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Journal of Catalysis 216 (2003) 23–31

JOURNAL OF CATALYSIS

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Concepts in homogeneous catalysis: the industrial view

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Received 11 July 2002; revised 30 August 2002; accepted 13 September 2002

Abstract

Homogeneous catalysis is among the most important areas of contemporary chemistry and chemical technology: new applications of transition metals as central atoms of ligand-modified complexes (and thus a tailoring and tuning of the whole catalyst system) opens novel routes to new compounds, together with new possibilities for reaction control and separation of the homogeneous catalyst from the reactants and the substrate.

Keywords: Carbonylation; Central atoms; Complex catalysts; Homogeneous catalysis; Hydroformylation; Immobilization; Ligands; Separation catalyst/products; Transition metals

1. If there is a choice: homogeneous catalysis—the challenge to heterogeneous catalysis

Catalysis as a whole comprises the varieties of heterogeneous, homogeneous, and biological (enzyme) catalysis. In agreement with its historical development, heterogeneous catalysis was applied first commercially to a large extent. Enzymatic catalysis is the most recent discipline and has developed explosively, being included in many commercial applications. In between is homogeneous catalysis, which in fact started with the action of nitrous oxides in the lead chamber process and thus prior to the recognition of the effects of heterogeneous catalysts [1]. Now it is estimated that 85% of all chemical processes are run catalytically, with a ratio of applications of heterogeneous to homogeneous catalysis of appoximately 75:25. The focal point of occupation as far as scientific *and* commercial papers are concerned is quite different: Taking the special issue "Industrial Catalytic Processes" (edited by W. Hölderich, a "heterogeneous" specialist as the state witness) as an example, the ratio of heterogeneous to homogeneous catalysis is roughly 60:40 [2]. It is true that homogeneously catalyzed processes such as hydroformylation, carbonylation, oxidation, hydrogenation, metathesis, and hydrocyanation contribute, with millions of tons, considerably to the inventory of bulk chemicals, but on the other hand the progress of homogeneous catalysis is also going on with fine chemicals, i.e., with products the manufacture of which ensures high atom economies [3] or *E* factors [4]. Thus, the goals of "green chemistry" as a synonym to environmentally benign chemicals and processes, including sustainable development, are afforded by homogeneous catalysis rather than heterogenous catalysts. And it is more than coincidental that the majority of the contributions of the journal *Green Chemistry* deals with *homogeneous* catalysis.

It has to be added that homogeneous catalysis does not suffer from the severe drawbacks of heterogeneous catalysis, such as the pressure gap or the lack of deeper mechanistic understanding of the multiphase processes on surfaces. The challenge of homogeneous catalysis, solving the problem of separating the reactants, the catalyst, and the reaction products (which are all *in the same phase*), is essentially made easier because of the fact the catalysts are unequivocally characterized chemically and spectroscopically, because the reaction kinetics are unequivocally related to each catalytically active metal atom, and because catalysts can be tailor-made for special purposes according to known principles and based upon rational design [5,6]. Prior to this, a tremendous amount of research work and applicational effort was done and it presents a bright outlook for further success in the future (and for competitive application of both homogeneous and heterogeneous catalysts for some reactions). With this

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doi:10.1016/S0021-9517(02)00128-8

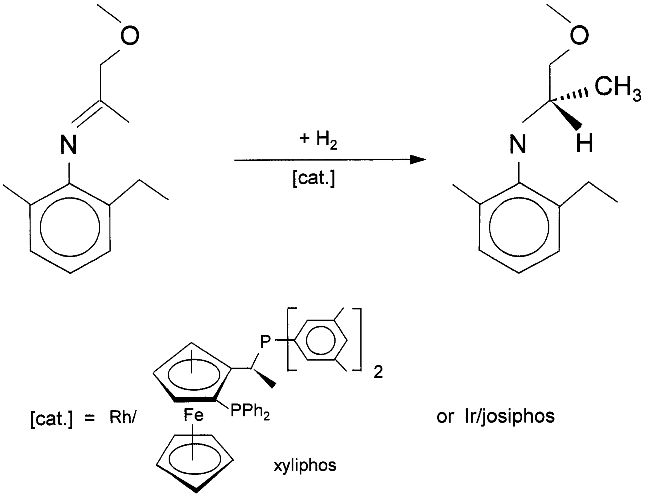
review, only typical examples are given to highlight the actual developments.

2. The homogeneous catalyst and its ingredients

Apart from homogeneous acid–base catalysts, the "classical" homogeneous and organometallic catalyst consists of the central atom and the ligand(s). Their interplay governs decisively activity, productivity, and selectivity of the catalytic system, as can be demonstrated for the example of hydroformylation (Table 1).

As indicated, the proper choice of tailor-made and fine-tuned ligands may change considerably the behavior of the catalytic system. Depending on the nature of the fed alkenes and on the desired product distribution, nearly all grades of combinations of activity ↔ productivity ↔ selectivity may be chosen. Additionally, novel variants, such as the aqueous-phase hydroformylation ([15a,22], together with variants such as the use of thermoregulated ligands [15b]) and other phase-separating means (supercritical solvents [16], ionic liquids [17], soluble polymer supports [18]), extend the degree of freedom of the reaction. This is true not only for rhodium, the "working-horse" of hydroformylation, but also for palladium in carbonylations and for all newly developed variants of ligand-modified Pd catalysts, for example, Heck reactions, alternating copolymerizations, Wacker oxidations, and Suzuki, Stille, or Negishi couplings [6,23].

Transition metals other than Pd and Rh deserve special attention for outstanding versatility: iridium, for large-scale carbonylations (Cativa process of BP [19]), as well as for hydrogenations [20a] or addition reactions [20b] in the fine chemical business (Eq (1); Solvias uses systems Rh/xyliphos or Ir/josiphos; see also Structure 12).



(1)

Table 1
Properties of homogeneous hydroformylation catalysts and their influence on activity and selectivity (partly simplified)

Catalyst (system)	Activity/ productivity	Selectivity		Refs.
		Chemo-	Regio-	
Cobalt, unmodified[a]	High	Medium	Medium	[7]
Co, ligand modified[b]	Low	Medium	Higher	[8]
Rhodium, unmodified[c]	Very high	Very high	Low	[9]
Rh, PR$_3$ modified[d]	Low	High	High	[10]
Rh, P–P modified[e]	Low	High	Very high	[11]
Rh, PR$_3$/P(OR)$_3$ modified[f]	Higher	High	Very high	[12,13]
Ph, phosphonites[g]	Lower	Lower	Lower	[14]
Rh, aqueous phase[h]	Low	High	High	[15]

[a] Classical oxo process.

[b] Selectivity higher compared to unmodified Co, i.e., Shell oxo variant.

[c] Unmodified Rh catalyst as used by ICI.

[d] Low-pressure oxo process as developed by Celanese and Union Carbide; modifier is triphenylphosphine (TPP; PPh$_3$).

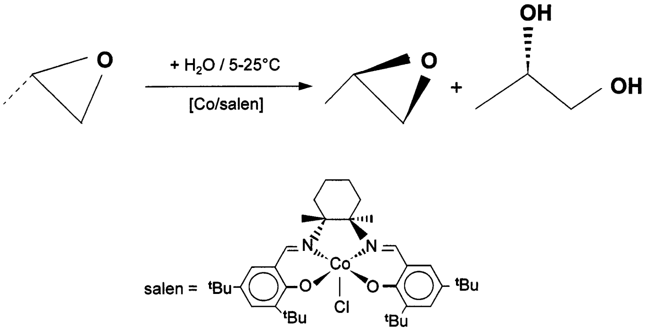
[e] Diphosphines as modifiers; so far not used commercially.

[f] Modifiers are phosphines/phosphites. Very selective but sensitive to moisture. Modifiers with stereogenic P atoms allow asymmetric hydroformylation.

[g] Activity and selectivity somewhat lower compared to other systems, but isomerization during hydroformylation is high.

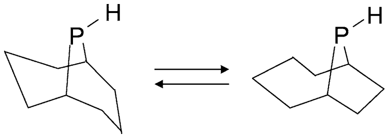
[h] Process needs water-soluble ligands, but reaction engineering is extremely simple and use of the heat of reaction is advantageous.

Ruthenium complexes tend to be the next generation of metathesis catalysts, mainly due to their high polar function tolerance (and despite their actual poor lifetimes; cf. Grubbs' catalysts of the first or second generation and Hoveyda–Grubbs catalyst) [20c]. The same is true for some applications for fine chemicals [20d]. Rare-earth metals, especially their triflates, are on the advance from homogeneously catalyzed aldolizations, Mannich, Michael, or Mukaiyama reactions to transesterifications, copolymerizations, hydroaminations, metallocene-induced polymerizations, and so forth. The recalling of proven transition metals such as iron, cobalt, and nickel yields new results, too. As an example (cf. Eq. (2)), the isomerization and hydration of propylene oxide is [21].

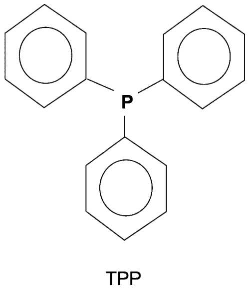


(2)

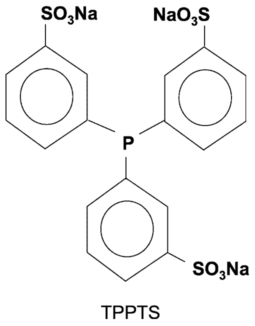
A similar development with much research work is under way as far as ligands are concerned. Since the success with phobane (cf. Structure 1, the ligand for Shell's Co-modified oxo process), triphenylphosphine (TPP; Structure 2) for Celanese's and UCC's LPO process [10] and trisulfonated TPP (TPPTS; Structure 3) for Ruhrchemie/Rhône-Poulenc's oxo process [22] have been developed as very different ligands. Structures 4–12 give an impression of the versatility of chemistry aiming at ligands with different (and directed) architecture, including various bite angles, electronic



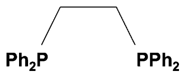
Structure 1.



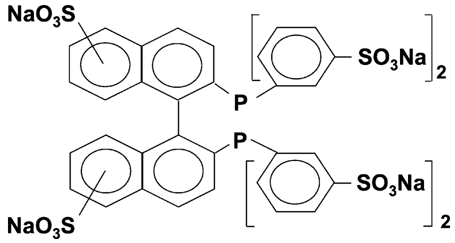
Structure 2.



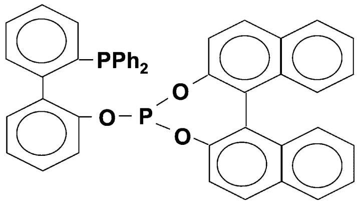
Structure 3.



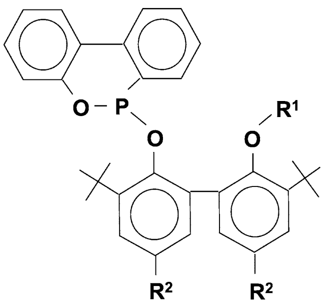
Structure 4.



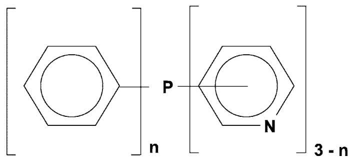
Structure 5.



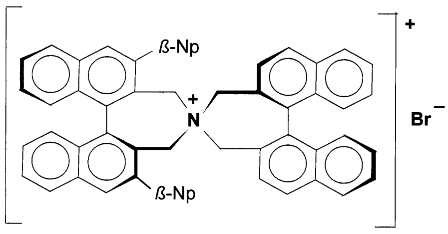
Structure 6.



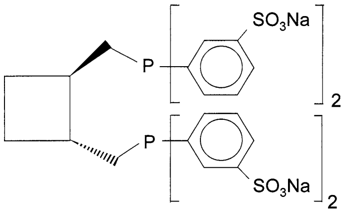
Structure 7.



Structure 8.



Structure 9.



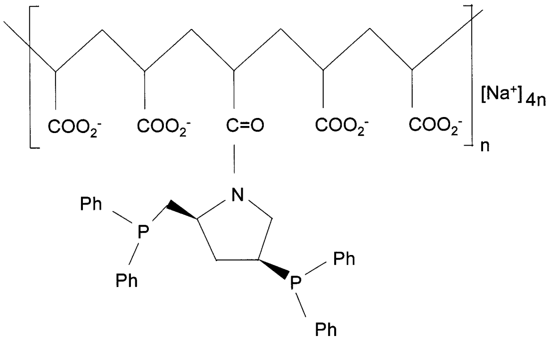
Structure 10.

properties, and stereogenic behavior. The many-sideness of Structures 4–12 gives evidence that the demands for ligands grow: the claims for suitable active and selective catalyst systems for the hydroformylation of propylene are different from those to convert octene, and the carbonylation of methanol—aiming at acetic acid or anhydride—is a completely different matter. Keeping in mind the tasks for modern chemical developments using homogeneous catalysts, e.g., stereoselective syntheses, the activation of colloidal organometals, and the use of multicomponent or multifunctional catalysts, makes the very different architecture of ligands self-explanatory.

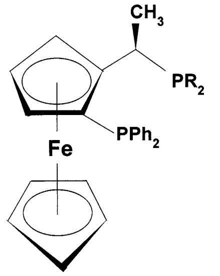
The “construction” of combinations of central atoms and ligands depends on a firm foundation of mechanistic studies, including thermodynamic considerations. This is a proven concept which ought to be complemented by in situ spectroscopic studies, conversion/time diagrams, and kinetic time laws. Such data will pave the way toward a mechanistic understanding and will eventually, through accurate mechanistic study, emerge with *new* catalysts. This was the case for many versatile reactions, such as Heck, Suzuki, Stille, Sonogashira, and other couplings (e.g., [23]), for which homogeneous catalysts (or their precursors) are now commercially available, for example, palladacycles, such as the SK series of Solvias AG [24] (Structure 13).

It is certainly not a matter of chance that the latest synthesis of the famous antitumor reagent taxol (Structure 14) depends on a (homogeneously catalyzed) intramolecular, palladium-catalyzed Heck coupling [25].

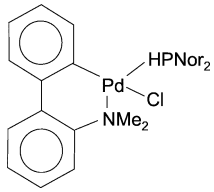
As far as ligands are concerned, there is a certain focus on the occupation with diphosphines, compounds with phosphine and phosphite backbones in the same molecule, and with amphiphilic ligands. Diphosphines offer the possibility of optimizing the bite angle of bidentate ligands and thus inducing large P–M–P angles (up to 138°) in transition metal complexes [26]. The special structure of the ligands (e.g., dppe; Structure 4) has an enormous impact on stability, reactivity, and selectivity of various transition metal-catalyzed reactions. Water-soluble derivatives, which offer the possibility of a process combination of highly sophisticated ligands with an advantageous change of the application phase, have also been described (Structure 5) [27]. Ligands containing phosphine/phosphite backbones (Structure 6, binaphos) [28] or phosphonites (Structure 7) [29] are



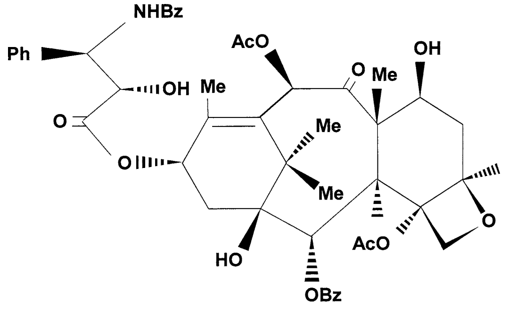
Structure 11.



Structure 12.



Structure 13.



Structure 14.

used for the isomerizing hydroformylation (see below). The concept of amphiphilic ligands (Structure 8) [30] is based upon compounds which are soluble in either an organic or aqueous phase, depending on the pH. In this case, the homogeneously catalyzed reaction, e.g., a hydroformylation, is first carried out in the organic phase (or in pure substrate). After the conversion, water of a certain pH is used to extract the catalyst. The aqueous phase with the water-soluble catalyst is then neutralized and the catalyst is extracted in a fresh organic phase. Thus, during the hydroformylation, the system is homogeneous with a concomitantly high reaction rate. This technique is a variant of aqueous-phase processes insofar as an effective separation between organic and aqueous phase (and thus between catalyst and reactants) is achieved.

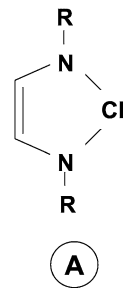
Apart from "proven" ligands (used for special, homogeneously catalyzed processes in small-scale operation for fine chemicals), such as BINAP, DEGUPHOS, BPM, and DuPHOS [20d], a multitude of other ligands, aiming at different targets, has also been developed (e.g., Structures 9–12). Above all these are ligands with stereo centers for asymmetric syntheses, such as NAS (Structure 9) [31], (R,R)-CBDTS (Structure 10) [32], PPM (Structure 11) [33], and josiphos (Structure 12) [34]—an important field of activity of homogeneous catalysis, which has been reviewed very recently by Blaser and co-workers, in particular regarding economically important processes [20a].

N-Heterocyclic carbenes (NHCs, derived from imidazole, pyrazole, and triazoles; cf. the ylides A–D as the precursors of the free carbenes) have become universal ligands in organometallic coordination chemistry *and* in homogeneous catalysis (Structures 15–18). Because of their specific coordination chemistry, they stabilize and activate metal centers in quite different key catalytic steps of organic syntheses, e.g., C–H activation and C–C, C–H, C–O, and C–N bond formation [35]. Other N-containing ligands (so-called "hard" ligands) are investigated thoroughly for the complexation of transition metal catalysts for polymerization of ethylene or propylene. Polymerization cocatalysts such as the activator methylalumoxane (MAO) are applied extensively, and other weakly coordinating anions [e.g., BARFs (boronarylfluorides)] are also under development.

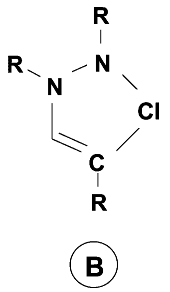
The scope of new ligands is wide and their synthesis is increasingly difficult and costly: no wonder the price of ligands, in addition to the cost of precious metals (such as Rh, Pt, and Ru), plays a more and more decisive role in the calculation of the catalyzed processes. This, in turn, requires a recycling of the ligand as well as the central atoms—an additional challenge. Research is in full progress, and it is expected that new combinations of central atoms and ligands will open exciting new horizons and possibilities for commercial applications.

3. Developments

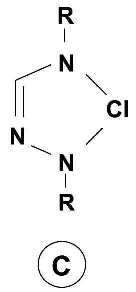
Modern homogeneous catalysis comprises more than the development of catalysts and catalyst–ligand systems. Catalyst performance is the result of tremendous effort, e.g., the *activity* of oxo catalysts has improved in the past 50 years by a factor of 10,000: the change from a triadic process technology to continuous plant operation, the replacement of Co by Rh catalysts, the tailoring of the ligand sphere, a change in the phase application (two-phase processes) [7]. At the same time, an important improvement of *selectivity* has been achieved. Similar developments occurred in other homogeneous catalyzed processes. These efforts are ongoing events for all industrial researchers. In academia, a certain focal point is research work using combinatorial homogeneous catalysis. Because of the inherent advantages of homogeneous catalysis, as mentioned above, and because of the fact that mass transfer restrictions are negligible, combinatorial catalysis basically can above all be used for tailoring and tuning homogeneous catalysts—in contrast to heterogeneous catalysis, where the "development funnel" (a vision by Weinberg; see [36]) is questionable. It is one thing to synthesize thousands of catalysts; it is another to screen



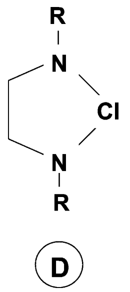
Structure 15.



Structure 16.



Structure 17.



Structure 18.

them (e.g., using high-throughput screening techniques) and to interpret the results: in heterogeneous catalysis, it is not the formula of the technical catalyst (or the protocol of its application) which is decisive but its recipe (including the know-how) for *technical feasibility and reproducibility* under the conditions of *technical catalyst manufacture*. Therefore, the development funnel has to be supplemented by the decisive "?," i.e., an additional stage to guarantee the complete transferability of the experimental results by development work which is close to practical use and which has been done by experienced teams (Fig. 1). On the other hand, the results of *homogeneous* combinatorial catalysis can easily be transferred to practice. The same is true for the introduction of microreactor technologies into the area of homogeneous catalysis [37].

More ongoing research work is the effort to immobilize homogeneous catalysts. Although it is clear that the strength of organometallic catalysts—*activity and chemo-, regio-*, and *stereoselectivity*—results from a simple concept, i.e., specific ligands keep the catalyst metal in a maximum mobile shape and low nuclearity, other work concentrates on immobilizing or anchoring the homogeneous species to heterogeneous supports, despite thousands of failures because of leaching or lesser activity. Except for enzyme catalysis (where immobilizing is the state of the art [38,39]), all experiments failed under industrial conditions, and it is unknown whether the approach via the borderline cases of phase transfer catalysis/surface organometallic catalysis (as indicated in the Fig. 2) will be successful.

The only exception known so far is UOP/Chiyoda's process proposal called Acetica, which delivers acetic acid from methanol and carbon monoxide in bubble-column operation over resin-based, immobilized rhodium catalyst (MeI promoted) at 160–200 °C and 3–6 MPa pressure. This process still has to prove its reliability, leaching resistance, and long-term stability under commercial conditions [70]. The target is rhodium losses in the parts per billion range, as proven in Ruhrchemie/Rhône-Poulenc's hydroformylation process: a goal difficult to reach!

A considerable part of the homogeneous community concentrates instead of on new—and promising—homogeneously catalyzed variants of two-phase processes. This is true for the use of ionic liquids (more exactly, for nonaqueous ionic liquids (NAILs) [40]) [41], supercritical (sc) solvents such as carbon dioxide or water [42], the application of fluorous phases [43], and polymer supports [18]. For the fluorous phases, this procedure is a preparative method rather than a commercial one: the ligands required are extremely expensive and their architecture, in most cases, contains components which may severely effect the environment when used in large amounts.

The other technologies mentioned are highly interesting and are a focal point of academia and industrial research work, but their status is bench scale at the extreme. An exemption is IFP's Difasol process for the dimerization of butylenes, catalyzed by Ni complexes in BMIC-type ionic liquids [71]. Other commercial uses are not in sight.

On the one hand, this is a consequence of limited knowledge about application and long-term stabilities of ingredients (and catalysts), and the other hand, these methods of

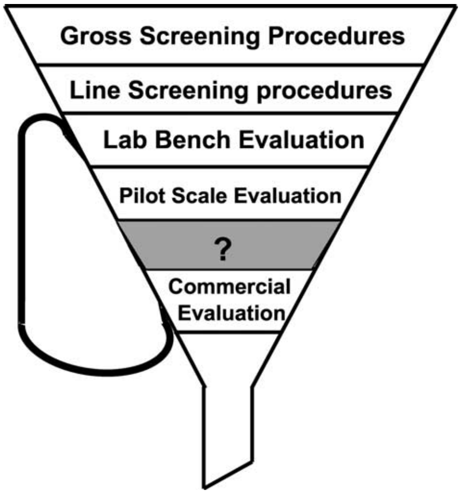


Figure 1. The realistic development funnel.

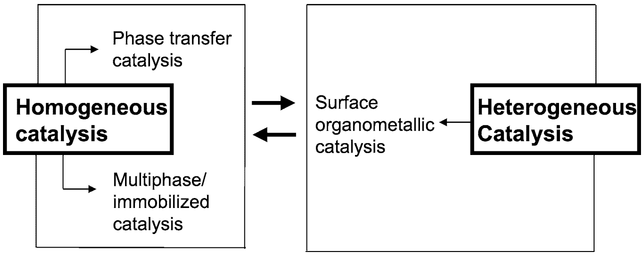


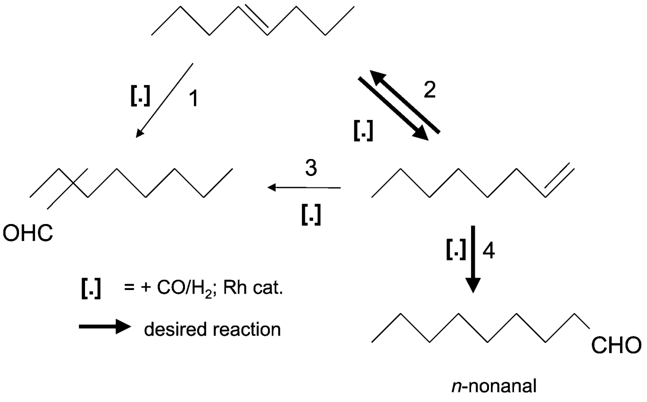
Figure 2. Links between homogeneous and heterogeneous catalysis.

two-phase technologies and their expected advantages so far do not pay the costs.

4. Applications

Development work in the area of homogeneous catalysis is manifold and comprises support of running processes and improvement of their feedstock base, as well as the search for new applications. The 10 “challenges for catalysis” [44] include five “eternal” goals, which are typical homogeneous targets (i.e., low-temperature epoxidation of propylene, direct syntheses to H_2O_2 from the elements, phenol from benzene and oxygen, aromatic amines from NH_3, selective oxidation of methane to methanol, and *anti*-Markovnikov addition of alcohols and amines to alkenes). These jobs for academic researchers deserve praise.

On a more applicable level there are some economic problems. One comprises the hydroformylation of (higher) alkenes, especially under isomerizing conditions. The most recent development in oxo technology—the aqueous-phase process [45]—suffers from the increasing insolubility of the feed alkenes within the catalyst solution with increasing C number. The search for more-suitable ligands, the addition of promoters, and the application of sonochemistry or microwaves are matters of research, as is the combination of the hydroformylation process with other two-phase variants, such as the use of ionic liquids or supercritical media (even fluourous phases have been proposed, despite their obvious disadvantages in this case [46]). To the extent this problem cannot be solved adequately (and this includes profitably), higher alkenes will be hydroformylated in the “old fashioned” way, with cobalt catalysts, which, as far as toxic properties and environmental harmlessness are concerned, are not without problems. This is also true for the hydroformylation of higher *internal* alkenes, which are very reasonable feedstocks when hydroformabled with rhodium catalysts. This in turn requires a “isomerizing hydroformylation” according to Eq. (3), since Rh catalysts—unmodified or modified by phosphines—do not promote the conversion of internal double bonds:

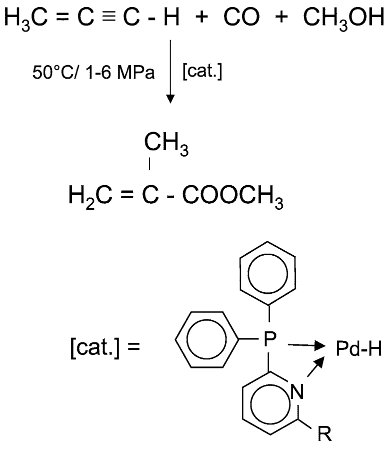


(3)

If straight-chain reaction products are required (e.g., for plasticizer or detergent applications), the catalytic system consisting of rhodium and ligand and the reaction conditions must be coordinated in such a manner that dynamic kinetic control of the reaction, based on isomerization to the thermodynamically less stable terminal alkene (step 2), occurs and this alkene rapidly undergoes the final *n*-regioselective hydroformylation (step 4). Steps 1 and 3 ought to be suppressed. Although the isomerizing hydroformylation proceeds easily with Co catalysts, for hydroformylation with ligand-modified Rh catalysts, special ligands have to be developed (cf. Table 1) [12–14].

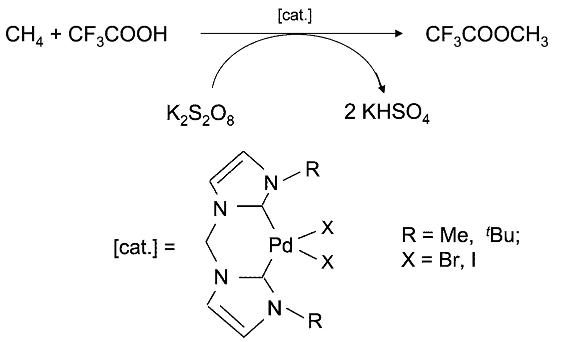
Listed under bench-scale tests are several (partly) homogeneously catalyzed reaction sequences, such as new routes to aromatic polyesters (Amoco, Eastman) [47–49]; Enichem’s cyclohexanone oxime process by reaction of cyclohexanone, ammonia, and H_2O_2 over titanium silicalite TS-1 catalyst, a process which is essentially $(NH_4)_2SO_4$ free [50]; and DSM/Shell’s Altam process [51] for the waste-free manufacture of caprolactam by multistep syntheses starting with butadiene, its bis-hydroformylation and bis-reductive amination with NH_3 to α,ω-aminohexane, and the subsequent cyclization to caprolactam. This process concept competes with other processes which at least partly contain homogeneously catalyzed steps, such as Rhodia’s caprolactam process [52], BASF/DuPont [53], and the Solutia–Boreskov Alphox process [54].

Also under intensive research are homogeneously catalyzed variants to methyl methacrylates [55,56a], concerning known technologies as well as the novel Shell/Linde MMA process comprising the hydrocarbonylation of propyne (methylacetylene) with ligand-modified palladium catalysts, according to Eq. (4) [57]:



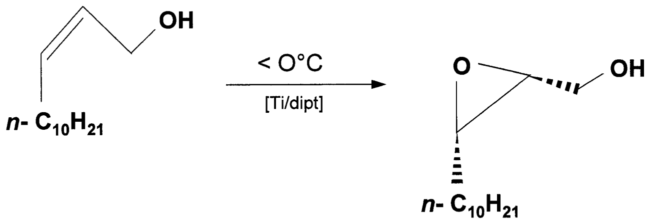
(4)

Some homogeneous variants of the often-discussed “direct syntheses” or “direct catalytic processes” are also in the stage of testing [56b]. The manufacture of methanol by functionalization of methane is of special interest. After the pioneering work of Shilov and Shteinman [58a], Fujiwara et al. [58b], and Periana et al. [58c], a new system consisting of a suspension of $K_2S_2O_8$ in trifluoroacetic acid and catalyzed by NHC palladacycles leads to the formation of trifluoroacetic acid methyl ester [59]:



(5)

The first industrial application of the Sharpless technology [60] has been described for the manufacture of an intermediate of Disparlure^R, a pheromone [61]:



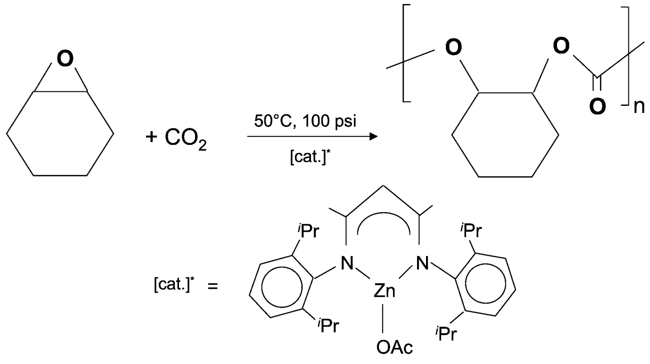
(6)

The *ee*-value reaches 91%, but commercial applicability is restricted due to the low temperatures required.

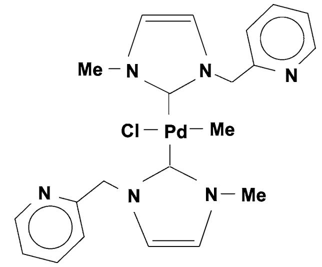
5. New proposals

Knowledge of the reaction principles of a multitude of central atoms, the special importance of the ligand architecture and its influence on steric and electronic properties of the system consisting of transition metal *and* ligand, and the vast amount of experience from the running homogeneous processes create an atmosphere in which new applications grow incessantly.

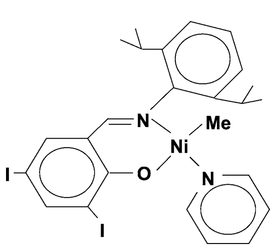
On the borderline for use of supercritical CO_2 is the synthesis of special polycarbonates from cyclohexene oxide and carbon dioxide as a reactant with a variety of Zn catalysts [62]:



(7)

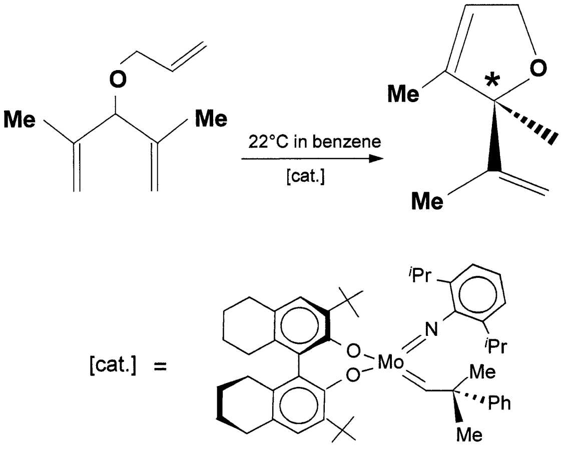


Structure 19.



Structure 20.

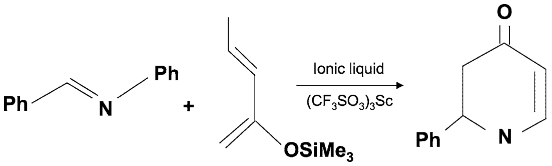
Efficient chiral molybdenum catalysts which are, at the same time, easy to handle were generated in situ without further purification in asymmetric alkene metathesis. For example, the ring-closing metathesis (RCM)—following Eq. (8)—yields $>$ 80% of the desired product at $>$ 88% *ee* [63]:



(8)

Highly active and stable catalysts for Heck, Suzuki, and Sonogashira coupling reactions were discovered in palladium(II) complexes of *N*-heterocyclic carbenes with “dangling” *N*-substituents, such as Structure 19 [35,64].

Ionic liquids as nonvolatile and nonflammable solvents for homogeneous catalysts may be tuned by varying the identities of the cations and anions, thereby tailoring the solvents to specific applications. An example is the aza-Diels-Alder reaction realized with microencapsulated Lewis acid catalyst ($ScTf_3$), which may be recovered and reused [65]:



(9)

A last example comes from the manufacture of high-molecular-mass polyethylene aqueous latexes by catalytic polymerization. By means of lipophilic, and as submicron-size compartemented Ni complexes of Structure 20 (in hydrocarbon solvent), the polymerization of ethylene takes place in the aqueous phase under high-shear (ultrasound) conditions [66]. This is a transition to homogeneous catalysis with polymer-bound but soluble catalysts [67], which have been under intensive research since the early days of

Bayer/Schurig [68] and Bergbreiter et al. [69]. They offer another possibility for “immobilizing” the homogeneous catalyst by means of “liqud supports.”

6. Conclusions

Today, we know much about how homogeneous catalysts are assembled, how they work, and how they can be improved: thanks to research in organometallic chemistry and its techniques and methods in experimental and theoretical concerns, and thanks to progress in chemical reaction engineering in processes using homogeneous catalysts. The level of knowledge improved considerably within the last 10 years. It seems to be typical for the area of homogeneous catalysis that as far as commercially important processes are concerned, the literature concerning the particularly attractive features is dominated by publications from industry, particularly patent literature.

Thus, ideas from academia are followed by initial experiments by industrial chemists and by their realization on a commercial scale. Cooperation between academia and industry is fruitful when confidence and mutual understanding occur on both sides—in our eyes a clear advantage over what occurs with heterogeneous catalysis, where gaps occur not only with the experimental work but also between the highly sophisticated experimenters and the daily application of catalysis.

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