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A Career in Catalysis: Jean-Marie M. Basset

Didier Astruc, Guy Bertrand, Mohamed Eddaoudi, Yu Han, Kuo-Wei Huang, Johannes Lercher, Catherine Santini, Kazuhiro Takanabe, Mostafa Taoufik, and Luigi Cavallo*

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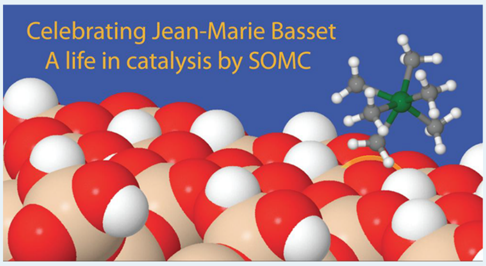
ABSTRACT: This account is to commemorate the retirement of Jean-Marie Basset from the KAUST Catalysis Center after a career spanning almost five decades. Jean-Marie has been a leading figure in the world of heterogeneous catalysis. Rather than studying supported catalysts through the traditional lens of surface science, he brought an approach of molecular organometallic chemistry to the field. In the process, Jean-Marie established the field of surface organometallic chemistry. During the first phase of his career, he pioneered ways to synthesize and characterize well-defined metal sites on oxide and metal surfaces. Through this work, the Basset group could establish structure–activity relationships on supported catalyst materials and also show that the rules known to govern the catalytic cycles of homogeneous catalysts could be employed to understand and enhance heterogeneous catalyst reactions. From this key insight, Jean-Marie developed the concept of heterogeneous catalysis by design, synthesizing surface organometallic fragments that were thought to form a part of the catalytic cycle. From this standpoint, the Basset group has improved the activity, selectivity, and sustainability of numerous known reactions and also discovered multiple reactions, including the Ziegler–Natta depolymerization, the metathesis of alkanes, the coupling of methane to ethane and hydrogen, the cleavage of alkanes by methane, the metathesis of imines, the metathetic cleavage of olefins to aldehydes by molecular oxygen, and the hydro-metathesis of olefins.



KEYWORDS: *homogeneous catalysis, heterogeneous catalysis, surface organometallic chemistry, catalysis by design, alkane metathesis*

■ STARTING CONCEPTS OF SURFACE ORGANOMETALLIC CHEMISTRY (SOMC)

Catalysis is the discipline of chemistry that deals with the rate of chemical reactions between molecules, molecules and solids, and between solids. It is a key discipline of chemical science, and one that has the potential for a major impact on the world economy, and on the future of our planet regarding environment, health, and energy.

Jean-Marie Basset describes his rich and productive, 45-year, independent research career with a concise mission statement. His sole scientific objective, he says, was to bring together two different disciplines: homogeneous catalysis on the one hand and heterogeneous catalysis on the other.

This simple statement encompasses considerable technical challenges. Traditionally, the two major fields of chemical catalysis have belonged to distinct research communities with little apparent overlap. The field of heterogeneous catalysis was oriented toward solid state chemistry and interpreted through the rules of surface science. Homogeneous catalysis research, in contrast, was closely connected with organometallic chemistry, governed in principle by the laws of molecular chemistry.

From the industrial chemistry perspective, heterogeneous catalysis offers key clear advantages of easy product separation and catalyst reuse. From the molecular point of view, however, the processes taking place on the catalyst surface were often poorly understood. The development of improved heterogeneously catalyzed reactions, or the discovery of new reactions, has therefore been a longstanding challenge—but one that has major implications for humanity, with significant potential gains for chemical industry sustainability.

Homogeneous catalysis research, in contrast, has benefited from the considerable structural and molecular mechanistic insights that could be gained from the ready transfer of tools and concepts developed within molecular and organometallic chemistry research.

From the start of his career, Jean-Marie proposed that bringing a molecular chemistry like approach to heterogeneous catalysis could bring significant performance gains. Jean-Marie expected that the rules of molecular chemistry must apply, at least in part, to the rationalization of heterogeneous catalysis phenomena. His guiding and intuitive idea was that all heterogeneous catalysis must involve a “surface organometallic fragment” (SOMF), a reaction intermediate formed by the

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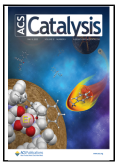

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chemical bond created between the surface and the incoming molecules during the elementary steps of the reaction.

In practical terms, the application of such concepts to industrial heterogeneous catalysis required methods to generate SOMF precursors on structural supports. The Basset group therefore developed "surface organometallic chemistry" (SOMC), which involves taking organometallic complexes derived from molecular chemistry, and reacting them with oxide (or metal) surfaces to produce a new family of heterogeneous catalyst with well-defined structural features.[1−6]

Jean-Marie thereby pioneered a new discipline of chemistry that has generated numerous improved or entirely new heterogeneous catalytic reactions. Along the way, he published more than 700 publications, took 68 patents, with the help of about 140 Ph.D. or postdocs. He established from scratch a world-renowned center for catalysis at the King Abdullah University of Science and Technology (KAUST), Saudi Arabia, that will be a long-standing legacy of his vision.

TOOLS OF SOMC

In 1970, Jean-Marie left France to take up postdoctoral fellowships at the University of Toronto with W. F. Graydon, and then at Imperial College London in the group of Geoffrey Wilkinson. His stay with Wilkinson, Nobel laureate with E.O. Fischer in 1973, convinced him of the strength of homogeneous catalysis to rationalize heterogeneous catalysis. When Jean-Marie returned to France in 1975 to commence his independent research career, it was to take up a position at the Research Institute on Catalysis (IRC), where he later followed in Marcel Prettre's footsteps to become vice-director of the institute (Figure 1).

Figure 1. At the Couturier Defense: Jean-Marie Basset (front right) with Yves Chauvin (front left), Jacques Gore (middle left), Michel Leconte (upper right), John Osborn (middle right), and Agnes Choplin (middle right).

In the 1970s, industrial heterogeneous catalysts largely remained "black box" materials. Even when the catalyst surface could be characterized, the small number and the diversity of metal sites on the surface of heterogeneous catalyst prepared by traditional impregnation protocols, increased the challenge of identifying catalytically active sites. Lack of knowledge on the active catalyst structure largely precluded rational improvement of catalyst performance.

Grafting well-defined organometallic fragments onto surfaces such as metals or oxides, potentially, was recognized by Jean-Marie to represent a method for generating heterogeneous catalysts with well-defined active sites. To pursue this molecular chemistry-like approach to heterogeneous catalysis, the Basset group identified that the first step was to develop new specific tools to interrogate and characterize the molecular structure of catalytic clusters on surfaces. These tools were essential to establish the structure of organometallic complexes formed on surfaces, from which the structure−activity relationships of these new types of catalyst could be probed. Most of these tools appear to be in situ spectroscopic techniques, including in situ infrared (IR), in situ X-ray photoelectron spectroscopy (XPS), in situ extended X-ray absorption fine structure (EXAFS), in situ microanalysis to name a few.

But solid-state 1D and 2D nuclear magnetic resonance (NMR) spectroscopy has also proven a powerful technique for SOMC structure determination. The Basset group has continued to contribute advances in the characterization techniques for SOMC catalysts. One enduring research topic has been the characterization of tantalum organometallic complexes on silica support. In the study of one such grafted tantalum complex, $[(\equiv SiO-)Ta(=CH^{t}Bu)(CH_2{}^{t}Bu)_2]$, the Basset group demonstrated the value of 2D HETCOR solid-state NMR spectroscopy to unequivocally assign ^{1}H and ^{13}C chemical shifts for surface organometallic complexes.[7] In the same study, the team confirmed that polyhedral oligomeric silsesquioxanes are a good solution-state model of partially dehydroxylated silica, from which information could be inferred about the coordination sphere of metal complexes directly supported on oxides such as silica. A strong collaboration with Lyndon Emsley, Swiss Federal Institute of Technology in Lausanne, began during this period.

Recently, the Basset group extended insights into the formation of silica-supported tantala-aziridine intermediates $[(\equiv Si-O-)Ta(\eta^2\text{-}NRCH_2)(\text{-}NMe_2)_2]$ using solid-state NMR. This study exemplifies Jean-Marie's approach of combining detailed structural characterization with computational modeling, in the form of density functional theory (DFT) calculations, to gain additional mechanistic insights.[8]

Jean-Marie is quick to acknowledge that his early focus on thorough characterization of surface organometallic complexes may initially have slowed progress in the new field of surface organic chemistry.[2] However, the strong foundations laid down by the development of advanced characterization tools ultimately underpinned a new branch of chemistry, and Jean-Marie's entire career of catalyst development.

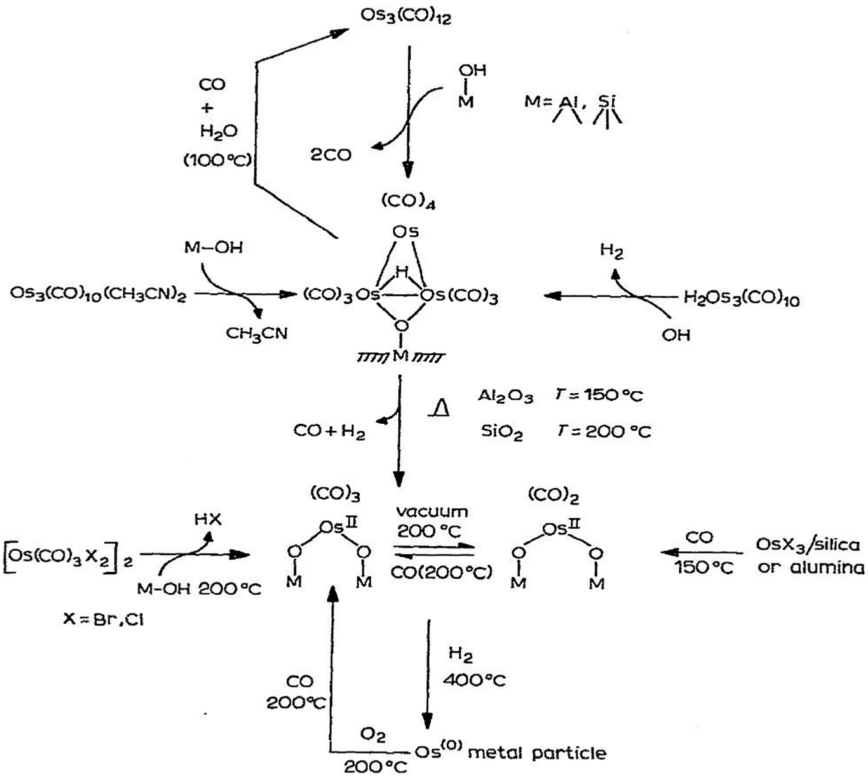
BONDING BETWEEN CHEMISORBED MOLECULES AND METALLIC PARTICLES

Jean-Marie initially used IR spectroscopy to illuminate the nature of surface-bound catalytic metal complexes. Infrared spectroscopy of the chemisorbed CO "ligand" provided early evidence that the rules of molecular chemistry, known to govern organometallic chemistry (the $\sigma-\pi$ type of bonding (Duncanson model)) its structure and reactivity, also at least partially applied to surface-adsorbed complexes.

Jean-Marie's forays into this space were stimulated by studies published in the late 1960s and early 1970s, while undertaking his Ph.D. and postdoctoral training, which examined the IR signal of CO bonded to supported and unsupported platinum. In these studies, he noted the observed $\nu(CO)$ frequency appeared to shift when different gases interacted with the metal.

As already described, adsorption on platinum involves two forms of bonding. In addition to the σ bond, a π bond is formed

Scheme 1. Early explorations of the reaction of osmium carbonyl clusters on oxide supports. Reproduced with permission from ref 19. Copyright 1981, Elsevier B.V.



by back-bonding of metal d electrons to an antibonding orbital of CO. Jean-Marie showed that the ν(CO) vibration of CO adsorbed on platinum is very sensitive to the extent of the back bonding.[9] When Lewis bases such as ammonia or pyridine were adsorbed on platinum, the effect of the adsorbed base was to increase the electronic density of the platinum crystallite and the back-donation to the carbonyl group. This resulted in a shift of ν(CO) frequency toward low wave numbers.

Conversely, when electron-acceptor atoms such as chlorine or oxygen were attached to platinum, the back-donation is lowered, resulting in a shift of the ν(CO) frequency toward high wave numbers. The highest upward shift was observed when two chlorine atoms were adsorbed on the same platinum atom as CO.

This systematic study showed that the ν(CO) shift could be used to probe the bonding state of molecules adsorbed on metals' surface. Through this work, Jean-Marie discovered the first analogies between the bonding in chemisorbed species and the bonding of ligands in organometallic chemistry. The study extended the Dewar−Chatt−Duncanson model, which described chemical bonding in transition metal organometallic complexes involving ligands with orbitals available for back-bonding: it showed that it was analogous to the bonding behavior metals on surfaces when they feature ligands such as CO with orbitals available for back-bonding.

Following the publication of this study, CO IR spectroscopy was widely adopted as a tool to study adsorbed species on surface-supported metallic elements. The Basset group went on to explore the IR signature of other ligands absorbed to supported metals, including showing for example, that benzene interacts with individual supported platinum atoms by means of a π complex.[10]

Through such work, Jean-Marie progressively discovered that the bonding of chemisorbed species, especially on metal particles, could be rationalized by the Green formalism of ligand coordination to the metal. As with molecular organometallic complexes, ligands bonded to chemisorbed metals could be classified as X, L, or Z depending on whether the ligand donates one, two, or zero electrons.

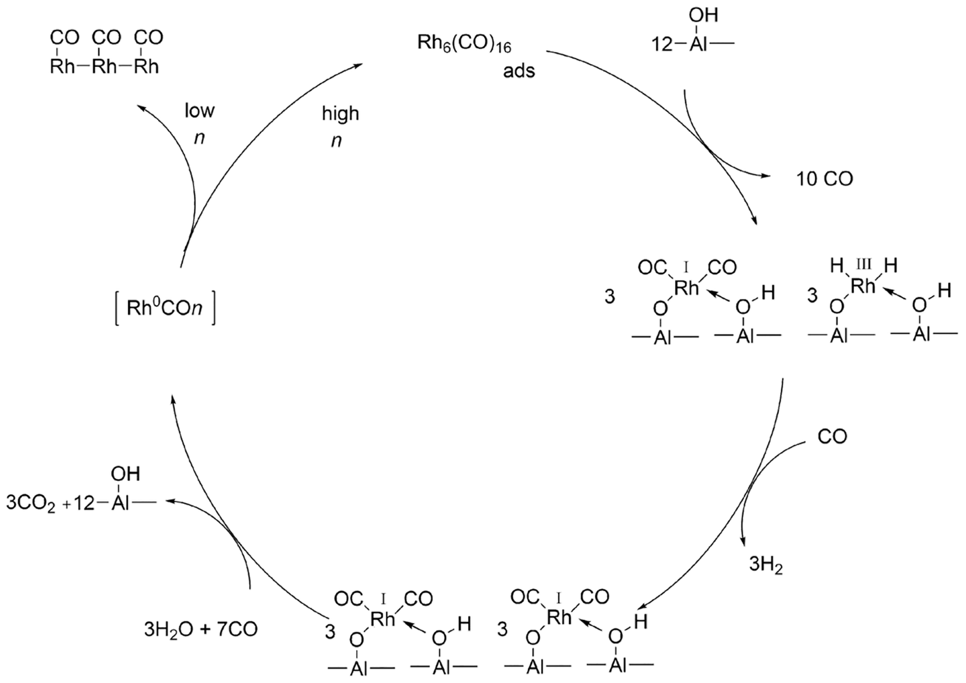
■ THE CLUSTER SURFACE ANALOGY

During the mid-1970s, Jean-Marie was in the vanguard of researchers who noticed a potential new way to study one major group of heterogeneous catalysts, which consisted of nanoparticles of transition metal atoms adsorbed onto a surface. In each case, the catalytic entity was thought to consist of a small number of metal atoms.[11] In 1975, Jean-Marie noted the potential analogy between these supported metal nanoparticles, and discrete molecular transition metal cluster complexes. He was the first to report on the analogy between small nanoparticles of Pt and molecular Pt clusters.[12] These giant molecular clusters were made, at that time by the late Paolo Chini. A typical example was $(Pt_{38}(CO)_{44})^{2-}$.[13]

At that period Basset's important scientific collaboration and friendship with Renato Ugo, also a pioneer in the field of relations between homogeneous and heterogeneous catalysis, has to be mentioned.[14] Starting from 1977 an important and stimulating scientific collaboration was born between the Basset group and that of Ugo in Milano, which led to the development of SOMC.

Unlike supported metal nanoparticles, which remained difficult to characterize at the atomic and molecular level, cluster complexes were relatively easily characterized and their reactions, both stoichiometric and catalytic, could be followed by kinetic and spectroscopic analysis. Cluster complexes

Scheme 2. Rhodium carbonyl clusters supported on alumina catalyze the water−gas shift reaction. Adapted with permission from ref 21. Copyright 1982, Royal Society.



therefore potentially represented more readily studied models for chemisorption and for heterogeneous catalysis by metal surfaces.

Jean-Marie's study of the cluster/surface analogy really opened the field of SOMC. The initial idea that he explored was that nanoparticles in heterogeneous catalysis and molecular cluster have a metallic frame, so the molecular clusters could be adsorbed onto a surface by reversible loss of a ligand such as CO.

Extending his work studying surface-supported metals via the IR spectra of their CO ligands, Jean-Marie examined a series of transition metal cluster complexes, such as the rhodium cluster compound $Rh_6(CO)_{16}$, which possessed activity as a homogeneous catalyst for oxidation and hydrogenation reactions.[11] Jean-Marie studied the adsorption and decarbonlyation of $Rh_6(CO)_{16}$ onto an alumina surface.[15] He showed that a partially decarbonylated metal cluster quickly formed on the surface of silica by oxidation at room temperature. This process could be reversed to regenerate the initial cluster compound by heating under a carbon monoxide atmosphere at 200 °C. Decarbonylation of $Rh_6(CO)_{16}$ at higher temperatures produces a new metallic material on the surface, characterized by two distinct ν(CO) vibration bands, from which the initial cluster complex could not be regenerated.

The team soon expanded the carbonyl cluster compounds under investigation, to include osmium clusters such as $Os_3(CO)_{12}$. The team demonstrated reaction between the cluster and oxide surfaces including alumina, silica and magnesia.[16,17] The osmium cluster was initially weakly physisorbed onto the silica surface, the Basset group found. Upon heating, however, it reacted with the surface by oxidative addition of the silanol group into the Os−Os bond of the triangular frame (Scheme 1). Upon further heating, the cluster was destroyed through reaction with hydroxyl groups on the support, producing mononuclear osmium fragments.[18,19]

The starting metallic frame hypothesis had proven to be wrong. However, by exploring the cluster/surface analogy, completely new chemistry was emerging based on the controlled synthesis of surface-supported organometallic fragments. This work effectively launched the new field of surface organometallic chemistry.[1] The novel materials that could be obtained via the emerging field of SOMC had clear potential as a new form of heterogeneous catalyst, and the application of surface organometallic chemistry on oxides to heterogeneous catalysis developed fast. Jean-Marie showed that the water−gas shift reaction could be catalyzed by oxide-supported rhodium clusters, including $Rh_6(CO)_{12}$ adsorbed on alumina and $Rh(CO)_2Cl_2$ adsorbed on alumina or certain zeolites (Scheme 2).[17,20]

The transition metal cluster complexes underpinning these new supported catalyst materials had shown potential as homogeneous catalysts; however, one major challenge was that, in their molecular form, the catalytically active coordinatively unsaturated species tended to fragment or form colloidal metal particles, with loss of catalytic function. By developing methods to adsorb cluster complexes onto an oxide support, the catalytically active species could be stabilized, and kept separate, overcoming this challenge.

For example, osmium carbonyl clusters were active but were unstable Fischer−Tropsch catalysts. Studying silica-supported osmium complexes, and their molecular counterparts, as ethylene hydrogenation catalysts, the Basset group showed how the molecular species was transformed under catalytic reaction conditions. The supported catalyst, however, retained its structure and activity, demonstrating the value of surface stabilization.[22]

Surface organometallic chemistry on oxides was expanded to other transition metal cluster carbonyls,[23] and SOMC on oxides has subsequently been developed and extended to include almost all the elements of the periodic table. SOMC was turning out to offer a significant step forward on the path to bring a molecular chemistry-like understanding to heterogeneous catalysis, with the potential for rational improvement in design.

■ THE SOMC ON METALS

The success of Jean-Marie's surface organometallic chemistry on oxides soon raised the possibility that this new chemistry could be extended to other types of surfaces. One fruitful exploration by the Basset lab, was surface organometallic chemistry on metals. Surface organometallic fragments could be stabilized on zerovalent metals, the team helped to show, leading to surface metal alloys. In particular, SOMC-on-metals research in Basset's lab developed into an effective approach for the controlled synthesis of supported bimetallic catalysts.[24]

Metallic surfaces, which consist of a transition metal on a SiO_2, ZrO_2, or Al_2O_3 support, prepared using conventional ion exchange methods followed by hydrogenation, have an established history of use in heterogeneous catalysis. However, it was also clear that catalyst activity and selectivity could often be enhanced by switching from a monometallic to a bimetallic catalyst.

SOMC potentially offered an improved way to produce novel bimetallic catalysts for a wide range of chemical transformations. In addition, the use of controlled surface reactions to generate well-defined bimetallic surfaces potentially offered a way to explore and understand the enhanced reactivity of bimetallic catalysts.

The first step was to develop methods to graft organometallic compounds onto metals. As the attachment of organometallic carbonyl clusters onto a metallic surface inevitably generates carbon monoxide, which can poison the metal, this required new synthetic modes for bonding organometallic clusters onto metal surfaces. In 1984, a series of reports showed that group IVa alkylmetals could be reacted with supported metallic surfaces to generate bimetallic catalyst systems.

Exploring the chemistry of this grafting reaction, Jean-Marie discovered that the surface reaction depends heavily on the oxidation state of the metal surface, with reduced metal surfaces producing the best results. The Basset group extended this chemistry to generate a range of bimetallic compounds, by reacting various reduced group VIII metal surfaces with alkyl complexes of groups II, III, IV, and VI.[24]

In one early example, Jean-Marie studied the reaction of $Sn(n\text{-}C_4H_9)_4$ with NiO/SiO_2 to generate a bimetallic Ni−Sn alloy. Changing the ratio of nickel and tin in the initial surface reaction enabled the team to alter the composition of the resulting bimetallic alloy. The material showed high selectivity in the catalytic hydrogenation reaction of ethyl acetate to produce ethanol.[25]

Similar catalytic results were seen with bimetallic Rh−Sn and Ru−Sn prepared by SOMC. Kinetic studies offered insights into the improved selectivity of the bimetallic catalyst toward alcohol formation from the ethyl acetate starting material, compared to a monometallic catalyst. The study suggested that single rhodium atoms isolated between tin atoms were the active site for the reaction.[26,27]

In line with his mission to bring a molecular chemistry-like approach to the study of heterogeneous catalysis, Jean-Marie continued to delve into the mechanism and ultimate structure of bimetallic catalysts produced by SOMC methods. He detailed the stepwise nature of the selective hydrogenolysis reaction between $Sn(n\text{-}C_4H_9)_4$ and the supported rhodium surface, using techniques including NMR and IR analysis to characterize the surface. By systematically varying the reaction temperature, and the quantity of the organometallic compound introduced, his team was able to generate partially dealkylated catalysts, $M[M'Rx]y$/oxide with desired values of x and y.[28]

The Basset group also applied thorough characterization to the bimetallic surface organometallic complexes such as formed between silica-supported rhodium and $Sn(n\text{-}C_4H_9)_4$. Applying a barrage of methods including EXAFS, IR spectroscopy, Mossbauer spectroscopy, and (XPS), the team established that by controlling the temperature they could generate partially dealkylated bimetallic catalysts with the formula $[Rh_sSn(n\text{-}C_4H_9)_2/SiO_2$. Molecular modeling suggested that, due to steric crowding, the material most likely had the complex structure $(Rh_s)_2Sn[Sn(n\text{-}C_4H_9)_3]_2$, involving a bridging tin atom.

In related work, Jean-Marie delved deep into the catalytic dehydrogenation of isobutane to isobutene by bimetallic platinum−tin catalysts.[29] These catalysts, when prepared by conventional coimpregnation methods to simultaneously impregnate a support with platinum and tin salts, had already shown improved activity and selectivity for isobutane dehydrogenation. However, this method of catalyst production did not exclusively generate the desired bimetallic particles: some monometallic tin and platinum particles also formed on the support surface, hampering selectivity and activity.

The Basset group overcame this limitation by applying the more controlled synthetic methods of SOMC to prepare well-defined bimetallic supported platinum−tin particles.[29] After characterization of the surface by elemental analysis, transmission electron microscopy, and IR chemisorption studies, catalyst performance at various platinum−tin ratios was measured. At a tin/platinum ratio of 0.85, the catalytic dehydrogenation of isobutane to isobutene reached selectivity greater than 99%, and with high activity, compared to monometallic platinum. The selectivity could be rationally explained by the single site effect, as isolating the platinum atoms between tin atoms suppressed several potential side reactions that could occur on surfaces featuring adjacent platinum atoms. The increased activity could be explained by the inhibition of coke formation.

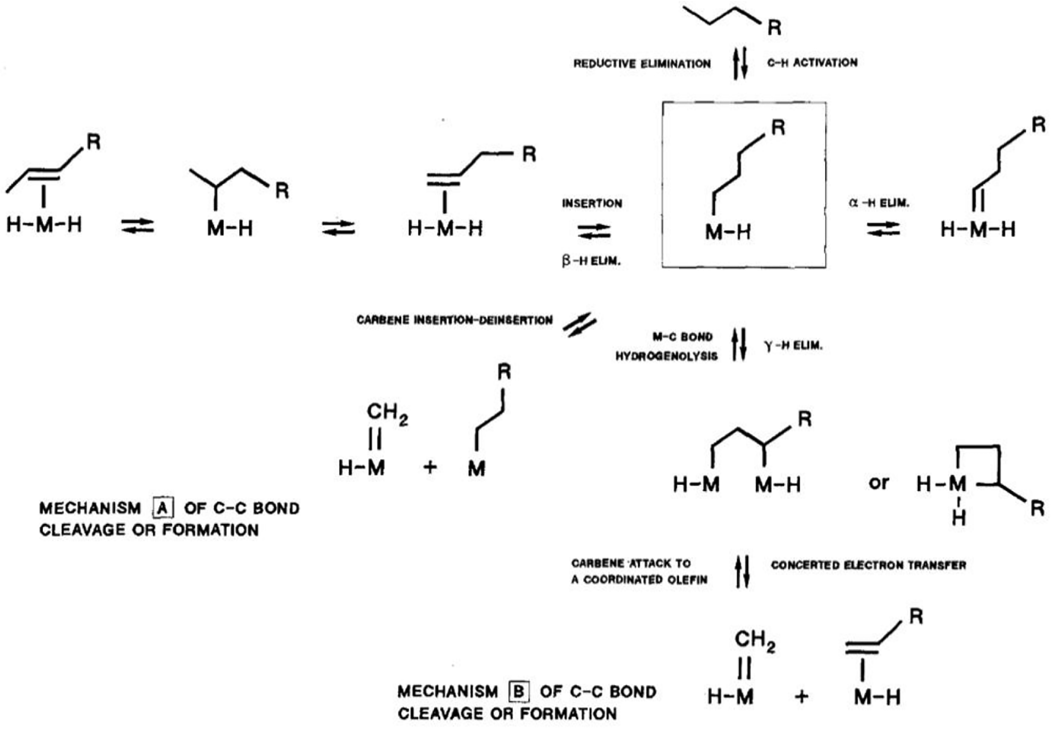
Jean-Marie continued to revisit and extend the field of SOMC on metals over the years. When interest in catalytically active gold nanoparticles began to grow, the Basset group applied SOMC principles to synthesize supported gold nanoparticles.[30] Well-defined and perfectly dispersed $[(\equiv SiO-)AuI]$ surface species supported on silica were produced, and readily transformed to gold nanoparticles supported on passivated silica. These particles were active in aerobic epoxidation and in the preferential oxidation of CO.

SOMC on metals also had applications beyond the synthesis. For example, Jean-Marie showed that supported nickel surfaces coated with hydrogen were able to adsorb toxic Cd^{2+} ions from wastewaters.[31] In the presence of Cd^{2+}, a redox reaction between the heavy metal ions and adsorbed hydrogen occurred, resulting in the release of two protons and the adsorption of $Cd^{(0)}$ onto the Nickle surface. This efficient capture of cadmium, and related toxic metal ions, offered a method of water purification for environmental protection.

■ THE MODES OF C−C BOND FORMATION IN HETEROGENEOUS CATALYSIS ON METALS

The Basset group's detailed study of the supported catalysts on metal prepared by SOMC, and the team's analysis of the carbon−carbon bond forming reactions catalyzed by these

Scheme 3. Mechanism of C−C bond and cleavage both in FT synthesis and olefins homologation with Ru nanoparticles. Reprinted with permission from ref 34. Copyright 1991, Elsevier B.V.



supported structures, proved to be a key opportunity to integrate certain concepts of homogeneous and heterogeneous catalysis. For Jean-Marie, extending the analogy between molecular chemistry and surface chemistry, to explore the mechanism of catalysis of heterogeneous SOMC on metals, was the next logical step in this work.

On the basis of his in-depth characterization of these well-defined catalytic surfaces, the research showed similarities between the elementary steps of carbon−carbon bond formation on molecular catalysts, and on the new surface catalysts the Basset group was generating.

One area of exploration was in the mode of C−C formation in Fischer−Tropsch synthesis and olefin homologation reactions catalyzed by SOMC on metals.[32] The team found that with Fe, Ru, Os, and Rh supported on silica, the selectivity of these two reactions was identical. This result suggested each reaction proceeded via the same mechanisms of C−C bond formation, in which C1 fragments add to the olefin carbon skeleton.[33]

The generation and addition of C1 fragments was found to be key in the homologation and hydrogenolysis of linear and branched butenes and butanes on Ru/SiO_2 catalysts.[34] On the basis of factors including the characterization of the catalyst surface, and the influence of the structure of the starting hydrocarbon on observed product ratios, two simple mechanisms were proposed to explain the simultaneous and reversible nature of the C−C bond cleavage and formation reactions involved in the homologation and hydrogenolysis process (Scheme 3). The reaction may proceed via the insertion−disinsertion of a metallocarbene into (or from) a metal−alkyl species (mechanism A), or via the formation−rearrangement of a dimetallacyclopentane intermediate (mechanism B). The latter mechanism has progressively become the more accepted reaction.

The intermediates involved in these mechanisms Jean-Marie found to be common to a wide variety of reactions of hydrocarbons that occur on metallic surfaces. For example, as discussed in the previous section, the selective dehydrogenation of isobutane into isobutene on supported bimetallic platinum−tin catalysts was a reaction that received detailed attention in the Basset lab. As well as examining the dehydrogenation reaction, they also explored the carbon−carbon bond formation reactions leading to the side products seen on monometallic platinum on silica. The metallocarbene insertion−disinsertion mechanism, or the dimetallacyclopentane intermediate formation-rearrangement, could again explain the observed reaction products (Scheme 4).[35]

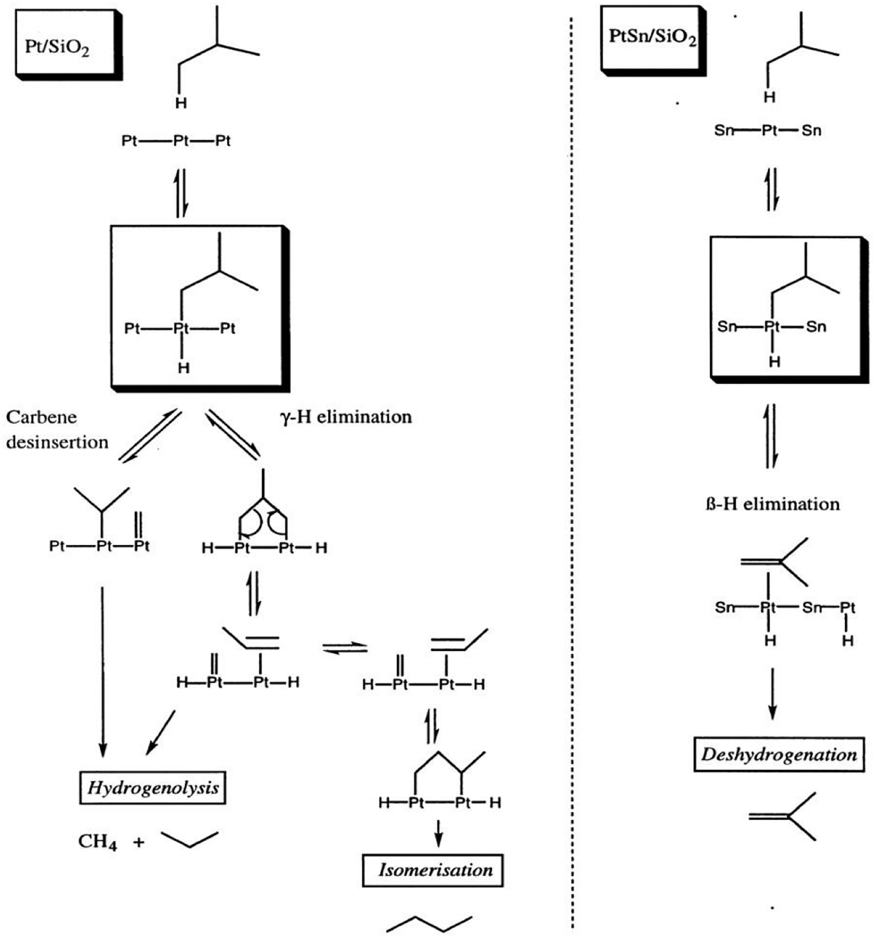
■ CATALYSIS BY DESIGN

Jean-Marie's development of metal hydride SOMFs therefore represented a rich new chemistry, including the transformation of polyethylene to diesel range gasoline or the transformation of polypropylene to polyethylene plus methane. However, they also offered a potential method for the recycling of all polyolefins, a very important target for plastic recycling, that Jean-Marie is now developing through a startup company, JMB SAS. Catalysis by design was gathering momentum, and Jean-Marie's early career bid to unite the rules and concepts of heterogeneous and homogeneous catalysis was paying spectacular dividends.

The mid-1990s, 20 years into Jean-Marie's independent research career, marked a key inflection point in his work. The various strands of his investigations into SOMC based catalysis came together to enable the major new theme that characterized the rest of his career: heterogeneous catalysis by design.

Traditional heterogeneous catalysis progressed by trial and error. The traditional methods for heterogeneous catalyst production had produced ill-defined, structurally diverse

Scheme 4. Explanation of PtSn effect on the selectivity of isobutane dehydrogenation. Reprinted with permission from ref 35. Copyright 1998, Elsevier B.V.



surfaces, which had often precluded the identification of the catalytically active sites. With this critical lack of structural information, it had been highly challenging to establish structure–activity relationships in heterogeneous catalysis research.

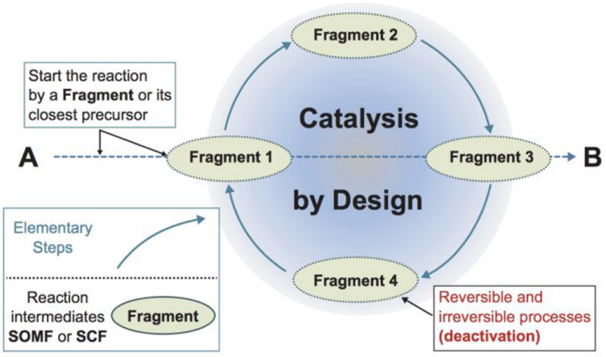
In the initial phases of Jean-Marie's development of SOMC, its potential implications in terms of rational catalyst design were not foreseen. However, one of the main achievements of Jean-Marie's pursuit of SOMC, both the creation of new SOMFs and the development of new analytical tools to study them, was that it provided the ability to prepare well-defined heterogeneous catalysts with a single site structure.

During the first phase of his career, Jean-Marie had systematically interrogated the catalytic properties of these well-defined heterogeneous catalysts to establish the molecular mechanism of key reactions. The development of SOMC on oxides and metals progressively led him to discover the validity of the following simple concept at the origin of catalysis by design: "Any catalytic reaction (known or unknown) can be rationalized or discovered by entering a pre-supposed catalytic cycle by a surface organometallic fragment (SOMF) or surface coordination fragment (SCF)".[36]

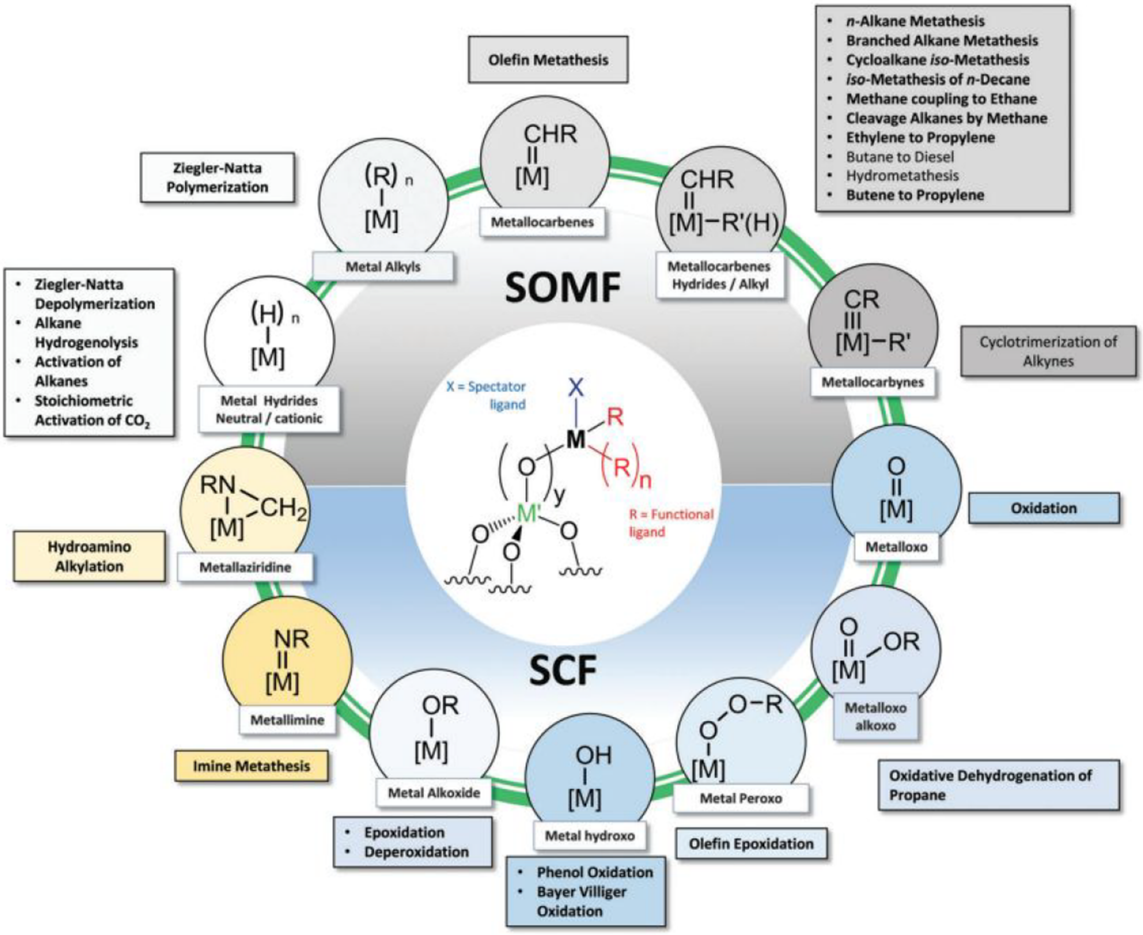
The heterogeneous catalytic cycle that Jean-Marie had established was just the juxtaposition of elementary steps already known in molecular chemistry. From the point of view of catalyst preparation, the objective was therefore to enter the catalytic cycle through a presumed catalytic intermediate, prepared from organometallic or coordination compounds to generate well-defined SOMFs or SCFs (Scheme 5).

Jean-Marie progressively developed his concept of "catalysis by design" throughout the rest of his career (Scheme 6). As outlined in the following sections, his catalysis by design approach allowed him to improve existing reactions, such as olefin metathesis, in terms of selectivity, activity or lifetime.

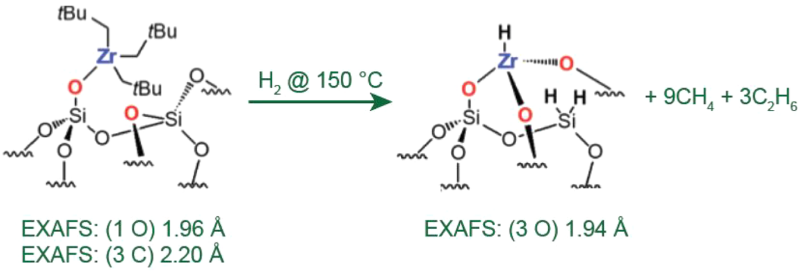
Scheme 5. Description of catalysis by design by entering a presumed catalytic reaction via a surface organometallic or coordination fragment. Reprinted with permission from ref 5. Copyright 2018, Oxford University Press.



Scheme 6. All the reactions carried out with the concept of catalysis by design. Reprinted with permission from ref 4. Copyright 2018, Royal Society of Chemistry.



Scheme 7. Formation of a highly reactive Zr H able to cleave a low temperature the CH bonds of alkanes and poly-olefins.



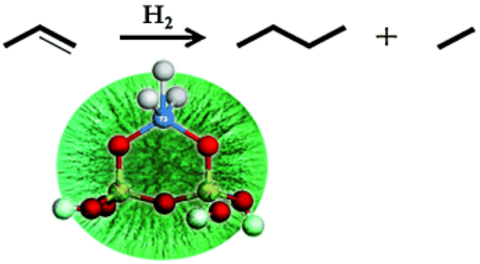
More significantly, the concept enabled him to discover reactions that were previously unknown. The list of reactions discovered in this way includes the Ziegler−Natta depolymerization; the metathesis of alkanes; the coupling of methane to ethane and hydrogen; the cleavage of alkanes by methane; the metathesis of imines; the heterometathetic oxidation of olefins with molecular oxygen to give aldehydes, the synthesis of ammonia, the synthesis of hydrogen from methane.

The basis of Jean-Marie's strategy for catalysis by design was to select SOMFs presumed to be intermediates in the catalytic cycle of the target reaction (Scheme 5). The simplest of these SOMFs, metal hydrides, provided some of the earliest and the most notable examples of catalysis by design to come from the Basset lab.

Metal hydride SOMFs could readily be made by hydrogenolysis of metal-akyl groups adsorbed onto a support. The most significant result in this area was the synthesis of highly electronically unsaturated species by reacting $ZrNp_4$ with silica, followed by hydrogen treatment. Using elemental analysis in combination with solid state NMR and EXAFS, Jean-Marie found that the resulting species featured three Zr−O bonds and had the structure $[(\equiv Si-O-)_3Zr-H]$ (Scheme 7). This highly electrophilic SOMF could activate the C−H and C−C bonds of alkanes or polyolefins. Under hydrogen, it was able to cleave the C−H and C−C bonds of any alkanes at moderate temperature, converting hydrocarbons into a range of types of gasoline. This hydrogenolysis reaction proceeded by elementary steps, already well-known in molecular organometallic chemistry, in a catalytic cycle proposed to feature sequential β-alkyl transfer and σ bond metathesis under hydrogen.[37] Previously, the industrially important catalytic transformation of higher alkanes to lower alkanes or to fuels could only be carried out at high temperatures using very acidic zeolites.

The related highly electrophilic SOMF, tantalum hydride on silica, also proved to be highly catalytically active. In the case of tantalum hydride supported on fibrous silica nanospheres (KCC-1), the SOMF catalyzed the direct conversion of olefins into alkanes that have higher and lower numbers of carbon atoms in the presence of hydrogen (Scheme 8). Jean-Marie named this novel transformation of olefins the "hydrometathesis reaction".[38] This catalyst showed remarkable catalytic activity and stability, with excellent potential for regeneration.

Scheme 8. Hydrometathesis of olefins with tantalum tris hydride supported on a highly fibrous nanosphere silica (KCC-1). Reprinted with permission from ref 38. Copyright 2011, John Wiley & Sons, Inc.



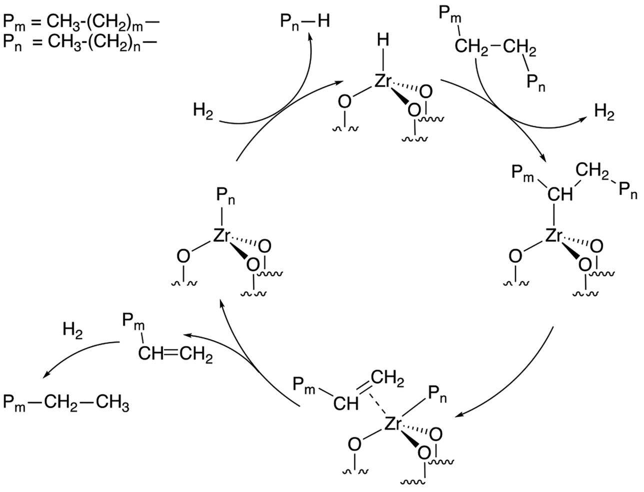
In a further notable example of metal hydride SOMF activation of C−H and C−C bonds via σ bond metathesis, the Basset group demonstrated the reversibility of Ziegler−Natta polymerization. Under hydrogen, Jean-Marie found that ($\equiv$Si−O−)$_3$Zr−H could break down polyethylene in a form of the Ziegler−Natta depolymerization process.[39]

Depending on the reaction conditions used, the Basset group was able to perform polymerization or depolymerization with the same catalyst. The ($\equiv$Si−O−)$_3$Zr−H catalyst system cleaves polyethylene and polypropylene under a hydrogen atmosphere, but is also capable of polymerizing ethylene or propylene to PE or PP. This result showed the close relationship between olefin insertion into a metal alkyl bond and β-alkyl elimination (Scheme 9).

In August 2008, Jean-Marie was offered a chance to undertake his own catalysis: the opportunity to perform a novel and challenging transformation that would convert an area of the Saudi Arabian desert into a world-class center for catalysis, at the newly conceived King Abdullah University of Science and Technology (KAUST). At the time, this new university was still on the drawing board. Jean-Marie accepted the chance to become the inaugural director of the KAUST Catalysis Centre (KCC), leading on key processes from laboratory design to faculty recruitment. Less than 18 months later, in December 2010, the new university in the desert was officially inaugurated, and the real work could begin.

Jean-Marie's research focus, which typically involved catalytic transformations of alkanes and alkenes, was an excellent fit for a catalyst center being founded in a country looking to leverage its 30% global oil reserves in new ways. The remit of the KCC included to become a hub of the global oil and petrochemical research and industrial community, as well as more forward-looking aims such as the reuse of CO_2 and the development of new energy carriers such as H_2.

Scheme 9. Possible mechanism of polyolefin depolymerization with Zr−H on silica (Ziegler Natta depolymerization). Adapted with permission from ref 39. Copyright 1998, John Wiley & Sons, Inc.



THE METATHESIS OF OLEFINS

Catalytic cycles involving double bond metathesis as a key elementary reaction step were a central theme of the catalysis by design era of the Basset group. However, Jean-Marie's investigation of metathesis dates back to his early work as an independent researcher.

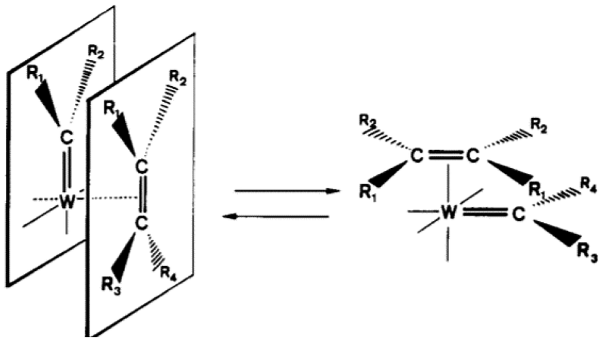
Olefin metathesis today is often associated with homogeneous catalysis, since the Nobel Prize in Chemistry 2005 was awarded jointly to Yves Chauvin, Robert H. Grubbs, and Richard R. Schrock for the development of the metathesis method in organic synthesis. However, the olefin metathesis reaction was originally discovered by classical industrial heterogeneous catalysis research during the 1950s and 60s. The silica- or alumina-supported transition metal oxides MoO_3 and WO_3, it had been shown, catalytically transformed propene into ethene and butene. However, the mechanism of the reaction was unknown.

In 1971, Chauvin proposed that the catalytic cycle proceeded via metallocyclobutane intermediates, and that the key catalytic species was a metal carbene. However, several details concerning the exact mechanism were yet to be determined: the Basset group set out to address this.

Jean-Marie's exploration of olefin metathesis was initially related to the stereochemistry of the reaction. Using several tungsten precursor complexes, he examined the metathesis of *cis*- and *trans*-2-pentene and the competing cis−trans isomerization reaction.[40] Studying the reaction kinetics, Jean-Marie proposed a mechanism of coordination of the internal olefin on the two different metallocarbene moieties, which accounted for the competitive cis−trans isomerization or formal metathesis of the starting olefin (Scheme 10).

Regarding the metathesis of olefins, the Basset group made several early contributions in the area of homogeneous olefin metathesis. Tungsten(VI) aryloxide complexes such as W(OAr)$_2$Cl$_4$ (OAr = $OC_6H_3Me_{2-2,6}$, $OC_6H_2Me_{3-2,4,6}$, $OC_6H_3Ph_{2-2,6}$, $OC_6H_3Br_{2-2,6}$, $OC_6H_3Cl_{2-2,6}$, or $OC_6H_3F_{2-2,6}$) had been shown to be active olefin metathesis catalysts when associated with a Lewis acid additive such as alkyl-aluminum, alkyl-tin, or alkyl-lead complexes. Studies had suggested that the

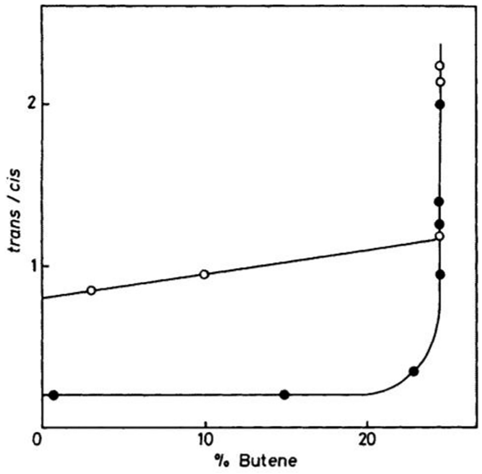
Scheme 10. Explanation of the selectivity in olefin metathesis. Formal metathesis degenerate metathesis and cis−trans isomerization. Reprinted with permission from ref 40. Copyright 1977, American Chemical Society.



catalytically active species was a complex of the type $W(OAr)_2Cl_2(=CHR')$.

Following his early principles of catalysis by design, Jean-Marie set out to synthesize such a complex directly to test its catalytic properties. His synthesis of $W(OAr)_2Cl_2(=CHR)(-CH_2R_1)(OR_2)$, (where Ar = 2,6-disubstituted phenyl; R_2 = Et or i-Pr) was one of the first examples of a well-defined, Lewis acid free, homogeneous olefin metathesis catalyst.[41] The activity and stereoselectivity of the metathesis reaction could be governed by the nature of the aryloxide ligands and of the coordinated ether. The extremely high stereoselectivities that could be achieved, combined with high conversion, were an early indication that homogeneous olefin metathesis catalysts would be useful in organic synthesis (Scheme 11).

Scheme 11. *Trans*/*cis*-2-butene ratio versus 2-butene yield in the metathesis of *cis*-2-pentene with B1 (black circles) and B3 (white circles) catalysts. Reprinted with permission from ref 41. Copyright 1985, Royal Society of Chemistry.



The catalyst was particularly active for the metathesis of olefins bearing polar groups. For example, it could be highly effective in metathesis of phosphorus-containing olefins.[42] Phosphane was metathesized intramolecularly to give the corresponding phospholene, and allyldiphenyl phosphane gives the corresponding bisphosphane (Scheme 12).

The Basset group subsequently returned to the question of olefin metathesis by heterogeneous catalysis. Some of the earliest recorded examples of olefin metathesis catalysts had been based on the impregnation of alumina with rhenium oxides. However, analysis had shown that less than 2% of the rhenium was catalytically active. The activity was associated with Re centers in proximity to highly active acidic sites of alumina.

Applying the principles of catalyst design, the Basset group used SOMC to produce well-defined rhenium complexes, such as $[(\equiv SiO-)Re(\equiv CtBu)(=CHtBu)(CH_2tBu)]$, supported on silica.[43,44] Different levels of reaction activity and selectivity were observed, which could be correlated to the nature of the metal center and identity of the spectator ligands of the SOMF. Molybdenum proved to be less active than rhenium, the group observed, and oxo spectator ligands led to a higher catalyst lifetime than imido ligands. This approach gave quite spectacular results with spectator ligands like oxo or amido and with functional ligands like carbenes (Scheme 13).[45]

In broader terms, the most significant result of this research was establishing the reaction cycle proceeded via a single-site cascade, involving the generation of several SOMFs on the same metal. The metal could sequentially, or simultaneously, exhibit two fragments: metallocarbenes with hydrides or metallocarbene with alkyls. Reactivity at the metal center was based on a double functional ligand structure, generating a multifunctional catalyst including a metal hydride for C−H bond activation and a carbene for metathesis.[36]

With this double functional ligand concept, Jean-Marie was able to design metathesis of alkanes, described in the following section, as well as to design methane coupling to ethane and hydrogen,[46] to cleave alkanes by methane,[47] to transform ethylene to propylene, to transform butane directly to gasoline, and to achieve the hydro-metathesis of olefins as previously described.

■ THE METATHESIS OF ALKANES

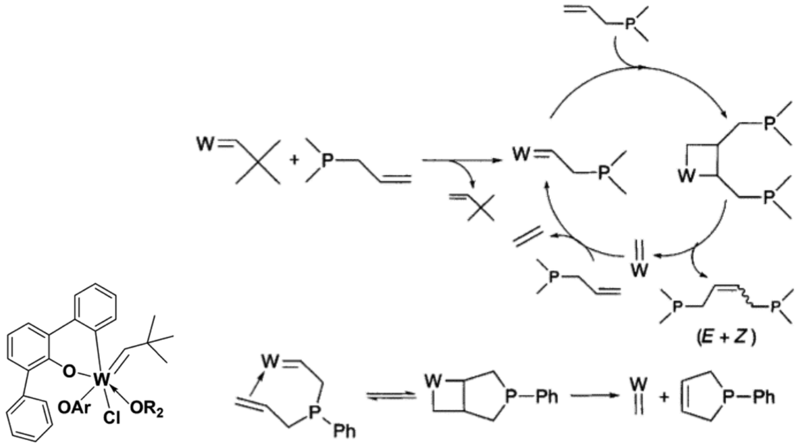
During the late 1960s and early 1970s, new research showed the catalytic conversion of alkanes into their higher and lower homologues at temperatures of 400 to 600 °C. The reaction was based on dual-function catalysts, combining tungsten oxide on silica and chroma or platinum on alumina.

In 1997, the Basset group applied their single site, dual functional catalysts to the reaction. They reported a silica-supported (Ta−H) catalyst that could achieve this alkane disproportion reaction at a much lower temperature of 150 °C.[48] The hydride was the precursor to the dual functional tantalum metallocarbene hydride catalyst (Scheme 14). Because of its similarity to olefin metathesis, the group named the new reaction “alkane metathesis”.

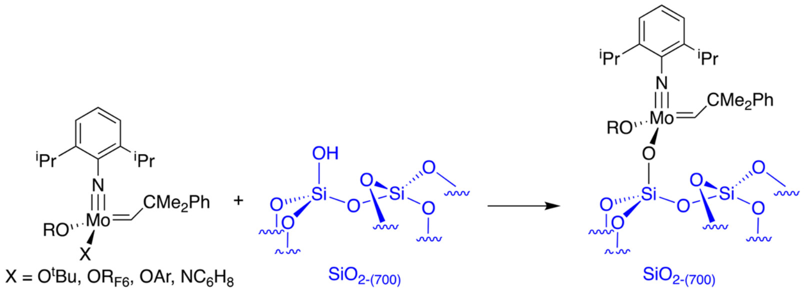
The Basset group used a continuous flow reactor to carry out kinetic studies of propane metathesis, to probe the reaction mechanism (Scheme 15). The initial steps are the σ bond metathesis reaction of Ta−H with propane to form Ta-*n*-propyl, with the evolution of hydrogen. This intermediate can then form [Ta]-*n*-propylidene hydride via α-H abstraction or produce propene via β-hydride elimination. These two products can then jointly participate in olefin metathesis, forming the new alkanes after reduction with hydrogen.[49]

Having established the most likely mechanism, Jean-Marie could apply catalysis by design principles to improve activity. On the basis of the discovery that the catalytic cycle incorporated olefin metathesis, attention initially switched to tungsten catalysts, which are known for their improved olefin metathesis performance compared to the corresponding tantalum catalyst.

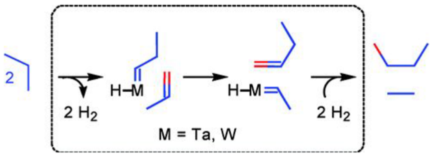
Scheme 12. Metathesis of P containing olefins with a homogeneous catalyst. Adapted with permission from ref 42. Copyright 1995, Royal Society of Chemistry.



Scheme 13. Mo-Based catalysts for olefin metathesis with spectator imido ligands. Adapted with permission from ref 45. Copyright 2006, John Wiley & Sons, Inc.



Scheme 14. Alkane metathesis on a single site catalysis. Reprinted with permission from ref 49. Copyright 2005, American Chemical Society.



The tungsten hydrides reached a TON of 129 for the propane metathesis reaction.

This first generation of catalyst had been based upon the corresponding hydrides of neopentyl complexes. To access the key metal carbene hydride catalyst more directly, the Basset group switched attention to metal methyl complexes. Jean-Marie was able to demonstrate that the precursor catalyst (≡Si–O–)WMe_5 was thermally transformed to the excellent [(≡Si–O–)WMe_2(≡CH)]. With this second-generation catalyst, a TON of 260 was reached for propane metathesis.[50]

The Basset group ultimately designed a third-generation alkane metathesis catalyst with far higher performance. From kinetic and DFT studies, the rate-determining step was understood to be the C–H bond activation. Based on previous experience with related catalyst systems, titanium was expected to be a good candidate for C–H bond activation. Jean-Marie therefore designed a catalyst with two adjacent single sites, combining tungsten and titanium on a single surface (Scheme 16). This material successively catalyzes C–H bond activation, (by synthesis of a metal alkyl from a Ti hydride by σ bond metathesis, followed by β-H elimination leading to olefin); and W based olefin metathesis via a metallocarbene fragment. TON with the Ti/W bimetallic system can reach 10 000. The proximity of the two metal centers on the catalyst surface was shown to be key to the synergistic effect of the bimetallic catalyst.[51]

THE METATHESIS OF CYCLOALKANES

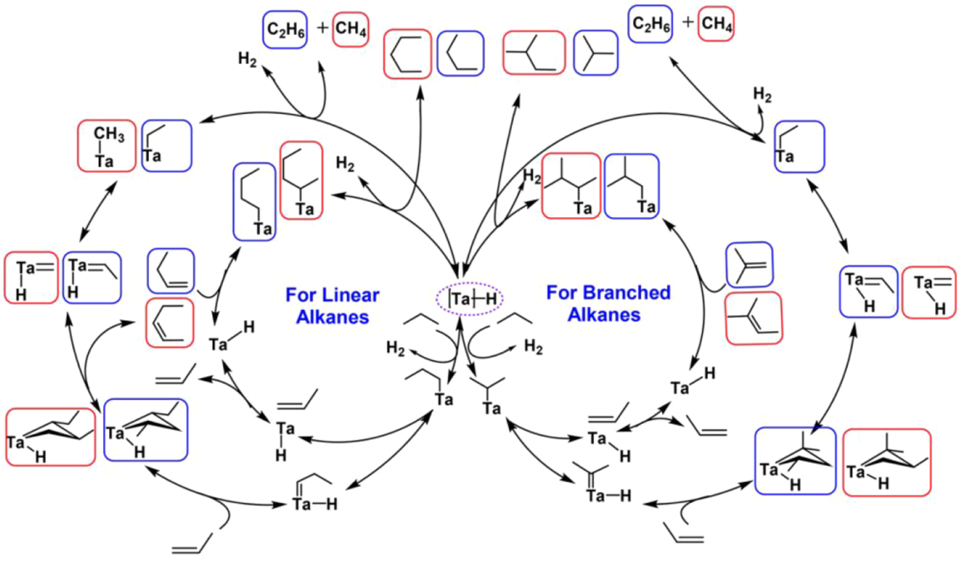
Taking the chemistry for linear alkane metathesis successfully developed by the Basset group, Jean-Marie examined the case of cyclic alkane metathesis. Alkane macrocycles are of interest to industry, particularly for flavor and fragrance applications, and are nontrivial to synthesize. Alkane metathesis of cyclooctane potentially offered a convenient route to alkane macrocycle synthesis.

In previous attempts with tandem system pairing iridium and molybdenum catalysts, alkane macrocycle production had been limited due to the formation of polymeric byproducts. This problem was overcome by the Basset group's single multifunctional catalyst, based on the metal surface precursor complex [(≡SiO)W$(Me)_5$].[52] The multifunctional, supported W single catalytic system led to an unprecedented distribution of macrocyclic alkanes in the range of C_{12} to C_{40}, with no polymer products detected (Scheme 17).

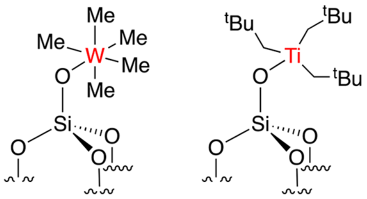
THE METATHESIS OF IMINES

In the wake of successful development in homogeneous olefin metathesis, a number of groups had explored the corresponding imine metathesis. Bergmann had reported that zirconium-

Scheme 15. Proposed mechanism of linear-alkane metathesis. Reprinted with permission from ref 6. Copyright 2020, American Chemical Society.



Scheme 16. Bimetallic precursors for highly active alkane metathesis catalysts. Adapted with permission from ref 51. Copyright 2017, American Chemical Society.



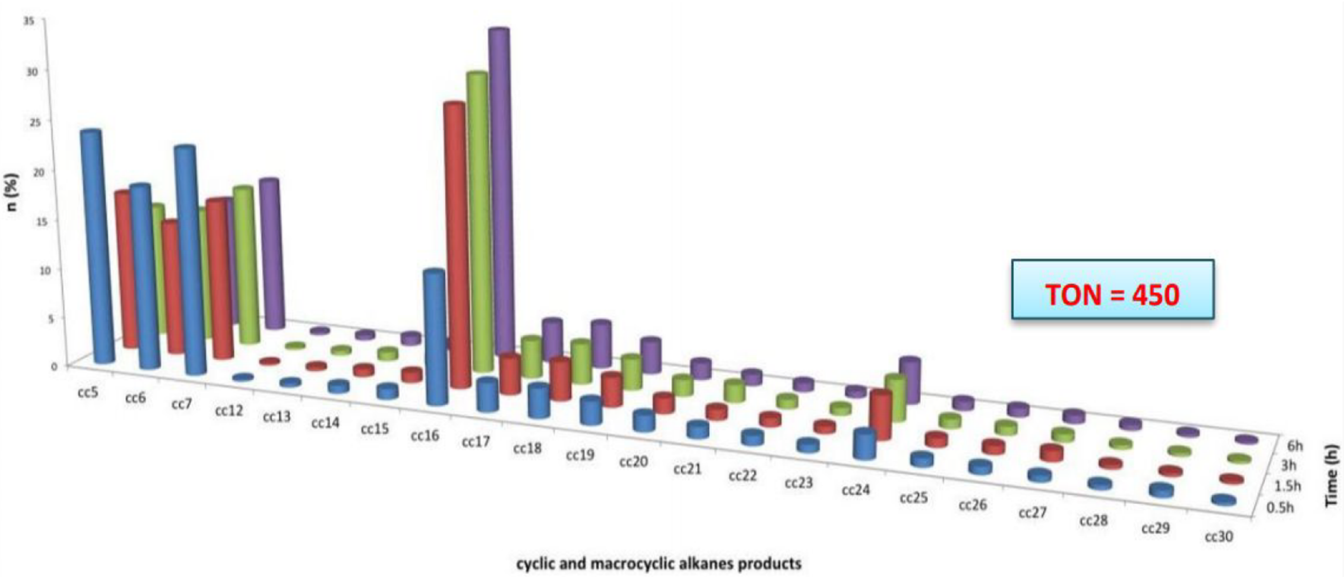
catalyzed imine metathesis proceeded in homogeneous catalysis through a Chauvin-type mechanism.

It was expected that in heterogeneous catalysis an imido ligand coordinated to a grafted metal, previously only employed as a spectator ligand, would be part of the catalytic cycle and would promote this reaction. This was confirmed when the Basset group reported the first example of a heterogeneous imine metathesis, using Hf or Zr imido complexes supported on silica.[53] The group demonstrated that the exchange of an imido ligand coordinated to Zr could metathetically exchange with an incoming imine (Scheme 18), a process analogous to the Chauvin olefin metathesis mechanism.

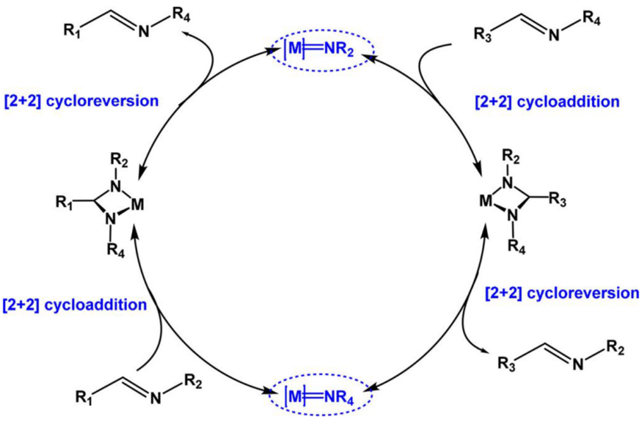
THE METATHETIC OXIDATION OF OLEFINS TO ALDEHYDES WITH MOLECULAR OXYGEN

Most recently, Jean-Marie has turned his attention to some of the largest-scale and oldest processes currently conducted by the petrochemical industry. The aim was to apply catalysis by design

Scheme 17. Product distribution in cyclooctane metathesis. Adapted reprinted with permission from ref 52. Copyright 2014, John Wiley & Sons, Inc.



Scheme 18. Metathesis of imines with supported imido ligands. Reprinted with permission from ref 6. Copyright 2020, American Chemical Society.

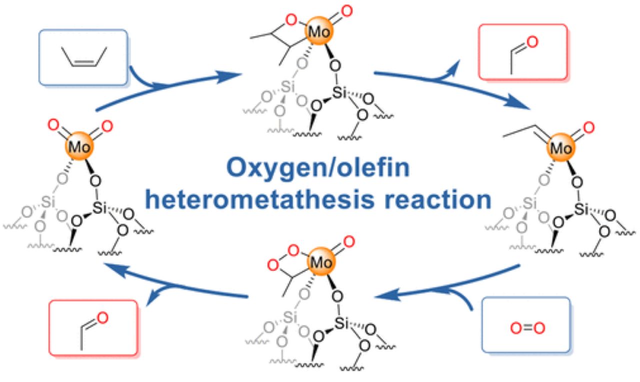


to these near-century-old processes, to improve the sustainability and reduce the environmental impact.

One example is the production of acetaldehyde, a feedstock for many important industrial products. Acetaldehyde is primarily made by the Wacker process, a $CuCl_2/PdCl_2$-catalyzed homogeneous reaction involves the oxidation of ethylene, to produce 800 000 tons of acetaldehyde annually. The process is complicated by the production of HCl as a byproduct, and the need to regenerate the homogeneous catalyst.

By analogy with olefin metathesis, the Basset group developed a way to generate acetaldehyde via the catalytic oxidation of *cis*-2-butene or propylene with molecular oxygen. The double bond of 2-butene could undergo a metathesis-like reaction with the double bond of molecular oxygen to generate 2 mols of acetaldehyde (Scheme 19). As molybdenum complexes are known olefin metathesis catalysts, the group developed a silica-supported Mo(bis-oxo) species, $[(\equiv SiO)_2Mo(=O)_2]$ as a single-site metathetic oxidation catalyst. Using a *cis*-2-butene/O_2 feed at 350−400 °C, the catalyst yielded a conversion of approximately 10% and an acetaldehyde selectivity of approximately 70%. This performance is maintained up to an experimental time of 20 h in a continuous flow reactor.[54]

Scheme 19. Silica-supported bis-oxo complex catalyzed the heterometathesis reaction between *cis*-2-butene and molecular oxygen. Reprinted with permission from ref 54. Copyright 2018, American Chemical Society.



The Mo(bis-oxo) surface compound was fully characterized by multiple spectroscopic techniques as well as surface microanalysis. The results from quantum mechanics calculations indicate that the reaction proceeds via a [2 + 2] cycloaddition/cycloelimination steps with the formation of metalla-oxacyclobutane intermediates, analogous to the Chauvin mechanism in olefin metathesis

THE AMMONIA SYNTHESIS

An even bigger industrial reaction than the Wacker process, in terms of scale and environmental footprint, is the Haber−Bosch process for ammonia production. The approximately 10^8 tons of ammonia produced industrially each year, mainly for synthetic fertilizer use, is roughly equal to the annual nitrogen fixation of biological systems.

In the latter case, the splitting of dinitrogen to generate ammonia is catalyzed by nitrogenase enzymes with an iron molybdenum sulfur cluster active site. The Haber Bosch process, in contrast, is an energy-intensive homogeneous process involving a surface of iron or ruthenium atoms, conducted at high temperature and pressure. But in each case, the reaction was thought to proceed via the cooperation of multiple metals to break the very stable N≡N triple bond of dinitrogen.

Jean-Marie's initial exploration of ammonia synthesis was a mechanistic investigation of the reaction. He explored dinitrogen activation using highly electrophilic electron-deficient Ta hydrides. Following detailed characterization and theoretical simulations (Scheme 20), the Basset team discovered that N_2 could be transformed into an amido amino ligand on a single Ta hydride supported on silica. This result contrasted with the generally accepted belief that multiple cooperative metal centers are required to cleave the dinitrogen triple bond. The result suggested that the generally accepted mechanism of dinitrogen dissociation onto the Fe surface was probably not correct.[55,56]

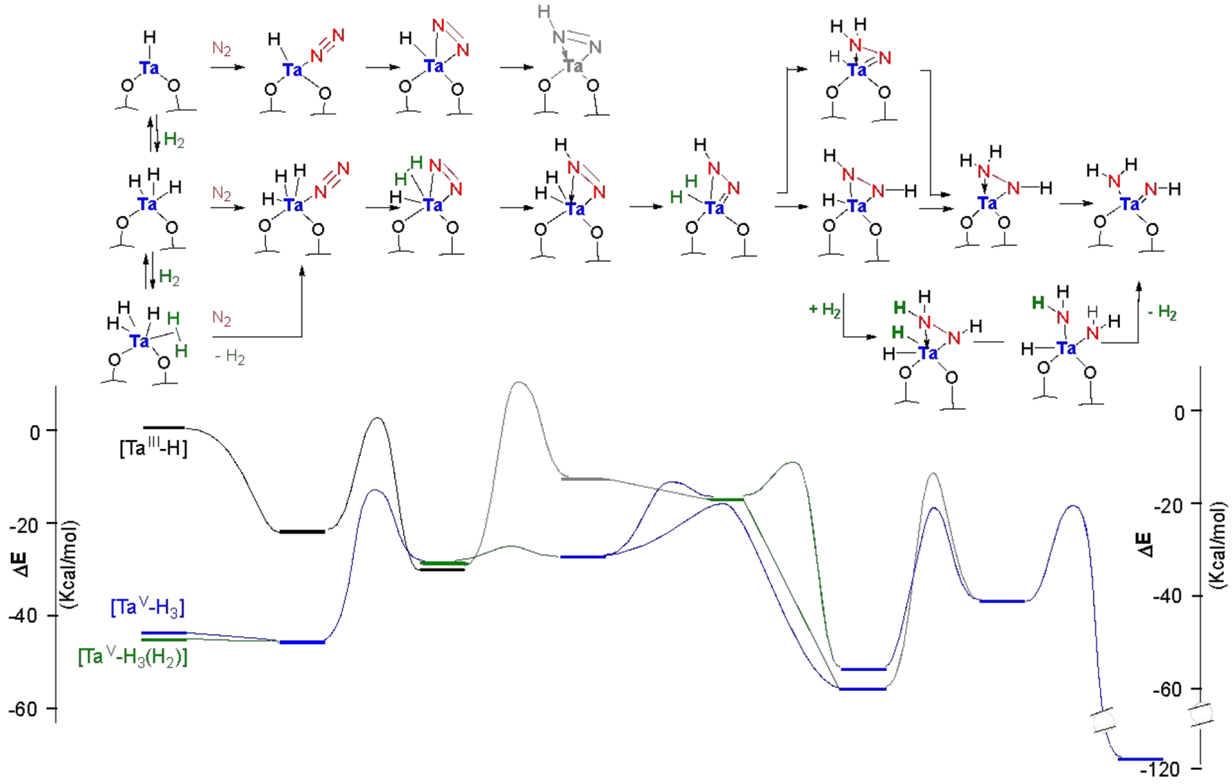
Although tantalum hydrides on silica achieved dinitrogen dissociation, the stability of the aminidated Ta center precluded NH_3 generation. The Basset group recently revisited the reaction, with the aim of total N_2 to NH_3 conversion by single-site heterogeneous catalysis. The team found that single atom Mo catalyst was efficient in ammonia synthesis, achieving NH_3 rates of approximately 1.3×10^3 μmol h^{-1} gMo^{-1} when reacted at atmospheric pressure and 400 °C.[57] A cobalt cocatalyst helped to increase the rate to 29×10^3 μmol h^{-1} gMo^{-1} when the pressure was increased to 30 atm.

Most recently, Jean-Marie took a quite different approach to create a novel heterogeneous ammonia synthesis catalyst. Rather than grafting a metal complex onto an oxide support, he developed of a new generation of catalysts obtained by decomposition of a molecular precursor phthalocyanine of Co.[58] Pyrolysis of these metal−organic compounds generated metal clusters confined within the cavities of the carbonized organic component. Using iron and/or cobalt metal, combined with alkali metal promoters, generated highly active and stable ammonia synthesis catalysts when operated at high temperatures. Unusually, the rate-determining step shifts from dinitrogen activation to NH_3 formation, potentially inspiring new areas for ammonia catalyst development (Scheme 21).

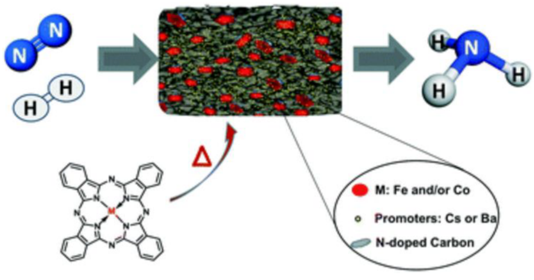
THE FUTURE OF CATALYSIS BY DESIGN

The future of catalysis by design is strongly linked to the development of material science that produces new supports for catalysis by design, to the demand of society in terms of environment and energy

Scheme 20. Plausible mechanism of N_2 transformation into an amido amino ligand on a single Ta hydride supported on silica. Adapted with permission from ref 56. Copyright 2012, American Chemical Society.



Scheme 21. Schematic representation of catalysts for ammonia synthesis based on metal phthalocyanine materials. Adapted with permission from ref 58. Copyright 2020, Royal Society of Chemistry.



The first example comes from the new MOF developed by Yagi and Eddaoudi. With Eddaoudi, Jean-Marie most recently extended SOMC to the field of metal−organic frameworks (MOFs).[59] The team anchored a $W(\equiv CtBu)(CH_2tBu)_3$ complex on the highly crystalline and mesoporous MOF Zr-NU-1000, using the SOMC concept and methodology. As predicted, the new material was a highly active single-site catalyst for the metathesis of olefins.

The second challenge is the huge environmental problem of our societies. One of them is the rising explosion of plastics across terrestrial, freshwater, and marine environments, including microplastics found within the tissues of some organisms. Jean-Marie and his colleagues have discovered depolymerization by a simple mechanistic reasoning of the reversibility of olefin polymerization/polyolefin depolymerization under hydrogen. This is one of the most crucial applications of catalysis by design. This reversibility of depolymerization of polyolefins led to Jean-Marie creating a startup, called JMB SAS, for recycling plastic. His catalysts are able to cleave all polyolefins to waxes and hydrogen a new major component of the future of energy vector.

The third challenge is energy and new vectors for energy preserving the environment. There is no doubt that hydrogen will progressively replace petroleum. The Basset group is producing hydrogen for about half the current cost of producing hydrogen, with about half of the CO_2 current produced by steam reforming of methane.

Jean-Marie's intuitive idea that the rules and concepts developed for homogeneous catalysis must be transferable to heterogeneous catalysis, has underpinned a rich and highly impactful career. His development of the concept of SOFC, supported by SOMC to generate the tailored catalytic surfaces he conceptualized, led to improvements in known catalyst performance, and to the discovery of new catalytic reactions at the rate of one every six months.

The new discoveries enabled by catalysis by design show no sign of slowing. The concepts pioneered by Jean-Marie will continue to generate new catalytic materials with considerable potential for industrial benefit, long after his retirement from KAUST in July 2021. It is doubtless that some of those new discoveries will be made in Jean-Marie's own new lab, at a start-up in the premises of the Ecole Nationale Supérieure de Chimie de Paris.

■ AUTHOR INFORMATION

Corresponding Author

Luigi Cavallo − *KAUST Catalysis Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia;*

orcid.org/0000-0002-1398-338X; Email: luigi.cavallo@kaust.edu

Authors

Didier Astruc − *ISM, UMR CNRS 5255, Univ. Bordeaux, Talence Cedex 33405, France;* orcid.org/0000-0001-6446-8751

Guy Bertrand − *UCSD-CNRS Joint Research Laboratory (IRL 3555), Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093-0358, United States*

Mohamed Eddaoudi − *Functional Materials Design, Discovery and Development Research Group, Advanced Membranes and Porous Materials Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia;* orcid.org/0000-0003-1916-9837

Yu Han − *Advanced Membranes and Porous Materials Center, Physical Sciences and Engineering Division, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia;* orcid.org/0000-0003-1462-1118

Kuo-Wei Huang − *KAUST Catalysis Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia;* orcid.org/0000-0003-1900-2658

Johannes Lercher − *Department of Chemistry and Catalysis Research Center, Technische Universität München, 85747 Garching, Germany;* orcid.org/0000-0002-2495-1404

Catherine Santini − *Université Lyon 1, CNRS UMR 5265, C2P2 CPE Lyon, F-69616 Villeurbanne, France*

Kazuhiro Takanabe − *Department of Chemical System Engineering, School of Engineering, The University of Tokyo, Tokyo 113-8656, Japan*

Mostafa Taoufik − *Université Lyon 1, CNRS UMR 5265, C2P2 LCOMS Lyon, F-69616 Villeurbanne, France;* orcid.org/0000-0002-3627-5263

Complete contact information is available at:
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Notes

The authors declare no competing financial interest.

REFERENCES

(1) Basset, J. M.; Choplin, A. Surface organometallic chemistry: A new approach to heterogeneous Catalysis? *J. Mol. Catal.* **1983**, *21*, 95−108.

(2) Copéret, C.; Chabanas, M.; Petroff Saint-Arroman, R.; Basset, J. M. Homogeneous and heterogeneous catalysis: bridging the gap through surface organometallic chemistry. *Angew. Chem., Int. Ed.* **2003**, *42*, 156−181.

(3) Lefebvre, F.; Candy, J. P.; Santini, C. C.; Basset, J. M. Surface organometallic chemistry on metals. Application to chemicals and fine chemicals. *Top. Catal.* **1997**, *4*, 211−216.

(4) Samantaray, M. K.; Pump, E.; Bendjeriou-Sedjerari, A.; D'Elia, V.; Pelletier, J. D. A.; Guidotti, M.; Psaro, R.; Basset, J. M. Surface organometallic chemistry in heterogeneous catalysis. *Chem. Soc. Rev.* **2018**, *47*, 8403−8437.

(5) Basset, J. M.; Pelletier, J. D. A. Predictive approach of heterogeneous catalysis. *Natl. Sci. Rev.* **2018**, *5*, 633−635.

(6) Samantaray, M. K.; D'Elia, V.; Pump, E.; Falivene, L.; Harb, M.; Ould Chikh, S.; Cavallo, L.; Basset, J. M. The comparison between single atom catalysis and surface organometallic catalysis. *Chem. Rev.* **2020**, *120*, 734−813.

(7) Chabanas, M.; Quadrelli, E. A.; Fenet, B.; Copéret, C.; Thivolle-Cazat, J.; Basset, J. M.; Lesage, A.; Emsley, L. Molecular insight into surface organometallic chemistry through the combined use of 2D HETCOR solid-state NMR spectroscopy and silsesquioxane analogues. *Angew. Chem., Int. Ed.* **2001**, *113*, 4625−4628.

(8) Hamzaoui, B.; Pelletier, J. D.; Abou-Hamad, E.; Chen, Y.; El Eter, M.; Chermak, E.; Cavallo, L.; Basset, J. M. Solid-state NMR and DFT studies on the formation of well-defined silica-supported tantallaaziridines: From synthesis to catalytic application. *Chem.—Eur. J.* **2016**, *22*, 3000−3008.

(9) Primet, M.; Basset, J. M.; Mathieu, M. V.; Prettre, M. Infrared study of CO adsorbed on PtAl2O3. A method for determining metal-adsorbate interactions. *J. Catal.* **1973**, *29*, 213−223.

(10) Basset, J. M.; Dalmai-Imelik, G.; Primet, M.; Mutin, R. A study of benzene hydrogenation and identification of the adsorbed species with PtAl2O3 catalysts. *J. Catal.* **1975**, *37*, 22−36.

(11) Smith, A. K.; Basset, J. M. Transition metal cluster complexes as catalysts. A review. *J. Mol. Catal.* **1977**, *2*, 229−241.

(12) Primet, M.; Basset, J. M.; Garbowski, E.; Mathieu, M. V. Properties of supported platinum. Analogy with cluster compounds. *J. Am. Chem. Soc.* **1975**, *97* (13), 3655−3659.

(13) Chini, P. Large metal carbonyl clusters (LMCC). *J. Organomet. Chem.* **1980**, *200*, 37−61.

(14) Basset, J. M.; Ugo, R. Structure and Electronic Relations Between Molecular Clusters and Small Particles: An Essay to the Understanding of Very Dispersed Metals. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; Springer: Dordrecht, 1977; pp 137−183.

(15) Bilhou, J. L.; Bilhoubougnol, V. S.; Graydon, W. F.; Basset, J.-M.; Smith, A. K.; Zanderighi, G. M.; Ugo, R. Surface-supported metal cluster carbonyls - chemisorption, decomposition and reactivity of Rh6(CO)16 supported on silica. *J. Organomet. Chem.* **1978**, *153*, 73−84.

(16) Smith, A. K.; Theolier, A.; Basset, J. M.; Ugo, R.; Commereuc, D.; Chauvin, Y. Hydrocarbon formation from metal carbonyl clusters supported on highly divided oxides. *J. Am. Chem. Soc.* **1978**, *100*, 2590−2591.

(17) Smith, A. K.; Hugues, F.; Theolier, A.; Basset, J. M. M.; Ugo, R.; Zanderighi, G. M.; Bilhou, J. L.; Graydon, W. F. Surface-supported metal cluster carbonyls. Chemisorption decomposition and reactivity of Rh6 (CO)16 supported on alumina, silica-alumina, and magnesia. *Inor. Chem.* **1979**, *18*, 3104−3112.

(18) Theolier, A.; Smith, A.; Leconte, M.; Basset, J. M.; Zanderighi, G. M.; Psaro, R.; Ugo, R. Surface supported metal cluster carbonyls. Chemisorption decomposition and reactivity of Rh4(CO)12 supported on silica and alumina. *J. Organomet. Chem.* **1980**, *191*, 415−424.

(19) Psaro, R.; Ugo, R.; Zanderighi, G. M.; Besson, B.; Smith, A. K.; Basset, J. M. Surface-supported metal cluster carbonyls. Chemisorption, decomposition and reactivity of Os3(CO)12, H2Os3 (CO)10 and Os6(CO)18 supported on silica and alumina and the investigation of the fischer-tropsch catalysis with these systems. *J. Organomet. Chem.* **1981**, *213*, 215−247.

(20) Basset, J. M.; Theolier, A.; Commereuc, D.; Chauvin, Y. The water gas shift reaction catalyzed by Rh6(CO)16 adsorbed on alumina or [Rh(CO)2Cl]2 adsorbed on alumina, Na-Y zeolite and HY zeolite. *J. Organomet. Chem.* **1985**, *279*, 147−158.

(21) Basset, J. M.; Besson, B.; Choplin, A.; Theolier, A. Catalysis by supported clusters: Two examples of catalytic reactions that involve a molecular cluster frame. *Philos. Trans. R. Soc. London A* **1982**, *308*, 115−124.

(22) Choplin, A.; Besson, B.; D'Ornelas, L.; Sanchez-Delgado, R.; Basset, J.-M. Surface organometallic chemistry - hydrogenation of ethylene with Os3(CO)10(MUH)(MU-OsI[-) and OS3(CO)10-(MU-H)(MU-OPh) - evidence for cluster catalysis. *J. Am. Chem. Soc.* **1988**, *110*, 2783−2787.

(23) Zanderighi, G. M.; Dossi, C.; Ugo, R.; Psaro, R.; Theolier, A.; Choplin, A.; D'Ornelas, L.; Basset, J. M. Surface supported metal cluster carbonyls. Chemisorption, reactivity, and decomposition of Ru3 (CO)12 on silica. *J. Organomet. Chem.* **1985**, *296*, 127−146.

(24) Candy, J. P.; Didillon, B.; Smith, E. L.; Shay, T. B.; Basset, J. M. Surface organometallic chemistry on metals: a novel and effective route to custom-designed bimetallic catalysts. *J. Mol. Catal.* **1994**, *86*, 179−204.

(25) Agnelli, M.; Candy, J. P.; Basset, J. M.; Bournonville, J. P.; Ferretti, O. A. Surface organometallic chemistry on metals: III. Formation of a bimetallic Ni-Sn phase generated by reaction of a Sn (*n*-C4H9)4 and silica-supported nickel oxide. *J. Catal.* **1990**, *121*, 236−247.

(26) Didillon, B.; Candy, J. P.; Le Peletier, F.; Ferretti, O. A.; Basset, J. M. Surface Organometallic Chemistry on Metals; Selective hydrogenation of citral on silica supported Rhodium modified by tetra-n-butyl Germanium, Tin and Lead. In *Studies in Surface Science and Catalysis*; Guisnet, M.; Barbier, J.; Barrault, J.; Bouchoule, C.; Duprez, D., Pérot, G., Montassier, C., Eds.; Elsevier, 1993; Vol. *78*, pp 147−154.

(27) Ferretti, O. A.; Bournonville, J. P.; Mabilon, G.; Martino, G.; Candy, J. P.; Basset, J. M. Surface organometallic chemistry on metals: Part IV. Selective hydrogenation of ethyl acetate to ethanol on Rh—Sn/SiO2 bimetallic catalysts: A mechanistic study. *J. Mol. Catal.* **1991**, *67*, 283−294.

(28) Didillon, B.; Houtman, C.; Shay, T.; Candy, J. P.; Basset, J. M. Surface organometallic chemistry on metals. Evidence for a new surface organometallic material, $\text{Rh}[\text{Sn}(\text{n-C}_4\text{H}_9)_\text{X}]_\text{Y}/\text{SiO}_2$, obtained by controlled hydrogenolysis of Sn(n-C4H9)4 ON A Rh/SiO2 catalyst. *J. Am. Chem. Soc.* **1993**, *115*, 9380−9388.

(29) Humblot, F.; Candy, J. P.; Le Peltier, F.; Didillon, B.; Basset, J. M. Surface organometallic chemistry on metals: Selective dehydrogenation of isobutane into isobutene on bimetallic catalysts prepared by reaction of tetran-butyltin on silica-supported platinum catalyst. *J. Catal.* **1998**, *179*, 459−468.

(30) Gajan, D.; Guillois, K.; Delichere, P.; Basset, J. M.; Candy, J. P.; Caps, V.; Copéret, C.; Lesage, A.; Emsley, L. Gold nanoparticles supported on passivated silica: Access to an efficient aerobic epoxidation catalyst and the intrinsic oxidation activity of gold. *J. Am. Chem. Soc.* **2009**, *131*, 14667−14669.

(31) Godard, G.; Mallmann, A. D.; Candy, J. P.; Fiddy, S.; Basset, J. M. Reductive adsorption of Cd2+ on a nickel surface in aqueous solution: Characterization of surface adatoms by in situ EXAFS. *J. Phys. Chem. C* **2008**, *112*, 12936−12942.

(32) Commereuc, D.; Chauvin, Y.; Hugues, F.; Basset, J. M.; Olivier, D. Catalytic synthesis of low molecular weight olefins from CO and H2 with Fe(CO)5, Fe3(CO)12, and [HFe3(CO)11]-supported on inorganic oxides. *Chem. Commun.* **1980**, *4*, 154−155.

(33) Leconte, M.; Theolier, A.; Rojas, D.; Basset, J. M. Stoichiometric and catalytic homologation of olefins on the Fischer−Tropsch catalysts Fe/SIO_2, Ru/SIO_2, Os/SIO_2, AND Rh/SIO_2. Mechanistic implication in the model of CC bond formation. *J. Am. Chem. Soc.* **1984**, *106*, 1141−1142.

(34) Rodriguez, E.; Leconte, M.; Basset, J. M. Homologation and hydrogenolysis of linear and branched butenes and butanes on Ru/SiO2 catalysts. *J. Catal.* **1991**, *131*, 457−481.

(35) Humblot, F.; Candy, J. P.; Le Peltier, F.; Didillon, B.; Basset, J. M. Surface organometallic chemistry on metals: Selective dehydrogenation of isobutane into isobutene on bimetallic catalysts prepared by reaction of tetran-butyltin on silica-supported platinum catalyst. *J. Catal.* **1998**, *179*, 459−468.

(36) Pelletier, J. D.; Basset, J. M. Catalysis by design: well-defined single-site heterogeneous catalysts. *Acc. Chem. Res.* **2016**, *49*, 664−677.

(37) Corker, J.; Lefebvre, F.; Lécuyer, C.; Dufaud, V.; Quignard, F.; Choplin, A.; Evans, J.; Basset, J. M. Catalytic cleavage of the CH and CC bonds of alkanes by surface organometallic chemistry: An EXAFS and IR characterization of a Zr-H catalyst. *Science* **1996**, *271*, 966−969.

(38) Polshettiwar, V.; Thivolle-Cazat, J.; Taoufik, M.; Stoffelbach, F.; Norsic, S.; Basset, J. M. Hydro-metathesis" of olefins: A catalytic reaction using a bifunctional single-site tantalum hydride catalyst supported on fibrous silica (KCC-1) nanospheres. *Angew. Chem., Int. Ed.* **2011**, *50*, 2747−2751.

(39) Dufaud, V.; Basset, J. M. Catalytic hydrogenolysis at low temperature and pressure of polyethylene and polypropylene to diesels or lower alkanes by a zirconium hydride supported on silica-alumina: a step toward polyolefin degradation by the microscopic reverse of Ziegler-Natta polymerization. *Angew. Chem., Int. Ed.* **1998**, *37*, 806−810.

(40) Bilhou, J. L.; Basset, J. M.; Mutin, R.; Graydon, W. F. A stereochemical study of metathesis and cis-trans isomerization of 2-pentenes. *J. Am. Chem. Soc.* **1977**, *99*, 4083−4090.

(41) Quignard, F.; Leconte, M.; Basset, J. M. Synthesis and catalytic properties of $\text{W(OAR)}_2\text{Cl}_2(\text{CHCMe}_3)(\text{OR}_2)$, and $\text{W(OAR)}_2\text{Cl}(\text{CHCMe}_3)$ $(\text{CH}_2\text{CMe}_3)(\text{OR}_2)$ (AR = 2,6-disubstituted phenyl; R= Et or Pr i), new uni-component catalysts for metathesis of acyclic and cyclic olefins, with or without functional groups. *Chem. Commun.* **1985**, *24*, 1816−1817.

(42) Leconte, M.; Jourdan, I.; Pagano, S.; Lefebvre, F.; Basset, J. M. Metathesis of phosphorus-containing olefins catalysed by a cyclometallated aryloxo (chloro) neopentylidene-tungsten complex. *Chem. Commun.* **1995**, *8*, 857−858.

(43) Chabanas, M.; Copéret, C.; Basset, J. M. Re-based heterogeneous catalysts for olefin metathesis prepared by surface organometallic chemistry: Reactivity and selectivity. *Chem.—Eur. J.* **2003**, *9*, 971−975.

(44) Chabanas, M.; Baudouin, A.; Copéret, C.; Basset, J. M. A highly active well-defined rhenium heterogeneous catalyst for olefin metathesis prepared via surface organometallic chemistry. *J. Am. Chem. Soc.* **2001**, *123*, 2062−2063.

(45) Blanc, F.; Copéret, C.; Thivolle-Cazat, J.; Basset, J. M.; Lesage, A.; Emsley, L.; Sinha, A.; Schrock, R. R. Surface versus molecular siloxy ligands in well-defined olefin metathesis catalysts: [{(RO)3SiO} Mo (=NAr)(=CHtBu)(CH2tBu)]. *Angew. Chem., Int. Ed.* **2006**, *118*, 1238−1242.

(46) Soulivong, D.; Norsic, S.; Taoufik, M.; Coperet, C.; Thivolle-Cazat, J.; Chakka, S.; Basset, J. M. Non-oxidative coupling reaction of methane to ethane and hydrogen catalyzed by the silica-supported tantalum hydride:(≡ SiO)2Ta- H. *J. Am. Chem. Soc.* **2008**, *130*, 5044−5045.

(47) Soulivong, D.; Copéret, C.; Thivolle-Cazat, J.; Basset, J. M.; Maunders, B. M.; Pardy, R. B.; Sunley, G. J. Cross-metathesis of propane and methane: A catalytic reaction of C−C bond cleavage of a higher alkane by methane. *Angew. Chem., Int. Ed.* **2004**, *116*, 5480−5483.

(48) Vidal, V.; Théolier, A.; Thivolle-Cazat, J.; Basset, J. M. Metathesis of alkanes catalyzed by silica-supported transition metal hydrides. *Science* **1997**, *276*, 99−102.

(49) Basset, J. M.; Coperet, C.; Lefort, L.; Maunders, B. M.; Maury, O.; Le Roux, E.; Saggio, G.; Soignier, S.; Soulivong, D.; Sunley, G. J.; Taoufik, M.; Thivolle-Cazat, J. Primary products and mechanistic considerations in alkane metathesis. *J. Am. Chem. Soc.* **2005**, *127*, 8604−8605.

(50) Maity, N.; Barman, S.; Callens, E.; Samantaray, M. K.; Abou-Hamad, E.; Minenkov, Y.; D'Elia, V.; Hoffman, A. S.; Widdifield, C. M.; Cavallo, L.; Gates, B. C.; Basset, J.-M. *Chem. Sci.* **2016**, *7*, 1558−1568.

(51) Samantaray, M. K.; Kavitake, S.; Morlanés, N.; Abou-Hamad, E.; Hamieh, A.; Dey, R.; Basset, J. M. Unearthing a well-defined highly active bimetallic W/Ti precatalyst anchored on a single silica surface for metathesis of propane. *J. Am. Chem. Soc.* **2017**, *139*, 3522−3527.

(52) Riache, N.; Callens, E.; Samantaray, M. K.; Kharbatia, N. M.; Atiqullah, M.; Basset, J. M. Cyclooctane metathesis catalyzed by silica-supported tungsten pentamethyl [(≡SiO)W(Me)5]: distribution of macrocyclic alkanes. *Chem.—Eur. J.* **2014**, *20*, 15089−15094.

(53) Hamzaoui, B.; Pelletier, J. D.; Abou-Hamad, E.; Basset, J. M. Well-defined silica-supported zirconium-imido complexes mediated heterogeneous imine metathesis. *Chem. Commun.* **2016**, *52*, 4617−4620.

(54) Le Quéméner, F.; Barman, S.; Merle, N.; Aljuhani, M. A.; Samantaray, M. K.; Saih, Y.; Szeto, K. C.; De Mallmann, A.; Minenkov, Y.; Huang, K. H.; Cavallo, L.; Taoufik, M.; Basset, J. M. Metathetic oxidation of 2-Butenes to acetaldehyde by molecular oxygen using the single-site olefin metathesis catalyst (≡SiO)2Mo(=O)2. *ACS Catal.* **2018**, *8*, 7549−7555.

(55) Avenier, P.; Taoufik, M.; Lesage, A.; Solans-Monfort, X.; Baudouin, A. D.; De Mallmann, A.; Veyre, L.; Basset, J. M.; Eisenstein, O.; Emsley, L.; Quadrelli, E. A. Dinitrogen dissociation on an isolated surface tantalum atom. *Science* **2007**, *317*, 1056−1060.

(56) Solans-Monfort, X.; Chow, C.; Gouré, E.; Kaya, Y.; Basset, J. M.; Taoufik, M.; Quadrelli, A.; Eisenstein, O. Successive heterolytic cleavages of H_2 achieve N_2 splitting on silica-supported tantalum hydrides: A DFT proposed mechanism. *Inorg. Chem.* **2012**, *51*, 7237−7249.

(57) Azofra, L. M.; Morlanes, N.; Poater, A.; Samantaray, M. K.; Vidjayacoumar, B.; Albahily, K.; Cavallo, L.; Basset, J.-M. Single-Site Molybdenum on solid support materials for catalytic hydrogenation of N_2-into-NH_3. *Angew. Chem., Int. Ed.* **2018**, *57*, 15812−15816.

(58) Morlanés, N.; Almaksoud, W.; Rai, R. K.; Ould-Chikh, S.; Ali, M. M.; Vidjayacoumar, B.; Al-Sabban, B. E.; Albahily, K.; Basset, J. M. Development of catalysts for ammonia synthesis based on metal phthalocyanine materials. *Catal. Sci. Technol.* **2020**, *10*, 844−852.

(59) Thiam, Z.; Abou-Hamad, E.; Dereli, B.; Liu, L.; Emwas, A. H.; Ahmad, R.; Jiang, H.; Isah, A. A.; Ndiaye, P. B.; Taoufik, M.; Han, Y.; Cavallo, L.; Basset, J. M.; Eddaoudi, M. Extension of surface organometallic chemistry to metal-organic frameworks: Development of a well-defined single site [(≡Zr-O-)W(=O)(CH2 t Bu)3] olefin metathesis catalyst. *J. Am. Chem. Soc.* **2020**, *142*, 16690−16703.