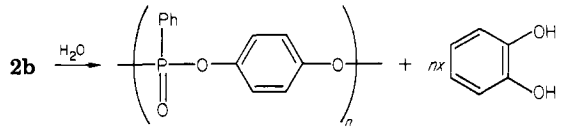
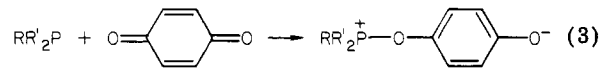
ination of pyrocatechol was a main pathway to polymer **2b′**, whose ^{31}P NMR signal appeared at +15.9 ppm.



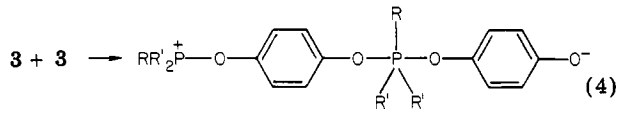
2b′

Reactions 3 and 4 are proposed to explain the course of



(3)

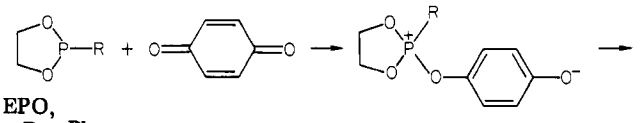
3



(4)

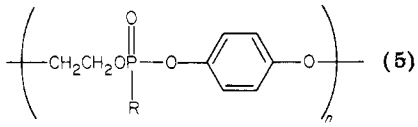
4

the polyphosphoranylation. The first step probably involves formation of the phosphoniumphenolate-type zwitterion **3**. Two molecules of **3** give dimeric zwitterion **4**. Successive reactions between zwitterions such as **3** and **4** and oligozwitterions lead to macrozwitterions of polyphosphoranes, **1** and **2**. A Japanese patent claiming copolymerization of ethylene phenylphosphonite (EPO) or ethylene phenyl phosphite (EPI) with BQ to produce alternating copolymer **6** was granted in 1971[17] and is similar to the present copolymerization. Sequence **5** was used to



EPO, R = Ph
EPI, R = PhO

5



(5)

6

explain the reaction of the patent. First, zwitterion **5** is formed which is polymerized to **6**. Propagation consists of opening of the phosphonium ring in **5** by nucleophilic attack of phenoxide anion of other zwitterions according to an Arbuzov-type reaction.[18] The phosphorus(III) monomers employed in the present study prevent the Arbuzov-type reaction involving **3** and hence allow it to undergo the polyphosphoranylation.

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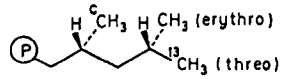
Comment on Proposed Mechanisms for Formation of Isotactic Polypropylene

In a recent paper, Zambelli et al. concluded that metallacyclobutanes are not involved in the δ-$TiCl_3$–$Al(CH_3)_2I$ polymerization of propene.[1] Here, we challenge that mechanistic interpretation.

Zambelli et al. carried out an elegant ^{13}C NMR analysis of the isotactic polypropylene formed from the δ-$TiCl_3$–$Al(^{13}CH_3)_2I$ catalyzed polymerization of propene.[1] They determined that the enriched ^{13}C methyl carbon was located only in the isopropyl end group and predominantly at the threo position relative to $^{\alpha}C$. Since neither a chiral carbon atom nor a spiralized chain participates in the first two addition steps, they concluded that the observed steric control must arise from the chirality of the catalytic center. We do not challenge these experimental results or conclusions.



Zambelli et al. point out that these results are in good agreement with a polymerization mechanism involving coordination of propene to a chiral surface M–$^{13}CH_3$ initiator followed by insertion of propene into the M–$^{13}CH_3$ bond.[2] However, Zambelli et al. contended that their results were inconsistent with the metallacyclobutane mechanism proposed by Green et al. in 1978.[3] We challenge this latter contention.

A variation[4] on Green's original mechanism of Zeigler–Natta polymerization involves (a) insertion of a metal into an α-CH bond of a metal alkyl to form a metal–carbene–hydride complex, (b) reaction of an alkene with the metal–carbene unit to produce a metallacyclobutane–hydride intermediate, and (c) reductive elimination of hydride and an alkyl group to produce a chain-lengthened metal alkyl. As Zambelli et al. correctly point out, the simplest version of Green's mechanism cannot account for the failure to observe ^{13}C label incorporated into the isobutyl methylene carbon of the right end group (Scheme I) or for the stereospecific placement of enriched methyls at the right end groups.

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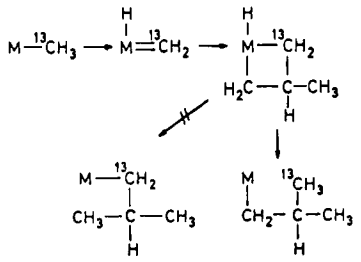
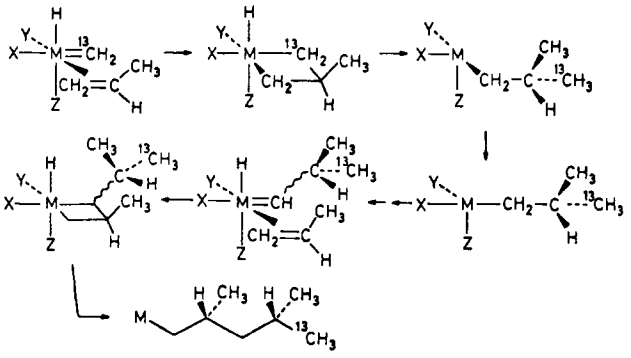
Scheme I



Scheme II



However, Green's mechanism can explain the observed structural data if a *chiral* metal environment is assumed. (It should be noted that Zambelli et al. were able to explain the structural data by using the normal insertion mechanism only if a chiral metal center was assumed.) Scheme II shows how a chiral metal center can lead to stereospecific polymerization of polypropylene.

There are several key features of this scheme. (1) Propylene coordinates at only one site on the metal (trans to Y) and the same face of propylene always coordinates to the chiral metal atom—this is controlled by chiral ligand environment (X, Y, Z) at the metal. (2) Only the alkyl group trans to X in the metallacycle undergoes reductive elimination of alkane; this precludes the formation of M-$^{13}CH_2CH(CH_3)_2$.[5] (3) The resulting metal alkyl group which is initially trans to Y isomerizes to a position trans to X; this opens the position trans to Y for coordination of propene. The stereospecific coordination of propene at the chiral metal center is ultimately responsible for the observation of $^{13}CH_3$ label at the threo site in the isopropyl end group. This scheme fully accounts for the observed stereochemistry of the $^{13}CH_3$ label incorporated from Al-($^{13}CH_3$)$_2$I in the initiation of the polymerization of propene.

In conclusion, Zambelli's experimental results are in equally good agreement with either the alkene insertion mechanism of polymerization or with Green's metallacarbene–metallacyclobutane mechanism of polymerization. For both mechanisms, the data require a chiral metal environment. The alkene insertion mechanism requires only a stereospecific coordination of propylene to explain the stereochemical and ^{13}C-labeling results while the metallacyclobutane mechanism requires this and an additional stereospecific reductive elimination step. This added requirement, however, makes the metallacyclobutane mechanism no less likely.

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(4) Green's original proposed mechanism involved a M–CHR–CH_2–CHR metallacycle. The formation of isotactic polypropylene cannot involve this type of intermediate since the polymer has isopropyl end groups. However, a variation on Green's original proposal involving a M–CH_2–CHR–CH_2 species is possible and is the type of metallacyclobutane considered here and in Zambelli's paper.[1]

(5) There is no precedent in the literature for such ligand control of reductive elimination. It would be a challenge to devise a system for testing the influence of trans ligands on reductive elimination of alkanes from a *fac*-dialkylmetal hydride.

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