Synthesis of Stereoregular Polymers through Ring-Opening Metathesis Polymerization

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S *Supporting Information*

CONSPECTUS: Some of the most readily available and inexpensive monomers for ring-opening metathesis polymerization (ROMP) are norbornenes or substituted norbornadienes. Polymers made from them have tacticities (the stereochemical relationship between monomer units in the polymer chain) that remain after the C=C bonds in the polymer backbone are hydrogenated. Formation of polymers with exclusively a single structure (one tacticity) was rare until approximately 20 years ago, when well-defined ROMP catalysts based on molybdenum imido alkylidene complexes that contain a chiral biphenolate or binaphtholate ligand were shown to yield *cis,isotactic*-poly(2,3-dicarbomethoxynorbornadiene) and related polymers through addition of the monomer to the same side of the M=C bond in each step.

Over the past few years, molybdenum and tungsten monoaryloxide pyrrolide (MAP) imido alkylidene initiators have been found to produce *cis,syndiotactic* polynorbornenes and substituted norbornadienes through addition of the monomer to one side of the M=C bond in one step followed by addition to the other side of the M=C bond in the next step. This "stereogenic metal control" is possible as a consequence of the fact that the configuration of the stereogenic metal center switches with each step in the polymerization. Stereogenic metal control also allows syndiotactic polymers to be prepared from racemic monomers in which enantiomers of the monomer are incorporated alternately into the main chain. Because pure *trans* polymers have not yet been prepared through some predictable mechanism of stereochemical control, it seems unlikely that all four basic polymer structures from a single given monomer can be prepared simply by choosing the right initiator. However, because tactic, and relatively oxygen-stable, hydrogenated polymers are often a desirable goal, the ability to form pure *cis,isotactic* polymers (through enantiomorphic site control) and *cis,syndiotactic* polymers (through stereogenic metal control) is sufficient for preparing hydrogenated polymers with a single structure. It is hoped that the principles of forming polymers that have a single structure through ring-opening metathesis polymerization will be general for a relatively large number of monomers and that some important problems in ROMP polymer chemistry can benefit from knowledge of polymer structure at a molecular level. With an increase in knowledge concerning the mechanistic details of polymerization by well-defined initiators, more elaborate ROMP polymers and copolymers with stereoregular structures may be possible.
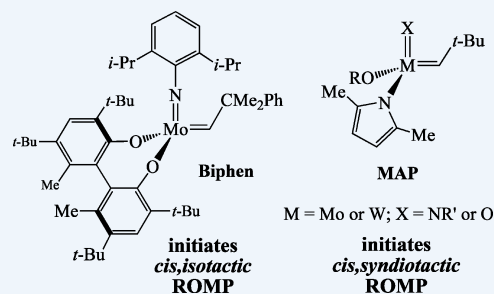
■ INTRODUCTION

Since the discovery of synthetic polymers in the mid 20th century, it has become clear that polymers with a single structure often have more desirable properties, one of which is an ability to crystallize and to have a relatively distinct melting point.[1] Perhaps the best known example is polypropylene, which has two stereochemically regular forms: isotactic (in which the configuration of the chiral carbon formed in each step is the same) and syndiotactic (in which the configuration alternates). If the initiator in a propylene polymerization is achiral, then polymer growth is regulated by the stereochemistry in the last inserted monomer unit. This "chain-end control" is usually regarded as the weakest form of control compared to others discovered through studies in organometallic chemistry during the last 25 years.[1] Homogeneous catalysts have been designed that will produce, virtually exclusively, one stereochemistry or the other in a mechanistically well-understood and efficient manner. For example, bidentate C_2-symmetric ligands are often employed (in *ansa*-metallocenes) to form isotactic polypropylene; in this case, propylene is forced to add to a given metal center through the same enantiotopic face of the olefin in each step. This "enantiomorphic site control" is a more efficient and more predictable way to control the stereochemistry of a growing polymer chain.[1] Syndiotactic polypropylene can be formed with, for example, a *meso* metallocene having large and small connected cyclopentadienyl-like rings that force propylene to add to the metal center sequentially through alternating enantiotopic faces.[1]

Formation of polymers from strained cyclic olefins through ring-opening metathesis polymerization (ROMP)[2,3] was an important application of olefin metathesis before the types of alkylidene initiators present in various "classical" catalyst systems were known. Once isolable, well-defined alkylidene complexes of Mo,[4] W,[4] and Ru[5] were prepared and employed
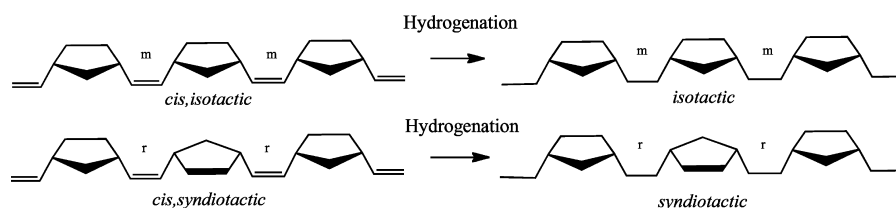
Figure 1. Two regular *cis* structures for polyNBE and hydrogenated or H-polyNBE.

as initiators, it became possible to control, to some degree, the formation of *cis* or *trans* double bonds, molecular weight, and dispersity in the resulting ROMP polymer through a careful design of the catalyst on a molecular level. (Well-defined catalysts are those whose structures are known and whose reactivities and selectivities can be varied in a knowledgeable manner through ligand design.)

Some of the most readily available monomers for ROMP are norbornenes or disubstituted norbornadienes. Polymers made from them have tacticities that remain in the polymer backbone after the C=C bonds in the polymer backbone are hydrogenated. Formation of polymers with exclusively one tacticity employing classical catalysts or well-defined catalysts was relatively rare until approximately 20 years ago, when well-defined ROMP catalysts based on molybdenum were found to yield *cis,isotactic* polynorbornenes through enantiomorphic site control. Over the last 5 years, catalysts have been designed based on Mo and W that produce *cis,syndiotactic* polynorbornenes through what is called "stereogenic metal control". Stereogenic metal control has made it possible to form a third regular structure, syndiotactic polymers prepared from racemic monomers that contain alternating enantiomers within the main chain. Most of the information concerning highly tactic ROMP polymers has been obtained through polymerization of a few monomers such as 2,3-dicarbomethoxynorbornadiene (DCMNBD and its relatives) or *rac*- or enantiomerically pure *exo,endo*-5,6-dicarbomethoxynorbornene (DCMNBE and its relatives). In this Account, I will review what is known about preparing ROMP polymers with essentially a single primary structure with well-defined Mo and W imido alkylidene initiators. A summary is provided in tabular form as Supporting Information. An account of early findings (i.e., the role of *syn* and *anti* alkylidene isomers, their interconversion, and other mechanistic details) can be found in articles published in 2007[6] and 2011.[7] So far, formation of ROMP polymers with a single tacticity employing well-defined Ru initiators is rare.[5,6,8] Extensive theoretical studies have been carried out over the last several years on various aspects of Mo and W metathesis catalysts.[9]

Cis,Isotactic Polymers

ROMP is most successful when the cyclic olefin is highly reactive and the double bonds in the resulting polymer are relatively unreactive toward secondary metathesis reactions, as is the case with norbornene-like monomers. In the simplest example, norbornene itself, the *exo* face of the C=C bond is proposed to add to a M=CHR bond to form a *cis* or *trans* intermediate metallacyclobutane complex that opens to give a *cis* or *trans* (respectively) C=C linkage between monomer units in the resulting polymer.[7] If the norbornene adds to one face of the M=CHR bond in a propagating alkylidene intermediate repeatedly and in the same manner (*cis* or *trans*), then the resulting structure will be isotactic. If the norbornene adds alternately to one face of the M=CHR bond

and then the other, the resulting structure will be syndiotactic. Therefore, four stereoregular polynorbornenes can be formed. The two *cis* forms of polynorbornene, and their hydrogenated versions, are shown in Figure 1. As discussed below, *cis* bonds appear to be the easiest to form. The stereochemical relationships (*meso* (m) and *racemic* (r)) between the carbon atoms on each side of the double bond are maintained in the saturated polymers formed upon hydrogenation of the C=C bonds in the main chain. Hydrogenated (saturated) polymers are relatively insensitive to oxygen compared to that of the unsaturated polymers, which have allylic protons. Repeating structures other than those in Figure 1 can be imagined; for example, ...mrmrmr..., although the mechanisms required to form them are not known.

Formation of highly stereoregular polymers from a monomer such as DCMNBD (DCMNBD = 2,3-dicarbomethoxynorbornadiene) employing first-generation Mo(NR)(CHR′)(OR″)$_2$ initiators enjoyed limited success.[7] While *cis* ROMP polymers often can be formed, especially at low temperatures,[10] a single tacticity (>95%) was rarely achieved with Mo(NR)(CHR′)(OR″)$_2$ initiators, perhaps in part because tacticity can arise only through chain end control if the initiator is not chiral. Exceptions include formation of a *cis,isotactic* polymer from the pantolactonyl ester analogue of DCMNBD and Mo(NAr)(CHCMe$_2$Ph)[OC(CF$_3$)$_3$]$_2$ as the initiator.[11b]

Second-generation imido alkylidene complexes that contain a biphenolate or binaphtholate ligand (generically, Biphen; i.e., Mo(NR)(CHR′)(Biphen)) were prepared in 1993 with an eye toward asymmetric metathesis reactions when the Biphen is enantiomerically pure (Figure 2).[11,12] Racemic Mo(NR)-
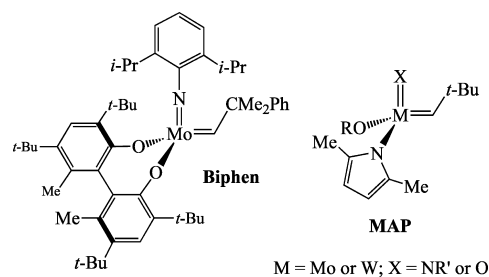

Figure 2. Examples of Biphen and MAP catalysts.

(CHR′)(Biphen) catalysts also were found to give *cis* poly(DCMNBD) with a single tacticity. If the monomer is enantiomerically pure (denoted by * in Figure 3) and a pure *cis* polymer with a single tacticity is formed, then mirror planes disappear, but the r (C$_2$ axis) relationship between monomer units remains. Therefore, the two olefinic protons (H$_a$ and H$_b$) are inequivalent and coupled to each other in the *cis,isotactic* polymer but are not coupled to each other (H$_c$ and H$_d$) in the *cis,syndiotactic* polymer. A simple proton NMR experiment could then determine whether the polymer is *syndiotactic* or
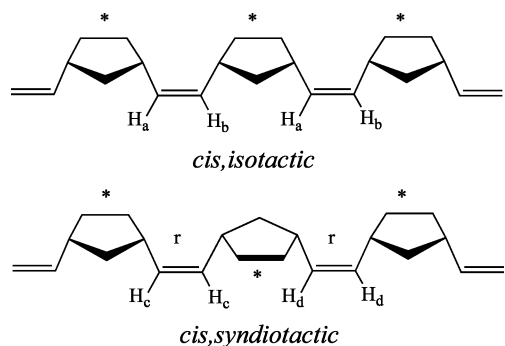
Figure 3. Four olefinic protons in *cis,tactic* polymers made from an enantiomerically pure monomer.

isotactic. The same is true in a *trans,tactic* polymer. In a *cis,tactic* polymer made from 2,3-dicarbo*menthoxy*norbornadiene (or the pantolactonyl ester analogue) and a Mo(NR)(CHR′)(Biphen) initiator, the inequivalent olefinic protons were found to be coupled by ~11 Hz.[11] Therefore, this polymer is *cis,isotactic*, a structure that is proposed to be a consequence of enantiomorphic site control by the Biphen catalyst. The tacticity cannot be determined directly for polyDCMNBD or any other polymers prepared from achiral monomers because the olefinic protons are equivalent. Therefore, one has to accept the proposal that the *methyl* ester derivative yields the same stereoregular structure as that of the *menthyl* or *pantolactonyl* ester derivatives.

The arguments above concerning direct measurement of tacticity are valid with respect to a *cis,tactic* polymer derived from an enantiomerically pure 5,6-disubstituted norbornene, namely, R = CO$_2$Me, CH$_2$OMe, or Me (Figure 4).[11b]
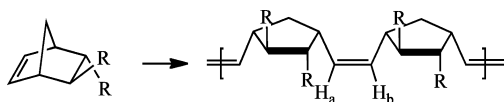

Figure 4. A *cis,isotactic* dyad formed from an enantiomerically pure disubstituted norbornene.

Cis,isotactic polymers that contain inequivalent olefinic protons (H$_a$ and H$_b$) are formed with a molybdenum imido Biphen catalyst. Although polymers that are not highly *cis* and/or highly tactic may result upon attempted polymerization of some monomers with biphenolate and binaphtholate catalysts, if the resulting polymer is highly *cis* and highly tactic, then the probability that it is a *cis,syndiotactic* structure instead of a *cis,isotactic* structure would seem to be low.

An issue associated with polymerization of an enantiomerically pure monomer with a catalyst that contains a racemic Biphen ligand is that two polymers with the same *cis,isotactic* structure, but slightly different lengths, may form from each enantiomer of the racemic initiator, because of different rate constants for initiation, propagation, or both. In polymers with a narrow molecular weight distribution, different molecular weights have been detected by GPC and attributed to this phenomenon.[11b,c] For similar reasons, it is possible that only one enantiomer of a racemic monomer could be polymerized by an enantiomerically pure initiator. Although this degree of kinetic resolution has not yet been observed in ROMP chemistry, it has been observed for other types of polymers.[1]

Cis,Syndiotactic Polymers

Monoaryloxide pyrrolide (MAP) imido alkylidene catalysts (Figure 2),[4] in which a large aryloxide ligand (OR) is present, have been found to promote the formation of *Z* double bonds in metathesis reactions of acyclic olefins.[13] It is proposed, on the basis of structural studies of relatively stable unsubstituted metallacyclobutanes (Figure 5), that only *cis* C=C bonds can
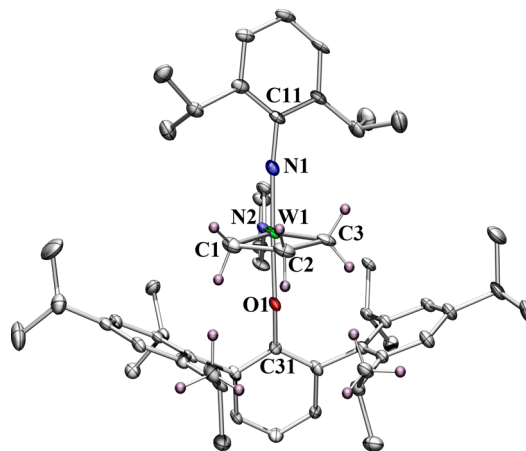

Figure 5. Thermal ellipsoid drawing of W(NAr)(C$_3$H$_6$)(C$_4$H$_4$N)-(HIPTO) (50% probability). (Only protons on C1−C3 are shown.)

form readily because a large OR group in MAP species (e.g., the OHIPT group in the structure in Figure 5; OHIPT = O-2,6-(2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$) limits formation of metallacyclobutane intermediates to only those in which the substituents point away from the bulky OR group. Mo(NAdamantyl)-(CHCMe$_2$Ph)(Pyrrolide)(OHIPT) and related initiators will form *cis,syndiotactic* polymers,[14a,17] as was proven in the case of the polymer formed from 2,3-dicarbo*menthoxy*norbornadiene.[14a] The formation of *cis,syndiotactic* polymers has been most successful when the OR groups in MAP initiators are 2,6-disubstituted phenoxides (2,6-terphenoxides) such as OHIPT (Figure 5) or OHMT (OHMT = O-2,6-(2,4,6-Me$_3$C$_6$H$_2$)$_2$C$_6$H$_3$).

The proposed mechanism of formation of *cis,syndiotactic* polymers is shown in Scheme 1. The monomer approaches the *syn* isomer of the alkylidene *trans* to the pyrrolide ligand in one enantiomer of the MAP catalyst to form a four-coordinate TBP metallacyclobutane, with all substituents pointing away from the bulky 2,6-terphenoxide (OR″). The pyrrolide ligand continues to move to the rear and the OR″ ligand to the front as the new *cis* double bond forms *trans* to the pyrrolide ligand. This type of "turnstile" rearrangement may actually consist of a series of Berry-type rearrangements before the MC$_3$ ring opens,[15] but the overall result of one step is inversion of the configuration at M, from (*R*) to (*S*) in the example shown in Scheme 1. The monomer then approaches the front face of the M=C bond to reform the (*R*) configuration at the metal and produce a *cis,syndiotactic* relationship between monomer units in the second insertion product. Repetition of this process leads to the *cis,syndiotactic* polymer. It should be noted that the only TBP metallacyclobutane complexes that have been isolated and structurally characterized have no substituents on the ring (as in Figure 5). Trisubstituted metallacyclobutane intermediates in a ROMP reaction may have more distorted MC$_3$ rings and less ideal TBP structures.[16]

Scheme 1. Proposed Mechanism for Forming *Cis,Syndiotactic*-Poly(dicarboalkoxyNBD) Using Molybdenum- or Tungsten-Based MAP Initiators
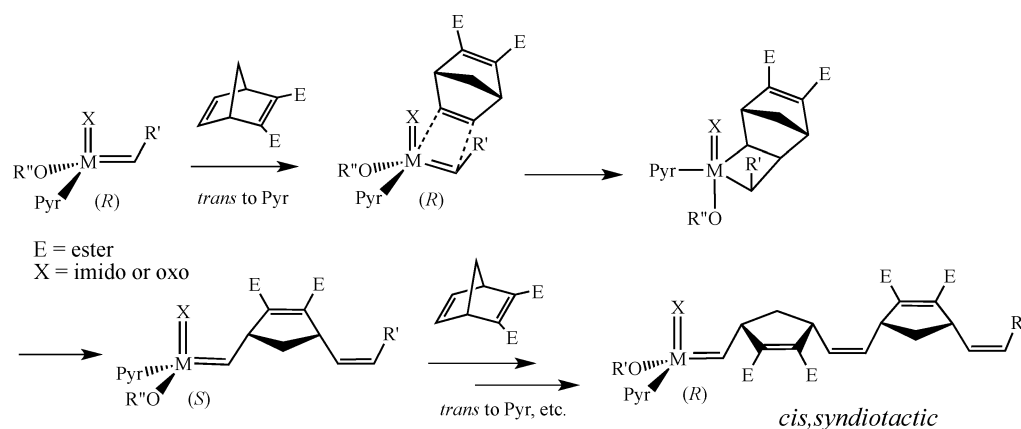
Inversion of the stereogenic metal center with each insertion in a ROMP reaction has been called "stereogenic metal control". Inversion of configuration at the metal could be said to be required in order to eject the product C=C bond in the same manner as that of the monomer added to the alkylidene (*trans* to the pyrrolide). No chiral ligands are present except for the chiral chain end after the first and each subsequent insertion. After each insertion, diastereomers are present as a consequence of one chiral center being present at the metal center and one in the chain end. It has been proposed that stereogenic metal control, like enantiomorphic site control, will dominate chain end control in most circumstances, although this proposition is a topic of continuing study. Polymers such as *syndiotactic* polypropylene are prepared via a mechanism that resembles that shown in Scheme 1, but we have not yet been able to find a strict analogue in the literature of what we have called stereogenic metal control.

When stereogenic metal control leads to a basic *cis,syndiotactic* structure, an interesting question is whether racemic monomers would be incorporated at random or whether a preferred diastereomeric combination of catalyst and monomer could lead to incorporation of enantiomers in a perfectly alternating fashion. A *cis,syndiotactic* structure in which the enantiomers have been incorporated alternately has been found for several monomers when Mo imido alkylidene MAP initiators are employed.[17] These have been called *cis,syndiotactic,alt*, or *c,s,a*, structures, where *alt* refers to the alternating incorporation of enantiomers. The *c,s,a* structure shown in eq 1
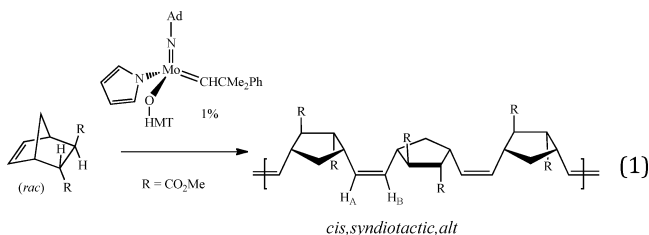
is made from *rac*-5,6-*exo,endo*-dicarbomethoxynorbornene and a molybdenum-based MAP initiator.[17] The two types of coupled olefinic protons in this case appear as pseudo triplets in the proton NMR spectrum (Figure 6). The ^{13}C NMR spectrum of the hydrogenated version of this polymer is clearly different from that of the hydrogenated *cis,syndiotactic* and hydrogenated *cis,isotactic* polymers formed from enantiomerically pure 5,6-
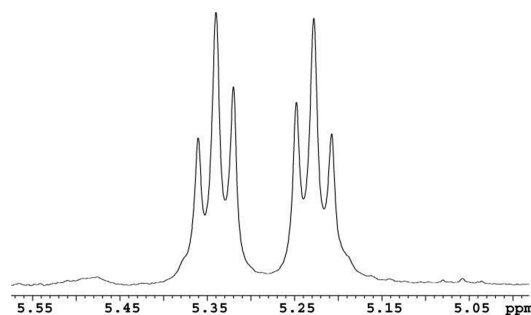

Figure 6. Olefinic region of the ^{1}H NMR spectrum of *c,s,a*-poly(*rac*-DCMNBE) formed with Mo(NAd)(CHCMe₂Ph)(Pyr)(OHMT) (CDCl₃, 500 MHz).

exo,endo-dicarbomethoxynorbornene (DCMNBE), as it should be.[17] A small amount (~5%) of what is proposed to be a *trans,iso,alt* (*t,i,a*) relationship (one of two resonances is at 5.47 ppm in Figure 6) is proposed to be present in addition to the *c,s,a* relationship as a consequence of an error similar to the mechanism that leads to formation of a largely a *trans,isotactic* polymer to be described in a section below. Similar *c,s,a* structures were formed from *endo,exo*-5,6-dicyanonorbornene and 1-methyl-5,6-dicarbomethoxy-7-oxanorbornadiene.[14]

A rare example of formation of a *c,s,a* polymer in the literature formed through ROMP employing a classical metathesis catalyst is polymerization of *rac*-1-methylnorbornene with ReCl₅.[18] The authors noted that "the inherent chirality of the metal seems to be of paramount importance in controlling tacticity...with little or no influence by chirality in the permanent ligands or in the polymer chain ends".[18b] The nature of the actual catalyst in this classical system is not known, but as the authors recognized, it seems likely to have a stereogenic metal center whose chirality inverts with each insertion and whose chirality controls the insertion process.

The rate of polymerization of (+)-5,6-*exo,endo*-dicarbomethoxynorbornene by W(O)(CH-*t*-Bu)(Me₂Pyr)(OHMT) (see later section) was shown to be approximately the same as the rate of polymerization of *rac*-5,6-*exo,endo*-dicarbomethoxynorbornene.[22] Therefore, the two enantiomers of *rac*-5,6-*exo,endo*-dicarbomethoxynorbornene react with alkylidene intermediates at approximately the same rate, which would explain why a *c,s,a* structure is not formed in polymerization of *rac*-5,6-*exo,endo*-dicarbomethoxynorbornene with W(O)(CH-*t*-Bu)(Me₂Pyr)(OHMT) as the initiator.

At least one anomaly has been found as far as forming *cis,syndiotactic* structures employing MAP catalysts is concerned; although $Mo(NC_6F_5)(CHCMe_2Ph)(Me_2Pyr)$-(OHMT) yields >98% *cis,syndiotactic*-poly(DCMNBD), Mo-$(NC_6F_5)(CHCMe_2Ph)(Me_2Pyr)(ODFT)$ (ODFT = decafluoroterphenoxide =2,6-$(C_6F_5)_2C_6H_3$) yields 95% *cis*, 91% *isotactic*-poly(DCMNBD).[19] This result could be taken as evidence that chain end control can override, or at least disrupt, stereogenic metal control in some circumstances.

Trans,Syndiotactic Polymers

High *trans*, highly tactic polymers were first prepared with a $Mo(NR)(CHR')(O\text{-}t\text{-}Bu)_2$ initiator through chain end control from 2,3-dicarbomethoxynorbornadiene (DCMNBD), 2,3-dicarbo*menthoxy*norbornadiene (DCMenNBD), the pantolactonyl ester analogue of DCMenNBD, and 5,6-bis-$(CF_3)_2$norbornadiene (NBDF6).[20] Poly(DCMenNBD) was proven to be *trans,syndiotactic* on the basis of the fact that the two olefinic protons observable in the proton NMR spectrum (H_c and H_d in Figure 3) are not coupled to one another.[11a] The polymer must be formed via a *trans* metallacyclobutane intermediate in each case, one that is formed either through *anti* addition of the monomer to a *syn* alkylidene (Figure 7; X = N-2,6-diisopropylphenyl) or through
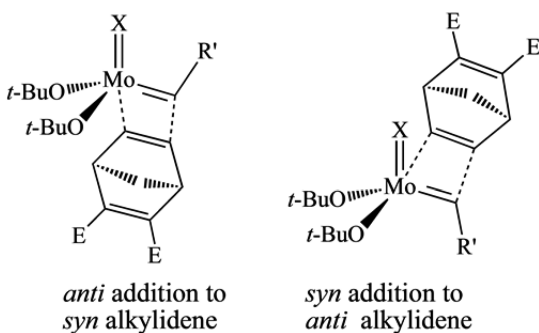

Figure 7. Two modes of addition of norbornene to the front face of *syn* and *anti* alkylidene isomers to give *trans* C=C linkages.

syn addition of the monomer to an *anti* alkylidene.[7] It has been proposed that the unobservable *anti* alkylidene is in rapid equilibrium with the *syn* alkylidene and is the much more reactive alkylidene isomer in this circumstance. It must be proposed that poly(DCMNBD) and poly(NBDF6) are also highly *trans* and highly tactic. There is no reason to change this proposal unless a method is developed for proving tacticity for each tactic polymer, and unless the application of that method yields results that are not consistent with expectations. It should become clear in this Account that catalysts can be surprisingly mercurial as far as the mechanism of formation and the structure of the resulting polymer are concerned, even when well-defined initiators are employed whose structures are known, and the lowest energy pathway is likely to depend, to some degree, on the monomer itself.

$W(NAr)(CH\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2$ does not readily polymerize 5,6-bis(CF_3)$_2$norbornadiene (NBDF6) at 22 °C.[20] Upon addition of NBDF6 to $W(NAr)(CH\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2$ at 0 °C, a square pyramidal metallacyclobutane complex is formed and can be isolated. An X-ray study (Figure 8) showed that the metallacycle is indeed *trans* and that the *t*-butyl group on one of the α carbon atoms points toward the NAr group, as if the metallacycle were derived through *anti* addition of NBDF6 to a *syn* alkylidene isomer of $W(NAr)(CH\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2$ (Figure
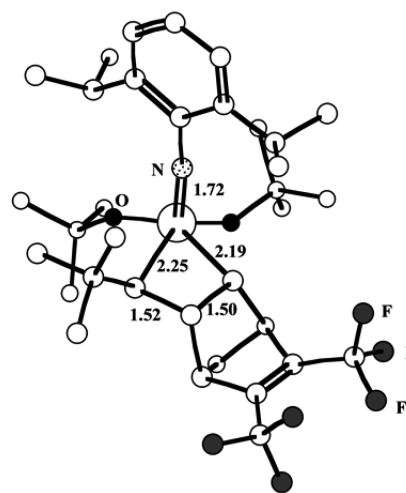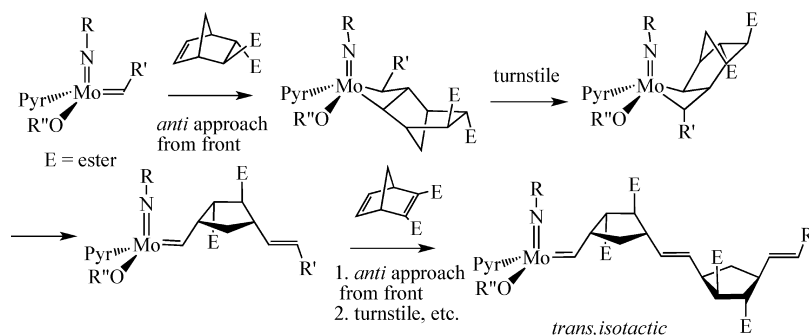

Figure 8. Structure of the tungstacyclobutane formed through addition of NBDF6 to $W(NAr)(CH\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2$.

8). However, that conclusion is not sound as a consequence of the likely fluxionality of the five-coordinate metallacyclic species; in other words, NBDF6 could add in a *syn* fashion to an *anti* alkylidene isomer of $W(NAr)(CH\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2$ (Figure 7) followed by a pseudorotation process to give the observed product. The metallacycle decomposes to the first insertion product, which is approximately a 9:1 mixture of what are proposed to be *syn* and *anti* alkylidene isomers. It was proposed that the molybdenum analogue of the observed tungstacyclobutane complex forms more slowly and rearranges more readily to the first insertion product than the tungstacyclobutane complex. In general, (i) tungstacyclobutane complexes appear to be more stable than molybdacyclobutane complexes toward loss of an olefin, (ii) square pyramidal complexes are believed to be favored relatively to trigonal bipyramidal metallacycles when relatively electron-donating alkoxides (e.g., O-*t*-Bu) are present, (iii) TBP metallacycles are observed when relatively electron-withdrawing alkoxides are present, and (iv) a TBP metallacycle has been proposed to be the one that rearranges most readily to an alkylidene. A square pyramidal molybdacyclobutane complex analogous to that shown in Figure 8 was isolated upon addition of 5,6-bistrifluoromethyl-7-oxanorbornadiene to $Mo(NAr)(CH\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2$.[21]

Trans,Isotactic Polymer

Attempts to polymerize (+)-5,6-dicarbomethoxynorbornene employing $Mo(NAd)(CHCMe_2Ph)(Pyr)(OHIPT)$ (Ad = 1-adamantyl; Pyr = pyrrolide = NC_4H_4) as the initiator led to a polymer in which ~92% of the dyads have a *trans,isotactic* relationship, with the balance (~8%) being *cis,syndiotactic*.[22] It was proposed that *cis,syndiotactic* dyads are formed when the monomer adds in a *syn* fashion to a *syn* alkylidene to give an all *cis* trisubstituted metallacyclobutane intermediate, as described earlier, but most of the time the monomer adds in an *anti* fashion to a *syn* alkylidene to give a metallacyclobutane that then undergoes a turnstile-type rearrangement before it opens (Scheme 2, where a square pyramidal "manifold" is employed for convenience). This "flipping over" of the metallacyclobutane ring is an alternative to the process shown in Scheme 1 in which aryloxide and pyrrolide ligands exchange positions; both are rearrangements of a five-coordinate metallacyclobutane intermediate. The resulting propagating alkylidene is the *syn*

Scheme 2. Formation of *Trans,Isotactic* Polymer without Interchange of Pyr and OR″ at the Metal

Since the present synthesis of tungsten oxo alkylidene complexes employs $W(O)(CHCMe_2Ph)Cl_2(PPh_2Me)_2$ or W-$(O)(CHCMe_3)Cl_2(PMe_2Ph)_2$ as a starting material, in most cases the isolated MAP species retains one equivalent of phosphine or acetonitrile (formed upon exposure of the phosphine adduct to neat acetonitrile) (i.e., $W(O)$-$(CHCMe_2Ph)(Me_2Pyr)(OAr)(L)$, where L is PPh_2Me or MeCN, Me_2Pyr = 2,5-dimethylpyrrolide, and OAr = a 2,6-terphenoxide).[28] When OAr is especially bulky (HMTO or dAdPO (O-2,6-Adamantyl$_2C_6H_3$), $W(O)(CHCMe_2Ph)$-$(Me_2Pyr)(OAr)$ complexes are isolated. In several cases, L can be removed from $W(O)(CHCMe_2Ph)(Me_2Pyr)(OAr)(L)$ complexes, usually through addition of $B(C_6F_5)_3$, and the base-free $W(O)(CHCMe_2Ph)(Me_2Pyr)(OAr)$ complex thereby prepared. Addition of 1 equivalent of $B(C_6F_5)_3$ to $W(O)$-$(CHCMe_2Ph)(Me_2Pyr)(OAr)$ results in a dramatic increase in the rate of polymerization of DCMNBD. In all circumstances, even after addition of 1 equivalent of $B(C_6F_5)_3$, the resulting polymer is *cis,syndiotactic*. All data suggest that (i) L must be lost to yield 14 electron $W(O)(CHCMe_2Ph)(Me_2Pyr)(OAr)$ in order to react with monomer, (ii) 1 equivalent of $B(C_6F_5)_3$ does not react destructively with the propagating species, and (iii) $B(C_6F_5)_3$ accelerates polymerization, probably through binding to the oxo ligand, as shown in Figure 9.[23a] NMR studies also have shown that $B(C_6F_5)_3$ binds preferentially to the oxo ligand in $W(O)(CH_2)(OHMT)_2$,[26] not to the methylidene carbon, although binding of $B(C_6F_5)_3$ to the methylidene carbon has been observed in $Cp_2Ta(CH_2)$-(CH_3).[29] All evidence suggests that *cis,syndiotactic*-poly-(DCMNBD) is formed through stereogenic metal control.

isomer, the same as the initial alkylidene, so no *syn/anti* alkylidene conversion is required as part of the polymerization process. The aryloxide and pyrrolide ligands do not exchange in this case, so an *isotactic* polymer is formed. This particular *trans* metallacycle intermediate may be especially prone to rearrangement and opening to an alkylidene, unlike the all *cis* metallacycle that leads to a *cis,syndiotactic* polymer. In summary, the overall result is decided on the basis of whether the monomer approaches a *syn* alkylidene in a *syn* fashion (→ *cis,syndiotactic*) or in an *anti* fashion (→ *trans,isotactic*). An "error" of this type obviously would doom formation of a hydrogenated polymer with one tacticity.

Tungsten Oxo Alkylidene MAP Initiators

Well-defined tungsten oxo alkylidene complexes[23] are of special interest because (*inter alia*) oxo alkylidene complexes are likely to be found in many classical metathesis catalyst systems. Oxo alkylidene complexes can be especially *Z*-selective when the aryloxide in a MAP species is an appropriate bulky 2,6-terphenoxide.[24] A Lewis acid ($B(C_6F_5)_3$) has been shown to add reversibly to the oxo ligand in $W(O)(CH-t-Bu)(OHMT)$-(Me_2Pyr) (Figure 9)[25] and to accelerate processes that are
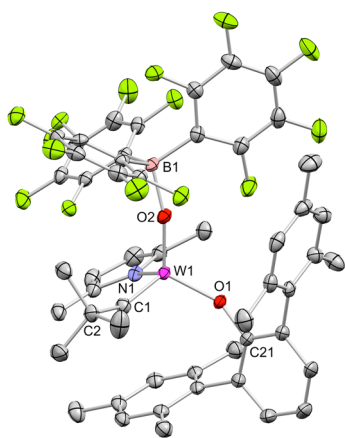

Figure 9. Thermal ellipsoid drawing (50% probability) of $W(OB$-$(C_6F_5)_3)(CH-t-Bu)(OHMT)(Me_2Pyr)$.

It is interesting to note that $W(O)(CH-t-Bu)(Me_2Pyr)$-$(OHMT)(PMe_2Ph)$ produces ~99% *cis,syndiotactic*-poly((+)-5,6-dicarbomethoxynorbornene),[22] in contrast to the *trans,iso-tactic*-poly((+)-5,6-dicarbomethoxynorbornene) produced with a Mo imido alkylidene initiator, as described above (Scheme 2). The five-coordinate rearrangement of the tungstacyclobutane that would lead to *trans,isotactic* polymer must be slow relative to the exchange of aryloxide and pyrrolide ligands in the tungstacyclobutane intermediate and formation of *cis,syndiotactic* polymer. The apparent mismatch between the chirality at W and the chirality of the monomer seems to be tolerated and part of the polymerization process.

3-Methyl-3-phenylcyclopropene (MPCP)

It is important to establish whether the principles proposed for polymerization of a small selection of norbornenes and norbornadienes hold for other types of polymerizable cyclic olefins. Several years ago, the ROMP polymerization of 3-methyl-3-phenylcyclopropene (MPCP) by molybdenum imido
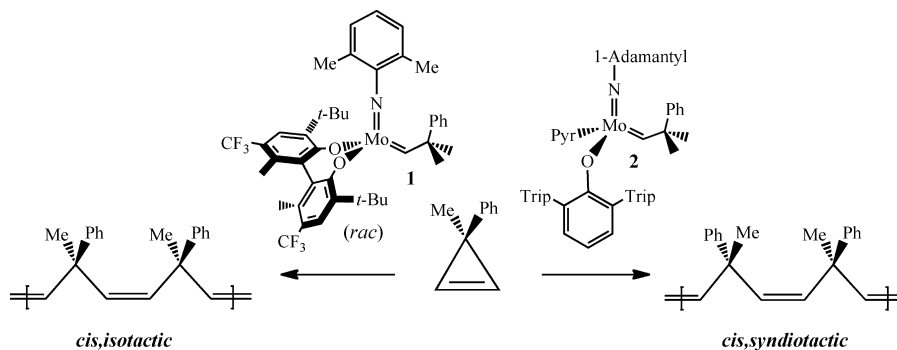
relevant to olefin metathesis.[26] Because Lewis acids (e.g., Al compounds) are often present in classical metathesis catalyst systems, the most active catalysts may in fact be Lewis acid-activated[25] oxo alkylidene complexes and therefore could be present as only a very low percentage of the total metal concentration. Possible alternatives to Lewis acid-activated oxo complexes are cationic complexes that do not contain an oxo ligand.[27]

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Scheme 3. Formation of *Cis,Isotactic* and *Cis,Syndiotactic*-Poly(MPCP)

alkylidene bisalkoxide initiators was reported.[30] Polymerization of MPCP with biphenolate and binaphtholate initiators yielded a highly tactic polymer that was proposed to be *trans* on the basis of IR absorptions near 980 cm^{-1} characteristic of *trans* double bonds, but the tacticity was not assigned.[31] An expanded investigation of poly(MPCP) revealed that another highly tactic poly(MPCP) could be prepared with MAP initiators.[14b] A complication with MPCP versus a norbornene or norbornadiene is that the C=C bond in MPCP could be attacked from either side. The current proposal is that the side toward which the methyl group points is the one that is attacked exclusively (for steric reasons). An interesting feature of the polymerization of MPCP is that the propagating alkylidene is closely related to the neophylidene in the initiator; therefore, the rates of initiation and propagation should be roughly the same. The absence of an allylic proton in poly(MPCP) is likely to result in these polymers being relatively stable to oxygen.

The carbon NMR spectra of poly(MPCP) prepared with **1** and **2** (Scheme 3) show that both polymers have highly regular structures. It was found that the absorption at ~980 cm^{-1} for each polymer is not intense enough to be characteristic of *trans* olefins, for example, as found in the largely *trans*-poly(MPCP) prepared with Mo(NAr)(CHCMe$_2$Ph)(O-*t*-Bu)$_2$. Therefore, both poly(MPCP)$_1$ (prepared with **1** as the initiator) and poly(MPCP)$_2$ (prepared with **2** as the initiator) are proposed to be *cis*. The two are clearly distinguished by the chemical shift of the methyl resonance in ^{13}C NMR spectra at 30.0 ppm in poly(MPCP)$_1$ and 32.0 ppm in poly(MPCP)$_2$ (in CD$_2$Cl$_2$). On the basis of the structures produced with **1** and **2** as initiators in norbornene and norbornadiene chemistry, it is proposed that poly(MPCP)$_1$ has a *cis,isotactic* structure (methyl shift of 30.0 ppm) and poly(MPCP)$_2$ has a *cis,syndiotactic* structure (methyl shift of 32.0 ppm, Scheme 3). The *trans* poly(MPCP) prepared with Mo(NAr)(CHCMe$_2$Ph)(O-*t*-Bu)$_2$ as the initiator is ~85% tactic, with the dominant methyl resonance being at 27.5 ppm in the ^{13}C NMR spectrum; this polymer is proposed to be biased toward a *trans,syndiotactic* structure, as found for polymers prepared from norbornenes and norbornadienes with Mo(NAr)(CHCMe$_2$Ph)(O-*t*-Bu)$_2$ as the initiator.

In contrast to polymerization of MPCP with **1** and **2**, polymerization of MPCP with Mo(NAr)(CHCMe$_2$Ph)-(OTPP)(Pyr) (**3**, Ar = 2,6-diisopropylphenyl, Pyr = pyrrolide, OTPP = 2,3,4,6-tetraphenylphenoxide) at 20 °C led to a polymer with no regular structure. However, poly(MPCP)$_3$ is formed at −78 °C, and that polymer is identical to *cis,syndiotactic*-poly(MPCP)$_2$ described above. As the temperature of polymerization is increased from −78 to 46 °C in

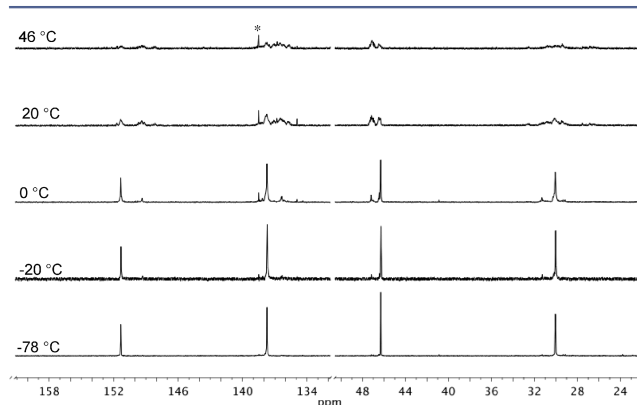separate experiments, the regularity of the polymer degrades steadily, as shown in Figure 10.

Figure 10. Partial ^{13}C{^{1}H} NMR spectra (CD$_2$Cl$_2$, 125 MHz) of poly(MPCP)$_3$ synthesized at various temperatures (*residual toluene).

It was shown in a series of ^{13}C labeling of the olefinic carbon atom in MPCP, along with kinetic and photochemical studies, that (i) the C=C bond in the first insertion product formed at −78 °C from the *syn* isomer of **3** is *trans*, (ii) the alkylidene in the first insertion product at −78 °C has the *anti* configuration, and (iii) this *anti* alkylidene is converted to the *syn* alkylidene product with $k = 2.9 \times 10^{-4}$ s^{-1} at −30 °C. Observation of a *trans* C=C bond in the first insertion product when MPCP is added to **3** at −78 °C suggests that a *trans* double bond is formed upon initiation at −78 °C, even though *cis* double bonds are formed upon propagation at −78 °C.

It was shown that the *anti* isomer of **3**, obtained through photolysis of **3** at −78 °C, is converted to the *syn* isomer upon warming the sample to higher temperatures. Rate constants for the conversion of *anti*-**3** to *syn*-**3** were obtained at several temperatures, and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were found to be 19.9 ± 2 kcal/mol and 8 ± 2 cal/mol K, respectively. At 298 K, the rate constant for conversion of *anti*-**3** to *syn*-**3** was shown to be 3 s^{-1}.

On the basis of the studies just described and related studies, it was proposed that the *anti* first insertion product is formed in the reaction between MPCP and *syn*-**3** at low temperatures and that *anti* insertion products do not readily convert to *syn* insertion products at low temperature. Therefore, *cis,syndiotactic*-poly(MPCP) (except for the first *trans* C=C bond) is formed as shown in Scheme 4. Only *anti* species are available on the time scale of the polymerization at low temperature. The polymer formed near room temperature has no regular

Scheme 4
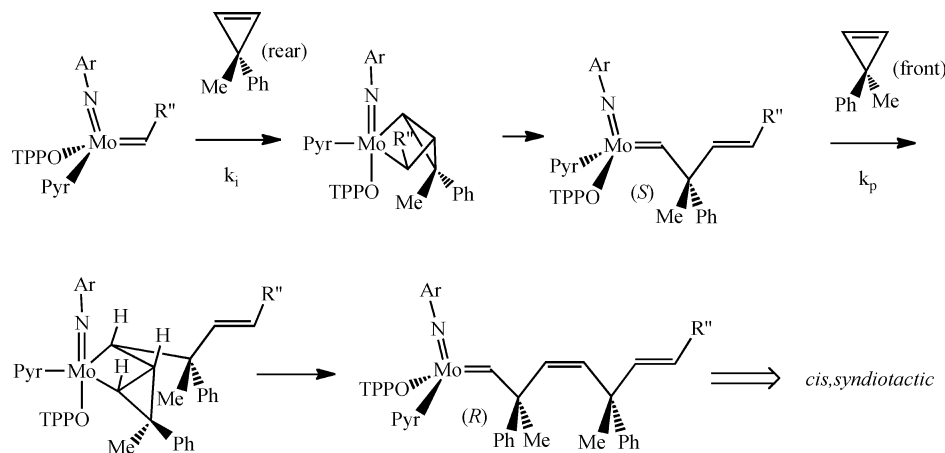
structure, in part because *anti* alkylidene insertion products are converted to *syn* insertion products at higher temperatures. MPCP also could attack a *syn* or *anti* alkylidene in a *syn* or *anti* fashion (because the OTPP ligand is not sufficiently bulky) and/or through both faces of MPCP.

The polymerizations of MPCP described in this section, and the structures and mechanisms proposed, are all completely consistent with the proposed structures and mechanisms associated with ROMP of norbornenes and norbornadienes. These studies also expose the role of temperature, inter-conversion of *syn* and *anti* alkylidene isomers, and mode of attack on one or the other alkylidene isomer in a ROMP polymerization.

■ CONCLUSIONS AND COMMENTS

We have now uncovered examples of the four basic stereoregular ROMP polymer structures for a small collection of monomers and have solid proposals as to how they are formed. The two *cis* forms can be obtained in >99% purity for several monomers. Because pure *trans* polymers have not yet been prepared through some predictable mechanism of stereochemical control, it seems unlikely that we will be able to form all basic polymer structures from a single given monomer simply by choosing the right initiator. However, as far as formations of tactic hydrogenated polymers are concerned, the ability to form pure *cis,isotactic* polymers (through enantiomorphic site control) and *cis,syndiotactic* polymers (through stereogenic metal control) is sufficient for preparing oxygen-stable hydrogenated syndiotactic and isotactic polymers.

Future goals include a broad exploration of the polymer-ization of different types of monomers. Second, it also would be desirable to prove polymer structures directly for each polymer in question. Third, we expect to encounter more differences between molybdenum and tungsten in the sensitive and complex ROMP reaction. Some of the differences may be traceable to the pervasive and often significant relativistic effects[32] for a third-row metal (W) versus a second-row metal (Mo). (Opportunities to compare a second-row metal with a third-row metal that is subject to significant relativistic effects in a catalytic reaction are rare.[33]) Fourth, we look forward to understanding more about tungsten oxo initiators, especially when activated through addition of a Lewis acids to the oxo ligand. Fifth, it would be desirable to apply the possibility to form stereoregular ROMP polymers to problems in polymer chemistry that can benefit from stereoregularity and knowledge of structure on a molecular level. With an ever increasing basis set of catalysts and results in hand, we are optimistic about being able to further refine and apply the principles uncovered during the last several years that have allowed stereoregular polymers to be prepared through ring-opening metathesis polymerization.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

List (with references) of all stereoregular polymers prepared so far with well-defined Mo and W catalysts. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

Biography

Richard R. Schrock was born in Berne, Indiana, in 1945. He received his B.A. degree from the University of California at Riverside in 1967 and his Ph.D. in inorganic chemistry from Harvard University in 1971. After 1 year as an NSF Postdoctoral Fellow at Cambridge University and 3 years at the Central Research and Development Department of E. I. DuPont de Nemours and Co., he moved to M.I.T. in 1975, where he became full Professor in 1980 and the Frederick G. Keyes Professor of Chemistry in 1989. His present interests include early metal complexes that contain an alkylidene ligand, the catalytic reduction of dinitrogen, and applications of olefin metathesis chemistry in organic and polymer chemistry. He is a member of the National Academy of Sciences and a Foreign Member of the Royal Society of London. He shared the Nobel Prize in Chemistry in 2005 with R. H. Grubbs and Y. Chauvin.

■ ACKNOWLEDGMENTS

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Identification of the Chain Carrying Carbene Complexes in a Highly Active Catalyst System. *J. Chem. Soc., Chem. Commun.* **1982**, 514−516.

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■ NOTE ADDED AFTER ASAP PUBLICATION

This paper published to the Web on June 6, 2014, with an error to the Conclusions and Comments section. The corrected version was reposted on June 18, 2014.