

Maurice Brookhart: A Legacy to Organometallic Chemistry

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As he approaches his 80th birthday, Maurice Brookhart, known to his students, colleagues, and friends as “Brook,” has built an impressive legacy of scholarship in organometallic chemistry. In addition, he has been a kind and welcoming member of the broader organometallic community. For those who have had the opportunity to work in Brookhart’s lab, it is very likely that the first discussion of “Brook” as a potential advisor included a mention of his welcoming demeanor and empathy as well his scientific achievements. Indeed, working in the Brookhart group is a very memorable experience, combining cutting-edge research and a supportive, collaborative environment. Brookhart’s keen intellect, enthusiasm for organometallic chemistry, and calm approach have been instrumental in training several generations of organometallic chemists.

Brook used to show up in the lab every day with a yellow notebook and a pen in his left hand, eager to discuss chemistry with his students, postdocs, and visiting scientists. He always treated his students and postdocs as full collaborators and encouraged them to generate new ideas and solutions. There is no doubt that his retirement will leave a gap in the organometallic community, even as many of his discoveries have spawned new areas of ongoing research.

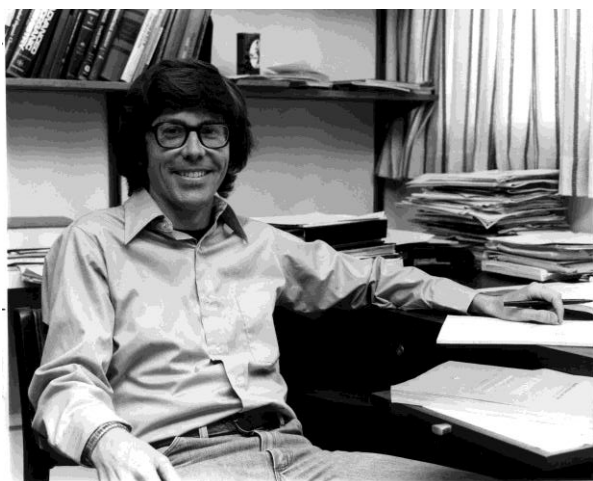
Brookhart’s influence on organometallic chemistry is profound and broadly spans fundamental concepts, novel transformations, and practical applications.¹ Although he is internationally well-known and has an impressive list of recognitions, we thought a brief overview of the main contributions from the Brookhart lab over the years could be useful for those new to the field, particularly in the context of the parallel evolution of organometallic chemistry and of Brookhart’s research directions. With that aim, this perspective will cover five general topics: transition-metal carbene complexes (1970’s), three-center two-electron (agostic) bonds (1980’s), detailed studies of migratory insertion reactions (late 1980’s-early 1990’s), late-metal olefin polymerization reactions (1990’s), and catalytic reactions involving C-H bond activation (2000’s). For a more extended description of such advances and others, we refer to an excellent article by Daugulis, MacArthur, Rix and Templeton on occasion of receiving the Gabor A. Somorjai



Maurice Brookhart during the writing of his Ph.D. Thesis at UCLA (1968, top) and receiving the Gabor A. Somorjai Award for Creative Research in Catalysis at the ACS Meeting at Denver (2015, bottom).

Award for Creative Research in Catalysis, as well as references therein.² We also take this opportunity to point the broader research community to an accompanying collection of articles published by some of Brook’s many former students, postdocs, and collaborators on this occasion and assembled in this issue, “Organometallic Chemistry Inspired by Maurice Brookhart.” The forty papers in this issue are contributed by Brook’s friends, colleagues, and former

students and postdoctoral researchers. Much of the re-



Brook at his office in Kenan Laboratories at University of North Carolina, Chapel Hill (about 1973, top; early 1980s, bottom) A messy desk has accompanied him throughout his career.

search intersects with the areas covered in this editorial or Brookhart's legacy is evident in other ways. At the same time, the wide range of topics, methods and applications presented provide a nice snapshot into how the field of organometallic chemistry has evolved in the last five decades. During this time, the demographics of the people doing organometallic chemistry have changed dramatically and the field become more diverse. This diversity has long been present in the Brookhart group, and we have tried to reflect that in this special issue of *Organometallics*

EARLY LIFE, EDUCATION AND RECOGNITIONS

Maurice Brookhart (b. 1942) grew up in the mountains of western Maryland and attended Johns Hopkins University in Baltimore, where he received an A.B. degree in chemistry in 1964. He carried out doctoral work in physical organic chemistry at UCLA under the direction of Saul Winstein. After receiving his Ph.D. degree in 1968, he spent six months as a National Science Foundation postdoctoral fellow at UCLA with Winstein and Frank Anet. He then spent a year at Southampton University as a NATO

postdoctoral fellow, where he began studying organometallic chemistry. Brookhart joined the University of North Carolina faculty in 1969 and retired as a William R. Kenan, Jr. professor of chemistry in 2014. In 2015 he joined the faculty at the University of Houston to conduct joint research with Prof. Olafs Daugulis. He has spent sabbaticals in Rennes, Oxford, Berkeley, Seville, Marburg, and the Max Planck Institute in Mülheim. From 1990 to 1996 he served as an Associate Editor of *Organometallics*.

The list of recognitions along his career is impressive (Table 1). He has been the recipient of *four ACS national awards*: Organometallic Chemistry (1992), A. C. Cope Scholar (1994), Polymer Chemistry (2003), and the Somorjai Award for Creative Research in Catalysis (2015). He was elected to the U.S. National Academy of Sciences in 2001.

Table 1. Selected Awards and recognitions

| | |
|-----------|---|
| 1986 | Chair, GRC on Organometallic Chemistry |
| 1989-91 | ACS Petroleum Research Fund Advisory Board |
| 1990-1996 | Associate Editor, <i>Organometallics</i> |
| 1992 | ACS Award in Organometallic Chemistry |
| 1994 | ACS A. C. Cope Scholar Award |
| 1995 | National Science Council (Taiwan) Distinguished Lectureship |
| 1995 | Japan Society for the Promotion of Science (JSPS) Fellowship |
| 1996 | American Academy of Arts and Sciences Fellow |
| 1997-2001 | Medicinal Chemistry Study Section, DRG, NIH |
| 1998 | PMSE Cooperative Research Award in Polymer Science and Engineering with L. K. Johnson |
| 1998 | Charles H. Stone Award (Piedmont Section, ACS) |
| 2000 | Royal Society of Chemistry Centenary Lecturer |
| 2000 | Honorary Doctorate, University of Rennes, France |
| 2001 | Fellow, American Association for the Advancement of Science |
| 2001 | Senior Humboldt Research Fellowship |
| 2001 | Member, National Academy of Sciences |
| 2002-2006 | Chemistry Division Review Committee, Los Alamos National Laboratory |
| 2003 | ACS Award in Polymer Chemistry |
| 2007 | ACS Sierra Nevada Section Distinguished Chemist Award |
| 2008 | North Carolina Award in Science |
| 2010 | Willard Gibbs Medal |
| 2015 | ACS Gabor A. Somorjai Award for Creative Research in Catalysis |
| 2016 | Oesper Award |

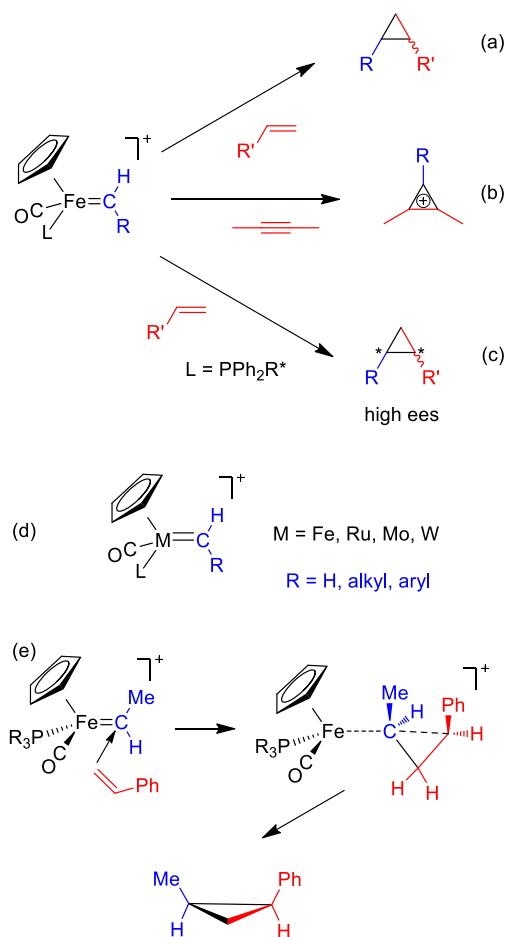
SELECTED ACHIEVEMENTS

Throughout his career, Brookhart has used a mechanism-based approach toward understanding fundamental organometallic reactions, with a particular interest in highly electrophilic complexes of the middle and late transition metals. This approach has been paired with a deep interest in novel types of catalysis and exploratory organometallic chemistry. Indeed, one hallmark of the Brookhart group is the broad range of chemistries explored. We briefly describe five key research areas from different eras of Brookhart's career below, including a bit of context to show how these seemingly diverse projects evolved and are intertwined.

Transition-metal carbene complexes

A breakthrough early in Brookhart's career was the discovery and development of cationic, highly electrophilic

Scheme 1. Isolated transition-metal carbene complexes and selected reactions.



secondary transition-metal carbene complexes $[\text{Cp}(\text{L})(\text{CO})\text{Fe}=\text{CHPh}]^+$ ($\text{L} = \text{CO}, \text{PPh}_3$) (Scheme 1).³ These iron species efficiently transfer the benzylidene unit to alkenes and alkynes⁴ to form cyclopropanes and cyclopropenium ions, respectively. (Scheme 1a,b). Reactions of chiral-at-iron complexes produced enantiomerically enriched cyclopropanes (Scheme 1c).⁵ Studies on electrophilic carbene

species were subsequently expanded to include stable methylene and ethylidene complexes of iron⁶ and ruthenium⁷, and methylene and benzylidene complexes of tungsten and molybdenum (Scheme 1d)⁸. These studies coupled with structural analyses and deuterium labeling experiments established details of the carbene transfer reactions.⁹ The most significant finding was that transfer oc-

Scheme 2. Observation of three center, two electron M—H—C bond in Fe (a) and Mn (b). (c) general schematic of agostic interactions.

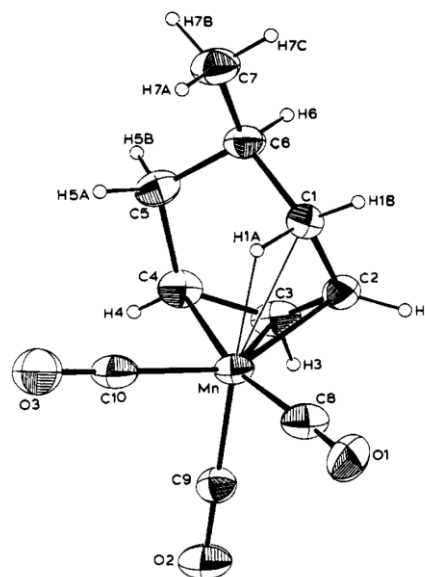
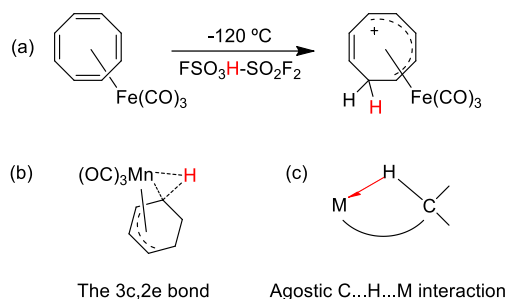


Figure 1. The molecular structure of the complex $[\eta^3\text{-C}_6\text{H}_8(\text{CH}_3)\text{Mn}(\text{CO})]$ (neutron diffraction). Reprinted from *J. Am. Chem. Soc.* (reference 11b).

curred not via a metallacyclobutane-like transition state similar to that observed for olefin metathesis, but rather via addition of the electrophilic metal carbene carbon to alkenes to generate a γ -carbocation followed by backside electrophilic attack on the metal-carbon bond to generate cyclopropanes (Scheme 1e).

Three-center, two-electron M...H...C Interactions: Agostic Bonds

In 1972, the Brookhart group reported that protonation of a cyclohexadiene iron tricarbonyl complex gave an unusual cationic species in which a 3-center, 2-electron (3c, 2e) bonding scheme was proposed as a possible structural

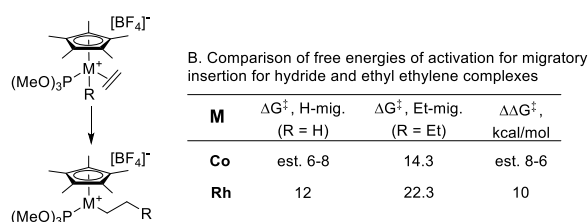
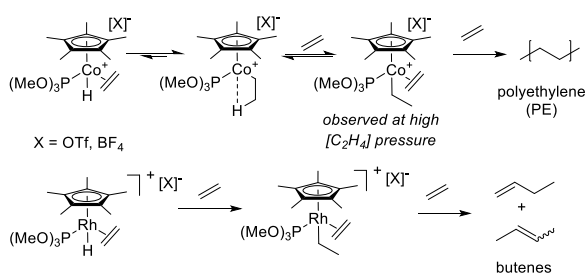
feature (Scheme 2a).¹⁰ In the early 80s, this discovery was followed up by the synthesis and investigation of the structures and reactivities of a series of neutral isoelectronic manganese complexes in which the 3c, 2e bonding scheme was verified (Scheme 2b). Analysis of the dynamics of these complexes showed the M—HC interaction to be on the order of 8–9 kcal/mol.¹¹ A neutron structure of a cyclohexenyl derivative carried out by scientists at Argonne National Laboratory established the precise details of the M—H—C interaction (Figure 1).

The identification of agostic interactions in olefin polymerization spurred an extensive and longstanding research effort in the Brookhart group. Indeed, this is perhaps the most significant and well-known contribution from the Brookhart lab and led to the development of a detailed understanding of the factors governing olefin migratory insertion and polymer chain growth and termination reactions. This led to the development of late-metal olefin polymerization catalysts.

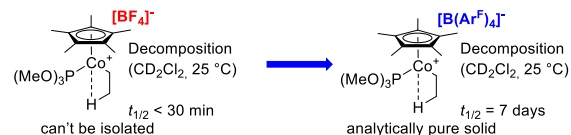
In 1983 Brookhart, Green and Pardy noted that protonation of Cp*Co(L)(ethylene) complexes resulted in an

Scheme 3. Representative agostic intermediates and migratory insertion reactions.

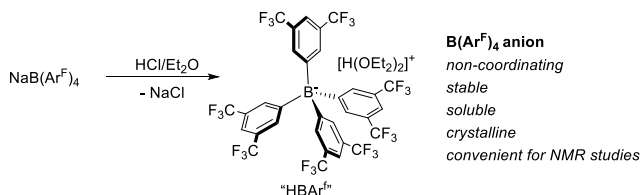
A. Reactions of cationic Cp* Co and Rh catalysts with ethylene



C. Anion effects on catalyst stability



D. Synthesis of "Brookhart's acid"



In 1982–1983, Brookhart spent a sabbatical in Malcolm Green's laboratory in Oxford. Green had identified early transition metal Ti(IV) alkyl species that also exhibited intramolecular (3c, 2e) M—H—C interactions. Together they realized that, in addition to their reports, there were a number of other complexes known that exhibited such intramolecular interactions and that this was a general but not well-recognized phenomenon and an unrecognized feature in many other systems. In a 1983 review,¹² Brookhart and Green summarized all the available evidence for such interactions and the distinguishing features of these types of bonding interactions. The shorthand term, agostic (ancient Greek, 'to hold close to oneself') was suggested by classics scholar Prof. J. Griffin to describe this interaction (Scheme 2c). Indeed, this term is now used extensively and hundreds if not thousands of complexes have been shown to possess such a bonding feature, including numerous additional examples from the Brookhart lab, particularly intermediates in metal-catalyzed olefin polymerizations. The 1983 review together with later reviews in 1988 with Wong¹³ and 2007 with Parkin¹⁴ have been cited thousands of times over the years.

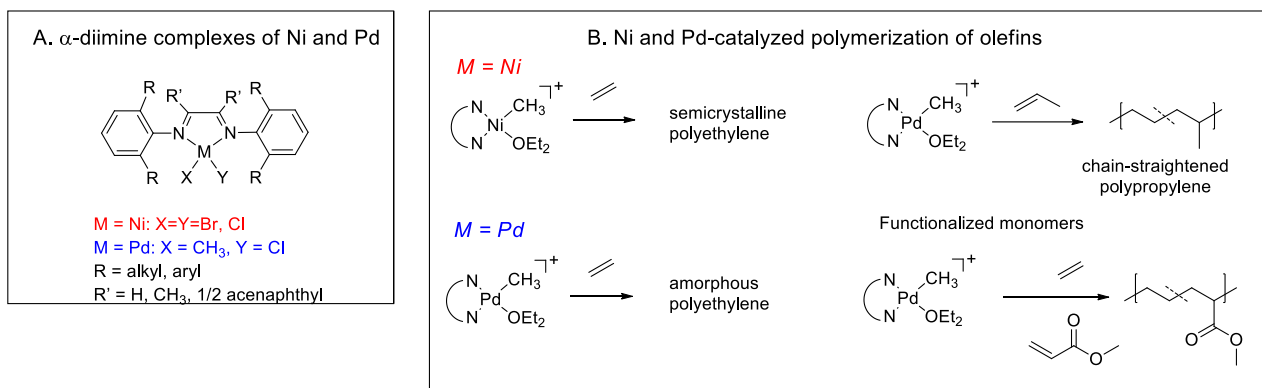
agostic ethyl complex rather than a cobalt ethylene hydride or undistorted ethyl complex.¹² Brookhart later proposed that if the stable form of an ethylene hydride complex is a bridged (agostic) species, then the factors that favor such a bridging hydride structure should also result in a lower energy difference between the analogous olefin alkyl metal complex and thus lower energy of the transition state for migratory insertion which would involve a bridging alkyl group. Because the agostic C—H interaction is readily displaced by incoming ligands, a metal complex possessing an agostic ethyl group should react with ethylene to yield an ethylene alkyl complex which would be expected to undergo rapid migratory insertion. Indeed, the agostic ethyl complex [Cp*(P(OMe)₃Co(CH₂CH₃)]⁺BF₄⁻ was shown to be an ethylene polymerization catalyst at 25 °C where agostic alkyl species are catalyst resting states (Scheme 3A).¹⁵

The Cp*Co alkyl ethylene intermediates are not observable and the lifetime of the catalyst is limited. In collaboration with Horvath (Exxon), high-pressure NMR experiments were performed. The alkyl ethylene intermediate was observed and the barrier of migratory insertion was determined to be 14.3 kcal/mol (Scheme 3B).¹⁶ This was the first NMR observation of an ethylene alkyl intermediate complex and direct measurement of an insertion barrier

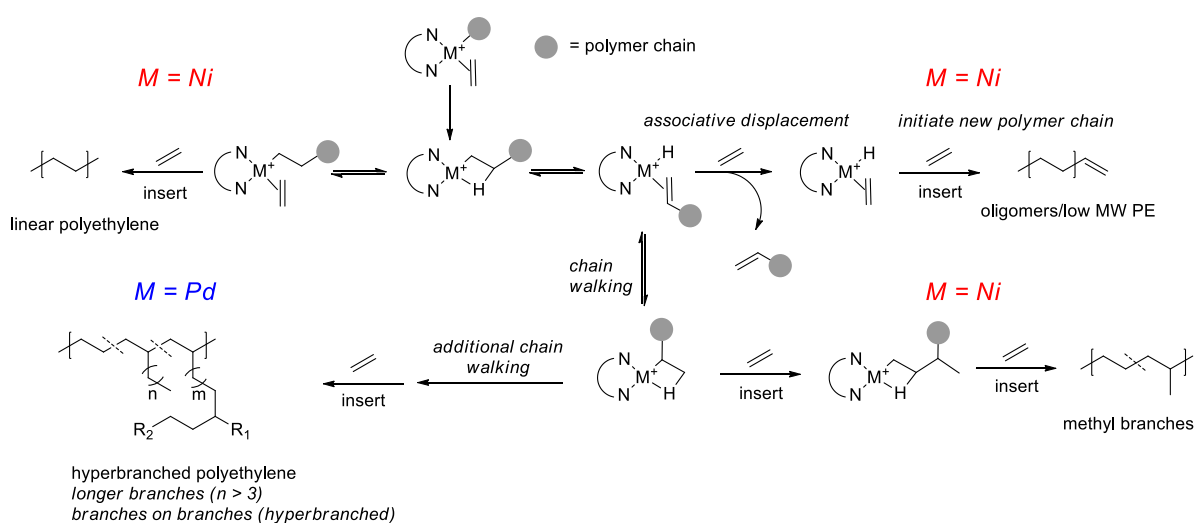
in the copolymerization (Scheme 5b).^{26,27} Investigation of Ni(II) analogs yielded insights into the migratory insertion reactions in these analogs and the importance of five-coor-

isoenriched, optically active poly(4-*t*-butylstyrene-*alt*-CO) and tacticity was determined by enantiomorphic site control. This difference in stereocontrol was used to prepare

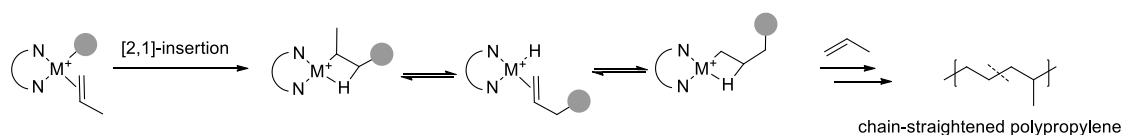
Scheme 6. Ni and Pd α -diimine catalysts for olefin polymerization.



C. Chain-walking leads to branched polymer microstructure



D. Mechanism of chain straightening in propylene polymerization



dinate intermediates.^{28,29}

Similar studies were performed for the copolymerization of *tert*-butylstyrene/CO by cationic palladium complexes of bipyridyl (bpy) and 1,10-phenanthroline (phen). Detailed studies of intermediates revealed that back to back styrene insertions occurred only once in 10^6 insertions.³⁰ Stereoregular, syndioenriched polyketone was isolated (Scheme 5c). The catalyst resting state(s) were determined to be acyl/CO complex(es) with migratory insertion of an acyl/styrene complex being rate-determining. Since the phen and bpy catalysts are not chiral, the polymer tacticity was proposed to result from chain end control. In contrast, palladium complexes of C_2 -symmetric enantiomerically pure bis-oxazoline ligands yielded

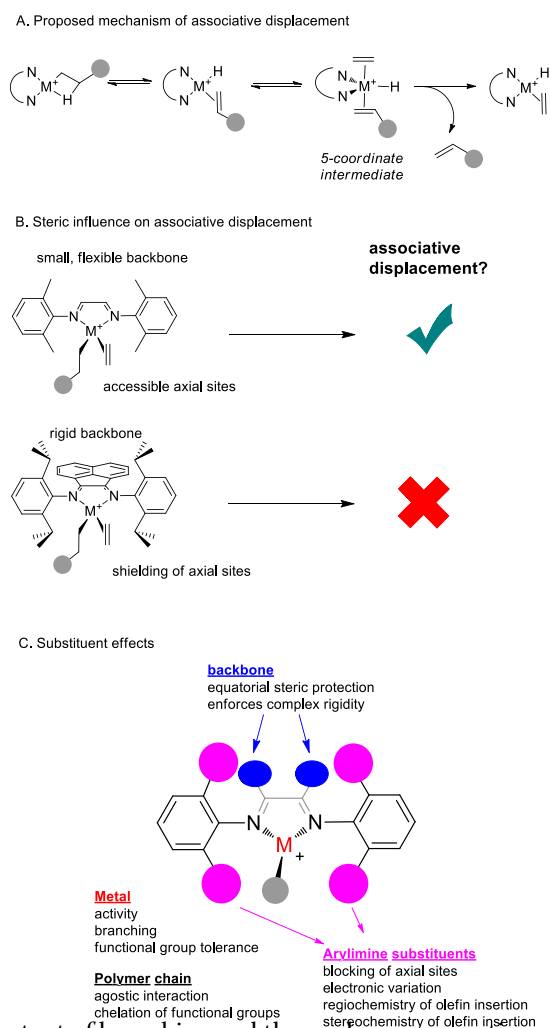
stereoblock copolymers were prepared by performing irreversible ligand exchange without chain transfer or catalyst decay.³¹

Late-Metal Olefin Polymerization and Copolymerization Catalysis

In 1992, during the course of extending these studies to nickel, Lynda Johnson found that the solubility of the (phen)Ni complexes was very low, rendering detailed NMR studies difficult. She then began studying bulky α -diimine analogs. These studies led to the discovery of the first late metal catalysts for the homopolymerization of ethylene; we think this is by far the most significant and well-known breakthrough from the Brookhart group. The α -diimine Pd

complexes are active catalysts for the polymerization of ethylene and α -olefins to high molecular weight, amorphous polymers with unique hyperbranched microstructures (Scheme 6).³² The nickel systems exhibit similar behavior but with much higher activities, in some cases approaching that of early metal catalysts. Although the nickel complexes also yield branched polymers, the branch number is lower and predominantly methyl branches are formed. In both metals, the branching is a result of “chain walking,” which is a unique mechanistic feature of these catalysts. The palladium complexes yielded highly branched amorphous polymers which resulted from chain walking in which the palladium was able to migrate along the chain prior to the next insertion. In the case of nickel,

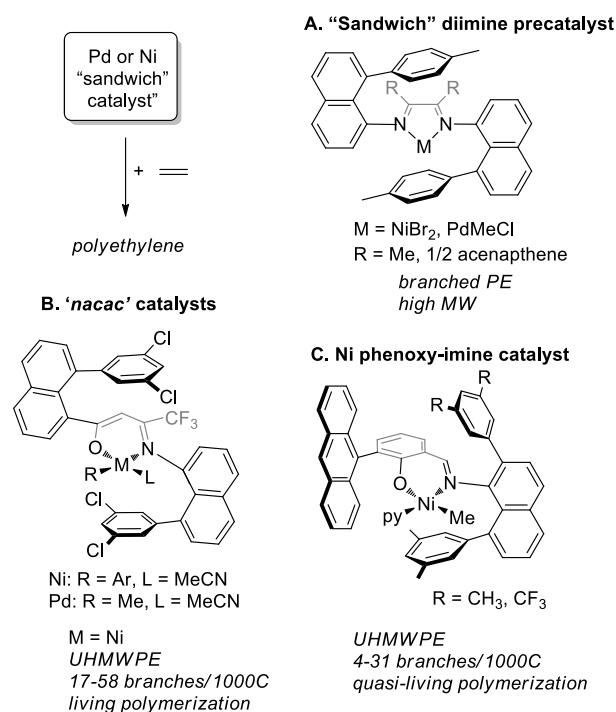
Scheme 7. Key points for catalyst design in the nickel and palladium olefin polymerization systems.



the extent of branching and thus polymer properties could be controlled via variation of temperature and pressure: increased pressure or decreased temperature reduced branching and thus polymer properties could be varied from amorphous to linear high-density polyethylene. Polymerization of α -olefins resulted in polymers with fewer branches than expected. This chain straightening polymerization is a result of 2,1 insertion followed by chain

walking to a primary carbon prior to the next olefin insertion event. The catalyst resting state(s) were alkyl olefin complexes and the turnover-limiting step was migratory insertion, thus the rate of chain growth was independent of olefin concentration. The key structural feature of these systems which allowed polymerization (rather than expected dimerization or oligomerization) was incorporation of axial bulk via the ortho-aryl substituents which retarded chain transfer which occurs via an associative process (Scheme 7A). This landmark article³² with thousands of citations sparked intense interest and activity in both industrial and academic labs which continues to this day. The simple idea of designing bidentate ligands which incorporate tunable axial and equatorial bulk opened up the investigation of numerous new catalyst designs incorporating

Scheme 8. Second generation imine catalysts for olefin polymerization.



this feature.³³

An intriguing property of electrophilic late-metal systems is their compatibility with functional groups in contrast to electrophilic early metal catalysts. The Brookhart group demonstrated that the palladium diimine catalyst was able to copolymerize ethylene with methyl acrylate to yield highly branched high molecular copolymers with ester groups on the end of branches (Scheme 6B). Mechanistic studies showed a chelate complex involving the ester group as the catalyst resting state.³⁴

A major effort aimed at investigating the α -diimine catalysts and related systems was launched following Johnson’s initial discovery and was additionally fueled by a close collaboration with DuPont. In-depth mechanistic studies proceeded over the next few years and provided an

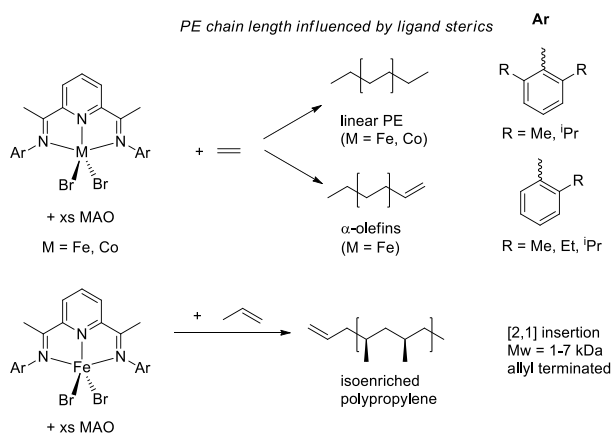
exquisitely detailed picture of the chain-growth processes, including delineation of the catalyst resting states, the barriers to migratory insertions in the palladium and nickel α -diimine systems, the observation that the intermediate alkyl complexes were β -agostic species together with the measurement of the barriers to chain walking in these systems.^{35,36}

Synthetic efforts continued with elucidation of living polymerizations of ethylene and α -olefins and generation of block copolymers,³⁷ analysis of the microstructures of poly(α -olefins),³⁸ and a detailed description of temperature, pressure and substituent effects on the microstructures of poly(ethylene)s generated from nickel α -diimine catalysts (Scheme 7C).³⁹

In 2013, Brookhart initiated a collaboration with Olafs Daugulis to study imine ligands containing 8-arylnaphthyl substituents (Scheme 8).⁴⁰ The use of the 8-arylnaphthyl substituents generates palladium and nickel α -diimine complexes with a sandwich-type structure. The capping aryl ligands further retard chain transfer and yield catalysts capable of generating much higher molecular weight polymers. In contrast to the first generation α -diimine ligands, hyperbranched polyethylene was obtained from both the palladium and nickel catalysts. In addition to the sandwich α -diimine complexes, the 8-arylnaphthyl anilines were used to prepare new bulky neutral nickel phenoxyimine catalysts, which were active for the preparation of ultra-high-molecular weight branched polyethylene (UHMWPE). Detailed investigations of the chain-growth process were performed.⁴¹

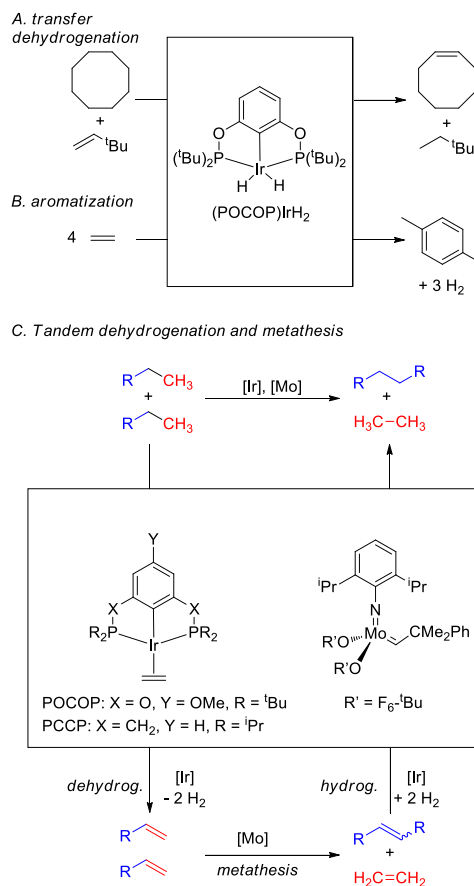
A second major advance in the area of late-metal polymerization catalysts was the discovery that bulky pyridyl diimine-complexes of iron and cobalt complexes (activated with aluminum alkyls) were highly active for ethylene polymerization (Scheme 9).⁴² The iron system was remarkably active, exhibiting a turnover frequency (TOF) of 10 million per hour at 60 °C. As was the case with

Scheme 9. Iron and cobalt catalysts for olefin polymerization.



the nickel α -diimine catalysts, the polymer molecular

Scheme 10. Selected catalytic reactions of [POCOP]Ir complexes.

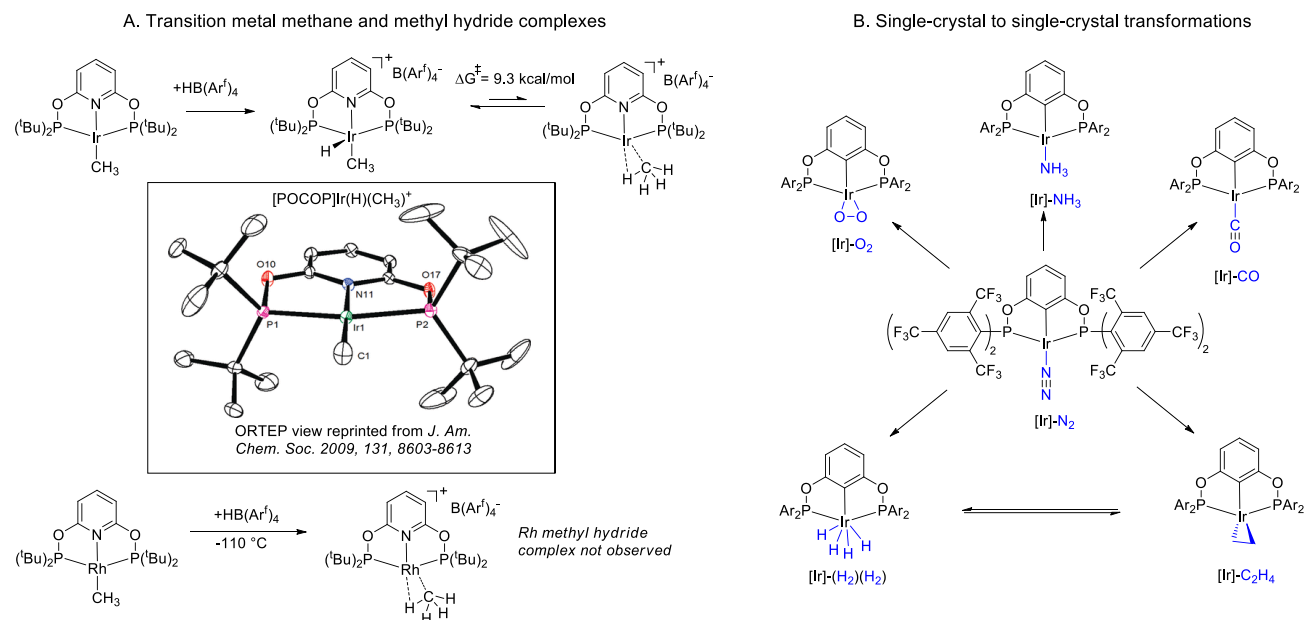


weight may be tuned by varying the sterics of the N-aryl substituents; less-hindered α -diimine iron catalysts were very active for the oligomerization of ethylene to a Shultz-Flory distribution of α -olefins. High selectivity for terminal olefins and remarkable TOFs up to 170 million per hour at 90 °C were observed.⁴³ The iron complex is also active for propylene polymerization, yielding iso-enriched polypropylene.⁴⁴ The iron and cobalt pyridyldiimine catalysts are still the subject of extensive research today, and have found use as earth-abundant catalysts for a variety of transformations, as well as examples of redox-active ligands.

Catalytic Processes Using Carbon Hydrogen-Bond Activation Reactions

Spurred by their ongoing interest in C-H activation chemistry, which arose out of studies of $Cp^*M(olefin)_2$ and Tp^*Pt complexes, in 2004 the Brookhart group reported a series of iridium bisphosphinite pincer ("POCOP") complexes, which catalyze transfer hydrogenation (Scheme 10).⁴⁵ (POCOP)IrH₂-catalyzes the transfer dehydrogenation of cyclooctane in the presence of neohexene, which serves as the hydrogen acceptor. In-depth mechanistic studies were performed., these studies led to a collaboration with Alan Goldman with the goal of developing a homogeneous dual catalyst system for alkane metathesis, funded through an NSF Center for Chemical Innovation

Scheme 11. Methane complexes and solid-state organometallic transformations.



(Center for Enabling New Technologies through Catalysis, CENTC) and led by Karen Goldberg. This team demonstrated that an iridium(I) pincer transfer-dehydrogenation catalyst working in tandem with a Schrock molybdenum olefin metathesis catalyst could achieve homogenous catalytic alkane metathesis. For example, hexane could be converted to ethane and decane by dehydrogenation to hexene, metathesis of hexene to ethylene and decene followed by hydrogenation to the alkanes to close the catalytic cycle (Scheme 10C). This permits inexpensive low molecular weight alkanes to be upgraded into higher value longer chain alkanes. More robust catalytic systems were developed by replacing the homogeneous molybdenum alkylidene catalyst with a rhenium oxide metathesis catalyst supported on alumina.⁴⁶ Additional studies by the CENTC team included development of heterogeneous recyclable iridium dehydrogenation catalysts⁴⁷ and a process for synthesis of *p*-xylene from ethylene as sole feed stock (Scheme 10B).⁴⁸

In collaboration with Goldberg, a study of the dynamics of the reversible cleavage of the C-H bond of methane by an iridium pincer complex⁴⁹ led to the first NMR characterization of a transition-metal methane complex, a cationic Rh(I) pincer complex (Scheme 11A).⁵⁰ An analogous ethane complex was generated, and the barrier determined for end-to-end migration of rhodium (7.2 kcal/mol). An additional noteworthy result by the CENTC team involved discovery of a crystalline fluorinated iridium pincer complex that exhibited a series of single crystal-to-single crystal transformations and selective hydrogenation of ethylene which occurred within the crystal lattice. (Scheme 11B).⁵¹

CONCLUSIONS

In this editorial, we have summarized a few highlights of Maurice Brookhart's many contributions to organometallic chemistry and described how the different areas of research developed and evolved throughout Brook's career. Brookhart's scientific achievements are outstanding, and his legacy as a mentor and collaborator is equally noteworthy. On the occasion of his 80th birthday, we are delighted to be able to revisit some of Brook's "greatest hits" for a new audience, and provide a platform for sharing the research of others whose work has been inspired by Brook's example.

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Notes

Authors declare no competing financial interests.

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