

REVISED

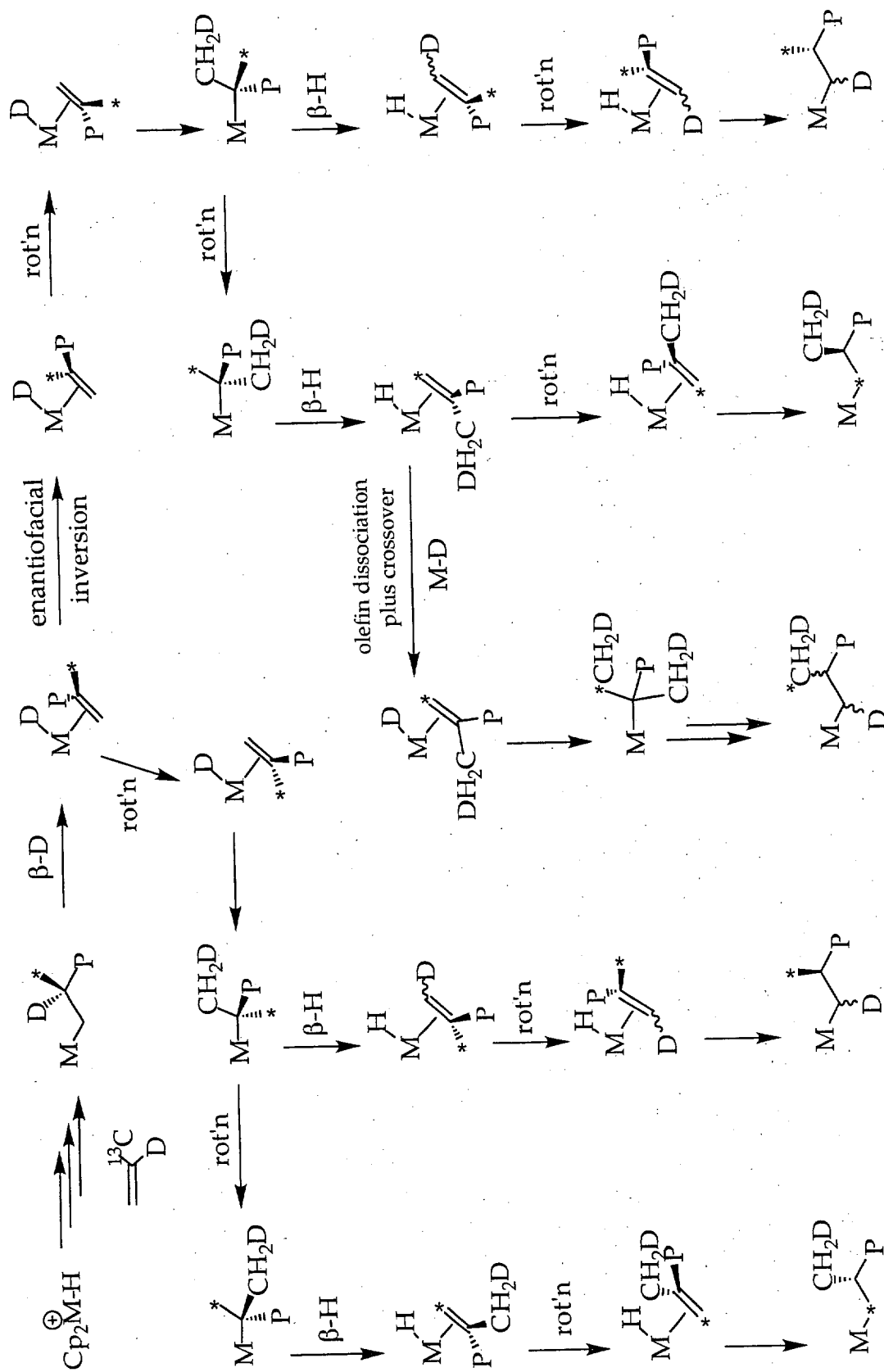
Chain Epimerization during Propylene Polymerization with
Metallocene Catalysts: Mechanistic Studies Using a Doubly-Labeled
Propylene

Jeffrey C. Yoder and John E. Bercaw*

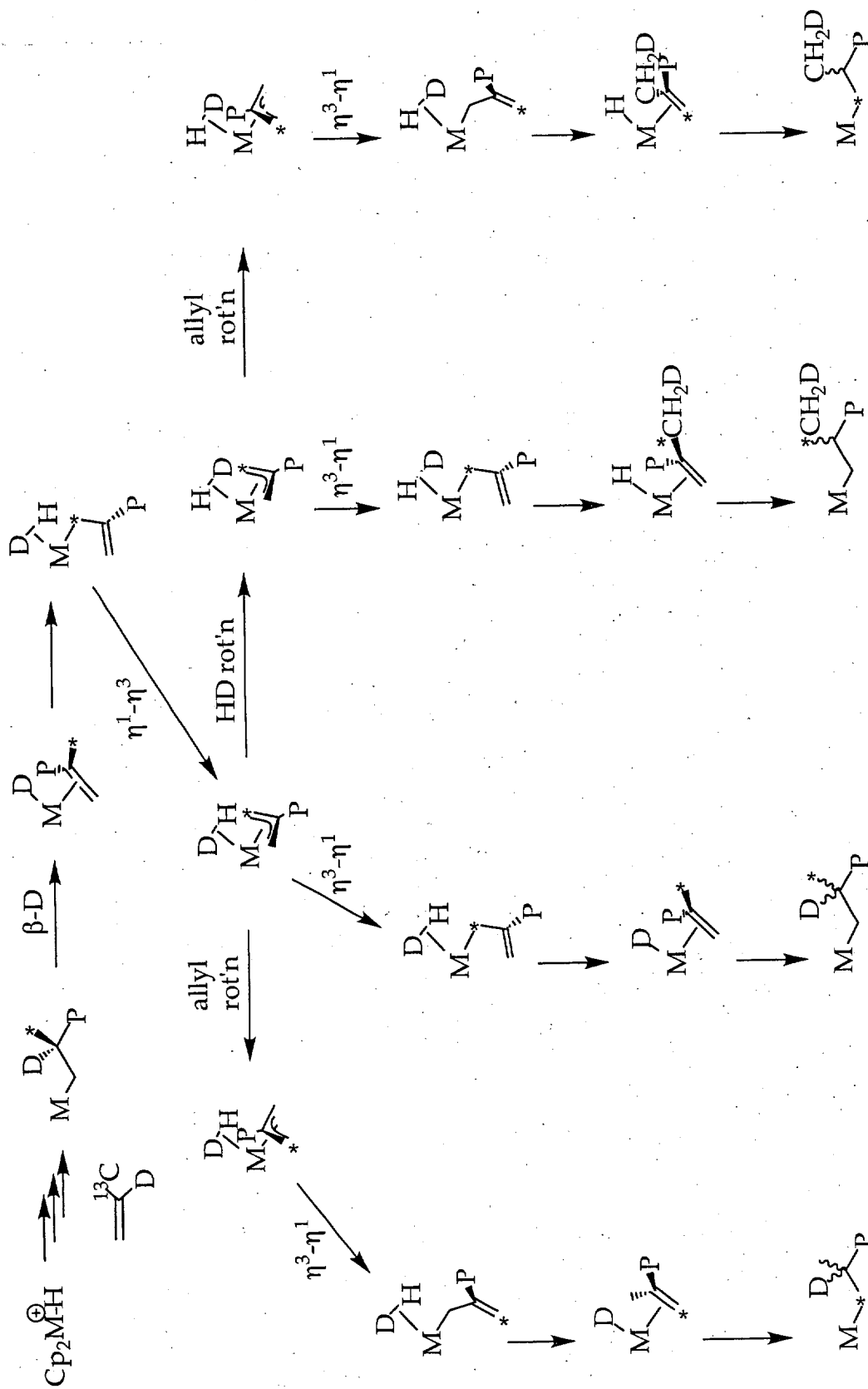
*Contribution from the Arnold and Mabel Beckman Laboratories of Chemical Synthesis,
California Institute of Technology, Pasadena, California , USA 91125.*

Received xxxx xx, 2001

Supporting Information: Schemes showing how the rearrangements according to Schemes 6 and 7 give rise to the structures labeled A through J. Schemes showing the predicted chain ends and ^{13}C NMR signals attributable to them and to regioerrors.

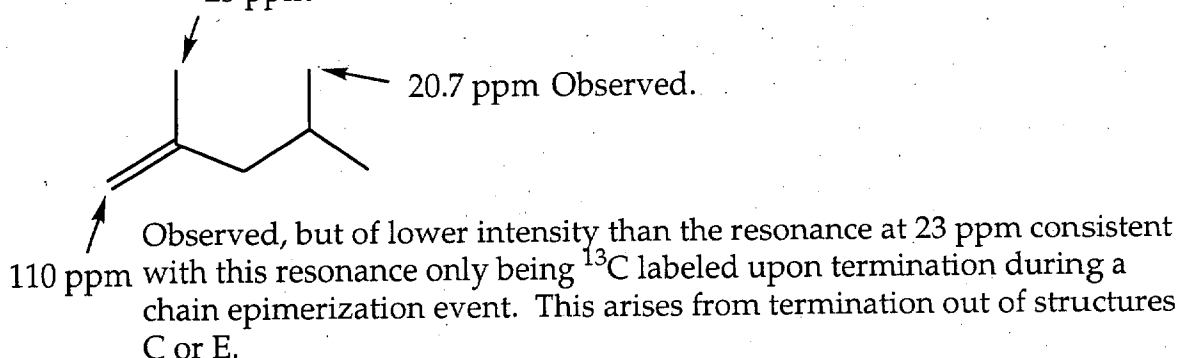


Scheme 1. Summary of proposed steps for chain epimerization using the tertiary-alkyl mechanism.

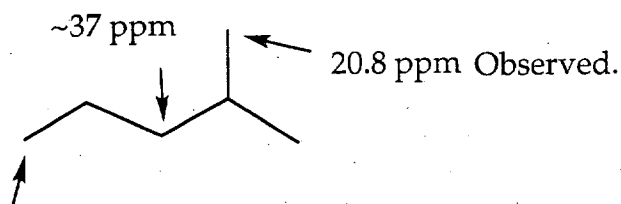


Scheme 2. Summary of proposed steps for chain epimerization using the allyl mechanism.

Chain Ends Observed. The position of this resonance should be insensitive to the presence of deuterium in the terminal vinyl position. Hence, this signal arises from termination out of structures A, B, D, or F.
23 ppm



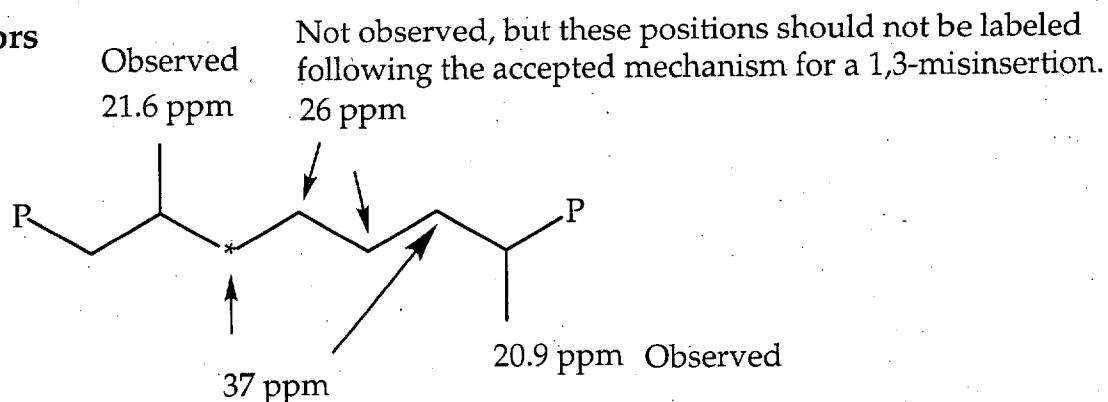
Observed. This position will be ^{13}C labeled only if chain epimerization occurs upon first insertion. This resonance is more likely due to a regioerror (see below).



~13 ppm Observed, but cut off from Figure 2 and not shown (unfortunately).

Integrations for 23 ppm, 20.7 ppm, 13 ppm, and 20.8 ppm resonances are identical, which is required by β -H elimination and then reinsertion to the M-H.

Regioerrors



Observed. The position labeled with an asterisk should be ^{13}C labeled in my system following the accepted mechanism for a 1,3-misinsertion.