalyst for this reaction, also affording a very high trans ($\sigma_c = 0.05$) and strongly isotactic polymer. The substituted double bond in **17** constitutes a Michael acceptor and we conclude that **1** is sufficiently basic to be partially poisoned by the π-acid. This concurs with a recent independent observation of this system[24] and also with Grubbs' observation[25] that **1** is a very poor catalyst for the polymerization of 2,3-bis(trifluoromethyl)norbornadiene where the $[-CF_3C{=}CCF_3-]$ moiety is also a Michael acceptor.

So far, where it could be ascertained, all the polymers made using **1** have shown a distinct isotactic bias. We were therefore surprised to find that analysis of poly(**12**) by ^{13}C NMR, according to previous assignments,[6f] indicated a slight syndotactic bias for the trans junctions with strongly syndiotactic cis junctions, according to the C^7 resonance, Figure 4a. Figure 4b shows the same resonance in the spectrum of an atactic polymer formed using a W-based catalyst system and it allows one to make a comparison with the present case (in contrast to the C^7 resonance in poly(**10**), Figure 3, the tt component now appears as a triplet while the cc component is barely affected by tacticity). In the ct sequence the tacticity of both cis and trans units is now important and the ct signal is resolved into a quartet: $\delta c_rt_r > \delta c_mt_r > \delta c_rt_m > \delta c_mt_m$. This group of signals provides a key to the tacticity of poly(**12**) formed using **1**. As can be seen in Figure 4a, the intensity of c_rt_r and c_rt_m signals exceeds that of c_mt_r and c_mt_m, which are discernible only as shoulders; this means that most of the cis double bonds are embraced by syndiotactic ring dyads. In fact, in the trans resonance, the t_rt_r component is slightly more intense than the t_mt_m component and therefore poly(**12**), in contrast to poly(**10**), has an overall syndiotactic bias. Hydrogenation of this polymer and comparison with published spectra of other hydrogenated examples[6c] confirms the syndiotactic bias.

This check, via the hydrogenated polymer, is important because we now recognize that polymers produced from substituted monomers with a given catalyst are generally more tactic than poly(**3**) and poly(**4**) and that the differences are also substantial between the polymers formed from substituted monoenes and those from the corresponding substituted dienes. Cis/trans ratios in ROMP show a strong monomer dependence,[1c] but a similar dependence of tacticity when comparing the norbornene and norbornadiene series, as illustrated above, is only beginning to emerge. We have found recently, for example, that when certain tantalum complexes, with only hydrocarbyl ligands, are used as ROMP catalysts, the polymers formed from **10** are highly isotactic whereas those formed from **3**, while still high cis, are essentially atactic.[26] We also believe that the all-anti poly(**13**) formed using **1** is also somewhat syndiotactic on the basis that the line order for the substituted C^7 in hydrogenated poly(**13**), Figure 5, is the same as that for C^7 in the unsubstituted hydrogenated poly(**3**) and poly(**4**). The degree of m/r splitting here is quite substantial.

Copolymerization. The study of the composition and microstructure of the low-yield products of ROMP copolymerization is a most useful methodology for

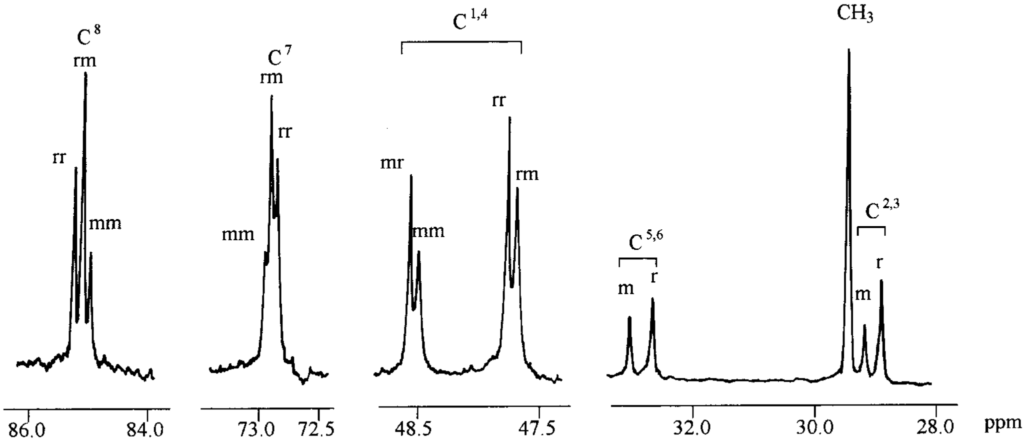


Figure 5. ^{13}C NMR spectrum of hydrogenated poly(**13**) showing multiple fine structure from tacticity effects. For clarity, different sections of the spectrum have different *x* and *y* scale expansions.

estimating relative reactivities of propagating metallacarbenes. Generally highly reactive metathesis catalysts do not discriminate much between monomers so that the composition of the copolymer merely reflects the feed ratio. On the other hand low catalyst reactivity results in preferential incorporation of the more reactive monomer, an extreme case being a competition ratio of 50 in favor of **3** in mixtures with **9** using $RuCl_3$; this high selectivity parallels the very high trans selectivity noted using this catalyst.[1c] We have also recently noted that the $MoCl_5/SnMe_4$/dioxan system affords very high cis poly(**3**) again with a very high competition ratio in favor of **3** over **9**.[18] The very reactive, nondiscriminating, catalysts are those which tend to produce homopolymers of **3** with $\sigma_c \approx 0.5$ and similar values of cis content for homodyads of **3** in copolymers with **9**.

We have found that **1** behaved in the same fashion as most other metathesis catalysts except that there is a tendency for it to be more selective; for example **10** is polymerized exclusively from a mixture of **10** and **11** in a manner analogus to the regioselective attack at the anti double bond of **12**, vide supra.

Copolymerization of the matched pairs of monomers **15**/**16** and **18**/**19** reveals that in each case the oxygen bridged analogue is preferentially incorporated into the respective copolymers, however the composition, Table 2, shows that there is a much larger incorporation of **16** than **19**. We believe this to be due to electron donation from the benzo ring in **16** via p-orbital conjugation through the oxygen bridgehead.[27] Such a factor must be involved since, using **1**, the ratio of units of **16** to **15** in the copolymer is high, (i.e., the same as with other catalysts) whereas the ratio **19** to **18** is unusually low.

The copolymerzation of norbornene, **3**, and norbornadiene, **4**, using **1**, is, as expected,[9a] azeotropic, but we have found that while the molecular weight of this copolymer is comparable to that of a homopolymer of the diene, **4** ($M_n = 1.2 \times 10^5$); both are considerably less than the molecular weight of a homopolymer of the monoene, **3** ($M_n = 8.2 \times 10^5$), Figure 6.[10,28] Consistent with this we have observed that the reaction mixture in the homopolymerization of **3** rapidly gels while little or no increase in viscosity is observed during the homopolymerization of **4** under identical conditions, even though high yields are recorded for both reactions. Furthermore, the molecular weight distribution of both poly(**4**) and copolymers of **3** and **4** is distinctly bimodal, like that recently reported[24] for the polymerization of **17** using **1**, and in contrast to poly(**3**), Figure 6. Clearly the formation of the actual chain-carrying metallacarbene from **1** is much more efficient with the diene than the monoene with many more growing chains being created with the former monomer. The reasons for this may be related to the recent observation[29] of the development of strong anion-radical concentrations in polymerizing mixtures of **1** and **4** which are much lower in corresponding mixtures of **1** and **3**. This phenomenon, as well as the bimodal MW distribution in the polymerization of **4** is the subject of ongoing studies.

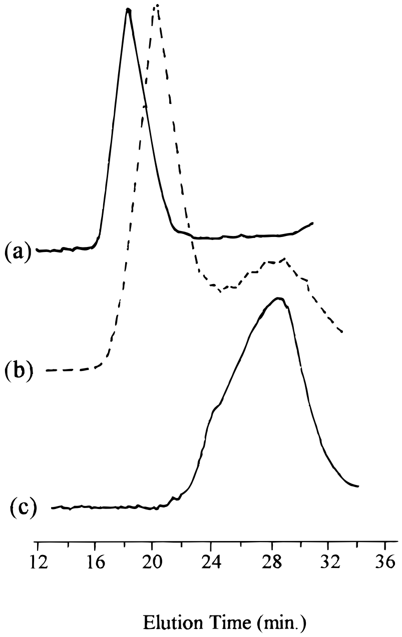


Figure 6. GPC analysis: (a) poly(**3**); (b) poly(**4**); (c) low MW fraction of poly(**4**) formed using **1**.

Efforts are now being directed toward increasing the activity of **1**[5,25] and related catalysts. We have recently carried out copolymerizations using noble metal salts in phenolic solvents and have noted an increased catalyst activity,[6h] so we decided to study the effect of phenolic solvents on the activity of **1**. The experiment recorded in Figure 7a used a 1:1 molar feed ratio of **3** and **9** in methylene chloride solvent. Here $\sigma_c = 0.13$ for M_2M_2 homodyads which is similar to homopolymers of **3**. Figure 7b shows that at the same feed ratio and conversion using chlorophenol solvent the competition ratio decreases to 1.5 (a value of 1.0 indicates no

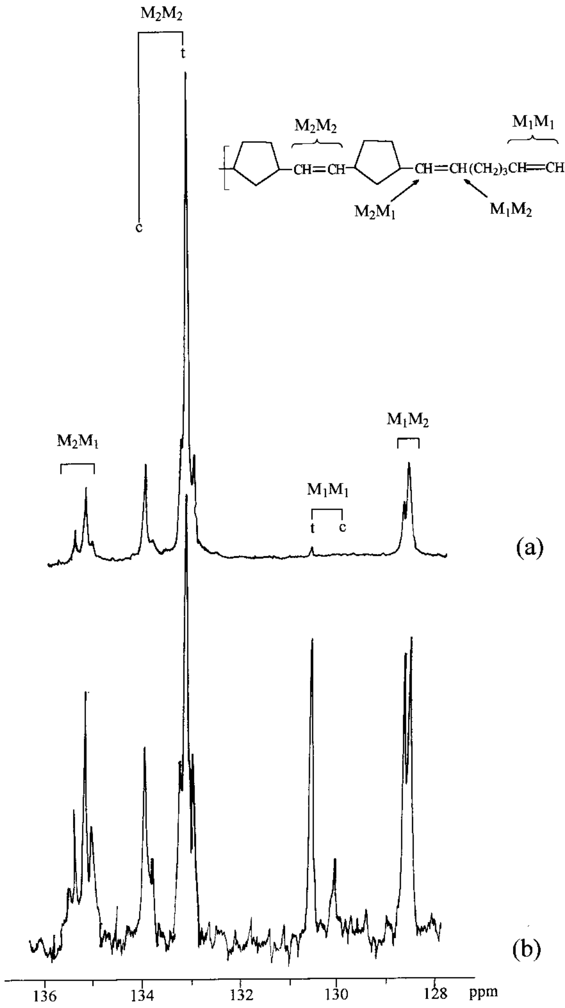


Figure 7. Olefinic region of the ^{13}C NMR spectra of copolymers of **3** (M$_2$) and **9** (M$_1$) formed using **1**: (a), methylene chloride solvent; (b), chlorophenol solvent.

selectivity) compared to 8.0 in CH$_2$Cl$_2$ and σ_c for M$_2$M$_2$ dyads rises to 0.28. The effect of chlorophenol is therefore to increase the reactivity and thus lower the selectivity of the propagating metallacarbene so that the selectivity parameters change in the same direction as when RuCl$_3$ was used in phenol.[6h]

There is good evidence[30] to support a hypothesis that the chloride ligands in RuCl$_3$- and OsCl$_3$-based catalysts, and **1**, hydrogen bond strongly to phenols and certain acidic alcohols; this would result in a net flow of negative charge away from the metal ion with concomitant increases in catalyst activity. This is reflected in a shift of λ_{max} for **1** in methylene chloride (λ_{max} = 522 nm) to λ_{max} = 572 nm in chlorophenol; metal-to-halide charge transfer is believed to be involved. A similar reduction in electron density at the metal ion center with concomitant increase in electrophilicity and reactivity of the carbene moiety has been suggested as the cause of similar changes in catalytic activity of a range of Ru-based initiators when acetate or chloride ligands are replaced by trifluoroacetate ligands.[21,31]

We cannot entirely rule out steric effects as being the cause of the increased incorporation of **9** in copolymers with **3** when **1**, in CH$_2$Cl$_2$, is compared to RuCl$_3$, as catalyst. The very bulky PCy$_3$ ligands should sterically crowd the propagating species to some extent and this might be expected to work to the disadvantage of the most sterically difficult propagating step, i.e., (1), among the four possible.

$$\mathrm{P_{NBE} + NBE \rightarrow P_{NBE}} \qquad (1)$$

$$\mathrm{P_{NBE} + CPE \rightarrow P_{CPE}} \qquad (2)$$

$$\mathrm{P_{CPE} + NBE \rightarrow P_{NBE}} \qquad (3)$$

$$\mathrm{P_{CPE} + CPE \rightarrow P_{CPE}} \qquad (4)$$

The more bulky metallacarbene is P$_{NBE}$ (NBE = **3** and CPE = **9**), but P$_{CPE}$ may be more relaxed than P$_{NBE}$ and therefore electronically less active, whereas **3** is more bulky than **9** but on electronic grounds is much more active.

P$_{NBE}$ n = 1,2 **P$_{CPE}$**

The net effect of all these factors is that step 4 is most disfavored while step 1 is the most prominent despite the potentially adverse steric factor. This leads to a tendency for the copolymer to alternate as can be seen from the value of 0.5 for $(M_1M_1/M_1M_2)(M_2M_2/M_2M_1)$, obtained from the peak integrals, Figure 7. When the value of this ratio is below unity the polymer is somewhat alternating. A more extreme example of this is that where RuCl$_3$ is used to copolymerize **3** and **9** in dry phenolic solvents where this ratio is as low as 0.01,[6h] indicating that step 1 is also now disfavored, leaving essentially only steps 2 and 3.

Conclusion

This extensive survey of **1** as a ROMP catalyst shows that it generally forms high trans, mainly isotactic polymers from a broad spectrum of monomers, although polydienes tend to be less isotactic and in one case show a distinct syndiotactic bias. The results further indicate that when derivatives of **3** and **4** are monomers, dramatic differences in polymer tacticities are observed and also that the distinction between monoenes and dienes in this respect is augmented. The catalyst is also highly regioselective, and with appropriate monomers this leads to high selectivity in copolymerization compared to other metathesis catalysts. The importance of steric factors associated with the bulky PCy$_3$ ligands is stressed and the differences in dienes and corresponding monoenes in influencing the efficiency of initiation and propagation is established. The basicity of **1** is also significant, as evidenced from selectivities in copolymerization of oxygen and methylene-bridged "matched pairs", the polymerization of 7-alkoxy norbornadienes, and the effect of phenolic solvents on the copolymerization of **3** and **9**.

Experimental Section

General Information. Polymer samples were dissolved in CDCl$_3$ and their ^{13}C NMR spectra recorded on a Bruker Advanc DPX 300 spectrometer at 75.45 MHz; chemical shifts were measured from TMS internal standard. GPC analyses were carried out at ambient temperature using a Perkin-Elmer instrument running in THF; samples were taken directly from the reaction mixture and injected for analysis. A 5 μm 500 Å column and a 5 μm mixed-bed Perkin-Elmer PL gel column, connected in series, were used at a flow rate of 0.5 mL/min. The system was calibrated using low polydispersity polystyrene standards. UV spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotomter at concentrations sufficient to give an absorbance reading of between 0.5 and 1.0 units.

Materials. Monomers **3**, **4**, **5**, **6**, and **9** were obtained from Aldrich and monomers **7**,[6a] **8**,[13] **10**/**11**,[6c] **12**,[6f] **13**,[6e] **14**,[32] **15**,[33] **16**,[34] **17**,[35] **18**,[36] **19**,[36] and **20**[36] were synthesized according to literature procedures; each of these, as well as the CH_2Cl_2 solvent was distilled from CaH_2 before use. Chlorophenol, received from Aldrich, was dried by distillation from P_2O_5. Catalyst **1** was obtained from Strem Chemicals, and $RuCl_3 \cdot nH_2O$, $OsCl_3$, $MoCl_5$, and WCl_6 were obtained from Aldrich; all were used as received.

Synthesis of Homopolymers. The following describes the general procedure used for homopolymerization reactions catalyzed by **1**: Dry Ar-sparged CH_2Cl_2 was used throughout. Solutions of the catalyst were freshly prepared for each reaction by adding 1.0 mL of CH_2Cl_2 to 5 mg of catalyst in a serum-capped flask. The catalyst solution was then transferred by syringe to a solution of 280 mg of the monomer in 1.0 mL of CH_2Cl_2. After approximately 2 h, the reactions were terminated by adding 50 mg of ethyl vinyl ether and the polymer was precipitated in methanol containing 5 mg of 2,6-diterbutlyphenol followed by drying *in vacuo*, giving moderate to high yields of soluble material.

For the polymerization of **4**, more dilute conditions were used to moderate the reaction. Here 1 mL of the catalyst solution prepared as above was added to 280 mg of the monomer now dissolved in 10 mL of CH_2Cl_2. Precipitation and drying rendered polymers formed from **4** insoluble. These samples were therefore solvent exchanged with $CDCl_3$ taking care not to allow the polymer to gel during successive solvent removal cycles on the rotary evaporator.

Polymers formed for comparison purposes using $RuCl_3$, $OsCl_3$ in ethanol/chlorobenzene solvent,[13] and WCl_6/Me_4Sn in chlorobenzene[6f] and dioxan[23] solvents were carried out according to literature procedures.

Synthesis of Copolymers. Copolymerizations involving monomers **3**/**9**, **15**/**16**, and **18**/**19** were carried out as above using 200 mg of an equimolar mixture of the respective monomers and keeping the yield of copolymer below 15% by a process of trial and error.

For the copolymerization experiments involving **3** and **4**, 5 mg of **1** dissolved in 1 mL of CH_2Cl_2 was added to 280 mg of an equimolar monomer mixture dissolved in 10 mL of methylene chloride. Samples for ^{13}C NMR analysis were obtained by solvent exchange as outlined above, and samples for GPC analysis were obtained by diluting the reaction mixture with dry THF (after destroying the catalyst by the addition of ethyl vinyl ether) to give approximately 25 mg/mL solutions. Homopolymers of **3** and **4**, for comparison of molecular weights, were prepared under identical conditions. Strict anaerobic conditions (Ar atmosphere) were observed throughout the preparation and isolation of samples for GPC analysis.

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