

## 1

## Introduction

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“Le nombre des corps capables de produire des catalyses est très grand, et ne cesse de s’augmenter par suite de progrès de la chimie.”<sup>1)</sup>

*Paul Sabatier (Toulouse, 1913)*

More than a century after the predictive statement of Paul Sabatier (1854–1941), the Nobel Laureate of 1912, catalysis has become a comprehensive technology in a great number of industries. It is, therefore, not surprising that numerous Nobel Prizes have been granted to the key pioneers in the field, with the most recent one being to Gerhard Ertl (Nobel Prize in Chemistry 2007) for his work on the mechanistic basics of surface-centered catalysis.

For a long period of time, homogeneous and heterogeneous catalysis were considered disjunctive subdisciplines, based on rather different operating regimes, which in fact resulted in different methodological ways of approaching the mechanisms of the underlying elementary steps. In the meantime, however, both areas have approached each other, in particular through so-called “organometallic surface chemistry.” Here, Jean-Marie Basset [1] may be seen as the most prolific protagonist: he was the first to achieve well-defined catalytically active organometallic species attached to solid-state surfaces.

### 1.1

#### Historical Pathways

The history of organometallic catalysis begun with a surprising discovery by the German chemist Otto Roelen (1897–1993) at Ruhrchemie (now Oxea) in

1) “The number of bodies that effect catalytic interactions is very large, and is still increasing incessantly with the progressive development of chemistry” [5d].

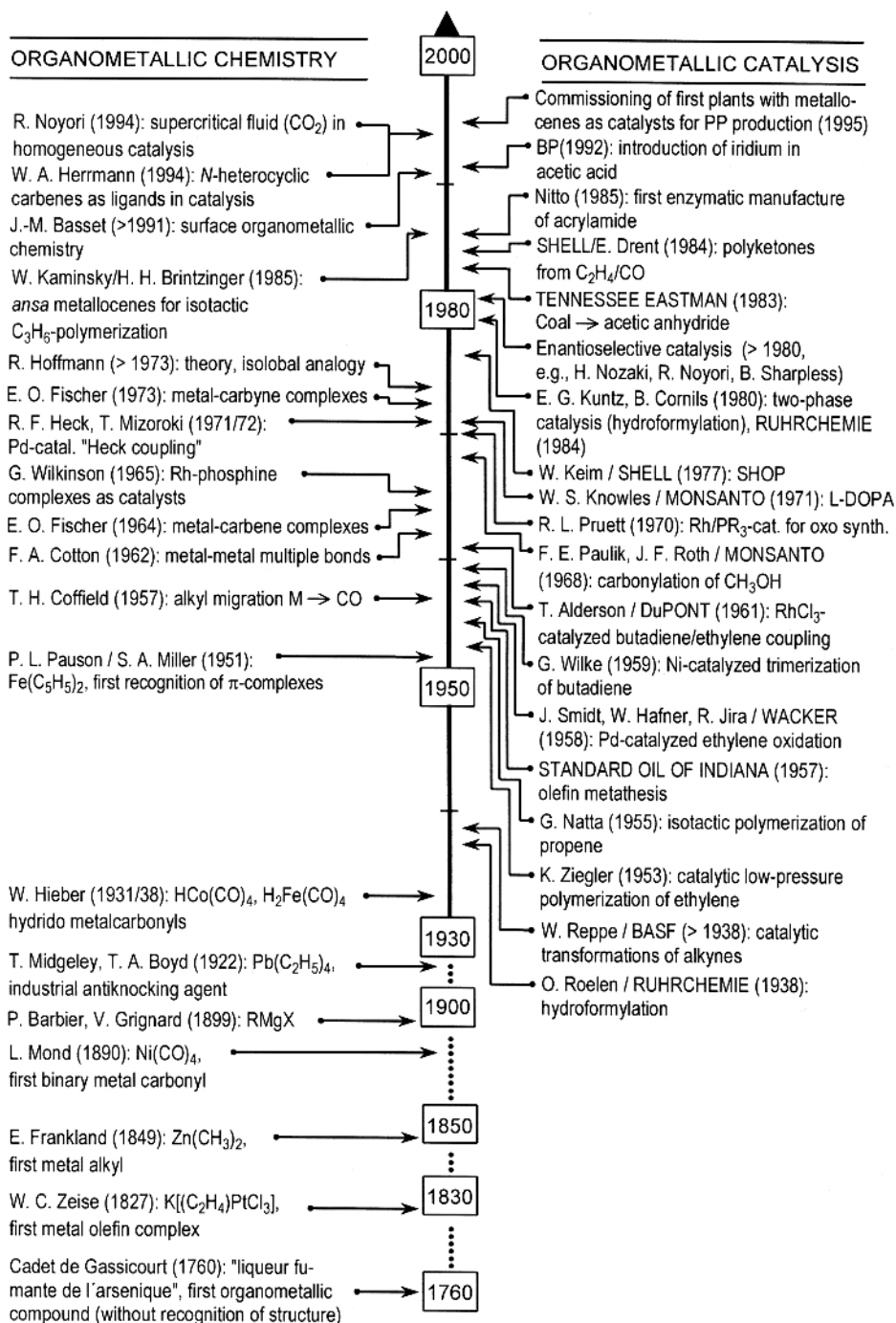
Oberhausen [2–4]. He is the *true pioneer* in this entire field, and he would clearly have deserved an early Nobel Prize.

Before 1938, when the landmark “oxo synthesis” was discovered by Otto Roelen (“hydroformylation,” “Roelen reaction”), *homogeneous catalysis* had received only occasional mention [2]. Sabatier and Mittasch [5] also made only passing reference to homogeneous catalysis. It was probably Sabatier (the discoverer of nickel-catalyzed hydrogenation) who gave a first rough classification of catalytic reactions: *homogeneous systems*, where all the compounds present, or at least one of them, are miscible with the catalyst (e.g., fermentations, Friedel–Crafts catalysts); and *heterogeneous systems* that are based upon a solid catalyst that is “in contact with a reactive liquid or gaseous phase. The effect takes place either on the surface of the catalyst if it is compact . . . or in its entire mass if it is porous . . .” [5c]. Mittasch in his notable *Kurze Geschichte der Katalyse in Praxis und Theorie* (*Short History of Catalysis in Practice and Theory*) mentioned homogeneous catalysis only incidentally [5e]. At that time, the term *catalysis* in its general usage was inseparably linked to large-volume industrial chemical syntheses (ammonia synthesis, coal hydrogenation, fat hardening, Fischer–Tropsch synthesis, mineral oil processing). Catalysis was thus synonymous with *heterogeneously* catalyzed reactions. Except for “exotic” applications (Grignard reagents, the Mond process, and Frankland organozinc reactions) organometallic compounds were not accorded any technical or commercial importance. Figure 1.1 demonstrates this clearly: after an initial period of synthetic organometallic chemistry the discoveries of Roelen, Reppe, Ziegler, and others sparked off a second, industrially oriented period of organometallic chemistry. Only since the 1950s has *homogeneous catalysis* been an established field of organometallic chemistry. It has now become a central feature within the chemical sciences.

Hence, unsurprisingly, Otto Roelen’s initial investigations into homogeneous coordination catalysts in oxo synthesis proved a source of much frustration (reviewed in Reference [2b]). It was only the work of Adkins and Krsek [6], Storch *et al.* [7], Berty and Markó [8], and Natta [9] that confirmed oxo catalysts to be homogeneous in nature. The intense activity associated with hydroformylation and oxo catalysts, with carbonylations as described by Reppe [10], and with Ziegler’s “borderline case,” the low-pressure polyethylene synthesis, highlighted the recognition of this new special type of catalysis (more historical information is given in References [11–13] and in the Historical Glossary below).

Table 1.1, showing the strengths and weaknesses of both methods, makes it easy to differentiate homogeneous from the older, successful heterogeneous catalysis [14–16].

The information given in Table 1.1 is discussed in numerous publications: a few typical ones are recommended for further details [17–23]. Despite the fact that heterogeneous catalysis has advantages in application (not without good reason do the most important mineral oil processing methods involve heterogeneous catalysis), the great challenge presented by homogeneous catalysis is the far better mechanistic understanding of its micro “processes” (catalytic cycles), with the possibility of influencing the steric and electronic properties of these



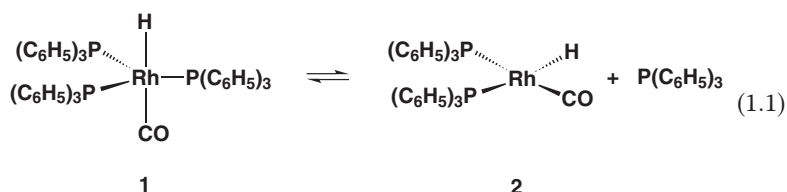
**Figure 1.1** Synoptic presentation of the development of organometallic chemistry and homogeneous catalysis.

**Table 1.1** Homogeneous versus heterogeneous catalysis.

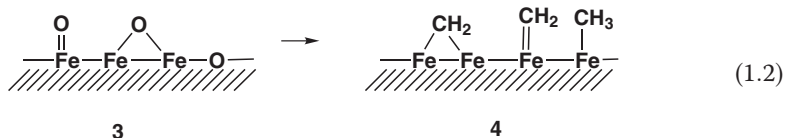
	Homogeneous catalysis	Heterogeneous catalysis
Activity (relative to metal content)	High	Variable
Selectivity	High	Variable
Reaction conditions	Mild	Harsh
Service life of catalysts	Variable	Long
Sensitivity toward catalyst poisons	Low	High
Diffusion problems	None	May be important
Catalyst recycling	Expensive	Not necessary
Variability of steric and electronic properties of catalysts	Possible	Not possible
Mechanistic understanding	Plausible under random conditions	More or less impossible

molecularly defined catalysts. It is thus possible to tailor optimized homogeneous catalysts to the particular problem involved, by adapting their chemical and structural basis: this is doubtless a clear advantage over heterogeneous catalysis, which is said to be an alchemist's "black art" [24] even though this statement is vehemently disputed [25].

The two "philosophies" are typically exemplified by hydroformylation (reaction (1.1)) [26] on the one hand and the Fischer–Tropsch reaction (reaction (1.2)) [7] on the other hand. They both represent catalytic carbon monoxide chemistry: in the first case the molecular structure of the *homogeneous* catalyst (structures **1** and **2**) is precisely known to be trigonal-bipyramidal,  $d^8$ -Rh<sup>I</sup>:

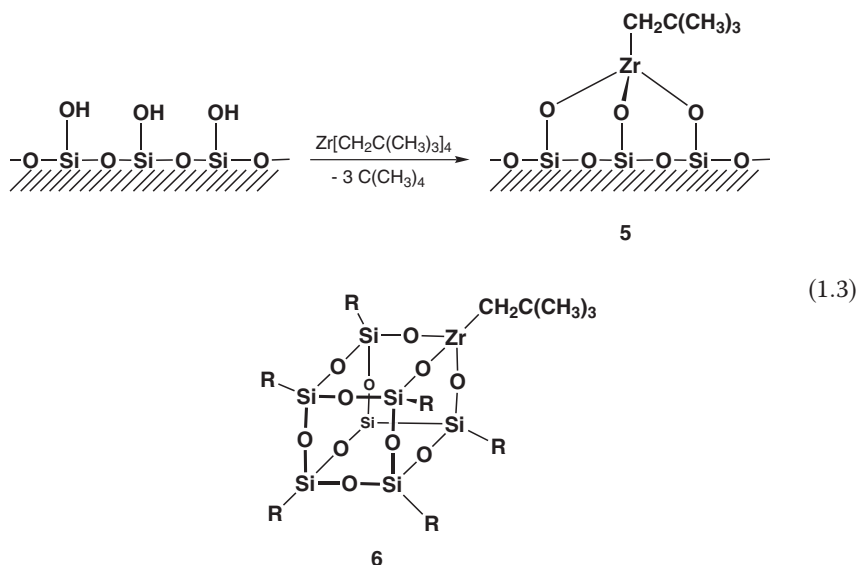


In contrast, Fischer–Tropsch chemistry requires *heterogeneous* catalysts of structures close to **3** and **4**, of which the surface structures are not precisely known, and for which therefore no clear molecular mechanism is known [27]:



"Organometallic surface science" [1, 28] seems to promise a bridge between the classical antipodes: by using well-defined molecular starting compounds such as metal alkyls and making them react in a defined way with surface species

(e.g.,  $\equiv\text{SiOH}$  groups), molecularly dispersed but immobile catalyst species in a more or less well-defined chemical environment can be produced. The alkylzirconium(IV) surface species **5** (which efficiently hydrogenates olefins) is an example (reaction (1.3)) [28b], and the molecular model (**6**) derived from a so-called silsesquioxane ( $\text{R} = \text{cyclopentyl/-hexyl}$ ) is related to it [28c,d]:



Bearing these facts in mind it is not surprising that a compromise between heterogeneous and homogeneous catalysts, made by combining the advantages of the two catalytic methods, has so far been attempted only from the homogeneous catalysis side, that is, by heterogenizing homogeneous catalysts and not vice versa. Most experiments with supported and therefore heterogeneous catalysts failed. In this respect Heinemann's question "Homogeneous and heterogeneous catalysis – common frontier or common territory?" still remains unanswered [29]. Taking all methods of mineral oil processing into account, the relative share of heterogeneous to homogeneous catalysis is approx. 85:15 [30].

Table 1.2 shows to what extent homogeneous catalysts are tailor-made and how variable and adaptable they are to the problem concerned by suitable reaction and unit processes, taking as examples the modern hydroformylation processes and catalysts. It clearly illustrates that various different solutions in terms of reaction conditions and product separation technologies are available to meet any list of requirements (specifications) of a modern oxo process [31, 32]. The technology and the homogeneous catalyst may be adapted to a mutual target, whereas with heterogeneous catalysis the choice of the catalyst determines the reaction conditions to a large extent (and usually the technical solution, too) (cf. References [33–37]).

An early example of the variability of highly sophisticated organometallic homogeneous catalysis is the synthesis of vitamin A, developed by Pommer

Table 1.2 Industrially important oxo processes [18,31,32].

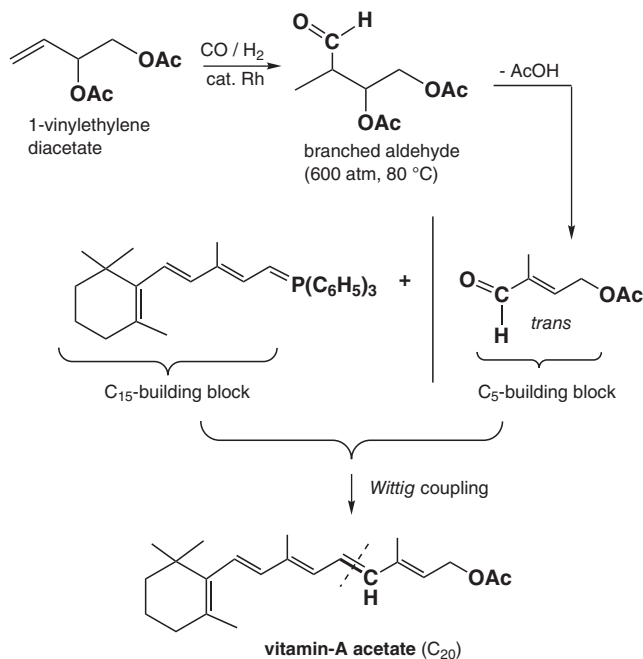
Parameter	Catalyst metal:					
	Cobalt			Rhodium		
Variant:	Unmodified	Modified	Unmodified	Unmodified	Modified	
Ligand:	None	Phosphines	None	None	Phosphines	
Process <sup>a)</sup> :	1	2	3	3	4	5
Active catalyst species	HCo(CO) <sub>4</sub>	HCo(CO) <sub>3</sub> L	HRh(CO) <sub>4</sub>	HRh(CO) <sub>4</sub>	HRh(CO) <sub>3</sub>	HRh(CO) <sub>3</sub>
Temperature (°C)	150–180	160–200	100–140	100–140	60–120	110–130
Pressure (MPa)	20–30	5–15	20–30	20–30	1–5	4–6
Catalyst conc. relative. to olefin (%)	0.1–1	0.6	10 <sup>−4</sup> –0.01	10 <sup>−4</sup> –0.01	0.01–0.1	0.001–1
LHSV <sup>b)</sup>	0.5–2	0.1–0.2	0.3–0.6	0.3–0.6	0.1–0.2	>0.2
Products	Aldehydes	Alcohols	Aldehydes	Aldehydes	Aldehydes	Aldehydes
Amount of byproducts	High	High	Low	Low	Low	Low
n/i ratio	80 : 20 <sup>c)</sup>	88 : 12	50 : 50	50 : 50	92 : 8	>95 : <5
Sensitivity to poisons	No	No	No	No	Yes	No

a) Key: 1 = BASF, Ruhrchemie; 2 = Shell; 3 = Ruhrchemie; 4 = Union Carbide (LPO); 5 = Ruhrchemie/Rhône-Poulenc.

b) LHSV = liquid hourly space velocity.

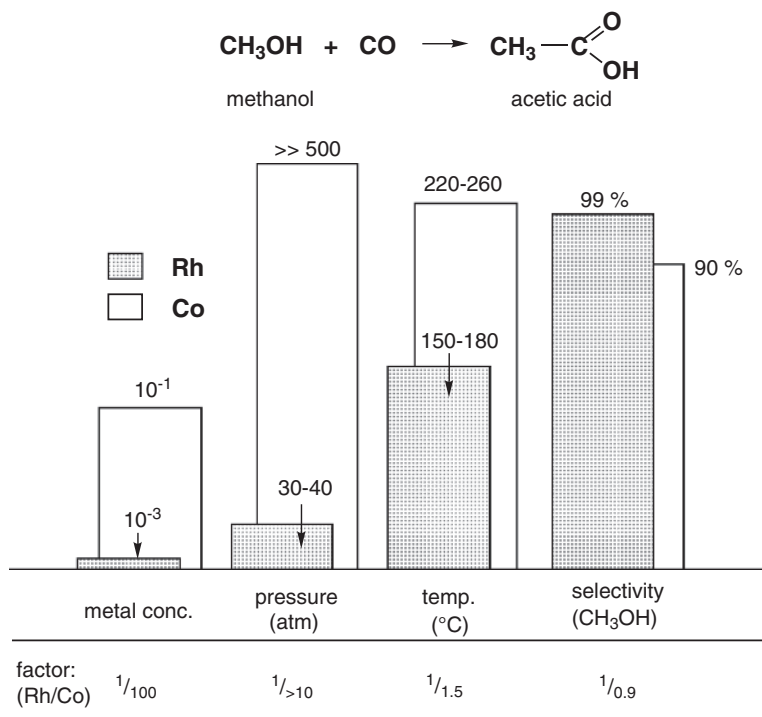
c) 65 : 35 at an early stage of development.

*et al.* at BASF AG in the late 1950s [38a]; a plant producing 600 tons per year has been operational since 1971 [38b]. While the key synthetic feature is a Wittig-type coupling between vinyl- $\beta$ -ionone ( $C_{15}$ ) and  $\gamma$ -formylcrotyl acetate ( $C_5$ ), there is also an earlier hydroformylation step in the synthesis of a precursor compound: 1-vinylethylene diacetate is hydroformylated under high-pressure conditions to yield the *branched* aldehyde with regioselectivities of up to 80%. This intermediate is then transferred into the  $\alpha,\beta$ -unsaturated derivative, which couples with the  $C_{15}$  ylide building block to form the  $C_{20}$  vitamin A according to Scheme 1.1 [39a–c]. An alternative Hoffmann–La Roche procedure also includes a hydroformylation step [39d]. These two processes share most of the vitamin A world capacity of approximately 3000 tons per year.



**Scheme 1.1** Vitamin A synthesis.

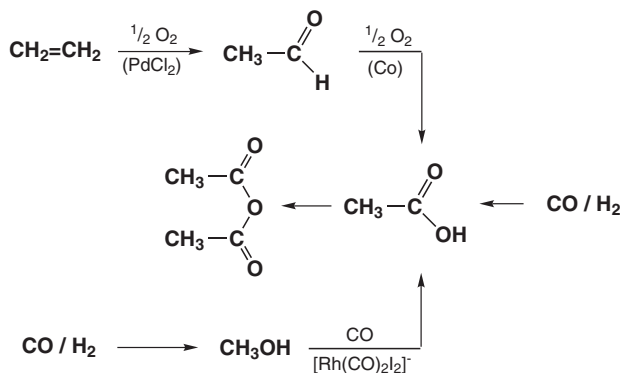
Another important and commercially essential example that proves the variability of homogeneous catalysis is the synthesis of acetic acid via carbonylation of methanol. Here, too, a breakthrough was achieved by employing milder reaction conditions and by increasing yield and selectivity as a result of switching from *cobalt* (in the old BASF process) to *rhodium* catalysts (Monsanto). This landmark change first introduced rhodium as a catalyst metal to the chemical industry. The effect of this change is seen impressively in Figure 1.2 by comparing the required metal concentrations, pressures, and temperatures of the methanol carbonylation, on the one hand, and the selectivities obtained on the other hand, for both catalyst metals.



**Figure 1.2** Catalytic breakthrough of rhodium versus cobalt in homogeneous catalysis: methanol carbonylation.

Parallel to this change of catalyst in methanol carbonylation, the feedstock for the manufacture of acetic acid was also changed at many sites, with ethylene being replaced by methanol (Scheme 1.2).

This development began to reduce steadily the capacities of acetaldehyde that previously had been made by oxidation of ethylene (Wacker–Hoechst process)



**Scheme 1.2** Alternative routes to acetic acid.

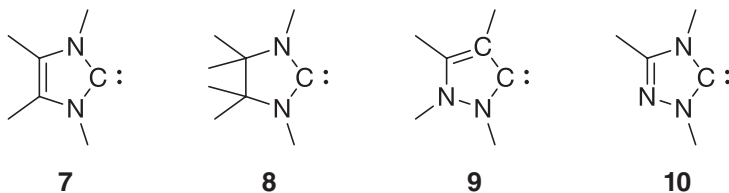


and then converted into acetic acid. Moreover, the Monsanto process, the second-generation process for methanol carbonylation, is now being followed by the third generation of highly efficient carbonylation processes, enabling acetic anhydride as well as acetic acid to be produced (cf. Scheme 1.2; Tennessee–Eastman [36] and BP [37] processes). The most advanced process (Hoechst [40]) has so far not been implemented industrially. It should be mentioned in passing that the Tennessee–Eastman technology is geared (although not necessarily) to coal as a raw material and to the synthesis gas made from it by coal gasification [12,41], and consequently a reference to the role of homogeneous catalysis in coal processing is made (cf. Scheme 1.2).

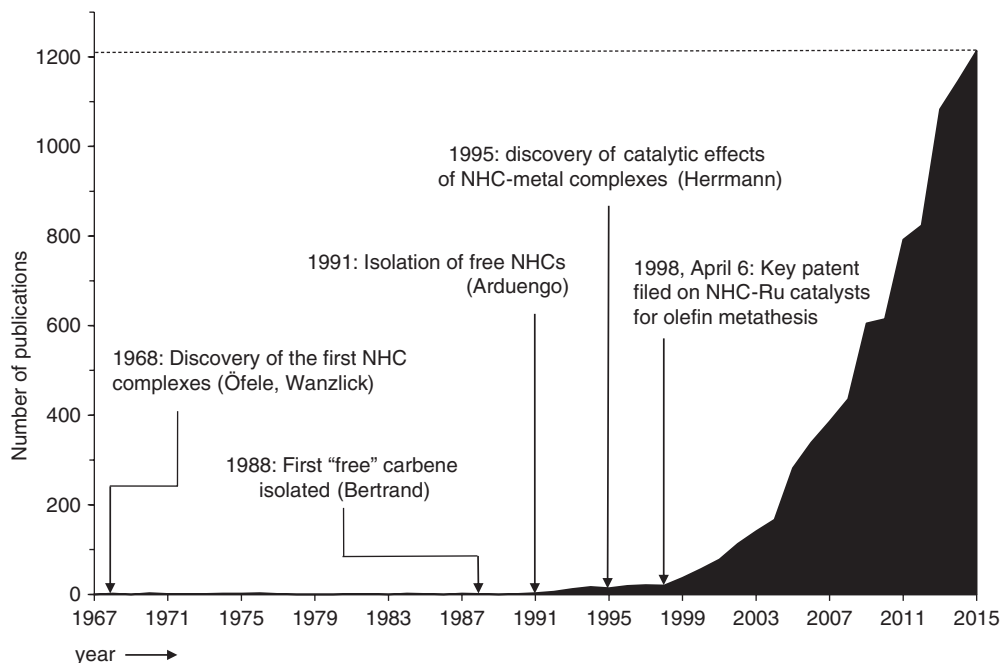
## 1.2

### Topical Developments Since Year 2000

Just at the time when the second edition of this book was published (2002), a tremendous new line of development became visible: *N*-heterocyclic carbenes (NHCs) began to unfold their efficiency as ligands in organometallic catalysis, as was highlighted in an early review article [42]. It was the Munich group of Herrmann who first demonstrated, back in 1995, the catalytic effects of palladium-NHC complexes in Heck-type CC-coupling reactions [43]. It soon became evident that these new catalysts are frequently superior to the standard phosphane ligands, in terms of structural diversity, easy accessibility, cheapness, and catalytic performance [42–44]. The most prominent examples belong to the structural varieties of type 7–10.

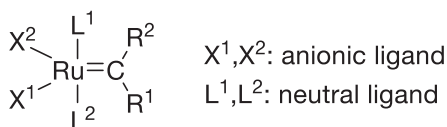


Before Herrmann's discovery, which obviously was stimulated by Arduengo's report on the isolation of a first "free" carbene (the bis-*N,N'*-mesityl-imidazolyli-dene) in 1991, this group of single-faced two-electron ligands had in fact played only a minor role in coordination chemistry, while nothing was known in the catalytic context. As can be seen from Figure 1.3, an exponential increase of journal articles, review articles, and patents appeared from many dozens of research groups around the world. Up to the end of 2015, a total of more than 1200 reports, which include about 70 patents, had appeared in the literature, covering the synthesis and (predominantly catalytic) applications of metal-NHC complexes. Curiously, even carbocyclic  $C_3$  and  $C_7$  carbenes complexes unfolded catalytic effects [45], albeit their efficiency has so far been inferior to their *N*-heterocyclic counterparts.



**Figure 1.3** Journal articles, review articles, and patents on "N-heterocyclic carbenes". Source: SciFinder, as of 14 January 2016.

The breakthrough in this development came from the beneficial catalytic effects of type-**11** ruthenium complexes in olefin metathesis, as first invented by the Munich group [46,47] and utilized in the subsequent work of Grubbs and many others. A combination of NHC-Ligands ( $L^1$ ) and other two-electron ligands ( $L^2$ , e.g. phosphanes, amines) commonly yield the best results in catalytic olefin metathesis.



## 11

In the meantime, *N*-heterocyclic carbenes represent a major field of organometallic chemistry and catalysis, with a plethora of benchwork and industrial applications. Thus, the prediction made in 2002 that "a revolutionary turning point in organometallic catalysis is emerging" has literally become true [42].

## 1.3

## Organization of the Third Edition

The extended scope of the third edition of “Applied Homogeneous Catalysis with Organometallic Compounds”, covering 1700 printed pages underlines the importance of this topic.

**Part A** is focused on **Applied Homogeneous Catalysis** (Chapters 2–9, pg. 27–692). The key topics center around industrially established processes such as those based on *carbon monoxide* and *hydrogen* (e.g. hydroformylation, hydrogenation), olefins with an emphasis on metathesis, oligomerization, (co-)polymerization, alkene carbonylation, and oxidation (e.g. Wacker Process, epoxidation, hydroxylation).

It is obvious, that homogeneous organometallic catalysis plays a major role in the industrial production of bulk and fine chemicals as well as pharmaceuticals. The landmark discovery dates back in the year of 1938, when Otto Roelen first observed the catalytic incorporation of carbon monoxide and hydrogen into simple olefins such as ethylene and propylene. Thus, the oxo synthesis became a pioneering success story by its own right, due to the disseminating research work performed at the Ruhrchemie company in Oberhausen/Germany (Chapter 21). Decades of research efforts finally yielded the two-phase Ruhrchemie-Rhône Poulenc Process in 1984 under the scientific leadership of Boy Cornils. It has become one of the most elegant catalytic production processes for bulk chemicals in industry.

Other pertinent carbonylation reactions are summarized in Chapter 3, including the industrially highly beneficial alternating copolymerization with carbon monoxide (Chapter 3.6).

The avant-garde of olefin polymerization/copolymerization was landmarked by the Brintzinger-Kaminsky discovery of metallocene-based catalysis and subsequent developments (Chapter 4). An additional driving force resulted from the “constrained geometry” of half-sandwich type catalysts, introduced by Jun Okuda in his Habilitation Thesis at the Technical University of Munich (Chapter 4.1). Yet more recent approaches stem from a variety of metal-based catalysts (including the lanthanoids) effective in the polymerization of 1,3-butadiene (Chapter 4.4). Finally, the elegant production of polycarbonates, an ever-growing group of technical polymers exhibiting beneficial material properties, has become a recent stronghold of applied organometallic catalysis, too (Chapter 4.5).

Chapter 5 summarized the present technical state of oligomerization, cyclooligomerization, and dimerization of olefins. A plethora of catalysts has recently become available, and the field is now open for efficient tailor-made catalysts, particularly in [2+2+2] cycloadditions.

Ever since the 2<sup>nd</sup> Edition got completed, cross coupling reactions have been developed and improved by numerous laboratories (Chapter 6). Particularly noteworthy are the Heck-Mizoroki, Suzuki-Miyaura, Kumada-Corriu, Negishi, and Sonogashira Reactions. Palladium continues to play the major role in

homogeneous catalysts to arrange known and novel types of C–N and C–O bond formations.

Oxidation has long been an overly neglected topic in organometallic catalysts. This picture has changed, however, by virtue of new catalysts, including those effecting decarbonylative and decarboxylative processes (Chapter 7).

Hydrosilylation (Chapter 8) and hydrogenation (Chapter 9) are among the classics of organometallic catalysis. Nevertheless, new approaches have been designed since the 2<sup>nd</sup> Edition of this monograph was completed.

**Part B** summarizes **Recent Developments** (Chapters 10–38, pg. 693–1700) and is organized in five thematic subparts:

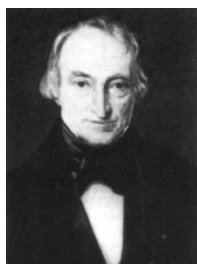
- 1) **Catalysts:** Here, new trends related to organometallic catalysts (Chapter 10) cover iron-based systems of various kinds, copper-catalyzed C–O, C–N, and C–C bond formation, rare-earth metal catalysts, and chiral “frustrated” Lewis pair catalysts. Great progress has also been made on new ligands (Chapter 11), with the *N*-heterocyclic carbones landmarking a new era in homogeneous catalysis. Other recent developments in the design of novel ligand systems are, for example, related to host-guest relations and self-organization (including uni-, supramolecular and self-assembled hosts), micellar catalysis, switchable catalysis, metal-pincer type complexes as well as the ever-growing sector of biocatalysis.
- 2) **Methods:** Chapters 12–20 are dedicated to methodological developments in organometallic catalysis. The following avant-garde topics have been selected: Computational chemistry, reaction engineering technologies, supported liquid phase catalysis, surface organometallic chemistry, high-throughput screening methodologies, organometallic photo catalysis, electrochemical water oxidation and reduction, multicomponent reactions, and supercritical fluids (reactions and separation techniques, respectively).
- 3) **Special Reactions:** An enormous variety of new approaches to organometallic bond making deemed necessary to be covered in the present new edition (Chapters 21–33). To give just a few selected examples, particular progress has been made in the C–H activation coupling, in the metathesis of alkenes and alkynes including totally novel industrial and pharmaceutical applications, in the catalytic hydroamination of non-activated CC multiple bonds and in amide bond-forming reactions, as well as in the selective alkane oxidation. Beyond that, catalytic “click reactions” and the role of sulfur in homogeneous catalysis have come to the fore ever since the second edition was completed.
- 4) **Alternative Feedstocks:** Regrowable (biogenic) and ubiquitous, abundant feedstocks landmark a new era in catalysis, with increasing significance to future chemical production. This field is now under active investigation both in academic and industrial laboratories. As a consequence, subpart 4 is dealing with oleochemistry, carbon dioxide as a building block feedstock, as well as biomass and biomass-derived platform chemicals (Chapters 34–36).
- 5) **Catalysis for Energy:** Photocatalytic processes dominate the hydrogen production assisted by earth-abundant metal-based molecular catalysts

(Chapter 37), while the well-established water-gas shift reaction (Chapter 38) forms an industrial basis of process energy.

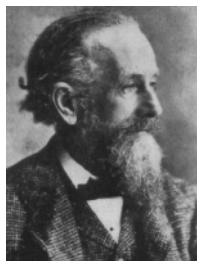
The Historical Glossary on the following pages refers to References [9, 10, 12, 48–50, 60]. No comprehensive history of organometallic chemistry is available as yet. A first review article was published in 1975 by Thayer [48], Werner has highlighted “Landmarks on Organo-Transition Metal Chemistry” in a recent monograph [61].

## 1.4

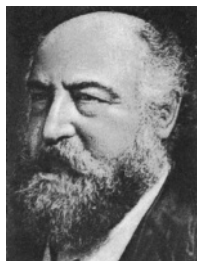
### Historical Glossary



*William Christopher Zeise* (1789–1847) was a Danish apothecary and professor in Copenhagen, Denmark. He synthesized the first metal–olefin complex by serendipity, when he treated platinum(IV) chloride with ethanol and potassium chloride:  $\text{K}[\text{PtCl}_3(\eta^2\text{-C}_2\text{H}_4)]$ , “*sal kalico-platinicus inflammabilis*” (cf. Reference [49]).  $\pi$ -Complexation of olefins at transition metals nowadays is a key feature of homogeneous catalysis in terms of olefin activation, with the Wacker–Hoechst process being a prominent example.



*Edward Frankland* (1825–1899) discovered the first transition metal alkyl complexes – diethylzinc (“*mobile fluid*”) and ethylzinc iodide (“*white mass of crystals*”) – while he worked in Robert Bunsen’s Marburg laboratory (1849). Frankland was later a professor of chemistry in London. Alkyl–metal bonding occurs in practically all catalytic processes involving hydrocarbons, for example, hydroformylation, hydrogenation of olefins, “hydrocarbon activation,” and C–H activation.



*Ludwig Mond* (1839–1909) was a German chemist who had emigrated from Kassel. He discovered the first binary metal carbonyl, the volatile, colorless liquid  $\text{Ni}(\text{CO})_4$ , in his soda factory at Widnes, UK [51]. This discovery not only initiated systematic research in this particular area but also had great relevance to the activation of carbon monoxide by transition metals. Mond’s discovery initiated Paul Sabatier’s study of the nickel chemistry of ethylene, in which context he found the catalytic hydrogenation of  $\text{C}=\text{C}$  double bonds.



*Victor A.F. Grignard* (1871–1935) was a student of Philippe Barbier. He discovered in 1899 the “Grignard” reagents, normally written as  $\text{RMgX}$  [50]. This class of compounds developed a broad chemistry as nucleophilic organyl-transfer reagents (“Grignard reaction”). Grignard was a professor of chemistry in Nancy and Lyon. He received the Nobel Prize in Chemistry (together with Paul Sabatier) in 1912.

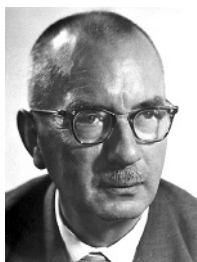
*Walter Reppe* (1892–1969) was the research director of Badische Anilin- & Sodafabrik (BASF) at Ludwigshafen, Germany. His research included metal-catalyzed reactions of acetylene (1938) and of carbon monoxide (1939). High-pressure catalytic acetylene chemistry is nowadays named after him. He also discovered the metal carbonyl-catalyzed cyclooligomerization of acetylene to yield styrene, benzene, and cyclooctatetraene (1948) [10,53].



*Walter Hieber* (1895–1976) was a student of Rudolf Weiland, who performed early experimental work on Alfred Werner’s theory of coordination compounds (*Hauptvalenzen*, *Nebenvalezen*). Hieber received his PhD in 1919 from Tübingen University on a topic concerning ferric complexes of hypophosphorous acid. He then developed metal carbonyl chemistry, mainly at Technische Hochschule München (1935–1964); he is now considered the pioneering researcher in this area of study. His name is associated with compounds like  $\text{HCo}(\text{CO})_4$  and  $\text{H}_2\text{Fe}(\text{CO})_4$  that are relevant to catalytic hydrogen-transfer reactions (hydroformylation). Nucleophilic addition to metal carbonyls, for example,  $\text{Fe}(\text{CO})_5 + \text{OH}^- \rightarrow [(\text{CO})_4\text{FeC}(\text{=O})\text{OH}]^-$ , is known as the “Hieber base reaction” (cf. Reference). Image reprinted with permission from Technische Universität München, Institute for Inorganic Chemistry.



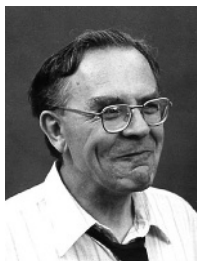
*Otto Roelen* (1897–1993) was a chemist at Ruhrchemie AG in Oberhausen, Germany [2]. He had received his training in (heterogeneous!) catalysis from Franz Fischer and Hans Tropsch at the Kaiser-Wilhelm-Institut Mülheim/Ruhr, Germany. Roelen discovered in 1938 the cobalt-catalyzed hydroformylation of olefins (“oxo synthesis,” “Roelen reaction”) [4]. This process has been improved ever since, when rhodium was discovered to be the much more active catalyst metal. Today the “Ruhrchemie-Rhône-Poulenc Process” developed under B. Cornils et al. [2b] landmarks the industrial best standard. Hydroformylation represents the largest-volume homogeneous catalysis process employing organometallic catalysts. Image reprinted with courtesy from Boy Cornils.



**Karl Ziegler** (1898–1973) headed the Max-Planck-Institut für Kohlenforschung in Mülheim/Ruhr, succeeding Franz Fischer (1877–1947) in this position. He was an organic chemist by training but developed the chemistry of lithium, potassium, and aluminum alkyls. His most revolutionary discovery was the alkyltitanium-catalyzed low-pressure/high-density polymerization of ethylene in the fall of 1953 [54]. The first polymerization plants for HDPE went into operation in 1955, simultaneously at Hoechst AG in Frankfurt, Germany, and at Ruhrchemie AG in Oberhausen, Germany (for ultra-high molecular weight polyethylene, UHMW) [55]. He received the Nobel Prize in Chemistry in 1963 together with Giulio Natta [56].



**Giulio Natta** (1903–1979), one of the early supporters of the oxo reaction [9,57], discovered in 1956 the isotacticity and syndiotacticity of olefin polymerization (e.g., propylene) using Ziegler's *Metallorganische Mischkatalysatoren* (see above). The industrial production of isotactic polypropylene started at Montecatini in Italy in 1956. Natta was a professor at the universities of Turin and Milan. He received the Nobel Prize in Chemistry together with Karl Ziegler in 1963 [56].



**Geoffrey Wilkinson** (1921–1996) was one of the pioneers of organometallic synthesis and catalysis. One of his far-reaching discoveries was the low-temperature/low-pressure hydrogenation of olefins by a then-new generation of (homogeneous) catalysts in 1965, such as  $\text{ClRh}[\text{P}(\text{C}_6\text{H}_5)_3]_3$  ("Wilkinson catalyst" [58]). This invention greatly spurred the industrial use of rhodium- instead of cobalt-based homogeneous catalysts, for example, in hydrogenation, hydroformylation, and the Monsanto acetic acid process (cf. Section 3.2). Wilkinson was a professor (emeritus) at Imperial College London. He received the Nobel Prize in Chemistry jointly with Ernst Otto Fischer (Technische Universität München) in 1973 [56]. Photo credit: Smokefoot.

**Günther Wilke** (1925–2016) received his PhD under the supervision of Karl Freudenberg at Heidelberg University. He developed the organonickel-catalyzed cyclooligomerization of butadiene (1956), for example, to 1,5,9-cyclododecatriene ("Wilke reaction"), with the latter being industrially converted into polyamide-12. Another landmark discovery relevant to homogeneous catalysis was nickel-(bis- $\eta^3$ -allyl) (1961). 1,5,9-Cyclododecatriene-nickel became famous as a source of "naked nickel." Wilke headed the Max-Planck-Institut für Kohlenforschung at Mülheim/Ruhr, Germany, from 1967 until 1992 [59], succeeding Karl Ziegler.





*Richard F. Heck* (1931–2015) was a student of Saul Winstein (UCLA) and Vladimir Prelog (ETH Zürich). He started mechanistic work on homogeneous catalysis in 1956 when he entered Hercules Inc. (Wilmington, Del., USA) as a research chemist. He pioneered the elucidation of reaction mechanisms of organometallic processes, for example, hydroformylation and Ziegler–Natta polymerization, and published a number of key papers about the chemical and mechanistic backgrounds of these reactions.

He was a chemistry professor at the University of Delaware from 1971 until his retirement in 1989. For the “Heck reaction” the reader is referred to Chapter 6. Photo credit: Holger Motzkau.

*Peter L. Pauson* (1925–2013) is among the pioneers of modern organometallic chemistry. In 1951 he discovered ferrocene,  $(C_5H_5)_2Fe$ , thus initiating the renaissance of inorganic chemistry. In 1971, he discovered the (cobalt-mediated) Pauson–Khand reaction, a triple C–C coupling leading to cyclopent-2-en-1-ones. Pauson was born in Bamberg, Germany, emigrated in the Nazi era with his parents to the United States of America, and started his scientific career in Pittsburgh and in Harvard where he met Wilkinson and Rosenblum. He spent most of his academic career at the University of Strathclyde in Glasgow, UK.



*Ernst Otto Fischer* (1918–2007) was a student of Walter Hieber at Technische Hochschule München where he received his PhD degree in 1948 in the field of synthetic metal carbonyl chemistry. He elucidated the molecular structure of ferrocene shortly after this compound was discovered. Further highlights in his life’s work were the synthesis of dibenzenechromium  $(C_6H_6)_2Cr$  in 1955 and the discoveries of the first metal-carbene (1967) and the first metal-carbyne complex (1971). In 1964 he succeeded Walter Hieber to the chair of inorganic chemistry at Technische Hochschule München, from which he retired in 1985. As a pioneer in organometallic chemistry [60], he received the Nobel Prize in Chemistry jointly with Geoffrey Wilkinson (Imperial College London) in 1973. Image reprinted with permission from Technische Universität München, Institute for Inorganic Chemistry.



*Ryōji Noyori* (born 1938) received his PhD from Kyoto University in 1967. Since 1972 he has been Professor of Chemistry at the Nagoya University and since 2000 Director of the Research Center for Material Science in Nagoya, Japan. In 1980 Noyori and his coworkers synthesized both enantiomers of the diphosphine ligand BINAP, a ligand for chiral catalytic reactions with rhodium complexes. To synthesize more generally applicable catalysts, Noyori replaced Rh(I) with Ru(II). The reactions catalyzed by



ruthenium(II)-BINAP complexes give high enantiomeric excess, high yields, and can be scaled up for industrial use; for example, as early as in 1980 with the catalytic synthesis of the chiral fine chemical L-menthol. Noyori received the Nobel Prize in Chemistry in 2001 together with William S. Knowles and K. Barry Sharpless. Photo credit: Brunei.

*K. Barry Sharpless* (born 1941) received his PhD in 1968 from Stanford University. Since 1990 he has been W.M. Keck Professor of Chemistry at the Scripps Research Institute in La Jolla, USA. Among several other important discoveries, Sharpless developed catalysts for asymmetric oxidations. In 1980 he achieved the catalytic asymmetric oxidation of allylic alcohols to chiral epoxides by utilizing titanium complexes with chiral ligands. One of the many applications of chiral epoxides is the use of the epoxide (*R*)-glycidol for pharmaceutical production of beta-blockers. Sharpless received the Nobel Prize in Chemistry in 2001 together with William S. Knowles and Ryōji Noyori.

*Richard R. Schrock* (born 1945) received his PhD under the supervision of John A. Osborn (1939–2000) at Harvard University (1971). After postdoctoral work in Cambridge/GB, he spent three years as a researcher at the Experimental Station of DuPont in Wilmington/USA. Since 1975 he has been a professor at MIT (Boston/USA), since 1989 as a Frederick G. Keyes Distinguished Professor. Among others areas, his research centered around olefin metathesis, for which reaction he developed structurally defined organometallic catalysts, in addition to his experimental contributions towards the understanding of the basic mechanistic principles (“Schrock-type carbenes,” metallocyclobutane mechanism). He received the Nobel Prize in Chemistry in 2005 jointly with Chauvin and Grubbs.



*Robert H. Grubbs* (born 1942) received his PhD under the supervision of Ronald Breslow at Columbia University, New York/USA (1968). After postdoctoral work with James Collman at Stanford, he was appointed to the chemistry department of Michigan State University, and in 1978 to the California Institute of Technology (USA). He is known for work on olefin metathesis, for which reaction he developed catalysts based on the initial discoveries of Wolfgang A. Herrmann (Technical University of Munich/Germany), see Chapter 1.2. He shared the Nobel Prize in Chemistry in 2005 with Yves Chauvin and Richard R. Schrock. Photo credit: Conrad Erb, Chemical Heritage Foundation.

*Yves Chauvin* (1930–2015) was a French chemist who received his PhD at the École Supérieure de Chimie Industrielle de Lyon (today CPE Lyon) in 1954. He spent his scientific career at the Institute Français du Pétrole (IFP) in Rueil-Malmaison near Paris. His industry-related research culminated in the epochal

discovery of olefin metathesis (1970), published in *Die Makromolekulare Chemie* (1971) vol. 141, pp. 161–176. For this truly pioneering work, he received the Nobel Prize in Chemistry along with Richard R. Schrock and Robert H. Grubbs in 2005.



*Jean-Marie Basset* (born 1943) received his PhD in 1969 from the University of Lyon/France. After postdoctoral research at the University of Toronto/Canada, he went to the Institute of Catalysis in Lyon/CNRS (1971). He then moved to the new King Abdullah University of Science and Technology (KAUST) in Saudi Arabia where he established the KAUST Catalysis Research Center and has been ever since. Basset is the highly recognized pioneer of organo-metallic surface chemistry, an area – bridging homogeneous and heterogeneous catalysis – he has developed with numerous fundamental contributions in CH-activation and alkane/olefin metathesis [1, 28b]. He has received an Honorary PhD from TU Munich and numerous further awards, for example, the Max Planck Research Award (Germany).

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