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Organometallic chemistry at the threshold of a new millennium. Retrospect and prospect*

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Abstract: The evolution of organometallic chemistry during the second half of the 20th century has transformed chemical science and technology to a degree and in ways that have rarely been matched throughout the history of chemistry. These include the discovery of radically new types of chemical compounds; novel structures and bonding modes; unprecedented reactivity patterns; unsuspected roles of organometallic chemistry in biology; powerful new synthetic methodologies; new materials; and whole new classes of catalysts and catalytic processes of extraordinary versatility and selectivity. The impact of these developments, which still are unfolding, has been truly revolutionary. Some milestones in this remarkable chapter of chemical history, as well as challenges and opportunities confronting organometallic chemistry today, will be examined.

INTRODUCTION

The remarkable flowering of organometallic chemistry, notably of the transition metals, during the second half of the 20th century, has enriched and transformed chemical science to a degree and in ways that have few parallels in the history of the discipline.

The full dimensions of this development cannot be easy to appreciate for anyone who was not around to witness the entire period. In 1950, the traditional branches of chemistry—physical, organic, and inorganic—already were mature disciplines, indeed, to the point that prompted many to wonder whether chemistry had already reached its full maturity with no really major new insights or discoveries remaining to be uncovered.

At the time, organometallic chemistry was a fledgling discipline—hardly recognizable as such. A striking reminder of the state of the field is provided by the organometallic literature—or lack thereof—of the period. Confronted with the massive current volume of literature on organometallic chemistry—journals, monographs, national and international conferences such as this one—it is hard to believe that a general monograph on organometallic chemistry—G. E. Coates' *Organometallic Compounds*—published in 1956, professed to cover the subject in less than 200 pages, of which fewer than 25 were devoted to the organometallic chemistry of the transition metals [1]. The ensuing growth of the field—and of the organometallic literature—were dramatic. Updated and expanded editions of Coates' monograph followed in rapid succession, a 360-page second edition in 1960 [2], and a two-volume 950-page third edition, co-authored by M. L. H. Green, P. Powell, and K. Wade, in 1971 [3]. The 1982 monograph *Comprehensive Organometallic Chemistry*, edited by G. Wilkinson, spans nine volumes occupying *ca* 9400 pages [4], and the 1994 supplement, covering the literature for 1982 to 1994, fills an additional 14 volumes and 9000 pages [5]. At the same time, the fraction of space devoted to

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the organometallic chemistry of the transition metals increased dramatically from 14% in the first edition of Coates [1] to 68% in Wilkinson's compendium [4].

HISTORICAL PERSPECTIVE

Some perspective on the extraordinarily rich landscape of discovery that characterized this period of explosive growth of organometallic chemistry is provided by the, admittedly incomplete and somewhat arbitrary, chronology of selected landmark advances in Table 1.

Table 1 Selected landmark advances in organotransition metal chemistry.

PRIOR TO 1950

- Zeise's salt, $K[(C_2H_4)PtCl_3]$
- Metal carbonyls
- Cobalt-catalyzed hydroformylation
- Reppe synthesis of cyclooctatetraene

1950 TO 1960

- Ferrocene and related metallocenes
- Dibenzenechromium and related arene complexes
- Fluxional behavior
- Ziegler-Natta catalysts for polyethylene and polypropylene
- Prediction and discovery of stable metal-cyclobutadiene complexes
- Pd-catalyzed oxidation of ethylene to acetaldehyde (Wacker)
- CO and olefin insertion reactions
- Stable transition metal hydrides and alkyls

1960 TO 1970

- Oxidative addition reactions
- Homogeneous catalytic hydrogenation
- Metal carbene (alkylidene) complexes
- Olefin metathesis
- Intramolecular C-H oxidative addition
- Heck-Breslow mechanism of Co-catalyzed hydroformylation
- Cossee mechanism of Ziegler-Natta polymerization
- Rhodium-catalyzed hydroformylation
- Bioorganometallic chemistry of cobalt (B_{12} coenzymes)

1970 TO 1980

- Rh-catalyzed carbonylation of methanol to acetic acid (Monsanto)
- Asymmetric catalytic hydrogenation
- Transition metal carbyne (alkylidyne) complexes
- Ni-catalyzed adiponitrile synthesis by hydrocyanation of butadiene
- Free radical pathways of hydrogenation and related reactions

SINCE 1980

- Intermolecular aliphatic C-H oxidative addition
- "Agostic" metal-CH interactions
- Metallocene and other "single site" catalysts for olefin polymerization
- Bio-organometallic chemistry of nickel (CO dehydrogenase; methyl coenzyme M reductase)

Although the organometallic chemistry of the main group elements also has experienced important advances, much of the focus of the modern era of organometallic chemistry—both conceptual and in terms of applications—has been on the transition metals, and it is with this branch of organometallic chemistry that the present account, and the entries in Table 1, are primarily concerned.

The early decades represented in Table 1, through about 1970, are characterized by three types of discoveries [6].

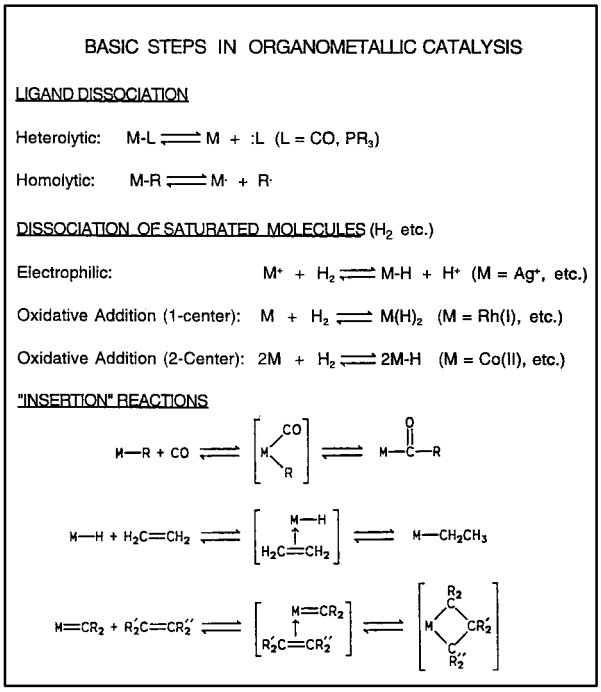
(a) New types of compounds, in many cases characterized by novel ligands and, in some cases, unprecedented metal-ligand bonding interactions. Early examples, notably metal carbonyls and olefin complexes, have been supplemented by the discovery since 1950 of a rich array of metallocenes, metal arene complexes, transition-metal hydrides, alkyls, carbene (alkylidene) and carbyne (alkylidyne) complexes, and, most recently, "agostic" metal complexes containing molecular H_2 and aliphatic C–H ligands.

(b) A variety of basic reactions, summarized in Scheme 1, that constitute the elementary "building blocks" of organometallic reaction chemistry [7]. These encompass conventional metal–ligand dissociation-association processes, as well as homolytic metal–ligand dissociation, distinctive for metal–alkyl complexes and reflecting the characteristic weakness of metal–alkyl bonds. Other characteristic elementary processes include dissociative reactions of saturated molecules with metal centers, and insertion of unsaturated molecules into metal–ligand bonds (migratory insertion reactions).

(c) Organic reactions, such as hydroformylation, hydrogenation, polymerization, oxidation, hydrocyanation, hydrosilylation, and metathesis of olefins, catalyzed by metal complexes, through organometallic pathways. Much of the importance and impact of organometallic chemistry during the past several decades is attributable to such processes.

PATHWAYS OF ORGANOMETALLIC CATALYSIS

Recognition of the basic reactions in Scheme 1 was followed almost immediately by appreciation of their potential role as component steps in the pathways of an extensive array of catalytic processes in organic chemistry.



Scheme 1

The mechanistic scheme of Fig. 1, essentially that proposed by Heck and Breslow [8] in 1961 to depict the pathway(s) of cobalt carbonyl-catalyzed hydroformylation (eq. 1), is prototypical. While

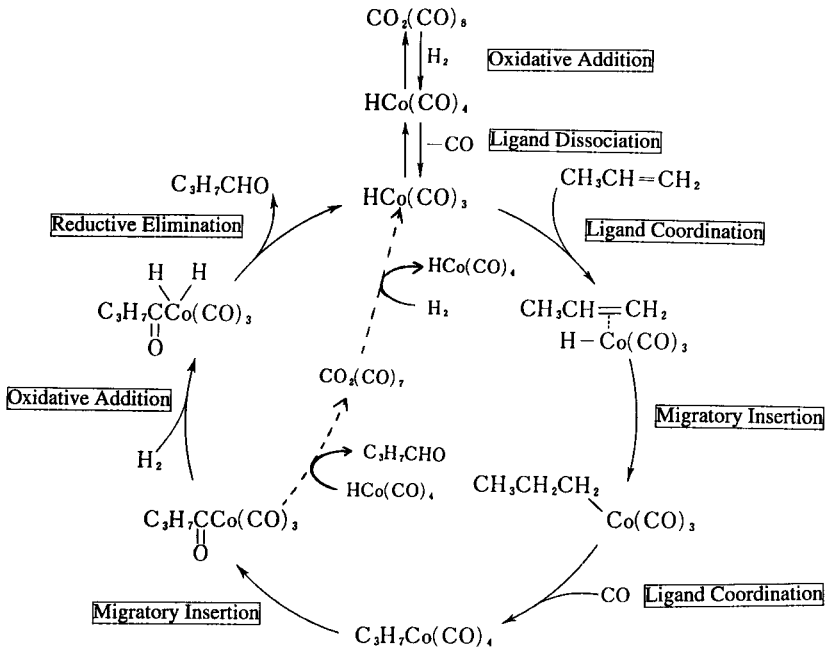


Fig. 1 Heck–Breslow mechanism of the cobalt carbonyl-catalyzed hydroformylation of propylene (adapted from ref. 8).

details of the mechanisms still await substantiation and the possible involvement of additional pathways still cannot be excluded, the essential features of this interpretation have withstood the test of time and analogous mechanistic schemes, involving combinations of the steps in Scheme 1, have been proposed, and come to be accepted, for most of the other catalytic reactions exemplified by those in Table 1.

$$RCH{=}CH_2 + H_2 + CO \rightarrow RCH_2CH_2CHO \quad (1)$$

Notwithstanding this basic understanding of the mechanistic framework of organometallic catalysis, the elucidation of the mechanisms of such reactions continues to be an active field of research with many challenges remaining to be surmounted. Increasingly detailed knowledge and understanding of such mechanistic pathways continue to be achieved through enhanced appreciation of the basic underlying chemistry, as well as increasingly powerful tools for elucidating elusive mechanistic details. Among the tools that are providing such important insights, are *in situ* spectroscopic methods, notably infrared and NMR, for identifying and structurally characterizing species present in solution, fast reaction methods such as flash photolysis that permit the detection of short-lived transient species and determination of the rates of their reactions in real time [9], and application of the chemically induced dynamic nuclear polarization (CIDNP) technique that permits identification of intermediates that do not accumulate in sufficiently high concentrations to be detected directly [10].

Illustrative of the progress that has been achieved is the evolution of our appreciation of the mechanism of olefin hydrogenation catalyzed by $[RhCl(PPh_3)_3]$ (Wilkinson's catalyst) one of the earliest, and most widely applied, homogeneous hydrogenation catalysts. Our current understanding [7] of the mechanisms of this reaction (Fig. 2), while retaining the essential steps originally proposed by Osborn, Jardine, Young, and Wilkinson [11] (Fig. 3), encompasses additional intermediates and an additional, previously unsuspected, pathway which, under certain conditions, accounts for most of the catalytic rate. The prospect cannot be excluded that further investigations will reveal yet additional mechanistic pathways.

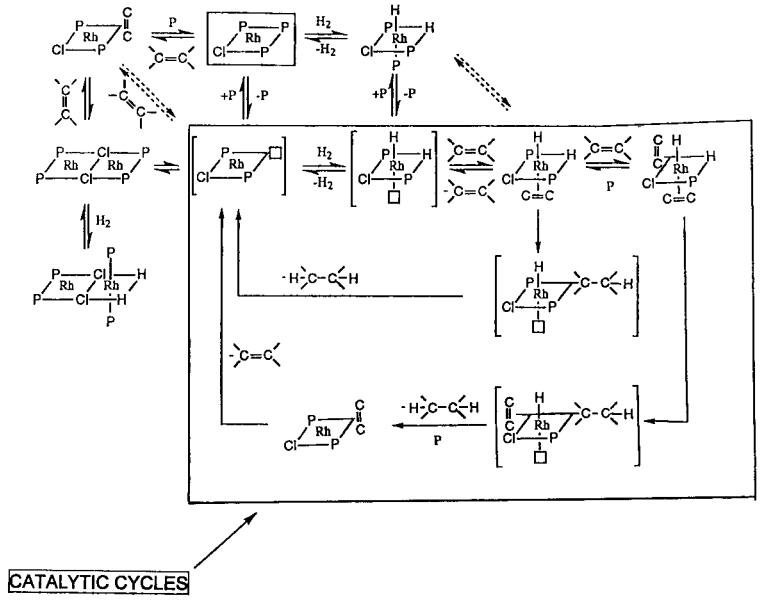


Fig. 2 Mechanistic scheme for the "$RhCl(PPh_3)_3$"-catalyzed hydrogenation of olefins (adapted from ref. 7).

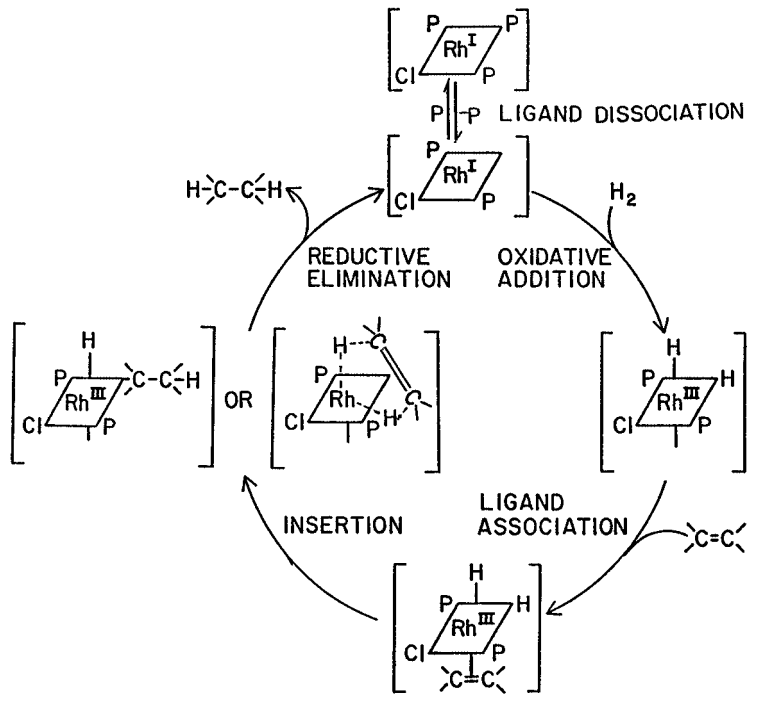


Fig. 3 Wilkinson mechanism of the "$RhCl(PPh_3)_3$"-catalyzed hydrogenation of olefins (adapted from ref. 11).

This system illustrates some of the challenges associated with the elucidation of the pathways of such catalytic reactions. The superposition of parallel multi-step sequences involving many species, often in rapid equilibrium, drastically curtails the extent and reliability of mechanistic information that

can be deduced from measurements of the kinetics of the overall catalytic reaction [12]. Misleading leads also may be provided by identification of the predominant species present in solution under reaction conditions. Thus, in the system under consideration (Fig. 2) none of the several species that have been directly identified as being present in solutions of the catalyst precursor, $[RhCl(PPh_3)_3]$, or under conditions of the catalytic reactions, actually lie within the catalytic cycle, details of which must be inferred from less direct criteria.

ASYMMETRIC CATALYSIS

Asymmetric catalysis, whereby complexes containing chiral ligands catalyze the conversion of achiral substrates to chiral products with high enantiomeric excess, must be counted as one of the major triumphs of organometallic chemistry [13,14]. The earliest such systems, reported in the early 1970s, and exemplified by eq. 2, involve the asymmetric hydrogenation of α-acetamidocinnamic acid derivatives, using rhodium catalysts containing chiral phosphine ligands [15].

$$R_1CH{=}C[COOR_2][NHC(=O)R_3] + H_2 \rightarrow R_1CH_2C^*H[COOR_2][NH(C=O)R_3] \quad (2)$$

This system, developed by scientists at Monsanto [15], found almost immediate application in the manufacture of the anti-Parkinson drug, L-Dopa, and has been followed by many other asymmetric catalytic systems, commonly based on organometallic chemistry, which are transforming not only the methodologies for synthesizing pharmaceuticals and other chiral compounds, but also our conceptual framework of understanding of the origin of catalytic entantioselectivity.

The mechanism of the reaction depicted by eq. 2 has been elucidated in exquisite detail (16) and is described in Fig. 4. While the basic features of the mechanism are conventional, comprising the familiar sequence of oxidative addition, migratory insertion and reductive elimination steps, elucidation of the mechanism revealed a remarkable, totally unexpected, feature. Contrary to the generally accepted prior view, it turned out that formation of the preferred product enantiomer results not from prefer-

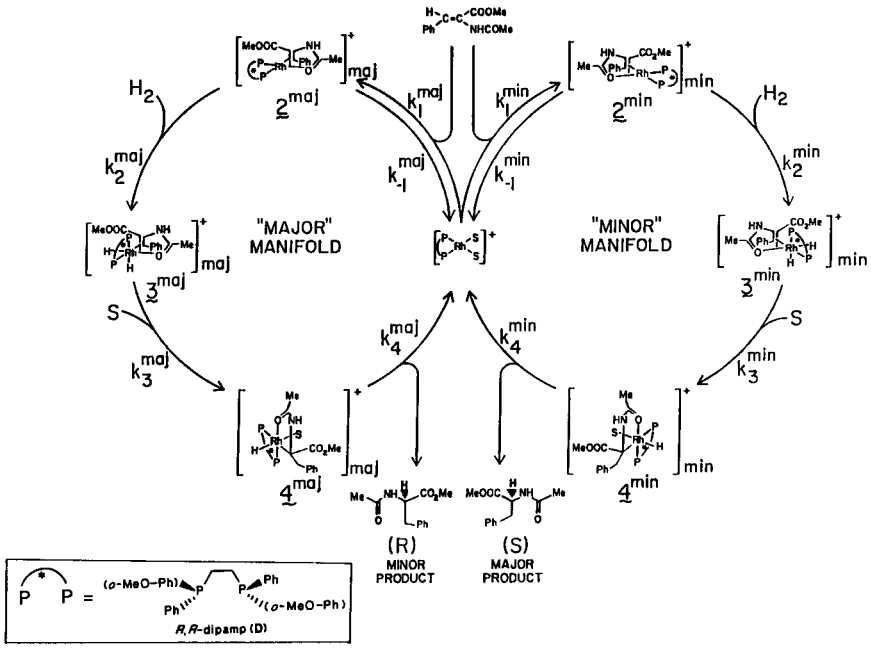


Fig. 4 Mechanistic scheme for the asymmetric hydrogenation of methyl-(Z)-α–acetamidocinnamate, catalyzed by {1,2-bis(phenyl-o-anisoylphosphino)-ethane}rhodium(I).

ence of the initial mode of binding of the olefinic substrate to the catalyst; instead, the predominant product enantiomer is derived from the *minor*, *less stable*, diastereomeric form of the catalyst-substrate adduct by virtue of its much higher reactivity toward H_2. This finding raises significant questions about the widely held "lock and key" interpretation of catalytic selectivity, with implications that extend considerably beyond organometallic chemistry.

ORGANOMETALLIC CHEMISTRY IN BIOLOGY

The totally unexpected finding in 1961, revealed by X-ray crystallography [17], that the biologically active forms of vitamin B_{12}, 5´-deoxydenosylcobalamin (coenzyme B_{12}, Fig. 5) and the corresponding methylcobalamin, are organometallic compounds containing covalent cobalt–carbon bonds, opened up a new field, bioorganometallic chemistry, spanning organometallic chemistry and biology, the full scope of which still is unfolding.

Coenzyme B_{12} is distinctive, not only because of its unprecedented metal–carbon bond, but also because the class of enzymatic reactions for which it serves as a cofactor, depicted schematically in Fig. 6, are unprecedented in nonbiological organic chemistry. The common feature of these reactions is the 1,2-interchange of a H atom and another substituent on adjacent saturated carbon atoms, as depicted in Fig. 6 [18], which also depicts schematically the mechanism that has been deduced for these reactions through a combination of eznymatic and chemical studies. The key stop in this mechanism is the enzyme-induced homolytic cleavage of the Co–C bond leading, ultimately, to formation of a substrate-derived radical which rearranges to the corresponding product radical.

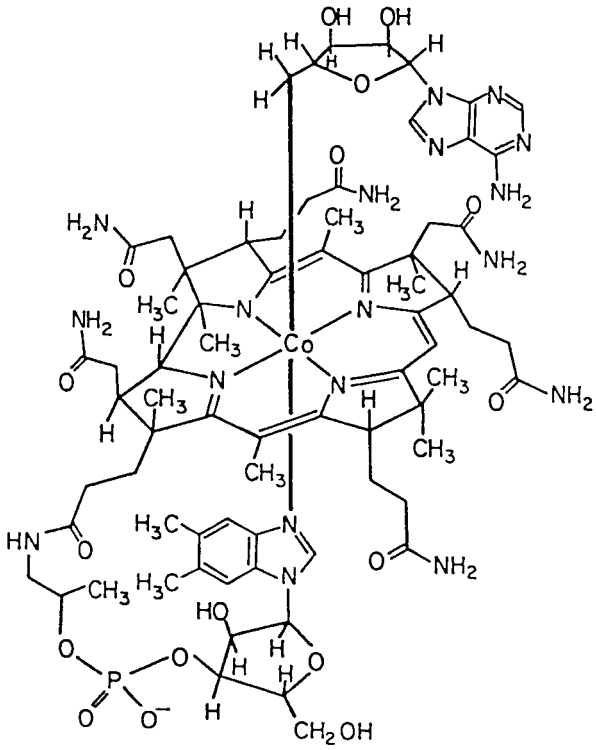


Fig. 5 5'-Deoxyadenosylcobalamin (coenzyme B_{12}).

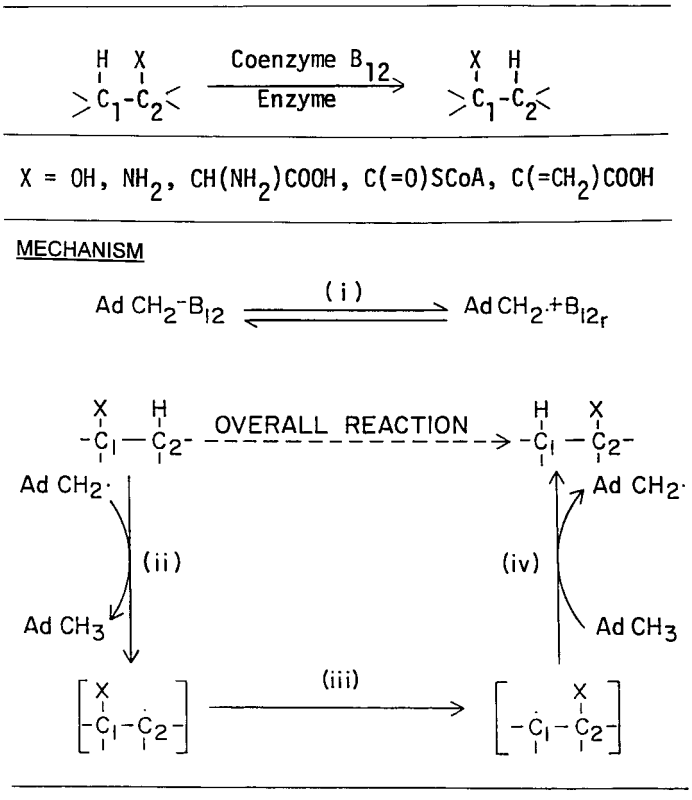


Fig. 6 Mechanistic scheme for coenzyme B_{12}-promoted enzymatic rearrangements ($AdCH_2$-B_{12} = 5'-deoxyadenosylcobalamin; B_{12r} = cob(II)alamin).

Organometallic chemistry also has been invoked to interpret the biological roles of some recently identified nickel-containing enzymes, notably methyl-coenzyme M reductase (19) and carbon monoxide dehydrogenase (CODH) [20]. The mechanistic scheme that has been proposed for the biosynthesis of acetyl-coenzyme A, CoAS-, (which undergoes hydrolysis to acetate) is depicted in Fig. 7B.

The evolution of the field of organometallic chemistry, with particular attention to lessons learned from its biological component, prompts two general observations.

First, the significance and impact of the discoveries that have marked this rapidly evolving field often extend beyond their immediate context and even beyond the broader landscape of organometallic chemistry. Thus, the immediate consequence of elucidation of the mechanistic features of coenzyme B_{12}-dependent reactions (Fig. 6), was the unfolding of the extensive and distinctive chemistry of a previously unrecognized class of organocobalt compounds. Beyond that, the search for understanding of the factors that influence cobalt–alkyl bond dissociation energies and contribute to the enzyme-induced Co–C bond weakening and dissociation that triggers the coenzyme B_{12}-dependent rearrangements has provided much of the motivation for measurements of transition metal–alkyl bond dissociation energies and has contributed significantly to our present extensive knowledge and understanding of such energies [21]. Finally, this system has revealed previously unrecognized dimensions of organic and organometallic free-radical chemistry [22], added to our understanding of free radical rearrangements, and uncovered new applications of free-radical chemistry in organic synthesis [23] and polymerization [24].

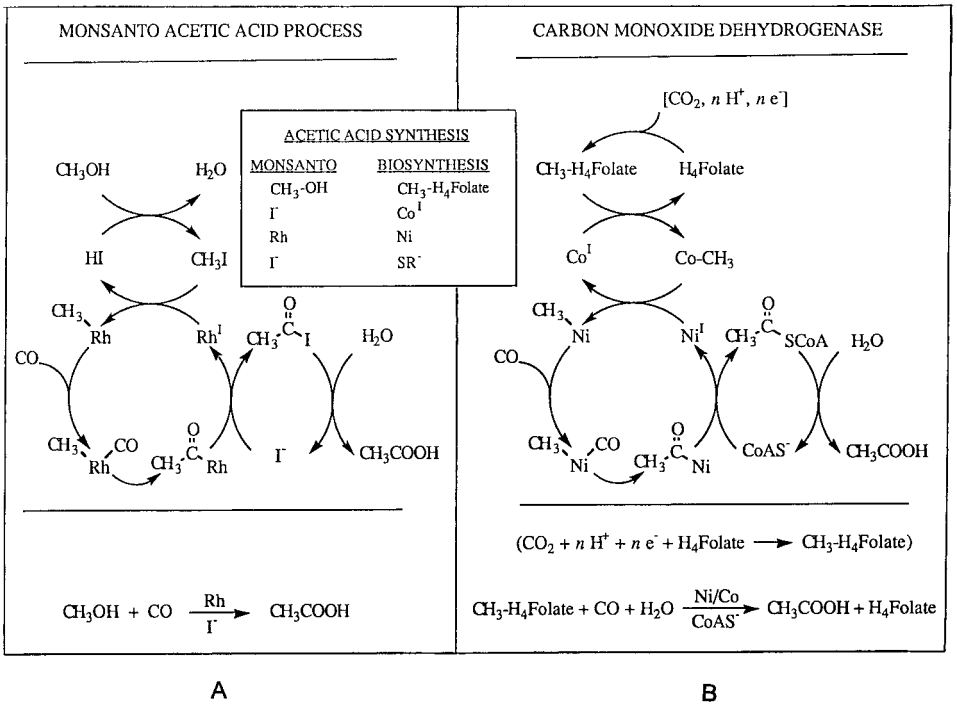


Fig. 7 (A) Mechanistic scheme for the rhodium/iodide-catalyzed carbonylation of methanol (adapted from Ref. 25). **(B)** Mechanistic scheme for carbon monoxide dehydrogenase (adapted from Ref. 21).

A second observation concerns the changing landscape of organometallic chemistry within which new discoveries are made. The structural characterization of coenzyme B_{12} in 1961 and its identification as an organocobalt compound provided virtually no insights into its role or mechanism of action, requiring them to be deduced from detailed enzymatic and chemical studies on the coenzyme, on its reactions, and on model systems. In contrast, when carbon monoxide dehydrogenase was characterized as a nickel-containing enzyme 20 years later, and found to exert its role in combination with a B_{12}-related cobalt-corrinoid, our knowledge and understanding of the organometallic chemistry of nickel and cobalt, and of the catalytic pathways of carbonylation reactions, had evolved to the point where a plausible mechanistic scheme, notably that depicted in Fig. 7B could be fairly readily constructed. Indeed, as comparison of Figs. 7A and 7B reveals, the proposed scheme parallels closely the previously deduced pathway of the Monsanto Rh/I-catalyzed synthesis of acetic acid from CO and methanol [25] developed in the early 1970s and employed today to produce most of the world's acetic acid.

Because we are always seeking to exploit our understanding of how biological systems work to devise more effective approaches to achieve chemical goals, it is reasonable to speculate whether an understanding of the mechanism of action of carbon monoxide dehydrogenase, had this understanding preceded discovery of the Monsanto acetic acid process, would have helped to guide that discovery. Possibly—but my suspicion is that it might well have had the opposite effect by encouraging attention to be focused on nickel, rather than rhodium, as a potential catalyst—an option that appears, in retrospect, to be much less promising.

CURRENT DIRECTIONS AND FUTURE OUTLOOK

Modern organometallic chemistry was shaped in many important respects during the three-decade "golden age" of the discipline, extending from about 1950 through the 1970s.

As documented in Schemes 1 and 2, much of the conceptual framework of the field evolved during this period, including: discovery of most of the basic metal–ligand combinations and elementary reaction steps that constitute the "building blocks" of organometallic chemistry; recognition of the role of organometallic chemistry in biology; discovery of many important organometallic-based catalytic processes, such as Ziegler–Natta catalysis, Wacker oxidation of ethylene, rhodium-catalyzed carbonylation of methanol, and olefin metathesis; as well as considerable progress toward the understanding of the mechanisms of these and related processes.

The ensuing evolution of organometallic chemistry has served to refine, extend, and exploit these groundbreaking discoveries and, thereby, to sustain the importance, distinctiveness and vitality of the field.

Notable recent advances and promising areas of current research include, but are not limited to, the following:

- *Catalysis*. Applications of organometallic catalysis to organic synthesis continue to expand, along with our understanding of their mechanistic pathways and our ability to design and "fine tune" catalytic activities and selectivities [26]. "Traditional" catalysts are being supplanted by new generations, for example Ziegler–Natta and olefin metathesis catalysts by significantly superior "single-site" variants [27,28]. At the same time, challenging targets, for example, the useful selective catalytic functionalization of alkanes, remain to be effectively achieved [29].
- *Theoretical studies*. The theoretical study of organometallic compounds and reactions employing extended Hückel and *ab initio* molecular orbital (MO) approaches [30], continues to be actively pursued. The impact of such studies to date has been only moderately encouraging, restricted, for the most part, to rationalizing known structures and reactivity patterns with only limited predictive power, particularly at the quantitative level. Discriminating among plausible alternative accessible reaction pathways with comparable rates, a common feature of organometallic reactions [31], is a particularly challenging task. Nevertheless, with the rapid pace of increasing computing power, this is likely to continue to be an active research field, and significant advances may be anticipated.
- *Mechanistic studies*. Increasingly powerful tools, notably spectroscopic techniques for identifying and structurally characterizing species in solution, as well as time-resolved infrared and optical spectroscopic methods for monitoring short-lived intermediates [9], are significantly enhancing our knowledge and understanding of the mechanistic aspects of both elementary and complex organometallic reactions. This continues to be an active and productive area of research.
- *"Unconventional" media*. Increasingly, reaction media, other than traditional organic solvents, are being employed as solvents for organometallic reactions. Such "unconventional" media include highly electrophilic solvents [32], aqueous solutions (using ligands with solubilizing substituents) [33], supercritical CO_2 and other fluids [34], as well as multiphase systems. Apart from practical advantages (e.g., environmental impact or superior separation properties) such media often significantly modify organometallic reactivities, thereby providing yet another tool for "tuning" catalytic systems. It is likely that this will continue to be an active and fruitful area of research and application.
- *Materials and supramolecular assemblies*. Mononuclear and polynuclear transition-metal centers are characterized by distinctive and potentially tunable electronic, magnetic and optical properties. Embedding such centers in, or attaching them to, organic matrices, or connecting them through organic bridges of specified architecture or electronic attributes, affords possibilities for the design of new organometallic materials with distinctive and useful characteristics. This currently is an active area of research that promises to expand significantly both the scientific framework and range of applications of organometallic chemistry. Recently reported examples of such compounds or materials include: mononuclear [35] or polynuclear [36] metal centers linked through conjugated polyalkynylene bridges ("molecular wires"); supramolecular constructs

exemplified by dendrimeric assemblies [37], by arrays of metal-containing moieties coordinated to sites on a fullerene surface [38] and by organometallic supracyclopentadienyl derivatives [39]; "molecular magnets", exemplified by tetracyanoethylene (TCNE)-linked arrays of metallocene units [40]; and organometallic materials with nonlinear optical properties [41]. This field is still at a relatively early stage, with promise of playing a prominent role in the future evolution of organometallic chemistry.

- *Bioorganometallic chemistry*. Although only a few roles of organometallic chemistry in biology have thus far been uncovered, the distinctive nature of these and the fact that their recognition was totally unexpected, suggests that such roles are considerably more widespread. Among other systems in which roles for organometallic chemistry (i.e., for metal–carbon bonds) have been suggested are several involving iron-containing enzymes [42]. The systems that have been identified thus far have yielded important new insights, for both chemistry and biology, and it is likely that this will continue to be an active and fruitful area of organometallic chemistry.

In the circumstances, there is every reason to anticipate that the extraordinary momentum and pace of discovery that have characterized organometallic chemistry during the past half century, and contributed so much to the vitality of chemical science during this period, will extend well into the new millennium.

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