



BISPHENOL LIGANDS IN THE STEREOCONTROL OF TRANSFORMATIONS CATALYZED BY TITANIUM AND TUNGSTEN

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Abstract—Bisphenol ligands have a rich coordination chemistry in the early transition elements. 1,1'-Bi-2-naphthols are of particular interest because of their continued utility in controlling the stereochemistry of metal catalyzed processes. In several projects in our laboratory, we have endeavored to examine the potential scope and mechanism by which modifications of bisphenolate ligands can influence the stereoselectivity of electrocyclic reactions. In this paper we discuss two of these studies: an examination of stereochemically modified ROMP precatalysts and a study of well characterized binaphtholate titanium chloride Lewis acid catalysts.

Diolate coordination complexes of both main group and early transition elements have achieved widespread usage in a range of metal catalyzed asymmetric protocols.¹⁻⁷ The focus of these studies, in which the topology of the catalysts range from D_2 through C_1 symmetric, is to allow the absolute stereochemistry of the metal coordination sphere to engender differences in alternative barriers along reaction coordinates that lead to enantiomeric products.⁸ Similarly, the goal of studies of C_2 symmetric metallocene polymerization catalysts is to engender stereoregularity in the backbone of a growing α -olefin polymer by enforcing the enantio-specific insertion of monomer units into the growing polymer chain. These processes, while encompassing very different product outcomes, have in common the requirement of exquisite control over the energetics of processes that may differ by only a few tenths of kilocalories per mole. If such processes are to be fully understood, a demanding interplay between catalyst and substrate, involving subtle elements of transition state structure and energetics, must be examined and understood.⁸

Our interest in early transition metal chemistry resulted in an understandable fascination with a range of bisphenolate units, both as potential ligands and as auxiliaries for enantiospecific and stereospecific transformations. One attraction of these ligands lay in their structural similarity to the 2,6-disubstituted phenoxide ligands widely used in the early transition metal, lanthanide and main group metal chemistry.⁹⁻¹² Another lay in the potential to broadly vary the steric and electronic characteristics of the ligands through choice of substituents on the phenol precursor. These attributes had already given rise to a great wealth of organometallic chemistry supported by phenoxide ligands in the Rothwell group,⁹ and was later exploited to tune the reactivity of a range of tungsten ROMP precatalysts by Bell at Hercules.¹⁰ Above these factors, there remained two more compelling rationales for undertaking a detailed study of the coordination chemistry and reactivity of a range of biphenoxide substituted early transition complexes. First, as demonstrated in the laboratories of Noyori and Mikami, 1,1'-bi-2-naphthol (BINOL or BINO), one member of a potentially broad class of bisphenoxide ligands, displayed exceptional promise as a stereogenic ligand.^{3,4,13} Second, the diverse ligand topologies generated by the different methods for connecting two phenol functional groups, as illustrated in Fig.

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1, promised the possibility of engineering subtle systematic variations in the stereochemical environment around the active catalyst center.

Having settled on a prototype ligand set, we decided to embark on a range of studies in the coordination chemistry and reactivity of early transition metal bisphenoxides. One of these studies was aimed at the generation of ROMP catalysts that would exhibit enantiomorphic site control over product stereochemistry. Ivin had previously conceived the possibility of such behavior in catalysts bearing chiral ligands, although no such studies had been reported at the inception of our project.¹⁴ A parallel study targeted the preparation of well characterized binaphtholate titanium chloride Lewis acid catalysts. Such species hold the promise of unraveling some of the mechanistic details observed in successful asymmetric titanate catalysts and should exhibit a yet broader range of stereocontrolled reactivity in Lewis acid catalyzed electrocyclic reactions and polymerization processes.

In this paper, we review some of the results of these studies.

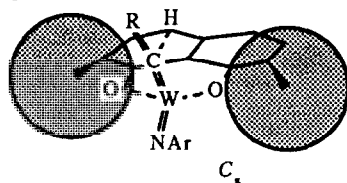
WELL CHARACTERIZED BINAPHTHOL TITANIUM CHLORIDE LEWIS ACIDS

Three basic forms of ligand were employed in these studies, including 10,10'-bi-9-phenanthrol (BIPHENO₂), 5,5',6,6',7,7',8,8'-octahydrobinaphthol (HYDBINO₂), and 3,3-disubstituted-1,1'-bi-2-naphthol (X₂BINO₂, X = Cl, Br, CH₃) (Fig. 2).¹⁵ Dinuclear titanium diolate dichloride complexes were prepared by two standard routes: lithium salts of the ligand were reacted with TiCl₄ in a non-coordinating solvent, or the bisphenolates were converted into their bis(silyl ethers),¹⁶ followed by reaction with TiCl₄ at low temperatures. This latter approach was applied successfully in the synthesis of complexes of empirical formula (bisphenolate)TiCl₂ for all of the ligand systems in moderate to excellent yield. Efforts to prepare crystalline, spectroscopically tractable derivatives of the parent binaphtholate and 3,3'-diphenyl substituted ligands (BINO and Ph₂BINO, respectively) by these routes proved unsuccessful. The products generated from the parent binaphtholate ligand often contained substantial quantities of insoluble material.

Molecular weight measurements¹⁷ on (Me₂BINO)TiCl₂ and (HYDBINO)TiCl₂ indicate that they are dinuclear in solution. Solubility constraints or complex instability prevented the acquisition of molecular weight data for the BIPHENO, Cl₂BINO, and Br₂BINO systems. However, studies of an equilibrium process involving (BIPHENO)TiCl₂ and TiCl₄ (*vide infra*) confirmed that (BIPHENO)TiCl₂ also exists as a dimer in solution. Based on simple model structures, we assume that the Cl₂BINO and Br₂BINO derivatives are also dinuclear in the rest state. Unlike the ¹H NMR spectrum of (*R,R*)-(Me₂BINO)₂Ti₂(OⁱPr)₄,¹⁸ which displays two distinct naphthoxide and isopropoxide environments at reduced temperature, the spectra of all of the diolate chloride complexes show that the molecules retain apparent D₂ symmetry at very low temperatures. Although all of these halide complexes could conceivably adopt both *rac*-(*R**,*R**) and achiral (*R,S*) diastereomeric structures, they each show only a single molecular entity in solution within the limits of NMR detection. This observation indicates that one of the two diastereomeric structures is significantly favored. ¹H NMR spectra of the complexes synthesized with enantiomerically pure ligands are identical to those of the respective racemic complexes, confirming that like (Me₂BINO)₂Ti₂(OⁱPr)₄, the homochiral (R₂BINO)₂Ti₂Cl₄ complexes are substantially more ther-

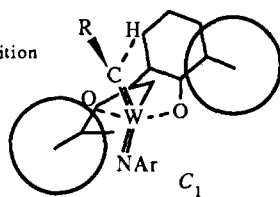
Strategy for developing isospecific ROMP catalysts

No ligand-induced face-selectivity during olefin binding

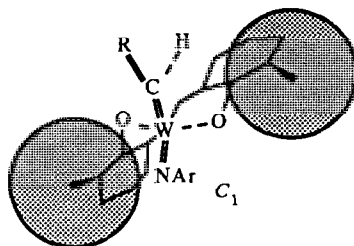


1,8-Dihydroxynaphthol

Expect increasingly face-selective olefin addition



1,1'-Biphenol



BIS-2-Phenolmethane

Fig. 1. Hypothetical topological environments for an ROMP active site in the presence of various bisphenolate ligands.

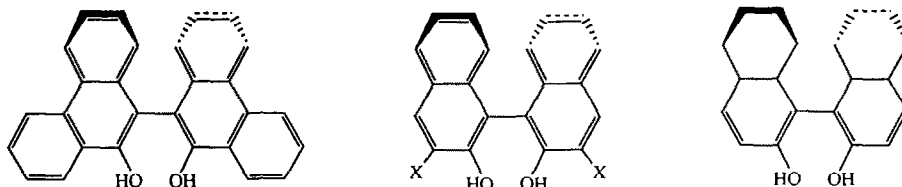


Fig. 2. Structures of three ligand systems employed in this study: 10,10'-bi-9-phenanthrol, 3,3'-disubstituted 1,1'-bi-2-naphthol ($X = \text{Cl}, \text{Br}, \text{CH}_3$) and 5,5',6,6',7,7',8,8'-octahydrobinaphthol.

modynamically stable than their mixed chirality diastereomers. However, the simplicity of the low-temperature NMR spectra of these dimeric (diolate) $_2\text{Ti}_2\text{Cl}_4$ complexes makes it impossible to determine whether the ground state structures of the complexes are open 14-membered metallacycles or if they retain a characteristic 1,3-dinaphthoxydititanacyclobutane core. In the absence of Lewis basic solvents, the dioxaditanacyclobutane-type structure is most likely the preferred configuration. The $(\text{HYDBINO})_2\text{Ti}_2\text{Cl}_4$ complex probably adopts an open structure in solution due to the dihedral constraints imposed on the HYDBINO ligand by the hydrogenated β -rings (*vide infra*).

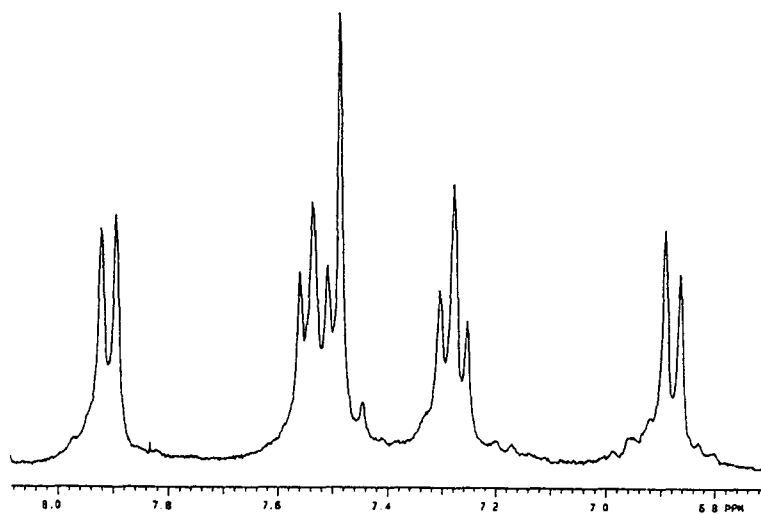
Although the Me_2BINO ligand forms the complex regardless of whether the dilithium salt or bis(silyl ether) is employed, the reactivity of the two $\text{Cl}_2\text{BINOH}_2$ derivatives toward TiCl_4 provided some unusual results. Reactions between $\text{Cl}_2\text{BINO}(\text{TMS})_2$ and TiCl_4 generate a product in 66% yield whose ^1H NMR spectrum is shown in Fig. 3(a). In contrast, the addition of TiCl_4 to a slurry of $\text{Cl}_2\text{BINOLi}_2$ under similar reaction conditions invariably produces a complex whose spectrum differs from that of the product generated with the bis(silyl ether) [Fig. 3(b)]. Notable differences in the spectra include an upfield shift of both the aromatic singlet and the most upfield doublet in the spectrum of the latter complex. Examination of the ^1H NMR spectra of crude reaction products of $\text{Cl}_2\text{BINO}(\text{TMS})_2$ reveals that traces of the second product are formed in these syntheses.

Several experiments were undertaken to determine a possible relationship between the structures of these complexes. The possibility that diastereomeric complexes have been formed is unlikely in light of the observation that neither the Me_2BINO or HYDBINO ligands form diastereomeric structures. Syntheses involving enantiometrically pure (*R*)- $\text{Cl}_2\text{BINO}(\text{TMS})_2$ or (*R*)- $\text{Cl}_2\text{BINOLi}_2$ produce complexes whose ^1H NMR spectra correspond exactly to those of the respective derivatives generated with racemic ligand, illustrating that, like the related binaphtholate systems discussed previously, only the homochiral diastereomer is significantly favored. The complexes may instead be different

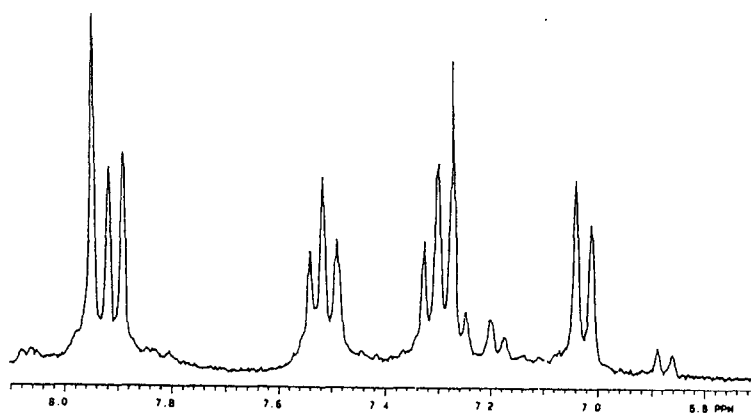
substitutional derivatives, as would be formed by the incorporation of varying stoichiometries of TiCl_4 and the Cl_2BINO ligand. When the complex generated via the lithium salt was treated with excess TiCl_4 , no change in the ^1H NMR spectrum was observed even after two days of incubation. The spectrum of the complex generated from the bis(silyl ether) precursor changed dramatically upon addition of TiCl_4 , although the resulting spectrum was different from those of either of the other Cl_2BINO complexes. The observations from these titration experiments combined with the results of Diels–Alder catalysis kinetics (*vide infra*) led to the assignment of the complexes from the lithium salt and the silyl ether precursors as $(\text{Cl}_2\text{BINO})_2\text{Ti}$ and $(\text{Cl}_2\text{BINO})_2\text{Ti}_2\text{Cl}_4$, respectively (Fig. 4). The latter complex could more easily react with excess TiCl_4 to form $(\text{Cl}_2\text{BINO})\text{Ti}_2\text{Cl}_6$ than the spirotitanate $(\text{Cl}_2\text{BINO})_2\text{Ti}$ derivative. The assignment of a dimeric structure for $(\text{Cl}_2\text{BINO})_2\text{Ti}_2\text{Cl}_4$ is based primarily on the similarity of its ^1H NMR spectrum to that of the known dimer $(\text{Me}_2\text{BINO})_2\text{Ti}_2\text{Cl}_4$.

The solid-state structure of the $(\text{Me}_2\text{BINO})_2\text{Ti}_2\text{Cl}_4$ molecule, represented in Fig. 5, is very similar to that determined previously for $(\text{Me}_2\text{BINO})_2\text{Ti}_2(\text{O}^i\text{Pr})_4$,¹⁸ with the dinuclear titanium core supported by identical unidentate-bridging Me_2BINO ligands, whose bridging naphthoxide units generate a classic d^0 – d^0 1,3-dioxaditanacyclobutane structure. Figure 5, plotted from the perspective of the Ti–Ti vector, illustrates the C_2 symmetry of $(\text{Me}_2\text{BINO})_2\text{Ti}_2\text{Cl}_4$ as well as the *syn* orientation of the binaphtholate ligands. This molecule appears to possess a vacant coordination site *trans* to the equatorial chloride ligand on each titanium center.

The structure of $(\text{HYDBINO})_2\text{Ti}_2\text{Cl}_4$ (Fig. 6) differs significantly from that of $(\text{Me}_2\text{BINO})_2\text{Ti}_2\text{Cl}_4$. The core of this molecule consists of a 14-membered dimetallacycle with bridging HYDBINO ligands of like chirality. As with other titanium binaphtholate complexes characterized in our laboratory,¹⁸ the homochiral complex is the exclusive product, with no apparent evidence of other diastereomers in the NMR spectra of crude reaction mixtures. By comparison, the solid-state structure of (dimethyl-



(a)



(b)

Fig. 3. Aromatic regions of ^1H NMR spectra of products generated by addition of TiCl_4 to $\text{Cl}_2\text{BINOLi}_2$ (a) and $\text{Cl}_2\text{BINO}(\text{TMS})_2$ (b) (CDCl_3 , 20°C , 300 MHz).

tartrato)zirconocene dimer forms an open ten-membered dimetallacycle with optically pure ligand, but exhibits a four-membered Zr_2O_2 core with unidentate bridging tartrates of unlike chirality when synthesized with racemic ligand.¹⁹ Four-coordinate titanium complexes such as $(\text{HYDBINO})_2\text{Ti}_2\text{Cl}_4$ are usually formed only when bulky aryloxy ligands prevent the formation of dative bridges.²⁰ In $(\text{HYDBINO})_2\text{Ti}_2\text{Cl}_4$, the 93° binaphthyl dihedral angle imposed by the three-dimensionality of the hydrogenated rings prevents the ligand from adopting a chelating structure. The $\text{Ti}-\text{O}$ bond lengths are extremely short at an average of 1.742 \AA , and the $\text{Ti}-\text{O}-\text{C}$ angle is nearly linear at 168° , indicating an unusually large degree of π -bonding character for a phenoxide

ligand. An alternative view of this molecule, depicted in Fig. 7(a), clearly illustrates the perpendicular orientation of the aromatic rings in each of the hydrogenated binaphtholate units. Unlike the configuration adopted by the naphtholate subunits in $(\text{Me}_2\text{BINO})_2\text{Ti}_2\text{Cl}_4$, the aromatic rings in $(\text{HYDBINO})_2\text{Ti}_2\text{Cl}_4$ are not in an orientation that favors π -stacking [Fig. 7(b)].

To develop a more quantitative comparison between the conformational flexibility of this ligand relative to binaphthol, calculations were undertaken to determine the effect of the dihedral angle on ligand energy. The free ligands were modeled as dimethyl ethers to eliminate any tendency for hydrogen bonding interactions to distort the dihedral angle. The results of these calculations,

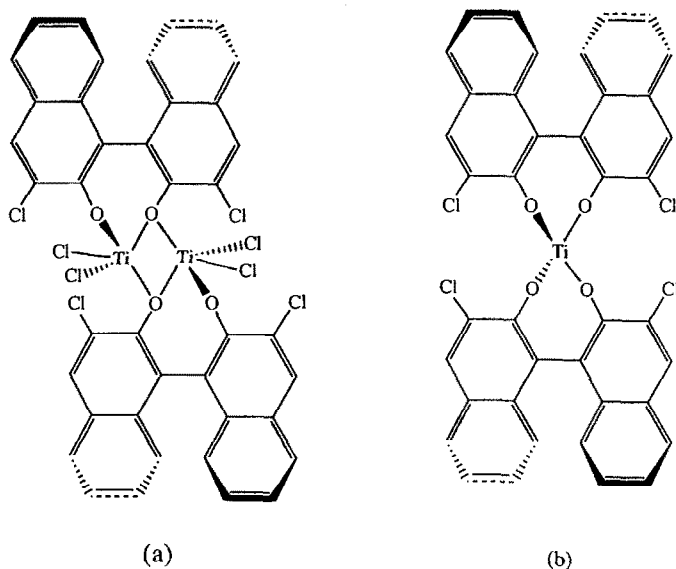


Fig. 4. Proposed structures of $(R^*,R^*)-(Cl_2BINO)_2Ti_2Cl_4$ (a) and $(R^*,R^*)-Cl_2BINO)_2Ti$ (b).

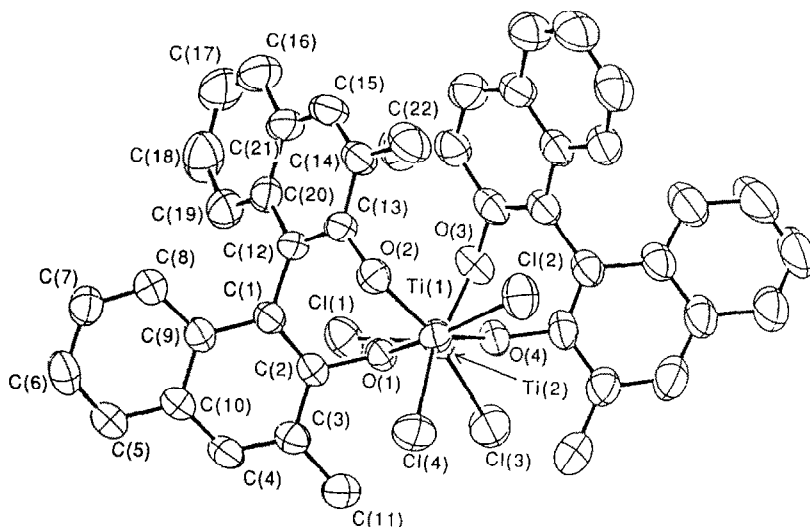


Fig. 5. X-ray structure of $(R,R)-(Me_2BINO)_2Ti_2Cl_4$, viewed along the titanium-titanium vector to illustrate the *syn* relationship of binaphtholate ligands.

illustrated in Fig. 8, reveal that the total energy curve of the $BINO(Me)_2$ displays a relatively flat minimum potential over the range of 60 to 120° . In contrast, the curve for the $HYDBINO(Me)_2$ is much more torsionally restricted. Its minimum energy value, like that for the $BINO(Me)_2$, is centered at 90° , but angular deviations beyond $\pm 10^\circ$ of this value cause precipitous increases in energy. These calculations parallel the range of dihedral angles found for $3,3'-R_2BINO$ ligands in a variety of binding modes. The O...O distance for a 60° dihedral was calculated at 2.78 \AA , while a 90° dihedral produced a 3.69 \AA distance. The 90°

dihedral enforces an O...O distance incompatible with $HYDBINO$ chelation to titanium.

As exemplified by " $(Cl_2BINO)TiCl_2$ ", these diolate chloride complexes can react with additional equivalents of $TiCl_4$ to form complexes of the general formula $(bisphenolate)Ti_2Cl_6$ (Fig. 9). The complex $(Me_2BINO)Ti_2Cl_6$ can be isolated in the solid state. Upon dissolution, this complex liberates $TiCl_4$ in an equilibrium process involving the concurrent formation of $(Me_2BINO)_2Ti_2Cl_4$. Figure 10 reveals the presence of these two complexes in the equilibrium mixture: the singlet at $\delta = 2.37$ represents the methyl protons of $(Me_2BINO)_2Ti_2Cl_4$,

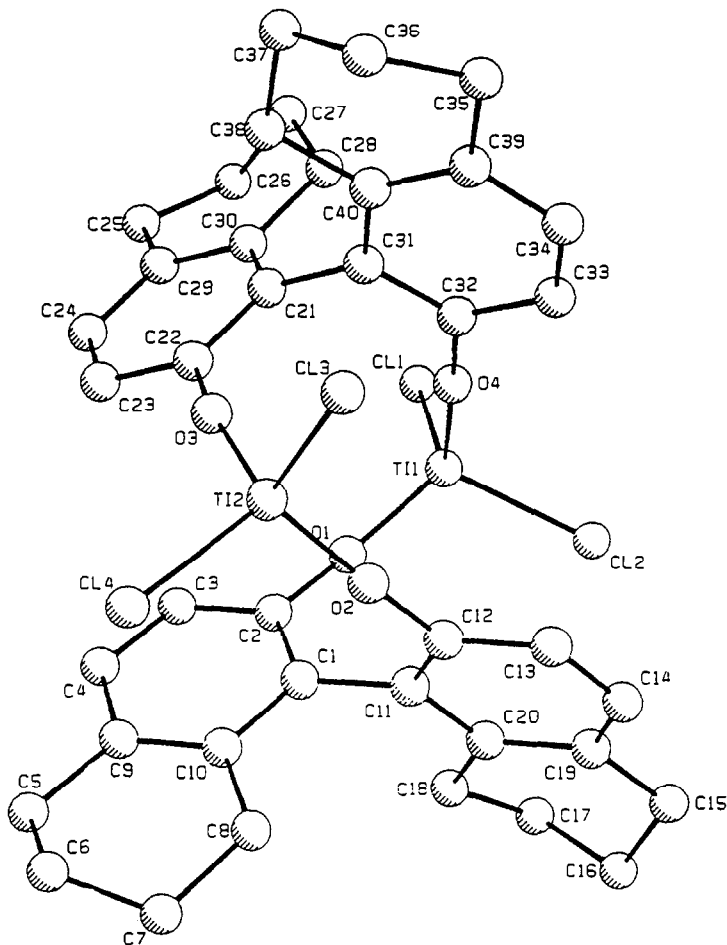


Fig. 6. X-ray structure of (S,S) -(HYDBINO) $_2$ Ti $_2$ Cl $_4$ depicting 14-membered metallamacrocyclic core.

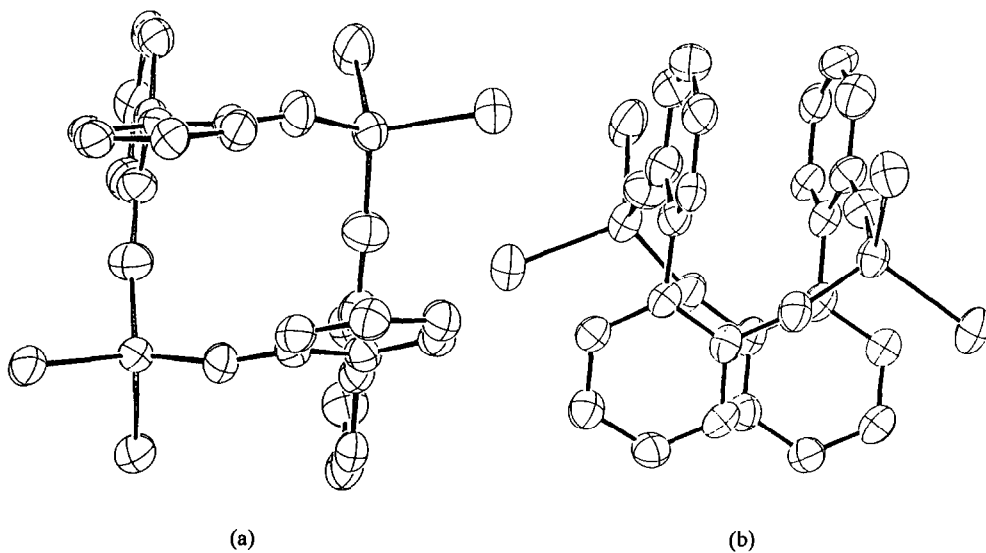


Fig. 7. Alternative views of (S,S) -(HYDBINO) $_2$ Ti $_2$ Cl $_4$ illustrating orthogonal relationship between naphthalene subunits within the same ligand (a) and parallel, displaced orientation of naphthalene subunits of different ligands (b).

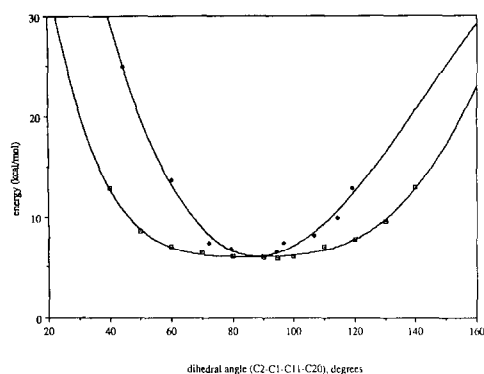


Fig. 8. Calculated energy values for bis(methyl ethers) of HYDBINO (upper curve) and Me_2BINO (lower curve) as a function of dihedral angle.

while that at $\delta = 2.73$ arises from the methyl protons of $(\text{Me}_2\text{BINO})\text{Ti}_2\text{Cl}_6$. This assignment was confirmed by the addition of excess TiCl_4 to the solution, driving the equilibrium completely toward $(\text{Me}_2\text{BINO})\text{Ti}_2\text{Cl}_6$. Although the (bisphenolate) Ti_2Cl_6 complexes were not isolable in the solid state, similar equilibria could be established for the BIPHENO and HYDBINO systems. Table 1 lists the thermodynamic parameters for these equilibria as determined by variable temperature ^1H NMR spectroscopy, as well as those determined for the related $(\text{Me}_2\text{BINO})_2\text{Ti}_2(\text{O}^i\text{Pr})_4/(\text{Me}_2\text{BINO})\text{Ti}_2(\text{O}^i\text{Pr})_6$ system. A comparison between the parameters for this isopropoxide system and the analogous chloride system reveals that, perhaps due to steric constraints, the isopropoxide system prefers the disubstituted form over the di-

meric $(\text{Me}_2\text{BINO})_2\text{Ti}_2(\text{O}^i\text{Pr})_4$ configuration. An additional consideration, the observed tendency of $(\text{Me}_2\text{BINO})\text{Ti}_2(\text{O}^i\text{Pr})_6$ to form intramolecular isopropoxide bridging interactions,¹⁸ may also assist in stabilizing this structure.

A second interesting characteristic of the $(\text{Me}_2\text{BINO})\text{Ti}_2\text{Cl}_6$ system is the solvent-dependent behavior of its equilibrium reaction. The negative entropy observed for the equilibrium in toluene solution seems inconsistent with the apparent change in molecularity of the reaction. The observation by Floriani and co-workers²¹ that TiCl_4 can form π -adducts with aromatic molecules, as evidenced by the solid-state structure of $[(\text{Me}_6\text{C}_6)\text{TiCl}_3][\text{Ti}_2\text{Cl}_9]$, may assist in the rationalization of the negative entropy of this equilibrium. Participation of toluene solvent molecules in the equilibrium results in a revised expression, $2(\text{Me}_2\text{BINO})\text{Ti}_2\text{Cl}_6 + 2\text{toluene} \rightleftharpoons (\text{Me}_2\text{BINO})_2\text{Ti}_2\text{Cl}_4 + 2\text{TiCl}_4 \cdot \text{toluene}$, whose overall decrease in molecularity is more consistent with the sign of the measured entropy.

The values listed in Table 1 for the equilibrium involving the BIPHENO ligand system stand out because of the large magnitudes of the equilibrium enthalpy and entropy. The potential ability of $(\text{BIPHENO})_2\text{Ti}_2\text{Cl}_4$ to participate in intramolecular π -stacking interactions may stabilize this species and contribute to the large enthalpy of reaction. The sizeable entropy of the equilibrium reaction may also, to some extent, be contributed to by the order engendered to the $(\text{BIPHENO})_2\text{Ti}_2\text{Cl}_4$ by these stacking forces.

$(\text{X}_2\text{BINO})_2\text{Ti}_2\text{Cl}_4$ ($\text{X} = \text{Cl}, \text{Br}, \text{CH}_3$) and (HYD-

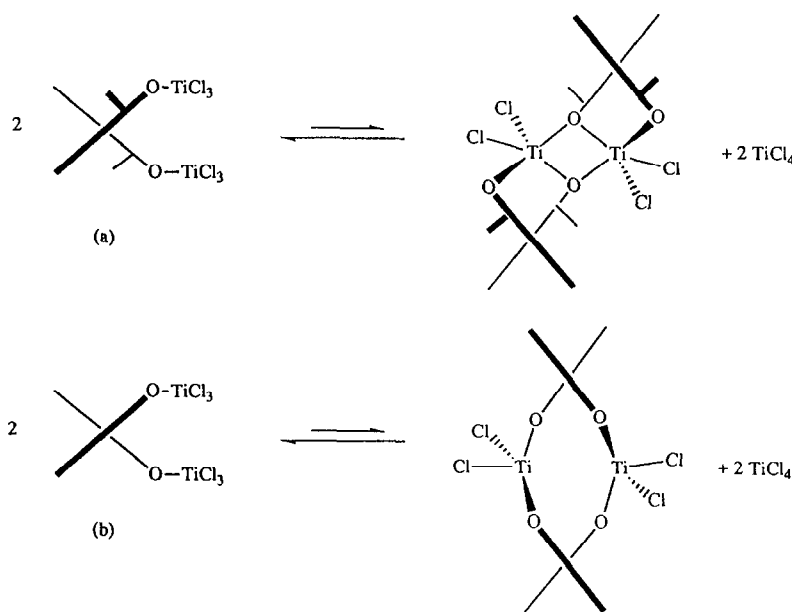


Fig. 9. Equilibrium scheme for $(\text{X}_2\text{BINO})_2\text{Ti}_2\text{Cl}_6$ (a) and $(\text{HYDBINO})_2\text{Ti}_2\text{Cl}_4$ (b).

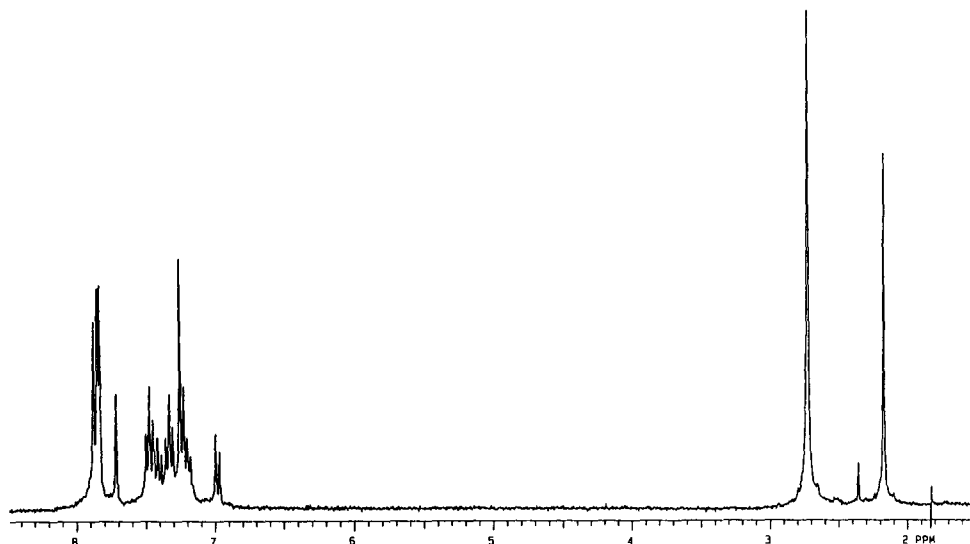


Fig. 10. ^1H NMR spectrum of equilibrium mixture of $(\text{Me}_2\text{BINO})_2\text{Ti}_2\text{Cl}_4$ and $(\text{Me}_2\text{BINO})\text{Ti}_2\text{Cl}_6$ (CDCl_3 , 20°C , 300 MHz).

Table 1. Summary of equilibrium data for loss of TiX_4 by (bisphenolate) Ti_2X_6 ($\text{X} = \text{Cl}$ or O^iPr) as monitored by variable temperature ^1H NMR spectroscopy

Bidentate ligand	Monodentate ligands	Solvent	ΔG_{298}° (kcal mol^{-1})	ΔH° (kcal mol^{-1})	ΔS° ($\text{cal mol}^{-1} \text{K}^{-1}$)
Me_2BINO	Cl	Chloroform- d_1	+2.8	+4.0	+4.0
Me_2BINO	Cl	Toluene- d_8	+3.3	+2.3	-3.6
Me_2BINO	O^iPr	Toluene- d_8	+1.2	+12.5	+38
BIPHENO	Cl	Chloroform- d_1	+4.5	+20.7	+54.2
BIPHENO	Cl	Benzene- d_6	+5.0	+10.0	+18
HYDBINO	Cl	Chloroform- d_1	+6.2	+8.6	+8.2

$\text{BINO})_2\text{Ti}_2\text{Cl}_4$ act as catalysts for the Diels–Alder reaction between methyl acrylate and cyclopentadiene in methylene chloride solution (Fig. 11), the kinetics of which can be monitored by ^1H NMR spectroscopy. All of these studies were run under pseudo-first-order conditions (excess cyclopentadiene). Over the conditions studied, the reactions remain strictly first-order in dienophile.

Moreover, doubling the concentration of diene doubles the rate of the catalyzed process, indicating that the reaction is also first-order in diene. The rate of the reaction in chloroform compared to that in benzene was 1.6, indicating that a more polar solvent only slightly accelerates the reaction. The *endo* isomer²² is the exclusive product generated in these titanium catalyzed reactions.

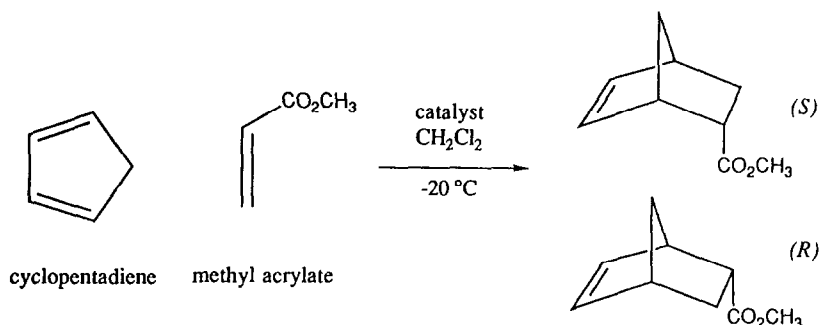


Fig. 11. Diels–Alder reaction between methyl acrylate and cyclopentadiene, generating *endo* adduct.

Plotting the determined rates of product formation against the catalyst concentration gives the simple first-order relationships shown in Fig. 12. For complexes of formula $(X_2\text{BINO})_2\text{Ti}_2\text{Cl}_4$, the substitution of electron withdrawing halide substituents at the 3- and 3'-positions of the ligand increases the reaction rate by rendering the titanium center more Lewis acidic. It seems remarkable that catalysis proceeds more slowly at the four-coordinate titanium centers in the HYDBINO complex than the initially five-coordinate centers in the $R_2\text{BINO}$ complexes. The slow reaction rate for the $(\text{HYDBINO})_2\text{Ti}_2\text{Cl}_4$ system could be explained in light of the substantial π -donation of the aryloxy groups as evidenced by the short Ti—O bond distances and obtuse Ti—O—C bond angles in the solid-state structure. The results of one kinetic study for $(\text{Cl}_2\text{BINO})_2\text{Ti}$ showed this species to be the least active catalyst, possibly due to the substantial electron-donating ability of the four oxygen ligands in this molecule or the increased steric demands engendered by the second binaphtholate group.

Figure 12 also depicts the linear dependence of the reaction on titanium concentration. This kinetic plot indicates that for titanium to dienophile ratios exceeding 1 : 10, a single catalyst species is involved in the reaction. Were a monomer/dimer equilibrium responsible for generating several catalytically active species, the plots would have exhibited non-linear character. This first-order behavior has two possible interpretations: either the dimer undergoes complete scission to generate an active mononuclear catalyst in the presence of coordinating methyl acrylate substrate or the catalyst maintains its dinuclear structure during the reaction. Rate data spanning a 50 degree temperature range of a 1 : 10 titanium to dienophile concentration for $(\text{Me}_2\text{BINO})_2\text{Ti}_2\text{Cl}_4$ give a good linear correlation,

also suggesting that a single catalyst species is active under these reaction conditions. Activation parameters for the Diels–Alder reaction obtained from the rate data ($\Delta H^\ddagger = 7.1 \pm 0.5 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -58 \pm 2 \text{ cal mol}^{-1} \text{ K}^{-1}$) are consistent with the cycloaddition step being rate-determining. These differ somewhat from the activation parameters for the uncatalyzed Diels–Alder process ($\Delta H^\ddagger = 12.6 \pm 0.3 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -35 \pm 2 \text{ cal mol}^{-1} \text{ K}^{-1}$). The higher entropic barrier for the catalyzed process is consistent with the additional requirements for organization, while the reduced enthalpic barrier is consistent with the Lewis acid induced polarization of the dienophile. Binding of the dienophile to the titanium center was examined for $(\text{Me}_2\text{BINO})_2\text{Ti}_2\text{Cl}_4$ and $(\text{HYDBINO})_2\text{Ti}_2\text{Cl}_4$. NMR spectroscopic studies performed at the concentrations employed in the catalytic experiments show no evidence of methyl acrylate binding to titanium. Moreover, spectra of the catalyst acquired in the presence of up to a thirty-fold excess of methyl acrylate and at temperatures as low as -55°C showed no perceptible changes, as would be expected if observable quantities of a monomer were present in solution or significant populations of acrylate-bound metal species were being formed. Based on the available data, it appears that these well characterized titanate Lewis acids are acting as intact dinuclear species.

Finally, the influence of titanium dimer concentrations on the percent enantiomeric excess (e.e.) of the Diels–Alder reaction between cyclopentadiene and methyl acrylate catalyzed by optically pure (R,R) -(diolate) $_2\text{Ti}_2\text{Cl}_4$ was determined. Table 2 shows the results of studies, in which the ratio of optically pure catalyst to methyl acrylate was varied from 5 mol% metal to up to 200 mol% metal for the Me_2BINO , HYDBINO , and Cl_2BINO catalyst systems. As is sometimes

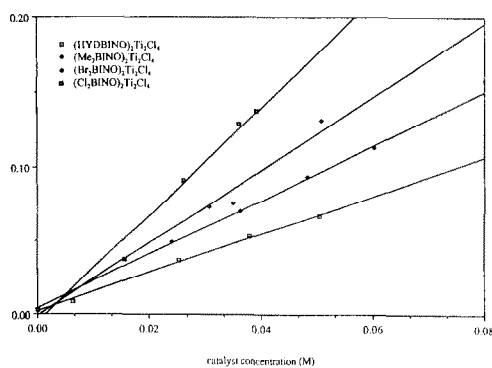


Fig. 12. Plots of pseudo-first-order constants vs catalyst concentration for $(X_2\text{BINO})_2\text{Ti}_2\text{Cl}_4$ ($X = \text{Cl}, \text{Br}, \text{CH}_3$) and $(\text{HYDBINO})_2\text{Ti}_2\text{Cl}_4$.

Table 2. Enantioselectivity of Diels–Alder reaction catalyzed by (R,R) -($\text{Me}_2\text{BINO})_2\text{Ti}_2\text{Cl}_4$ in the context of selectivities reported with catalysts generated *in situ*

Catalyst	Metal : dienophile	% e.e. (absolute configur- ation)
(R,R) -($\text{Me}_2\text{BINO})_2\text{Ti}_2\text{Cl}_4$	1 : 1	26 (S)
(R,R) -($\text{Me}_2\text{BINO})_2\text{Ti}_2\text{Cl}_4$	1 : 1	21 (S)
(R,R) -($\text{Me}_2\text{BINO})_2\text{Ti}_2\text{Cl}_4$	1 : 20	7 (R)
(R,R) -($\text{Me}_2\text{HYDBINO})_2\text{Ti}_2\text{Cl}_4$	1 : 1	11 (R)
(R,R) -($\text{Me}_2\text{HYDBINO})_2\text{Ti}_2\text{Cl}_4$	1 : 20	6 (R)
(S,S) -($\text{Cl}_2\text{BINO})_2\text{Ti}_2\text{Cl}_4$	1 : 1	13 (S)
(S,S) -($\text{Cl}_2\text{BINO})_2\text{Ti}_2\text{Cl}_4$	1 : 20	9 (S)

observed with metal-derived Lewis acids, the sign of the product enantiomeric excess for $(\text{Me}_2\text{BINO})_2\text{Ti}_2\text{Cl}_4$ showed a reversal on proceeding from catalytic stoichiometry to one in which the metal acts as a promoter for the reaction.²³ The best enantioselectivities for these well characterized catalysts were obtained for $(\text{Me}_2\text{BINO})_2\text{Ti}_2\text{Cl}_4$ at higher titanium to dienophile ratios.

The nature of the observed equilibria for the halide substituted complexes also provides some insight into the characteristics of the complexes during catalysis. Optically pure catalysts derived from TiCl_4 must not engage in equilibria that produce significant concentrations of free TiCl_4 , for fear that all productive catalysis will be channeled through this achiral molecule. We must conclude that the tendency of the $(\text{X}_2\text{BINO})\text{Ti}_2\text{Cl}_6$ systems to liberate TiCl_4 would prove detrimental to the enantioselectivity of reactions catalyzed by these complexes.

Because the $(\text{Me}_2\text{BINO})_2\text{Ti}_2\text{Cl}_4$ complex apparently remains dimeric during catalysis over a range of metal to dienophile ratios, changes in catalyst nuclearity cannot explain the reversal of enantioselectivity at different catalyst concentrations. This leads to the conclusion that variations in the product e.e. as a function of catalyst to dienophile ratio probably result from the ability of the active catalyst species to bind either one or two equivalents of organic substrate. The rapid reversible binding of either a second equivalent of dienophile or an equivalent of norbornene ester product at a site proximal to the reactive dienophile could alter the stereochemical environment at the first site and account for this effect (Fig. 13). A mechanism involving a heterolytically cleaved mononuclear catalyst seems unlikely in that the binding of a

second equivalent of substrate or product at the same cationic metal center might be expected to affect more directly the kinetics of cycloaddition at the reactive dienophile by decreasing the electron-withdrawing ability of the metal. In contrast, an intact dinuclear catalyst would separate the second substrate from the adjacent active site, affecting less directly the Lewis acidity of this metal center than would direct binding of the second dienophile to the same metal.

The study involving the optically pure catalysts emphasizes that Lewis acid catalysts that generate organic products with consistent enantioselectivity regardless of catalyst to substrate stoichiometry need to possess a single type of binding site that is sterically isolated from adjacent active sites. The $(\text{X}_2\text{BINO})\text{Ti}_2\text{Cl}_4$ catalyst systems exhibit many principles of structure and reactivity common to other diolate-substituted titanium catalyst systems. The most important of these observations appears to be that asymmetric catalysts with multiple stereochemically interacting ligand binding sites may not demonstrate uniform enantioselectivities over a broad range of catalyst: substrate ratios. These proximate metal centers could accommodate the binding of two Lewis base molecules, possibly altering the chiral environment about the reactive site during catalysis.

TOWARD STEREOCONTROL IN ROMP PROCESSES

A popular method for producing highly isotactic polypropylene in purely homogeneous catalyst systems is to incorporate C_2 -symmetric ligands in the metal coordination sphere. A well-known example

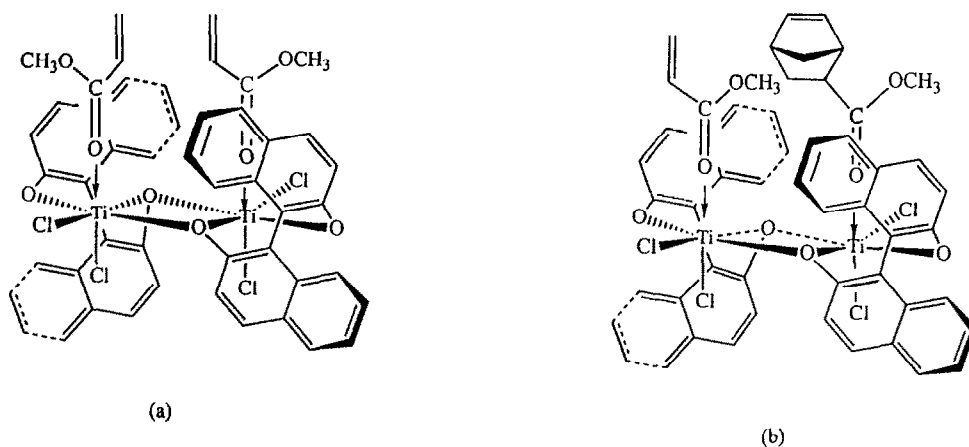


Fig. 13. Dinuclear structure of $(\text{Me}_2\text{BINO})_2\text{Ti}_2\text{Cl}_4$ catalyst which would allow for binding of one methyl acrylate at each metal center (a), or one methyl acrylate and one *endo*-5-carbomethoxynorbornene product at adjacent metal centers (b) (methyl substituents have been omitted).

of this approach is the Brintzinger chiral *ansa*-metallocene (1,1'-ethylenebis(indenyl))ZrCl₂²⁴ used in concert with a methylaluminumoxane cocatalyst.²⁵ The environment around the catalytic sites is modified by the presence of the C₂-symmetric ligand such that the enantioface selectivity of monomer insertion is controlled by steric interactions with the indenyl ligand and the growing polymer chain. While Ziegler–Natta chemistry has benefitted greatly from this ability to alter the catalyst environment to produce the desired tacticity of polymer, only recently have attempts to control the tacticity of ring-opening metathesis polymerization (ROMP) polymers been reported.^{26,27} Prior to these reports, relationships between catalyst type and geometric isomerism had been studied.¹⁴ Increased *cis* olefin content in polymerized norbornene derivatives has been related to increased ligand steric demand and more rapid rotation about the metal–carbon bond of the alkylidene ligand.²⁸ However, attempts to enforce face-selectivity in olefin coordination as in the poly(propylene) case through the incorporation of a C₂-symmetric ligand in a ROMP catalyst had not been reported. Face-selective addition to the alkylidene ligand in ROMP catalysis could, as in the Ziegler–Natta system, create stereoregular polymer microstructures possessing unique and desirable physical characteristics. A fundamental difference with the ROMP system, however, is that face selection must occur at the organometallic functional group (the alkylidene) rather than at the monomer in order to engender a tactically regular polymer.

A variety of microstructural types are possible for ROMP polymers, with some stereochemical elements depending on the nature of the monomer employed.¹⁴ These structural variations include *cis/trans* isomerism at the double bond, head/tail isomerism (which indicates the relative orientation of substituents in adjacent monomer units), and tacticity (Fig. 14). The chemical environment of the alkene can be sensitive to dyad effects, specifically to whether the nearest neighbor double bond has *cis* or *trans* stereochemistry. The nomenclature *cc* (Fig. 14) indicates that the carbon in question participates in a *cis* olefin linkage and that its nearest olefin neighbor also possesses *cis* stereochemistry. Alkene stereochemistry and tacticity are inherent to the structures of all ROMPed materials derived from norbornene-like polycyclic monomers, although only chiral monomers can exhibit head/tail isomerism. In Fig. 15, a *meso* (isotactic) dyad results when the monomer attacks the *re* face of the metal alkylidene, while attack at the *si* face generates a *racemic* (syndiotactic) dyad. Many of these structural characteristics can be elucidated to

some degree for a given polymer sample through a variety of NMR methods.¹⁴ Each of these methods is limited by the degree to which resonances attributed to the specific microstructural environments can be unequivocally assigned. The most common method employed for resonance assignment for an unsymmetrically substituted monomer is to polymerize one enantiomer independently, since the microstructures it can adopt are limited relative to those accessible by a racemic mixture of monomer.²⁹ Two limitations of this approach are that peak resolution is achieved only at the dyad level and many of the assignments are based on empirically derived substituent parameters. A new method reported by Schrock and co-workers²⁷ relies upon the change in symmetry of the various stereoregular oligomeric structures upon attachment of chiral substituents to the monomer. This alteration in monomer structure eliminates all mirror planes from these oligomers, thereby rendering the sets of olefin hydrogens unique. Because the *cis*, isotactic polymer contains no elements of symmetry, the olefinic hydrogens are no longer equivalent (designated as H_a and H_b) and, therefore, should exhibit coupling characteristic of *cis* olefin protons in simple alkenes. In contrast, the *cis*, syndiotactic oligomer contains a C₂ axis through the double bond, also resulting in the generation of two types of olefin hydrogens. The feature that distinguishes these two structures is that the inequivalent olefin hydrogens in the latter structure are not contained within the same double bond, so no coupling between these inequivalent hydrogen nuclei should be observed. The presence or absence of coupling can therefore allow for distinction between these microstructural forms.

The monomer 5,5-dimethylbicyclo[2.2.1]hept-2-ene (5,5-dimethylnorbornene, Me₂NBE) appeared to be an ideal substrate for our study of polymer tacticity due to its exhaustive study by Thoi *et al.*³⁰ This team of researchers assigned ¹³C NMR resonances for virtually every microstructural environment for both *cis* and *trans* polymers. This characterization involved the polymerization of both racemic and optically pure Me₂NBE: spectra of the latter polymer were simplified in that half of the 12 possible dyads, illustrated in Fig. 16, were not accessible to only a single enantiomer of monomer. Comparisons between these spectra and the spectra of polymer generated with racemic monomer allowed for the deductive assignment of the remaining resonances. Spectral regions exhibiting resonances derived from the olefinic carbons, unlike those in both *exo*- and *endo*-5-methylnorbornene studied previously by Ivin and co-workers, were the most well-resolved and therefore were chosen by

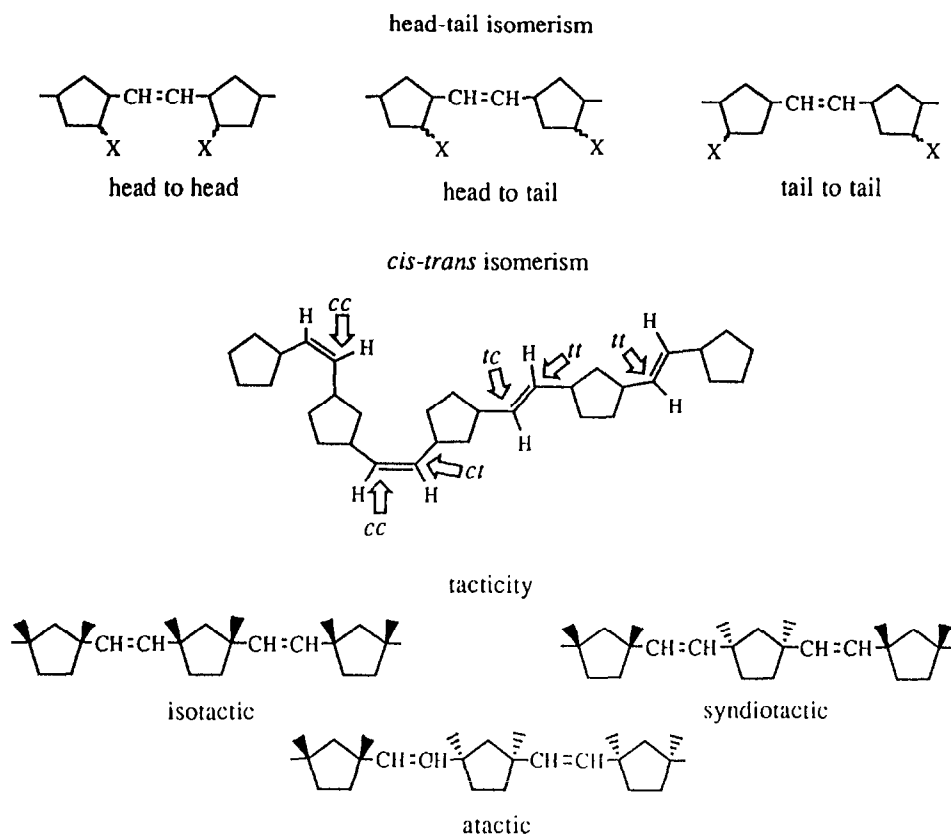


Fig. 14. Possible isomers of ROMP polymers. Head/tail isomerism is observed only in systems containing unsymmetrically substituted repeating units.

Ivin as the diagnostic tools in the assignment of tacticity.

The broad range of polymerization catalysts employed in Ivin's study allowed for correlations to be drawn between olefin isomer content and tacticity. *Cis* double bonds were associated with 50–100% *racemic* dyads (syndiotactic) and *trans* double bonds were associated with 50–100% *meso* dyads (isotactic). No correlation between degree of tacticity and percent *cis* content was apparent in these systems, except for all-*cis* polymers, which were found to be highly syndiotactic, and all-*trans* polymers, which showed a slight preference for isotactic microstructure. The incorporation of a C_2 -symmetric ligand in the metal coordination sphere may eliminate the bias of highly *cis* polymers to be syndiotactic and instead enforce a reaction mechanism which could lead to isotactic polymer.

Our studies of ligand induced stereochemical control focused on polymerization catalysts based on a range of tungsten(VI) templates.³¹ Tungsten oxo or arylimido precatalysts, similar to a series of compounds reported by Bell which are employed as components in industrial ROMP processes,¹⁰ were formed through reactions between diethyl ether

solutions of chelating phenolate ligands (Fig. 17) and $W(=X)Cl_4$ ($X = O$ or $N\text{-}2,6\text{-}C_6H_3Me_2$).³¹ These reactions result in the liberation of one equivalent of HCl to form complexes of the general formula $(X=)W(OArOH \cdot Et_2O)Cl_3$. When $X = N\text{-}2,6\text{-}C_6H_3Me_2$, reflux conditions were necessary to effect substitution. The discovery of both the oxo and aryl imido phenol-phenoxide derivatives has led to a broader study of d^0 and d^2 complexes containing hydrogen bonds in our group. A second type of precatalyst, $(Ph_2BINO)WCl_4$, was prepared via direct reaction of WCl_6 with Ph_2BINOH_2 in refluxing toluene,³² and the final precatalyst, $(Me_2BINO)(O^tBu)_2W(=CHPh)$, was formed by the reaction of $(^tBuO)_3W \equiv CPh$ with Me_2BINOH_2 in toluene at 0°C.³³

X-ray crystallographic and spectroscopic studies of the precatalysts show them to be structurally homologous, readily characterized molecules. As in a previous study of $d^3\text{-}d^3$ ditungsten binaphtholate complexes,³⁴ few of the candidate precatalysts formed more than one diastereomer, although, even in cases as simple as $(Me_2BINO)(O^tBu)_2W(=CHPh)$, such isomerism is possible.³³ Positive evidence of diastereomers were most commonly observed with

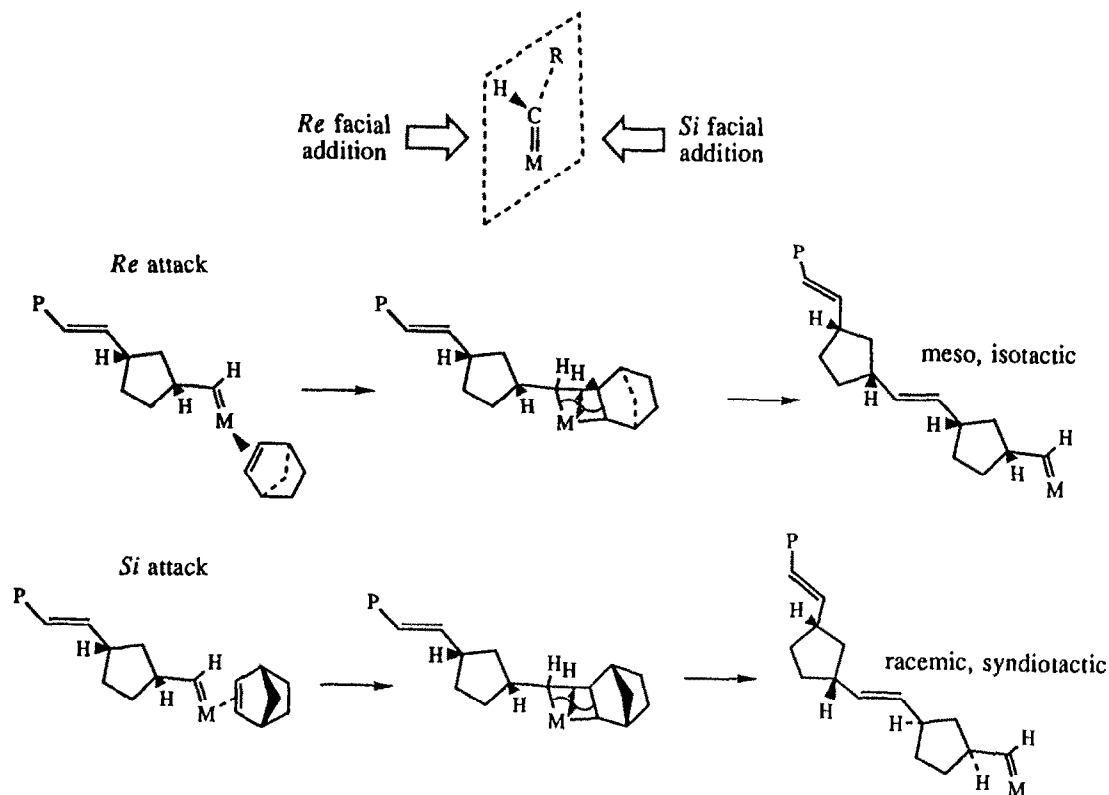
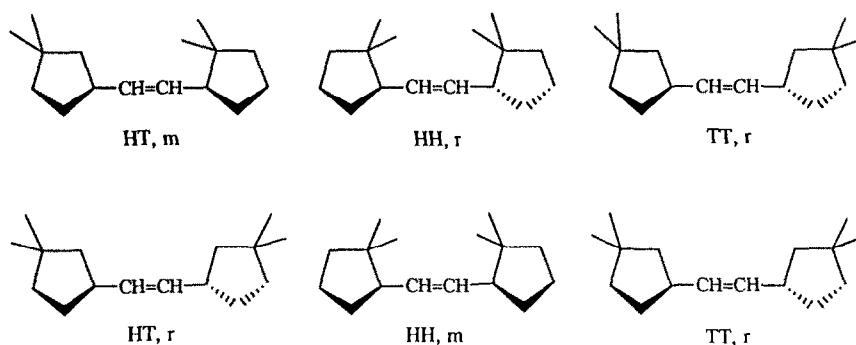


Fig. 15. Origin of tacticity in ROMP polymers.

Fig. 16. Possible dyads of 5,5-dimethylnorbornene. Each dyad can exist as a *cis* or *trans* geometric isomer. The lower three structures can be formed only when a racemic mixture of monomer is polymerized.

BINO ligands, as in the (*R,R,S*) and (*S,S,R*) isomers of $W(\text{BINO})_3$, which were separated by fractional crystallization.³² Initial studies of norbornene polymerization convinced us of three essential characteristics of the catalysts. Each precatalyst exhibited a distinct activity, conversion efficiency and product stereochemistry. This indicated that the precatalysts were generating unique catalyst species, despite the fact that most of our catalysts required an added alkylating or Lewis acid co-catalyst. Precatalysts whose coordination environments were largely congested with chelating bisphenoxide

ligands, notably $W(\text{BINO})_3$ and $(\text{Me}_2\text{B-INO})_2\text{W}(=\text{CHPh})$, showed greatly reduced or negligible polymerization activity, even in the presence of co-catalysts. Finally, crossover studies with preformed poly(norbornene) demonstrated that negligible quantities of depolymerization products were generated by the subject tungsten catalysts. This allowed us to examine our product distributions by NMR spectroscopy, confident that variations in polymer stereochemistry were determined at the time of monomer insertion and not by later "secondary metathesis" events.

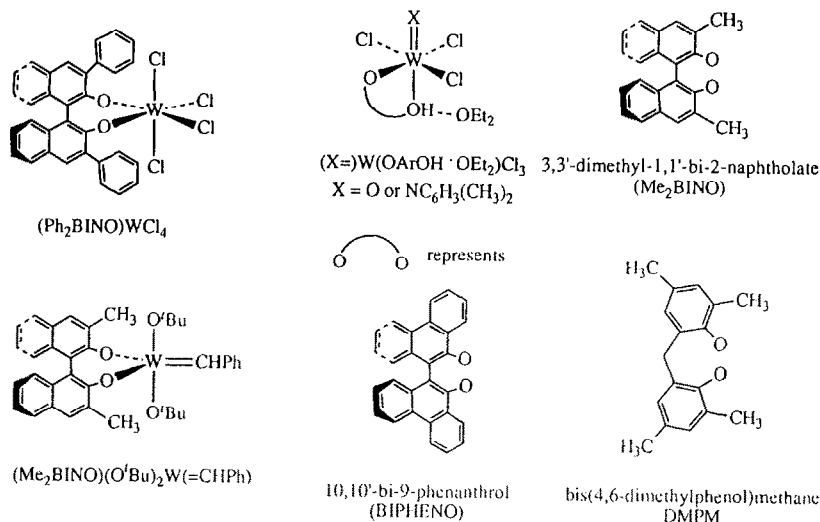


Fig. 17. Structures of the three forms of tungsten catalyst employed in the polymerization of 5,5-dimethylnorbornene.

The Me₂NBE monomer³⁰ was prepared by an alternative synthetic protocol (Fig. 18). Reaction of the commercially available aldehyde 5-norbornene-2-carboxaldehyde with formaldehyde in the presence of potassium hydroxide produced 5-norbornene-2,2-dimethanol, which was then mixed with *p*-toluenesulfonyl chloride in pyridine to yield the ditosylate derivative. Reduction of this ditosylate with LiAlH₄ produced the desired monomer with a 22% recovery yield. This low yield can be attributed in part to the difficulty in purifying Me₂NBE subsequent to the reduction step.³⁵ The byproduct of THF ring-opening reaction is recovered along with the monomer, and can be separated from the desired product only by a series of extractions and water washings.

Polymerization of this monomer was undertaken at 0°C. While the polymerization of norbornene by these catalysts occurs within a matter of minutes at this temperature, the increased steric demands of the Me₂NBE monomer required that reaction mix-

ture be stirred for 2 h to ensure complete polymerization. The reactions were quenched by the addition of acetone. The polymers were dried *in vacuo* then examined by ¹³C NMR in chloroform-*d*₁ solvent. The results of the polymer characterization for both norbornene and Me₂NBE can be found in Table 3.

The *cis* selectivity exhibited by most of these catalyst systems appears to be enhanced on changing the monomer from norbornene to Me₂NBE, suggesting that increasing the steric bulk of the monomer results in a greater energy difference between the transition states leading to *cis* and *trans* polymers. Previous studies involving catalyst systems related to (X=)W(OArOH·Et₂O)Cl₃ derivatives revealed that increasing the steric demands of ligands on the metal center by replacing X = O with N-2,6-C₆H₃Me₂ or by varying the size of the chelating phenoxide resulted in increased *cis* content in the resulting poly(norbornene). It is reasonable to expect that increasing the steric demands of the

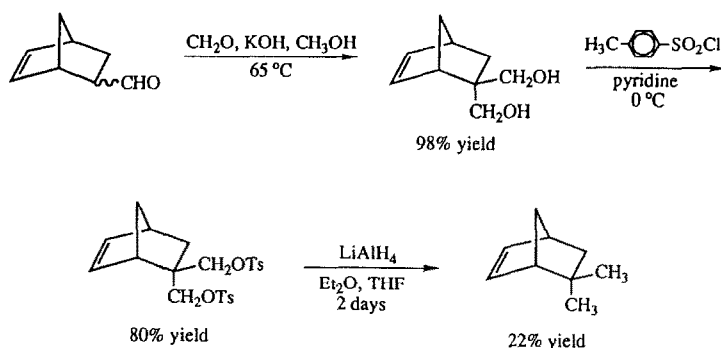


Fig. 18. Synthetic scheme developed for the production of 5,5-dimethylnorbornene.

Table 3. Microstructural data for poly(norbornene) and poly(5,5-dimethylnorbornene) generated by tungsten catalysts as determined by ^1H and ^{13}C NMR spectroscopy

Catalyst	Co-catalyst	<i>Cis/trans</i> ratio : norbornene	<i>Cis/trans</i> ratio : 5,5- dimethylnorbornene	Tacticity
$(\text{Me}_2\text{ArN}=\text{W})(\text{Me}_2\text{BINOH} \cdot \text{OEt}_2)\text{Cl}_3$	$2\text{Et}_2\text{AlCl}$	9.3	> 20	Fully syndiotactic
$(\text{Me}_2\text{ArN}=\text{W})(\text{BIPHENOH} \cdot \text{OEt}_2)\text{Cl}_3$	$2\text{Et}_2\text{AlCl}$	7.54	> 20	Fully syndiotactic
$(\text{Me}_2\text{ArN}=\text{W})(\text{DMPMH} \cdot \text{OEt}_2)\text{Cl}_3$	$2\text{Et}_2\text{AlCl}$	4.62	> 20	Fully syndiotactic
$(\text{Ph}_2\text{BINO})\text{WCl}_4$	$2\text{Et}_2\text{AlCl}$	0.78	0.72	44% syndiotactic
$(\text{Me}_2\text{BINO})(\text{O}^t\text{Bu})_2\text{W}(=\text{CHPh})$	2GaBr_3	0.32	0.69	48% syndiotactic

monomer may result in a similar increase in *cis* selectivity. Steric control over olefin selectivity has been rationalized³⁶ by the examination of reaction intermediates for formation of *cis* and *trans* alkene units, illustrated in Fig. 19. The metal alkylidene precursor to these intermediates could adopt two conformations that differ in the orientation of the growing polymer chain relative to the bulky ligands. Based on steric considerations, it is reasonable to expect the *anti* rotamer to be favored, as it best avoids contacts between these two large moieties. The inserting monomer unit can attack this alkylidene in one of two fashions: the bridging carbon could be oriented *syn* or *anti* to the polymer chain. The former approach would produce a *cis* alkene, while the latter would result in the formation of a *trans* olefin group. As the size of the bulky ligand *anti* to the growing polymer chain is increased, so too is its steric interaction with the bridging carbon of the monomer, thus disfavoring this mode of approach relative to that which would produce a *cis* polymer linkage.

The two polymer samples which were slightly enriched in *trans* linkages showed approximately equal quantities of syndiotactic and isotactic dyads.

NMR resonances representing *cis-cis* and *cis-trans* as well as *trans-cis* and *trans-trans* resonances overlap in several cases, preventing the determination of the blockiness of the polymer. It is therefore not possible to determine whether these latter polymers are composed of random *cis/trans* syndiotactic/isotactic blocks or if regions of *cis*, syndiotactic polymer and *trans*, isotactic polymer are present. Consistent with the findings of Thoi *et al.*, the highly *cis* polymers generated by the remaining three catalyst systems also exhibited syndiotactic microstructures. This correlation between *cis* linkage content and tacticity has been found in the polymerization of a variety of monomers. Four substituted norbornene monomers—*anti*-7-methylnorbornene,³⁷ *endo*-5,6-dimethylnorbornene,³⁸ *exo*-5-methylnorbornene,³⁹ and 1-methylnorbornene⁴⁰—form *cis* polymers that were found to be syndiotactic and *trans* polymers which were predominantly atactic. It appears that the presence of a C_2 -symmetric ligand in the coordination sphere of these tungsten catalysts could not override the tendency of *cis* polymer to favor syndiotactic linkages.

Molecular modeling studies of the four possible

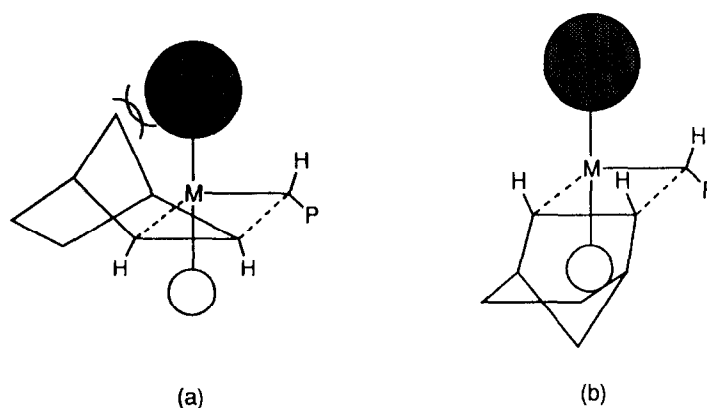


Fig. 19. Sterically demanding ligands in the metal coordination sphere result in the growing polymer chain as well as the monomer bridging group orienting downward, favoring intermediate (b), which leads to a *cis* olefin linkage.

microstructural variants to determine their relative stabilities were performed on an IBM RISC 6000 workstation with the Sybyl 5.5 Molecular Modeling program. Ethylidene-capped pentamers were constructed then minimized. The most stable oligomer is the *trans*, isotactic pentamer, which is only slightly more stable than its *trans*, syndiotactic counterpart. However, the energy difference between the isotactic and syndiotactic versions of the *cis* pentamer is significant. These results mirror the previous observations that *cis* polymers tend to be syndiotactic while *trans* polymers form isotactic structures. Unfortunately, examination of thermodynamic product distributions reveals no information about the source of the observed selectivity in this irreversible reaction. This association of predominantly syndiotactic microstructure with *cis* olefin linkages may have its root in steric interactions between the growing polymer chain and the catalyst center.¹⁴ A repeated shifting of the growing polymer chain to screen alternating enantiofaces of the alkylidene ligand results in the syndiotactic linkages seen in ROMPed poly(Me₂NBE).

Concurrent with our studies in this area, one report on the incorporation of C₂-symmetric ligands in the coordination sphere of ROMP catalysts to enforce tacticity control has appeared from the Schrock research group at MIT.^{26,27} Their approach involved the reaction of a range of C₂-symmetric ligands with catalyst precursors of the type (ArN=)Mo(CHR)(OTf)₂(DME) (R = CMe₂Ph or ^tBu; Ar = 2,6-C₆H₃ⁱPr₂) through triflate displacement reactions. These and related catalysts were then employed in the polymerization of 2,3-bis(trifluoromethyl)norbornadiene, 2,3-dicarboalkoxynorbornadiene and *endo,exo*-5,6-dimethylbicyclo[2.2.1]hept-2-ene. Values of the percentage of *cis* content in poly(2,3-dicarbomethoxynorbornadiene) varied from 93 to over 99%, while for poly(2,3-bis(trifluoromethyl)norbornadiene), a more broad range of 71 to over 99% was observed. Based on evidence collected by the polymerization of monomers bearing chiral substituents (*vide supra*) and of racemic and optically pure *endo,exo*-5,6-dimethylnorbornene, this group proposes that all of the high *cis* polymers generated in these studies have an isotactic bias.

It is not clear how significant the discrepancies in apparent polymer tacticities are between the materials observed in Schrock's and our studies. Our assignment of 5,5-dimethylnorbornene microstructure relies on the initial NMR assignments.³⁰ It is possible that the evident differences in monomer topology could be responsible for the apparent switch in tacticity, as could the requirement for alkylaluminum or Lewis acid co-catalysts in our two-component systems. Regardless, it is apparent

that both Schrock's and our studies suggest that the tendency of high *cis*-poly(norbornenes) to adopt highly-tactic microstructures and low *cis* norbornene polymers to exhibit atactic microstructure is not easily overcome by the use of group 6 catalysts bearing simple chiral diolate auxiliaries. Schrock has observed that polymerizations by catalysts similar in structure to his chiral molybdenum imido systems, but lacking chiral ligands, also generated a highly *cis*, isotactic polymer.²⁷ Because of the lack of chiral ligand on the metal center, enantiomorphic site control, in which the ligand environment about the metal influences insertion chemistry, is likely not operative. Both Schrock and we have suggested²⁷ that chain end control, in which the orientation of the last inserted monomer unit in the polymer chain influences stereochemistry of the subsequent insertion, is most likely the source of the preference for regular tacticity observed in the high *cis* polymers. This is in concert with the mechanism originally proposed by Ivin to explain the connection between *cis* olefin content and high tacticity in ROMPed polymers.¹⁴ The potential of monomers or the growing polymer chain to coordinate to the metal center may also explain the observed face-selectivity.¹⁴

Alternative catalyst structures containing more bulky chiral ligands or enforcing variations in the coordination number of transition state species may engender more efficiently face selectivity in the reactions of cyclic olefins, thereby enhance the directing effect of the ligand. Increasing the potential of the chiral ligand to interact with the active site, either through the use of substituted binaphthols or TADDOL systems containing bulkier substituents, or through relocation of the chiral element to another spectator functionality, may overcome the observed *cis*-highly tactic bias for Me₂NBE and other related norbornene-like monomers. The underlying cause-effect relationships outlined in this study more clearly define the problem and will eventually lead to a better understanding of the multitude of sources of tacticity control in ROMP polymerization.

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REFERENCES

1. R. O. Duthaler, A. Hafner, *Chem. Rev.* 1992, **92**, 807; K. B. Sharpless, S. S. Woodward and M. G. Finn, *Pure Appl. Chem.* 1983, **55**, 1823; T. A. Engler, J. P. Reddy, K. D. Combrink and D. Vander Velde, *J. Org. Chem.* 1990, **55**, 1248; T. Fujisawa, Y. Ukaji, T. Noro, K. Date and M. Shimizu, *Tetrahedron* 1992, **48**, 5629; M. Fetizon, M. Benchitch le-Hocine, D. D. Khac, F. Guir, Y. Guo and T. Prange, *Tetrahedron Lett.* 1992, 1443; E. Negishi and T. Takahashi, *Aldrichchim. Acta* 1985, **2**, 31.
2. A. Aoki, K. Mikami, M. Terada and T. Nakai, *Tetrahedron* 1993, **49**, 1783.
3. K. Mikami and S. Matusukawa, *J. Am. Chem. Soc.* 1993, **115**, 7039.
4. (a) K. Mikami, M. Terada, Y. Motoyama and N. Nakai, *Tetrahedron Asymmetry* 1991, **2**, 643. (b) M. Terada, S. Matsukawa and K. Mikami, *J. Chem. Soc., Chem. Commun.* 1993, 327.
5. K. Narasaka, M. Saitou and N. Iwasawa, *Tetrahedron Asymmetry* 1991, **2**, 1305.
6. K. Narasaka, *Pure Appl. Chem.* 1992, **64**, 889.
7. K. Mikami, M. Kaneko and T. Yajima, *Tetrahedron Lett.* 1993, **34**, 4841.
8. J. Halpern, in *Asymmetric Synthesis* (Edited by J. D. Morrison), Vol. 5, pp. 41–70. Academic Press, New York (1985).
9. (a) I. P. Rothwell, S. L. Latesky, J. Keddington, A. K. McMullen and J. C. Huffman, *Inorg. Chem.* 1985, **24**, 995. (b) I. P. Rothwell, L. D. Durfee, S. L. Latesky, J. C. Huffman and K. Foltz, *Inorg. Chem.* 1985, **24**, 4569.
10. (a) A. Bell, *J. Mol. Cat.* 1991, **76**, 165. (b) A. Bell, U.S. Patent, 16 March 1993, 5,194,534.
11. (a) A. R. Barron, M. B. Power, J. R. Nash and M. D. Healey, *Organometallics* 1992, **11**, 1830. (b) P. P. Power, X. Xu, H. Hope, G. Sigel and M. M. Olmstead, *J. Am. Chem. Soc.* 1987, **107**, 8087.
12. H. Yamamoto, K. Hatori and M. Miyata, *J. Am. Chem. Soc.* 1993, **115**, 1151.
13. (a) R. Noyori, K. Nashima, K. Duano, T. Ohta and H. Takaya, *J. Am. Chem. Soc.* 1979, **101**, 3129. (b) R. Noyori, *J. Am. Chem. Soc.* 1984, **106**, 6709.
14. K. J. Ivin, *Olefin Metathesis*. Academic Press, London (1983).
15. T. J. Boyle, N. W. Eilerts, J. A. Heppert and F. Takusagawa, *Organometallics* 1994, **13**, 2218.
16. J. F. Klebe, H. Finkbeiner and D. M. White, *J. Am. Chem. Soc.* 1966, **88**, 3390.
17. E. P. Clark, *Ind. Eng. Chem., Anal. Ed.* 1941, **13**, 820.
18. T. J. Boyle, D. L. Barnes, J. A. Heppert, L. Morales, F. Takusagawa and J. W. Connolly, *Organometallics* 1992, **11**, 1112.
19. G. Erker, S. Dehicke, M. Rump, C. Krüger, S. Werner and M. Nolte, *Angew. Chem., Int. Ed. Engl.* 1991, **30**, 1349.
20. S. L. Latesky, J. Keddington, A. K. McMullen, I. P. Rothwell and J. C. Huffman, *Inorg. Chem.* 1985, **24**, 995.
21. E. Solari, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Chem. Commun.* 1989, 1747.
22. J. M. Mellor and C. F. Webb, *J. Chem. Soc., Perkin Trans. II* 1974, 17.
23. (a) K. Narasaka, M. Inoue and T. Yamada, *Chem. Lett.* 1986, 1967. (b) T. Oh and P. Devine, *J. Org. Chem.* 1992, **57**, 396.
24. F. R. W. P. Wild, M. Wasiucionek, G. Huttner and H. H. Brintzinger, *J. Organomet. Chem.* 1985, **288**, 63.
25. W. Kaminsky, K. Kulper, H. H. Brintzinger and F. R. W. P. Wild, *Angew. Chem., Int. Ed. Engl.* 1985, **24**, 507.
26. D. H. McConville, J. R. Wolf and R. R. Schrock, *J. Am. Chem. Soc.* 1993, **115**, 4413.
27. (a) R. O'Dell, D. H. McConville, G. E. Hofmeister and R. R. Schrock, *J. Am. Chem. Soc.* 1994, **116**, 3414. (b) T. Sunaga, K. J. Ivin, G. E. Hofmeister, J. H. Oskam and R. R. Schrock, *Macromolecules* 1994, **27**, 4043.
28. R. R. Schrock and J. H. Oskam, *J. Am. Chem. Soc.* 1992, **114**, 7588. W. J. Feast, V. C. Gibson and E. E. Marshall, *J. Chem. Soc., Chem. Commun.* 1989, 1157.
29. H. H. Thoi, K. J. Ivin and J. J. Rooney, *J. Mol. Cat.* 1982, **15**, 245.
30. H. H. Thoi, K. J. Ivin and J. J. Rooney, *Makromol. Chem.* 1982, **183**, 1629.
31. (a) D. L. Barnes, N. W. Eilerts, J. A. Heppert, W. H. Huang and M. D. Morton, *Polyhedron* 1994, **13**, 1267. (b) M. D. Morton, J. A. Heppert, S. D. Dietz, W. H. Huang, D. A. Ellis, T. A. Grant, N. W. Eilerts, D. L. Barnes, F. Takusagawa and D. Vander Velde, *J. Am. Chem. Soc.* 1993, **115**, 7916.
32. S. D. Dietz, N. W. Eilerts, J. A. Heppert and M. D. Morton, *Inorg. Chem.* 1993, **32**, 1698.
33. J. A. Heppert, S. D. Dietz, N. W. Eilerts, R. W. Henning, M. D. Morton, F. Takusagawa and F. Kaul, *Organometallics* 1993, **12**, 2565.
34. (a) S. D. Dietz, J. A. Heppert, N. W. Eilerts and M. D. Morton, *Inorg. Chem.* 1993, **32**, 1689. (b) J. A. Heppert, S. D. Dietz and N. W. Eilerts, *Angew. Chem., Int. Ed. Engl.* 1992, **31**, 66. (c) J. A. Heppert, S. D. Dietz, T. J. Boyle and F. Takusagawa, *J. Am. Chem. Soc.* 1989, **111**, 1503.
35. J. March, *Advanced Organic Chemistry*, p. 441. Wiley, New York (1992).
36. D. L. Boutarja, F. Quignard, M. Leconte, J. M. Basset, J. G. Hamilton, K. J. Ivin and J. J. Rooney, in *Transition Metal Catalyzed Polymerizations: Ziegler-Natta and Metathesis Polymerizations* (Edited by R. P. Quirk), p. 695. Cambridge University Press, Cambridge (1988).
37. J. G. Hamilton, K. J. Ivin and J. J. Rooney, *J. Mol. Cat.* 1985, **28**, 255.
38. R. M. E. Greene, K. J. Irvin, G. M. McCann and J. J. Rooney, *Makromol. Chem.* 1987, **188**, 1933.
39. K. J. Ivin, G. Lapienis and J. J. Rooney, *Polymer* 1980, **21**, 436.
40. J. G. Hamilton, K. J. Ivin and J. J. Rooney, *Br. Polymer J.* 1984, **16**, 21. J. G. Hamilton, K. J. Ivin, G. M. McCann and J. J. Rooney, *Makromol. Chem.* 1985, **186**, 1477.