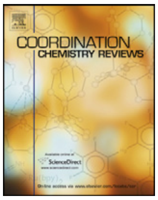
Coordination Chemistry Reviews 254 (2010) 646–660

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

The Baeyer–Villiger oxidation of ketones: A paradigm for the role of soft Lewis acidity in homogeneous catalysis

Rino A. Michelin[a,*], Paolo Sgarbossa[a], Alessandro Scarso[b], Giorgio Strukul[b,**]

[a] Dipartimento di Processi Chimici dell'Ingegneria, Università di Padova, Via F. Marzolo 9, I-35131 Padova, Italy
[b] Dipartimento di Chimica, Università Ca' Foscari di Venezia, Dorsoduro 2137, I-30123 Venezia, Italy

Contents

ARTICLE INFO

Article history:
Received 26 June 2009
Accepted 13 September 2009
Available online 20 September 2009

Dedicated to Prof. Fausto Calderazzo in occasion of his 80th birthday and in recognition of his great contribution to inorganic chemistry.

Keywords:
Baeyer–Villiger oxidation
Platinum diphosphine complexes
Metal Lewis acidity
Catalysis
Enantioselectivity

ABSTRACT

The Baeyer–Villiger oxidation of ketones to the corresponding esters or lactones is a valuable transformation that has been upgraded several times over the last century, from the original use of monopersulfuric acid as oxidant to more atom efficient and environmentally friendly oxidants such as hydrogen peroxide. The latter requires activation with organometallic complexes to explicate its oxidizing power. The catalytic version of the reaction can be achieved with several transition metal catalysts, but major differences are present among the various catalysts proposed in terms of scope of the reaction. In particular, most of the catalytic systems are active towards four-membered ring ketones leading to the corresponding substituted γ-butyro-lactones. Pt^{II} complexes characterized by the employment of chelating diphosphines turned out to be the most efficient in catalyzing the BV oxidation of a wider range of substrates, in particular cyclohexanones are suitable substrates and acyclic ketones can be converted into the corresponding esters, albeit with low turnover. As long as organometallic catalyzed BV reaction is concerned, Pt^{II} catalysts show the most versatile activity and selectivity. Such peculiar features are the result of the unique electronic properties of such metal combined with an easily tailored soft Lewis acid character modulated by the proper choice of the ancillary ligands. The enantioselective version of the reaction benefits from these properties and the compatibility of Pt^{II} species with water enabled the development of asymmetric catalytic BV reactions in water aided by the presence of micelles as dynamic self-assembled environments.

---

* Corresponding author. Tel.: +39 049 827 5522; fax: +39 049 827 5525.
** Corresponding author. Tel.: +39 041 239 8931; fax: +39 041 234 8517.
E-mail addresses: rino.michelin@unipd.it (R.A. Michelin), strukul@unive.it (G. Strukul).

0010-8545/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2009.09.014

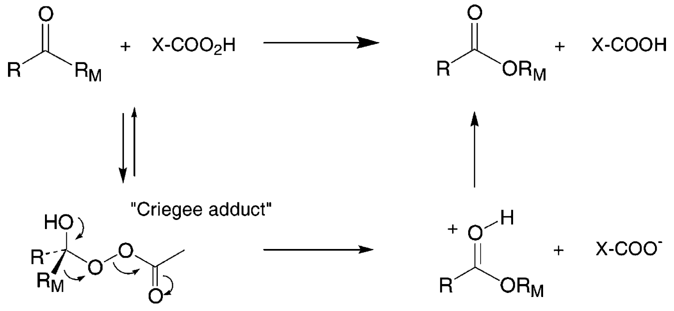


Fig. 1. The BV oxidation of ketones with organic peracids and its mechanism.

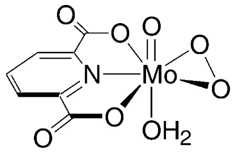


Fig. 2. Dipicolinato Mo^{VI} complex used as catalyst for the BV reaction.

1. Introduction

1.1. The Baeyer–Villiger oxidation of ketones

The Baeyer–Villiger oxidation of ketones (BV) is a one-century-old organic reaction [1] for the conversion of ketones into the corresponding esters or lactones using an organic peroxy acid as stoichiometric oxidant (Fig. 1). In the original version monopersulfuric acid (Caro's acid) was employed, generated by reaction of concentrated sulfuric acid with hydrogen peroxide. Over the years this reaction has been reviewed several times [2] and has become greatly successful in synthetic organic chemistry because of a series of advantages:

(i) the wide range of (relatively) stable organic peroxy acids that can be employed as oxidants;
(ii) its tolerance with respect to other functional groups that may be present in the molecule to be oxidized;
(iii) its regioselectivity that can be easily predicted on the basis of a well established migrating group (R_M in Fig. 1) priority order;
(iv) the stereoselective character of the reaction that proceeds with retention of configuration of the migrating C atom.

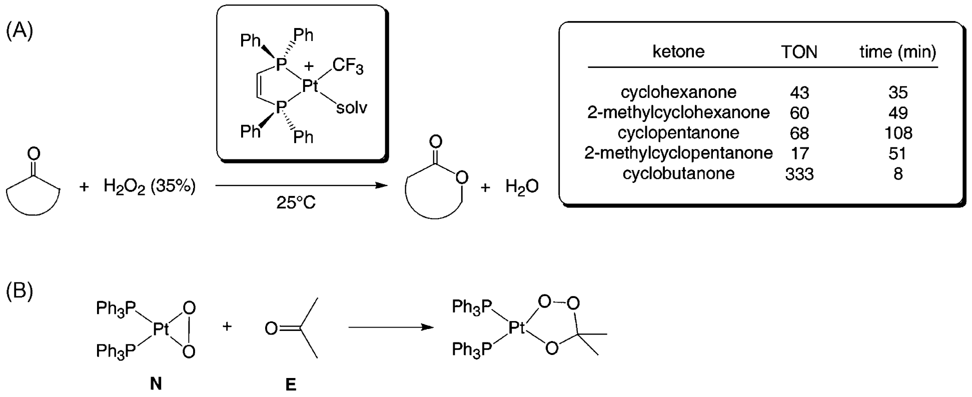
The mechanism of the reaction was studied some 60 years ago by Criegee [3] and consists (Fig. 1) in the nucleophilic attack of the peracid onto the electron-poor carbonyl carbon with concomitant protonation of the oxygen (the reactivity parallels the acid strength of the peracid), followed by the migration step with release of the carboxylate anion. The latter is the rate-determining step with a critical role played by the leaving group.

The use of organic peroxy acids as stoichiometric oxidants invariably produces one equivalent of carboxylic acid per unit of desired product. So, attempts to simplify the system by generating the peracid *in situ* have been known for a long time using sub-stoichiometric amounts of either carboxylic acids [2a] or benzeneseleninic [4] or arylarsonic [5] acids, the terminal oxidant being preferably H_2O_2. Major drawbacks were that either strained, easily oxidizable cyclic ketones were the only possible substrates, or the no longer commercially available 90% hydrogen peroxide was required. In all cases the strongly acidic medium caused the formation of significant amounts of hydrolysis products due to the concomitant presence of water. The alternative was to use the so-called Mukaiyama system based on a sacrificial aldehyde, O_2 and a catalyst to generate the peracid *in situ* but ultimately producing again carboxylic acids as by-products [6].

1.2. Catalysis with transition metal complexes and basic principles

Early attempts to introduce transition metal catalysis in the BV reaction started in 1978 with some contributions by Mares and coworkers [7] who reported the use of picolinato and dipicolinato Mo^{VI} peroxo complexes (see for example Fig. 2) as catalysts and 90% H_2O_2 as oxidant for the conversion of a series of cyclic ketones into the corresponding lactones in moderate yields. However, it was later found that the peroxomolybdenum complex (Fig. 2) failed to transfer oxygen to e.g. cyclopentanone as would be expected, the catalysis arising from H$^+$ dissociated from the strongly acidic transition metal species [8], thereby reflecting the intrinsic difficulty to apply to ketones the Halcon type chemistry originally developed for olefins, because of the intrinsic electrophilic nature of both reactants i.e. the metal coordinated peroxygens on the one hand and the carbonyl carbon on the other hand. In other words, the idea was good but the metal was wrong.

So it was not until 1991 that a genuine example of transition metal catalysis in the BV reaction appeared, based on a Pt^{II} complex as catalyst and commercial 35% H_2O_2 as the terminal oxidant [9] (Fig. 3A). Inspiration to this work came from the classical studies by Vaska et al. on noble metal dioxygen complexes published in the sixties [10]. Among these the well known $(PPh_3)_2Pt(O_2)$ complex was capable of reacting with ketones to give the corresponding peroxometallacyclic species [11] (Fig. 3B) simply because of the proper combination of electrophile (the carbonyl carbon) and nucleophile (the peroxy oxygen).



ketone	TON	time (min)
cyclohexanone	43	35
2-methylcyclohexanone	60	49
cyclopentanone	68	108
2-methylcyclopentanone	17	51
cyclobutanone	333	8

Fig. 3. (A) Catalytic BV oxidation of cyclic ketones using Pt^{II} as catalyst; (B) oxygen transfer to ketones by Pt peroxo complexes. N, nucleophile; E, electrophile. Note: Increase Fig. 3 dimension (ca. 10–20%).

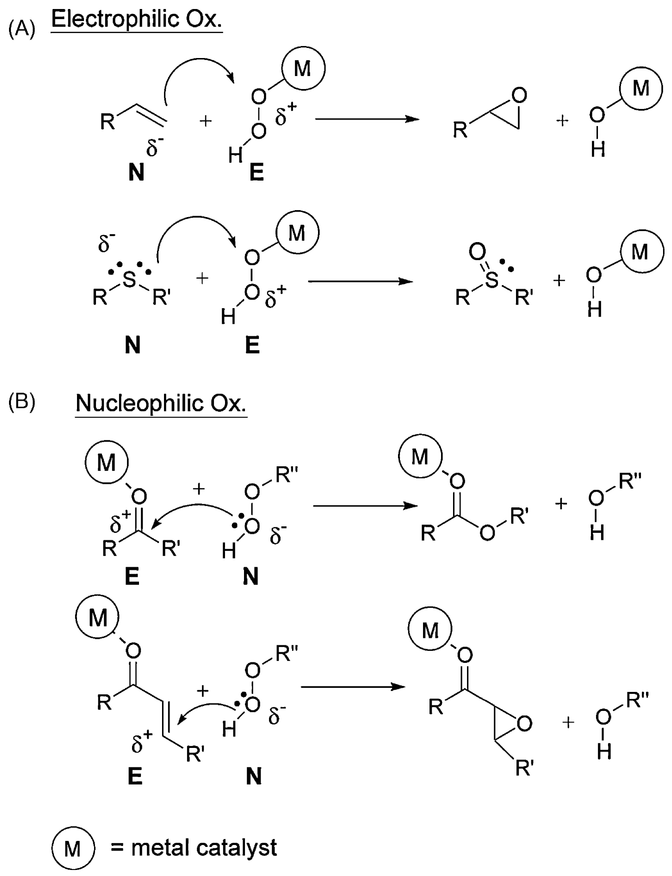


Fig. 4. Schematic representation of (A) electrophilic and (B) nucleophilic oxidation.

Unfortunately there is no way out for these structures leading to BV products, because of the intrinsic stability of the species and the lack, in the peroxometallacyclic species, of suitable leaving groups migrating on Pt and capable to provide the system with the driving force necessary to the rearrangement leading to the ester. Therefore, in order to put the system at work protonation at the peroxygen proximal to Pt (from a Pt hydroperoxide) is necessary [9].

These examples emphasize the principle of nucleophilic oxidation that applies to electron rich metal complexes as catalysts as opposed to the traditional electrophilic oxidation, typical of early transition metal complexes in their highest oxidation states (Halcon type catalysts). In Fig. 4 are reported typical examples of electrophilic oxidation like epoxidation and sulfoxidation where the electron-poor oxidant is attacked by the electron rich substrate (A), while in the nucleophilic oxidation the electron rich oxidant attacks electron-poor C atoms on the substrate like in the BV oxidation or in Julià–Colonna oxidation of α–β-unsaturated carbonyl compounds (B). Clearly the electrophilic and nucleophilic character of the reaction partners is often a consequence of transition metal coordination.

Other species have been used as catalysts for the BV reaction. These include Cu(OAc)$_2$ [6c], Ni(OAc)$_2$ [6c] and VMo heteropolyacids [6d] using the Mukaiyama system, as well as (Me)ReO$_3$ with hydrogen peroxide [12] and chiral Al and Mg species [13] as well as chiral Co, Zr and Pd complexes [14] developed for the asymmetric version of this reaction (*vide infra*) and also some heterogeneous systems based on Sn(IV) embedded in zeolites [15] or mesoporous silicas such as MCM-41 [16] or hydrotalcite [17]. It should be emphasized that in most cases these catalysts were found active only towards substituted cyclobutanones because of the intrinsic reactivity of the latter substrates caused by the presence of a strained four-membered ring. So the moderate to good reactivity observed relies more on the substrate properties than on catalyst efficiency. In the past 10 years the transition metal catalyzed BV reactions has been reviewed a few times [18].

2. The platinum system

2.1. Catalytic activity and selectivity

The complex shown in Fig. 3 is the prototype of a series of Pt^{II} catalysts that have been extensively studied in their many facets in the past 15 years, because they proved exceptionally reactive and still unsurpassed in terms of scope towards different substrates and flexibility with respect to stereochemical studies. Structure types are reported in Fig. 5: all of them are cationic and contain unusual ligands for oxidation reactions such as diphosphines.

Type **2** complexes have been the most thoroughly studied class of Pt^{II} catalysts and they share with the other types some essential features. First of all they are reactive towards a series of cyclic (4-, 5-, 6-membered rings) as well as acyclic ketones with high efficiency in the use of H_2O_2 (no oxidant is wasted in side reactions like dismutation) using a catalyst loading as low as 1% [19]. Although open chain ketones are oxidized slowly with generally poor yields (Fig. 6), these catalysts are the only ones known capable of doing so. From Fig. 6 it is also possible to observe that the catalytic activity depends on the nature of the migrating group (R_M) following the order: *t*-alkyl > vinyl > *sec*-alkyl > phenyl > *n*-alkyl that is the same recognized for the stoichiometric process with peroxy acids [2]. Similarly, the reaction proceeds also with retention of configuration at the migrating carbon as was shown in the case of menthone [20] and these features suggest that a similar reaction pathway is probably involved.

The reaction mechanism for the Pt^{II} catalytic BV oxidation reaction has been elucidated by means of kinetic investigations and is reported in Fig. 7 [18b]. It involves the initial splitting of the diplatinum dihydroxy core due to hydrolysis by hydrogen peroxide and concomitant coordination of the ketone. This leads to the formation of an intermediate monomeric species in which both reactants are coordinated and where the electrophilicity of the carbonyl carbon is increased and the nucleophilicity of the hydroperoxy anion is higher than in free hydrogen peroxide. Then a nucleophilic oxidation occurs with formation of a *quasi*-peroxymetallacycle.

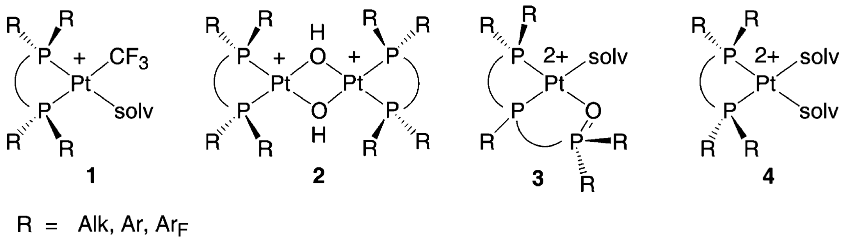


Fig. 5. Pt^{II} type complexes used as catalysts for the BV reaction with H_2O_2.

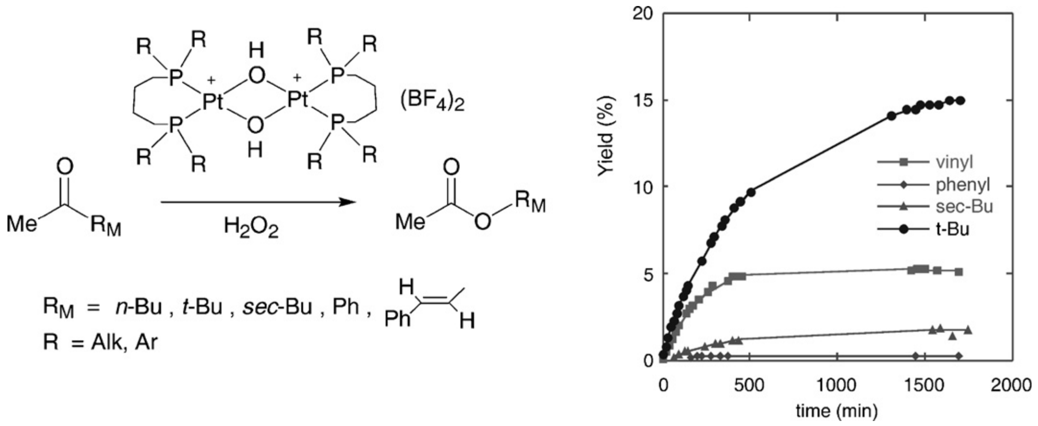


Fig. 6. Catalytic conversion of a series of acyclic ketones using Pt^{II} as catalysts.

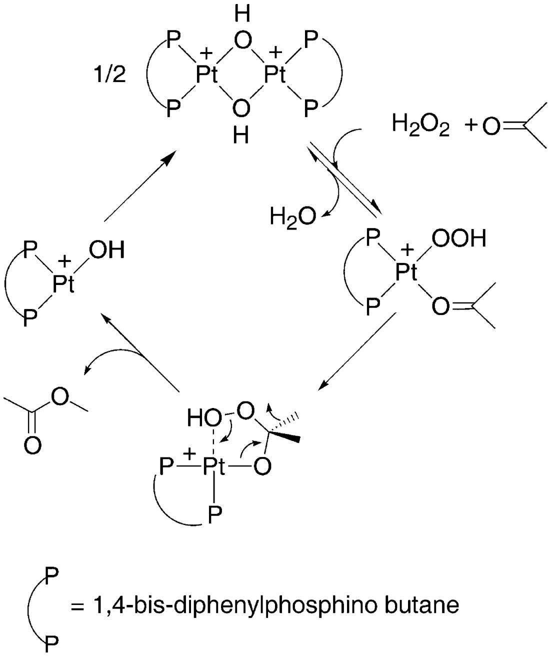


Fig. 7. Catalytic cycle for the BV reaction with type 2 Pt^{II} complexes. Diphosphines are omitted for the sake of clarity.

The structure of this intermediate strongly resembles that of the Criegee adduct identified in the stoichiometric reaction (Fig. 1) with Pt^+ mimicking the role of H^+. Similarly to the stoichiometric reaction the rate-determining step is the breaking of the C–C bond and migration onto the peroxy oxygen to form the ester aided by the facile leaving of –OH (per se a bad leaving group in the stoichiometric reaction) assisted by Pt. Dimerization of the Pt–OH species closes the catalytic cycle.

The similar role played by Pt^+ and H^+ in the reactive intermediate of both the catalytic and stoichiometric reaction respectively, suggested for the first time the possible role of the transition metal Lewis acidity in favoring the reaction.

Other complex types reported in Fig. 5 were found useful for the BV reaction. Among these type **1** were historically developed for accomplishing olefin epoxidation reactions using hydrogen peroxide as the oxidant and the first to be found active also for the BV reaction [9]. Type **3** have a double positive charge, that should increase their Lewis acidity, and similarly to **1** they are single site catalysts. They were developed to elucidate the parameters favoring BV vs. epoxidation reaction. So, while in competition experiments carried out mixing cyclooctene and 2-methylcyclohexanone, lactone vs. epoxide formation was favored by a factor of 2–3, with bifunctional substrates such as menthone and 2-allylcyclohexanone (Fig. 8) the BV product was the exclusive one [21].

Complexes **1** and **3** showed an identical BV oxidation mechanism [9b,22] (Fig. 9) and similar to that reported in Fig. 7 for complexes **2**. With both **1** and **3** the solvent is replaced by the ketone in the coordination sphere of Pt followed by external nucleophilic attack from free hydrogen peroxide leading to the *quasi*-peroxymetallacycle as in Fig. 9, then the rearrangement leading to the ketone takes place, followed by protonation of the Pt–OH intermediate to close the cycle.

Major differences between catalysts **1** and **3** on the one side and **2** on the other side are the following: (i) the former catalyze both

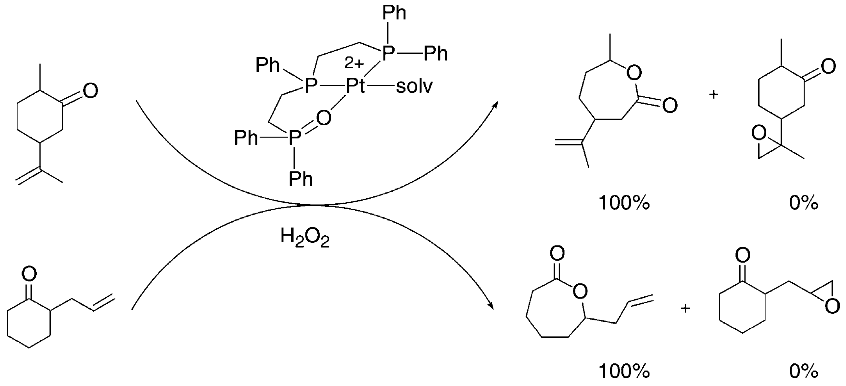


Fig. 8. BV vs. epoxidation behavior in the oxidation of bifunctional substrates with hydrogen peroxide using complexes 3 as catalysts.

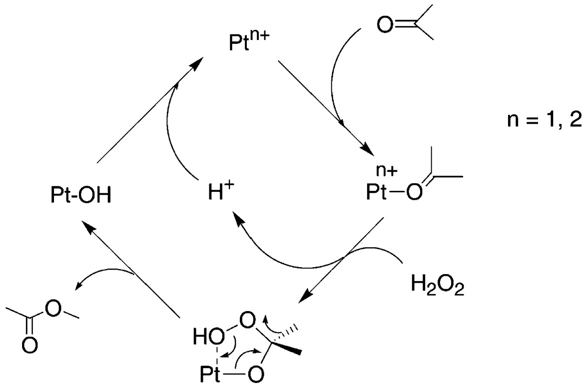


Fig. 9. The BV catalytic cycle in the case of complexes 1 and 3.

BV and epoxidation while the latter catalyze only BV; (ii) the former catalyze only the oxidation of cyclic ketones while the latter also of open chain ketones; (iii) the former are single site catalysts while the latter are two site catalysts and this allows the activation of both substrate and oxidant explaining their superior activity in BV as the nucleophilicity of coordinated –OOH is higher than free H_2O_2.

Despite their notable activity in BV oxidations, all Pt^{II} complexes considered so far have a limited lifetime in the strongly oxidizing reaction medium. In the (more or less) long term, deactivation occurs by oxidation of the diphosphine ligand to the corresponding dioxide and formation of unidentified, catalytically inactive Pt species.

Over the years, Pd complexes homologous to **1**–**3** have been tested in the same reaction, with the idea that Pd analogs would have been more active than Pt complexes. In all cases the Pd species survive only very shortly in the reaction medium so that they cannot be considered as efficient catalysts for such reaction.

2.2. Enantioselective BV oxidation

Most of the recent work on the BV oxidation has focused on the enantioselective version of the reaction, in particular in the catalytic version with organometallic catalysts and more recently with organic catalysts. The first report on such asymmetric transformation appeared about 15 years ago thanks to the pioneering work of Bolm [23] and Strukul [20]. These authors demonstrated, with two different catalysts and oxidant combinations, that a certain degree of stereocontrol on the Criegee intermediate rearrangement was possible, with ee up to 92% on chiral cyclobutanones and 58% in the kinetic resolution of chiral substituted cyclohexanones, respectively. Oxidation of larger ketones was successful only with Pt^{II} [9,19,20,28,24] or Cu^{II} [25] catalysts with moderate to good ee's. In the latter case chiral oxazoline complexes were capable of performing the kinetic resolution of 2-phenylcyclohexanone with 26% ee using the Mukaiyama approach to activate the terminal O_2 oxidant. On the other hand the dissymmetrization of *meso* 4-substituted cyclohexanones with hydrogen peroxide employing chiral Pt^{II} complexes was made possible by the use of a series of commercial chiral enantiopure diphosphines (binap, diop, pyrphos, norphos, Me-duphos, bppm) [28]. Fig. 10 shows some representative results obtained using the (*R*)-binap chiral auxiliary that proved the one giving the highest turnovers and ee's.

At present high conversions together with considerable enantioselectivities can be achieved either with chiral enantiopure organocatalysts based on phosphonic acids [26] or carboxylic acids like the system developed by Peris and Miller [27] where an aspartate-containing peptide mediates the oxidation of substituted cyclohexanones with hydrogen peroxide to give the corresponding lactones with up to 42% ee. As long as chiral organometallic catalysts are concerned, examples have been reported based on different metals. Worth of mention are catalysts based on Co [28], Cu [23,29], Pd [30], Pt [20,31], Zr [32], Hf [33] or non-transition metals like Mg [13b] and Al [34] all active towards *meso* or chiral cyclobutanone substrates which are intrinsically much more reactive compared to larger cyclic ketones. Some representative examples are reported in Fig. 11. However, only biocatalytic BV oxidations [35] performed with isolated enzymes or whole cells containing cyclohexanone monooxygenases (CHMOs) or BV monooxygenases (BVMOs) showed good conversions as well as enantioselectivity above 95% ee with cyclohexanones as substrates [36].

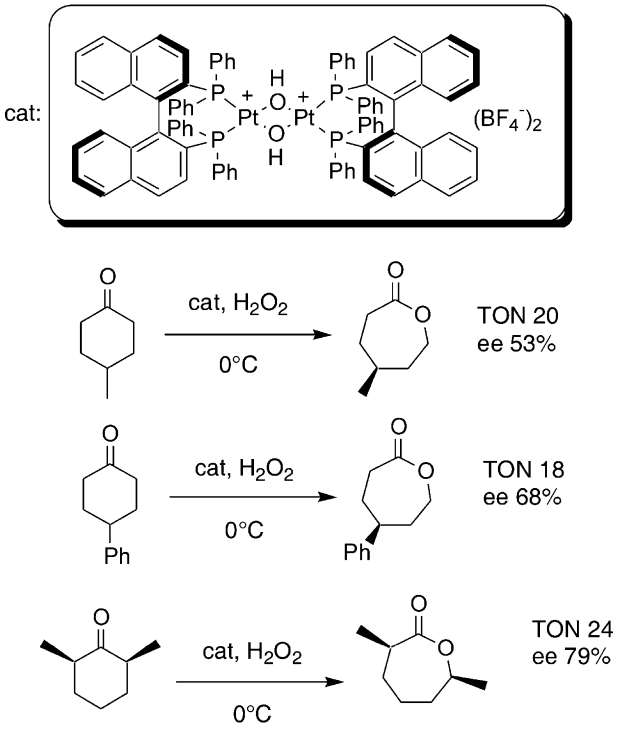


Fig. 10. Dissymmetrization of mesocyclohexanones via BV oxidation.

More recently, the enzyme like catalytic BV oxidation of substituted cyclohexanones and cyclobutanones in water as a green solvent was possible using hydrogen peroxide as the oxidant and mediated by Pt complexes of type **4**, modified with a variety of chiral mono and diphosphines thanks to the aid of surfactants capable of solubilizing the hydrophobic catalyst, substrate and product in micelles (Fig. 12) [37]. Micelles operate as nanoscopic reactors allowing to increase the enantioselectivity of the process with a combination of hydrophobic effect that confines the actors of the reaction in the micelles along with supramolecular interactions between the reaction partners within the ordered palisade provided by the alkyl chains of the surfactant. The confinement effect observed, reminds what observed for the Pt^{II} catalyzed BV reaction in organic media where biphasic systems with H_2O_2 in organic chlorinated solvents performed much better than in ethanol or in THF where a single liquid phase is present [38].

This reaction medium turned out to be remarkably effective to force otherwise inactive species to work with moderate activity and enantioselectivity. So, for example, the micellar environment enables catalytic, diastereoselective and enantioselective BV oxidation of cyclobutanones with H_2O_2 as oxidant using the Co(salen) complex shown in Fig. 13 that, according to Katsuki, should be inactive in the BV oxidation [25]. In micellar media this system shows ee up to 90% while it is inefficient in common organic solvents [39].

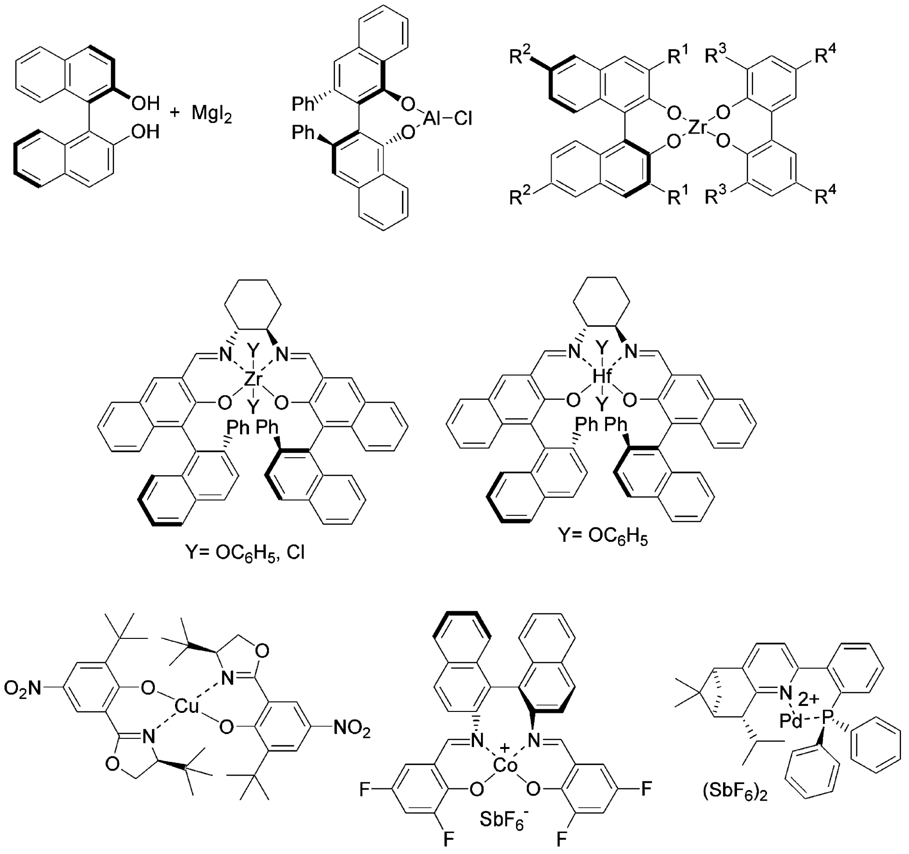


Fig. 11. Examples of chiral organometallic catalysts developed for the asymmetric BV oxidation of cyclic ketones.

2.3. Role of the ligand

Steric constrain is an important parameter to affect the selectivity in this reaction. As was shown in the enantioselective transformation, the rigidity of the diastereoisomeric transition states leading to enantiomeric discrimination can be improved by embedding the catalyst in a partially ordered system like a micelle [38,39]. A similar effect was observed by increasing the bite angle of the chiral diphosphine. In the dissymmetrization of cyclohexanones with type **2** complexes the use of chiral diphosphines with a larger bite results in an improvement of the ee of the lactone products [28]. For example, (*R*)-binap capable of making 7-membered rings with Pt^{II} causes systematically better enantioselectivities with respect to e.g. pyrphos or norphos (5-membered rings) because the larger bite forces the phenyl rings of the diphosphine to encumber the *quasi*-peroxymetallacycle (Fig. 7) limiting its flexibility and hence increasing the energy difference between the two diastereomeric intermediates.

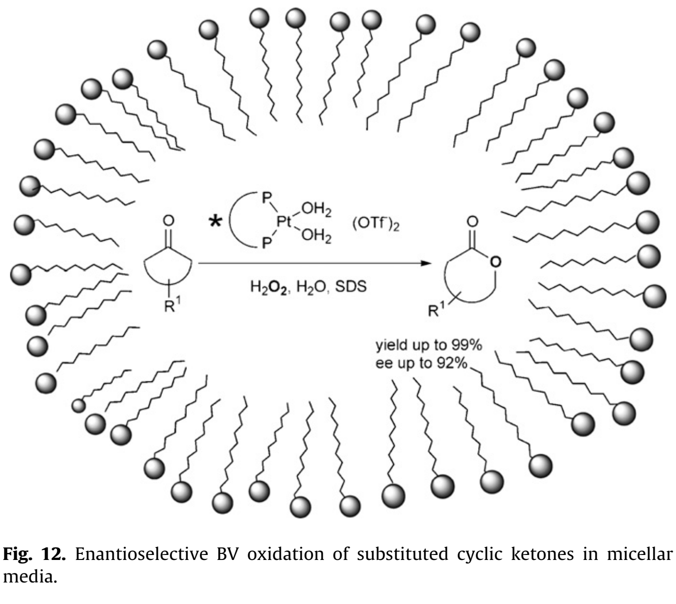
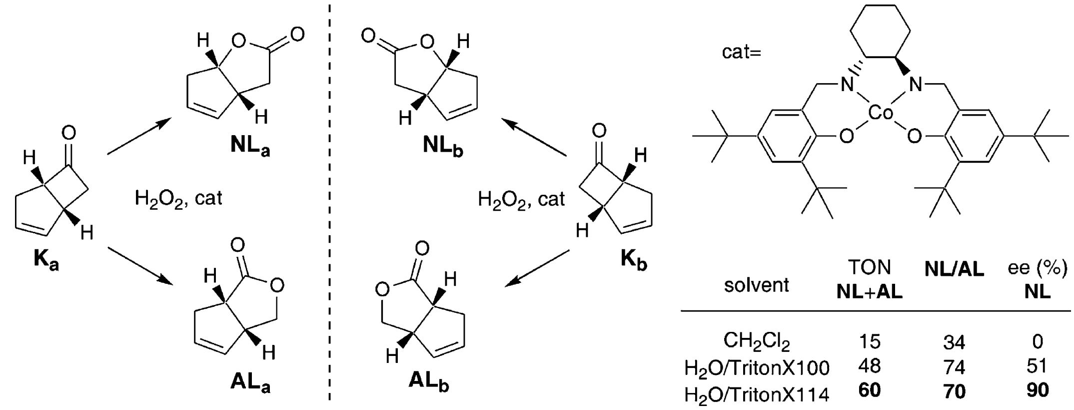


Fig. 12. Enantioselective BV oxidation of substituted cyclic ketones in micellar media.

Steric effects have also a strong impact on the catalytic activity of type **2** complexes as they help the splitting of the diplatinum dihydroxy core (Fig. 7). For example, it was observed that increasing the length of the chain linking the two P atoms in tetraaryl diphosphines, i.e. increasing their bite angle, increases the initial rate in the oxidation of methyl-cyclohexanone by about an order of magnitude (Fig. 14 left) [19b]. A similar effect (Fig. 14 right) is obtained also using tetraalky-diphosphinoethanes that make the complexes all similar in terms of Lewis acidity but characterized by different steric hindrance as a consequence of the size of the alkyl group, hence increasing their cone angle [24e].

The activity in the BV oxidation is strongly affected also by electronic factors and, more specifically, by the Lewis acidity of the soluble catalyst. The concept of Lewis acidity is central in catalysis with hydroperoxides. Halcon chemistry is based on Lewis acidic d^0 transition metal species (Ti^{IV}, V^V, Mo^{VI}, W^{VI}, etc.) capable of improving the electrophilicity of the coordinated hydroperoxide making it susceptible to nucleophilic attack by an external olefin. This is the principle of electrophilic oxidation (Fig. 4). In the BV oxidation some of the most active catalysts are based on Al^{III}, Mg^{II}, Sn^{IV}, i.e. typical Lewis acids. Cationic Pt(II) complexes that are the most active and versatile catalysts so far reported can be also considered Lewis acids as is suggested by the similar role of H^+ and Pt^+ in the reactive intermediates of the stoichiometric and catalytic reactions, respectively.



solvent	TON NL+AL	NL/AL	ee (%) NL
CH_2Cl_2	15	34	0
H_2O/TritonX100	48	74	51
H_2O/TritonX114	**60**	**70**	**90**

Fig. 13. The chiral catalyst Co(salen) is inefficient in the asymmetric BV oxidation reaction of chiral cyclobutanones when the reaction is performed in organic solvent, while it is active and highly enantioselective in micellar media.

This concept was systematically analyzed with type **2** complexes modified with diphenylphosphino ethanes where a variable number of fluorine atoms were present as substituents in the aryl groups. The F atoms would exert an electron-withdrawing effect on P and its donor capacities and hence decrease the electron density on Pt or, in other words, increase its Lewis acidity. Fig. 15 shows that on going from zero to five F atoms on the aryl groups the initial rate increases by an order of magnitude indicating that the higher the Lewis acidity of the catalyst the more favored is the catalytic activity in the BV oxidation of methyl-cyclohexanone, as a higher Lewis acidity would result in a higher electrophilicity of the carbonyl carbon upon coordination to platinum [24b].

The effect of the Lewis acidity of the complex was studied also in the epoxidation of simple terminal alkenes with hydrogen peroxide using $[(P–P)Pt(C_6F_5)(H_2O)](BF_4)$ catalysts. Here however, although the effect is still dramatic (two orders of magnitude difference in activity between diipe and dppe as ligands), an intermediate acidity is required as the largest activity is observed with dppe [40].

2.4. Other Pt^{II} Lewis acid catalyzed reactions

The soft Lewis acidity of these complexes makes them particularly tolerant to water, allowing its use as a reaction medium, as was reported above for the BV oxidation of cyclohexanones and cyclobutanones [38,39]. Nowadays, water is an especially attractive solvent for going green in organic transformations, because of its complete environmental compatibility and the occurrence of the so-called hydrophobic effect that, under entropic control, favors interaction between apolar surfaces when these cannot be efficiently solvated by water [41] and capable (in several cases) to improve the selectivity of processes, as shown above in Section 2.2. These properties were exploited in micellar media to accomplish other oxidation reactions in water namely sulfoxidation [42] and the epoxidation of simple alkenes [43], both in their enantioselective version and the latter with the possibility to recycle the catalyst (Fig. 16).

All oxidation reactions catalyzed by Pt^{II} complexes can be carried out at room temperature, in water, in air, with low catalyst loading, no need of over-stoichiometric amounts of oxidant yielding high activity, unsurpassed substrate selectivity and high enantioselectivity.

The soft Lewis acid properties were also exploited in some typically acid catalyzed reactions. Type **2** complexes were found very efficient catalysts for the acetalization and thioacetalization of aldehydes and ketones [44] while type **3** complexes could be used for the catalytic Diels–Alder reaction between dienes and unsaturated aldehydes or ketones as dienophiles both in the regular and the enantioselective version of this reaction [45]. Finally, the cat-

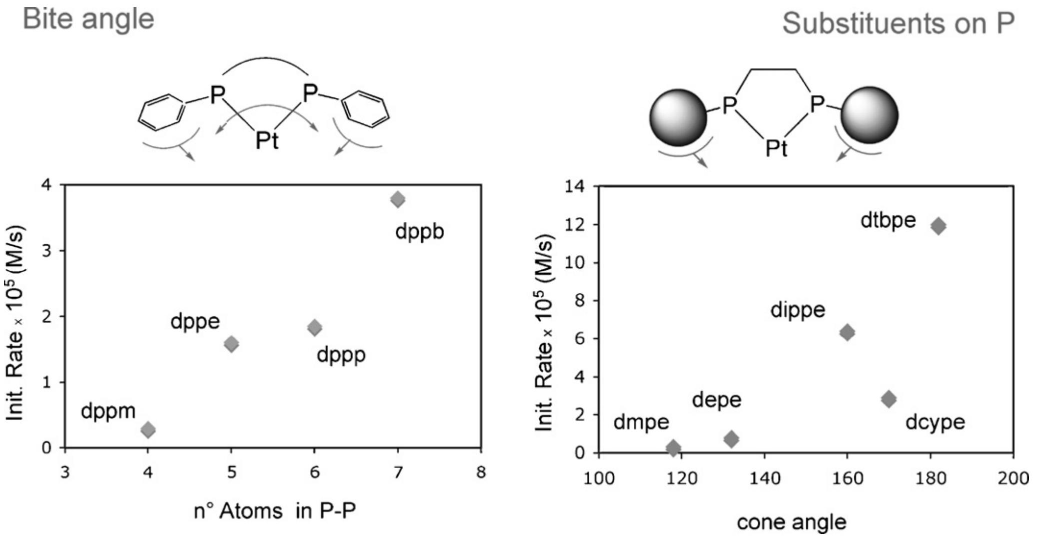


Fig. 14. Effect of the diphosphine in the BV oxidation of methylcyclohexanone. Left: dppm diphenylphosphinomethane, dppe diphenylphosphinoethane, dppp diphenylphosphinopropane, dppb diphenylphosphinobutane. Right: dmpe dimethylphosphinoethane, depe diethylphosphinoethane, diipe diisopropylphosphinoethane, dcype dicyclohexylphosphinoethane, dtbpe ditertbutylphosphinoethane.

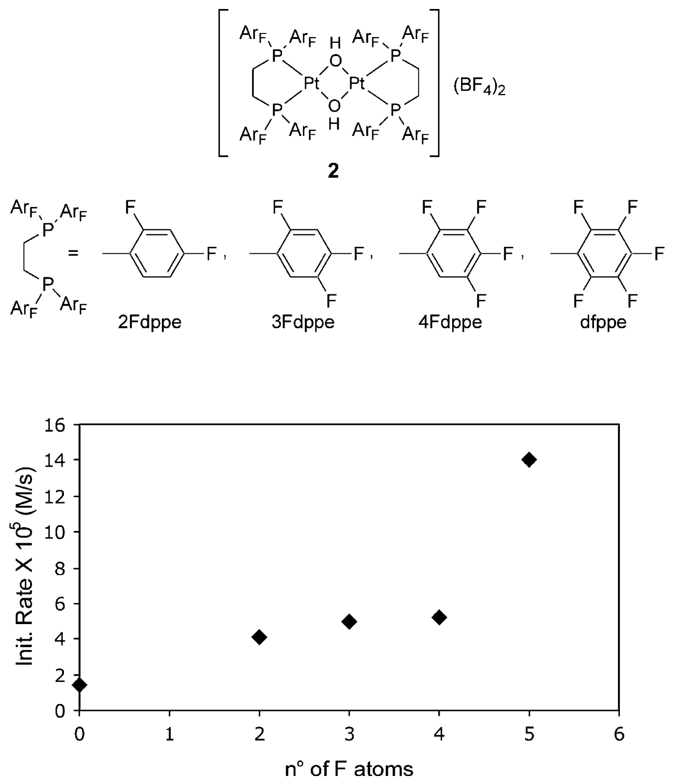


Fig. 15. Effect of F substitution on the aryl groups of the ligand on the catalytic activity of type 2 complexes in BV.

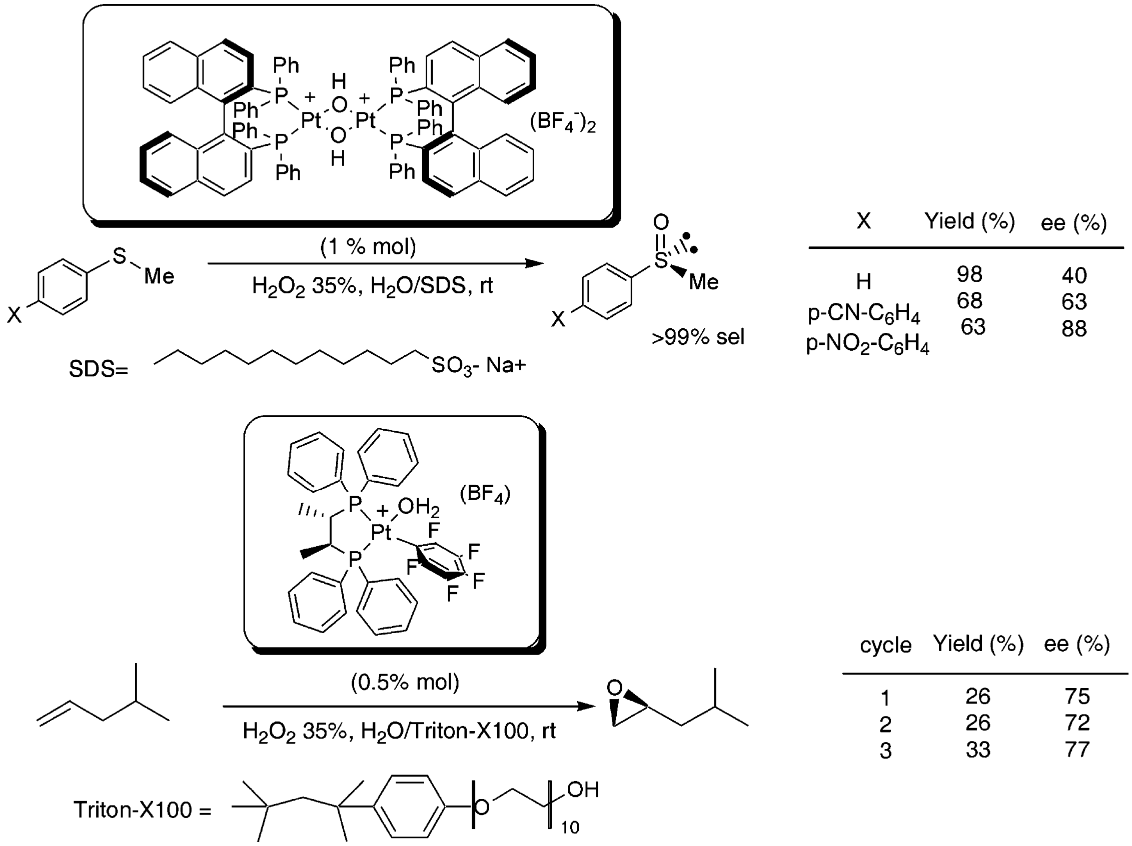
alytic isomerization of simple alkenes was made possible by the use of [(dppb)Pt(C_6F_5)(H_2O)](BF_4), allowing for example the efficient conversion of anethole into estragole with high stereoselectivity (Fig. 17) [46].

In all the above reported reactions, both in the oxidations and in the reactions shown in Fig. 17 the Pd homologous complexes failed to evidence any activity. The only exception was the Diels–Alder reaction where Pd^{II} *bis*-solvento complexes similar to those indicated showed comparable activity, but lower enantioselectivity. Interestingly similar Pd^{II} *bis*-solvento complexes were found by Inoue and coworkers [47] to induce excellent enantioselectivities in the same reaction but using *N*-acryloyl-oxazolidinone as the dienophile. This compound is very common in enantioselective Diels–Alder transformations and is capable to chelate on the metal and saturate both vacant coordination sites thereby yielding a very rigid intermediate during the [4+2] cycloaddition, a situation that is precluded when using simple dienophiles such as acrolein or methyl-vinylketone.

3. Analysis on the peculiarity of Pt^{II} catalysts for the BV reaction

3.1. Pt and Pd: why so different?

Apparently the answer to the question: *why platinum is more efficient than palladium in the catalytic Baeyer–Villiger oxidation of ketones?* is not an easy one. Although it can be observed that the two metals have similar features such as the atomic radii [48], the bond lengths in their homologous compounds [49], the M^{II} oxidation state where they both show a d^8 electronic structure of the outer shell and the same square-planar coordination geometry of their complexes, on the other hand they show a quite different reactiv-



X	Yield (%)	ee (%)
H	98	40
p-CN-C_6H_4	68	63
p-NO_2-C_6H_4	63	88

cycle	Yield (%)	ee (%)
1	26	75
2	26	72
3	33	77

Fig. 16. Other Pt^{II} catalyzed oxidations with hydrogen peroxide in micellar media.

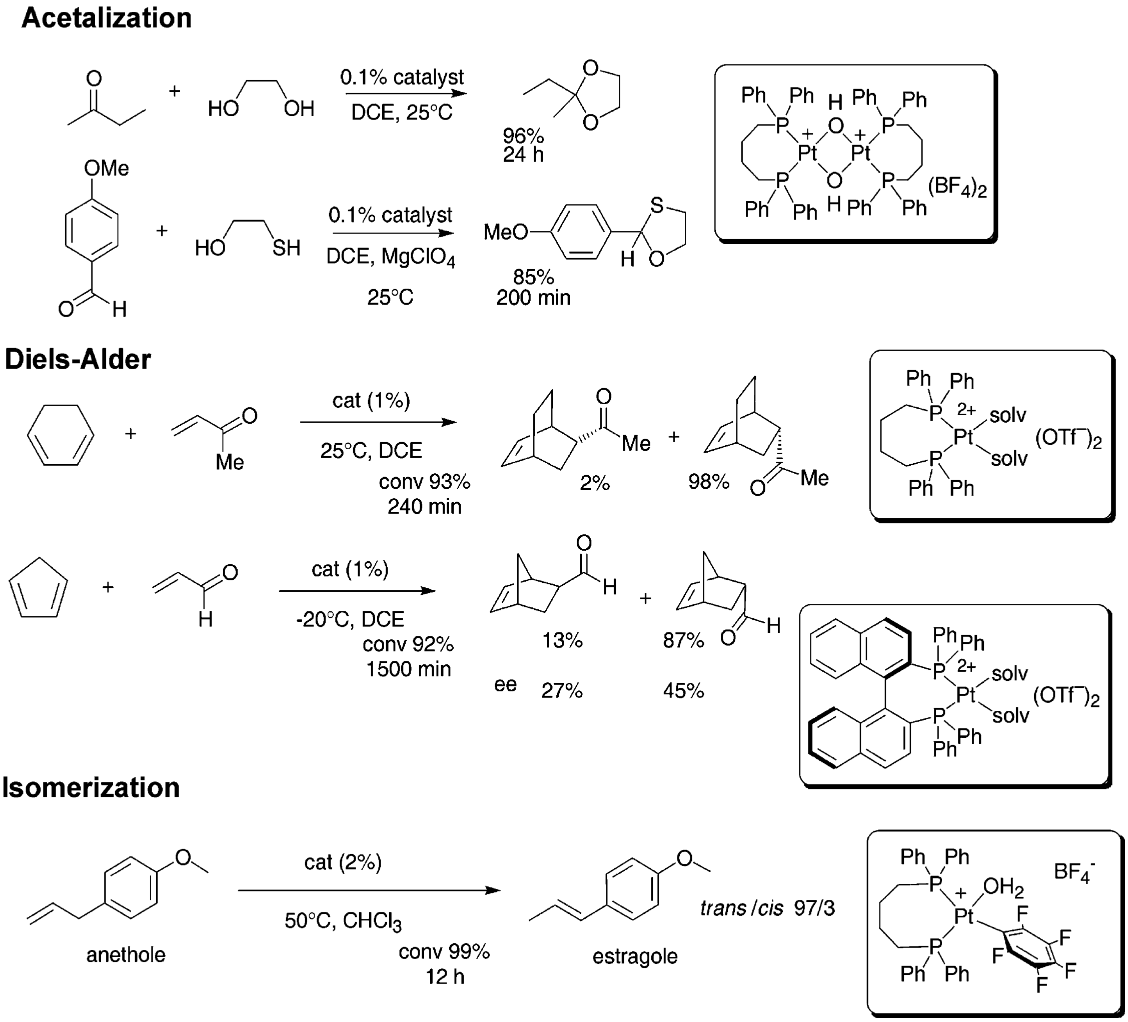


Fig. 17. Examples of other acid catalyzed reactions efficiently and selectively mediated by different classes of Lewis acidic Pt^{II} complexes.

ity both in terms of catalytic activity and type of catalyzed reactions [50]. In fact, platinum-based catalysts are not as common as those of palladium that in the past 50 years has been involved in a wide variety of catalytic transformations since the milestone discovery of the Wacker process for the oxidation of olefins to aldehydes [51].

A possible key for answering the above question can be based on the following considerations. First of all, the ligands coordinated to Pt^{II} are in general less labile than those bound to Pd^{II} complexes. This was observed in the past considering the rate of ligand exchange in a series of square-planar complexes [52] and the effect of ligands on those rates [53]. This property, while causing generally lower rates may be also the reason why Pt complexes survive much longer in a strongly oxidizing environment such as that involved in the present reaction. Moreover, palladium has a marked tendency to give parallel reaction pathways such as, β-hydride abstraction/reductive elimination processes, as was clearly observed in our attempts to use diphosphine Pd^{II} complexes as catalysts in the oxidation of olefins. In this type of reaction, the reported activity is rather low but, more importantly, the main product is not the epoxide but the corresponding methyl ketone. Similar results were first observed by Roussel and Mimoun in the oxidation of 1-octene with hydrogen peroxide, using different Pd(II) complexes [54] (Fig. 18).

Analogously, in the isomerization of allylbenzenes with Pt^{II} complexes as catalysts, we observed that the reaction mechanism proceeds via the formation of a hydride intermediate complex that reacts with the coordinated alkene through 1,2-hydrogen shift [46].

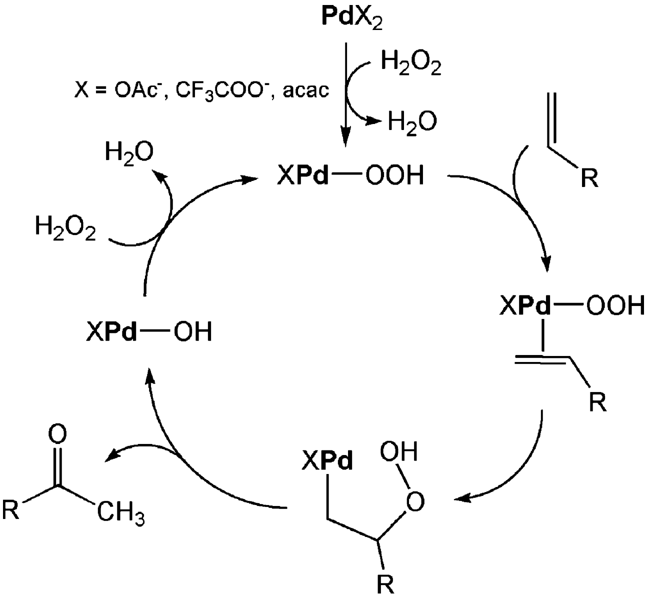


Fig. 18. Proposed mechanism for Pd(II) catalyzed epoxidation of 1-octene [54].

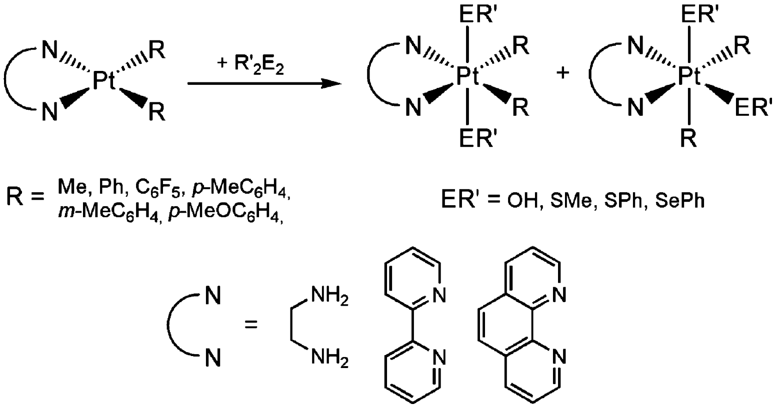


Fig. 19. Oxidative addition of H_2O_2, disulfides and diselenides to Pt^{II} diamine complexes.

Again, Pd^{II} was not active, as palladium usually isomerizes olefins through the formation of allylic intermediates (1,3-hydrogen shift), a pathway that is precluded with allylbenzenes because allyl complexes cannot be formed.

3.2. Effects of phosphines on the catalytic behavior

All the Pt^{II} complexes considered in our research work are d^8 square planar complexes. This class of complexes has received a great attention in the past and their relative stability has allowed the thorough understanding of their behavior, such as the cis/trans isomerism and ligand exchange phenomena and the effect of coordinated ligands on their stability [52,55]. Those fundamental studies have shown the stabilizing effect of phosphines towards a large number of transition metal centers, being good σ-donating ligands, and their high *trans*-effect [56], being able to labilize the ligands *trans* to them. Moreover, phosphines, differently from amines, can also act as π-acceptors, reducing the electron density on the metal center and increasing its Lewis acid character. So, they appear to be the ligands of choice in designing a series of possibly stable, Lewis acidic complexes able to coordinate the substrate and/or the oxidant but not too strongly to be blocked by them, being thus unable to act as catalysts.

Both monophosphines and chelating diphosphines have been thoroughly used as ligands in homogeneous catalysis in the last 60 years [57], as they are good nucleophiles, their steric and electronic properties can be easily tuned, and a large number of such type of ligands is presently commercially available.

Phosphine-based catalysts have been fruitfully applied to several catalytic reactions such as hydroformylation [58], hydrocarboxylation [59], hydrocyanation [60], cross-coupling [61], etc., but phosphines are odd ligands for oxidation reactions. In fact, they are usually reported to be readily oxidized, leading to subsequent decomposition of the metal complex [62] and deactivation of the catalyst. This feature was also observed with Pt^{II} systems (see Sections 2.1 and 2.3), as the main deactivation pathway involves the decomposition of the catalyst by progressive oxidation of the dissociated P-ligand by hydrogen peroxide. In the case of Pt diphosphine complexes, the oxidation process can be sufficiently slow to observe catalytic effects and much slower than that observed with Pd compounds since the diphosphine ligands are more strongly bound to the metal centre and less labile.

It should also be observed that P-ligands permit to avoid the oxidative addition of hydrogen peroxide at the metal center, thus behaving differently from chelating N-based ligands. In fact, as observed by Puddephatt and coworkers [63a] and subsequently by Deacon and coworkers [63b] and Rashidi and coworkers [63c], N-ligands such as bipyridyl, phenanthroline and diamines being more electron-donating ligands, they are able to activate the Pt^{II} square-planar complexes towards the oxidative addition of a variety of reagents such as hydrogen peroxide, disulfides and diselenides, to afford the corresponding octahedral Pt^{IV} *bis*-hydroxo, *bis*-thiolato and bis-selenolato complexes (Fig. 19), respectively.

Thus, focusing the attention to diphosphines, the possibility to modify their steric and electronic properties and consequently the properties of their complexes has allowed to readily determine how they affect the catalytic activity.

So far we have extensively studied such phenomenon preparing a wide series of complexes characterized by similar structures but also by the variation of pivotal features such as: (i) the bite angle of the chelating diphosphine, through the use of diphosphines with different bridges between the two P atoms; (ii) the electron withdrawing power of the groups on the P atoms, using both alkyl and aryl groups, both normal and fluorinated; (iii) the steric encumbrance of the groups on the P atoms.

As reported above, all of them have proved to have a major effect in driving the activity of the catalytic species, since more electron withdrawing groups on P and large bite angles gave the most active catalysts, while a more subtle effect of the steric bulkiness of the groups on P was observed.

The steric hindrance of the diphosphine and, more generally, its rigidity, in terms both of structure and coordination, is very important in the enantioselective reactions since it is a determining factor to get high asymmetric induction [64]. For instance, this is evident in a reaction such the above reported Diels–Alder cycloaddition, where the activity of Pd^{II} complexes is very similar to that of Pt^{II} ones. In this case the less labile complexes of platinum are responsible for a better enantioselectivity, giving higher ee's than the corresponding palladium based catalysts [45].

3.3. Lewis acidity: how could we measure it?

As mentioned in Section 2.3, a clear correlation was found between the predictable Lewis acidity of Pt^{II} complexes and their catalytic activity. In this perspective, it was interesting to find a correlation between the effect of the complex structure and of the type of ligands with the Lewis acidity and the activity of the catalysts.

In the past a few different methods were developed to assess the Lewis acidity of a homogeneous catalyst, most of them concerning the coordination to the metal centre of a probe molecule containing a spectroscopically detectable atom and/or functional group.

For instance, Childs et al. [65] developed a method based on the difference in chemical shift ($\Delta\delta$) of the proton bound to the C_3 in coordinated crotonaldehyde. Beckett et al. [66] modified the Gutmann method [67] by measuring the change in ^{31}P NMR chemical shift of a coordinated phosphine oxide or sulphide. Other

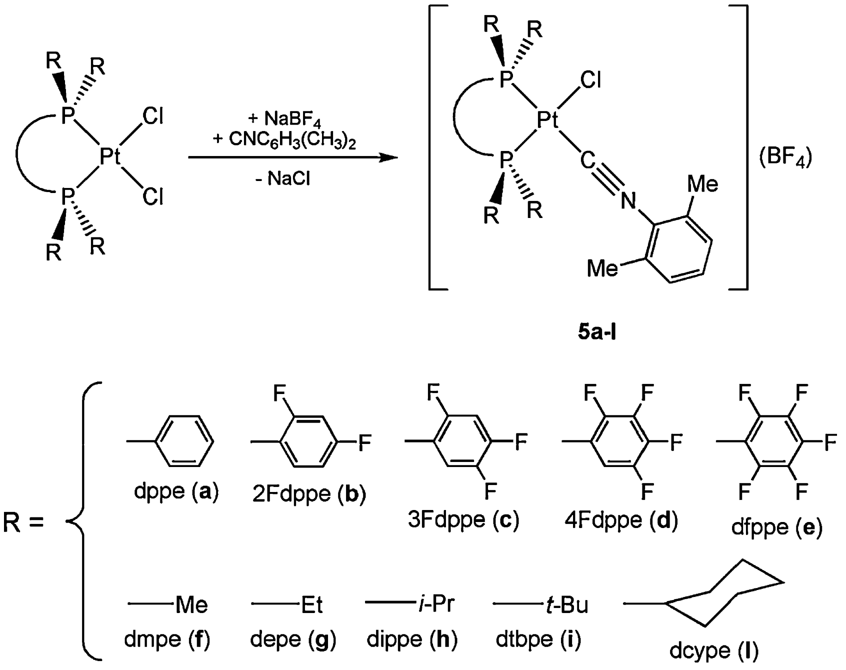


Fig. 20. Structure of the isocyanide complexes $[Pt(P\text{–}P)(CN\text{-}2,6\text{-}(CH_3)_2C_6H_3)Cl][BF_4]$ (**5a**–**l**).

approaches are based on the measurement of the acidity of a coordinated water molecule [68].

More recently various "quantitative" methods for Lewis acidity determination have been proposed. Fukuzumi and Ohkubo reported different spectroscopic series based on fluorescence measurements [69], or on the *g* values of ESR spectra of superoxide/metal ion complexes [70] while, Gasperini and Ragaini suggested a method based on the measurement of the equilibrium constant in the substitution reaction of a particular class of ligands [71].

Some of us have developed a method based on the correlation of the wavenumber shift $\Delta\nu$ ($\Delta\nu = \nu_{(C\equiv N)coord} - \nu_{(C\equiv N)free}$) of the IR C≡N stretching of a probe isocyanide molecule with the Lewis acidity of the metal centre. In fact, it is known [72] that the value of the $\nu_{(C\equiv N)coord}$ (or the $\Delta\nu$) of a transition metal-coordinated isocyanide gives information about the electrophilicity of the isocyanide carbon atom, which in turn is related to the electron density, hence to the Lewis acidity of the metal center. Thus, it was expected that a larger electron-withdrawing effect by the metal would give rise to a larger wavenumber shift.

On this basis, using 2,6-dimethylphenyl isocyanide as a probe molecule, we prepared a homologous series of isocyanide complexes **5** of general formula $[PtCl(CN\text{-}2,6\text{-}(CH_3)_2C_6H_3)(P\text{–}P)]^+$ (Fig. 20), which differ only in the diphosphine ligand, P–P being a fluorinated diphosphine of general formula $(C_6H_{5-n}F_n)_2PCH_2CH_2P(C_6H_{5-n}F_n)_2$ (with $n = 0$ in dppe, 2 in 2Fdppe, 3 in 3Fdppe, 4 in 4Fdppe, 5 in dfppe) or an alkyl-diphosphine of general formula $R_2PCH_2CH_2PR_2$ (with R = Me in dmpe, Et in depe, *i*-Pr in dippe, *t*-Bu in dtbpe, Cy in dcype). They have been obtained from the corresponding $[PtCl_2(P\text{–}P)]$ derivatives by single halide abstraction and treatment with a stoichiometric amount of the isocyanide ligand (Fig. 20).

The fluorinated diphosphines complexes **5b**–**e** displayed the $\Delta\nu$ values in the range 99–89 cm^{-1} (Table 1).

Table 1 shows that upon increasing the number of fluorine atoms in the phenyl groups of the diphosphine, $\Delta\nu$ increases and hence the acidity of the metal centre increases. Complex **5e** having coordinated dfppe, showed the highest wavenumber shift ($\Delta\nu = 99\ cm^{-1}$), and consequently it should possess the highest Lewis acidity among this class of complexes. This is in agreement with its highest catalytic activity in the oxidation of cyclic ketones.

On the other hand, the alkyl-diphosphines complexes **5f**–**l** displayed the $\Delta\nu$ values in the range 80–74 cm^{-1} (Table 1). The average $\Delta\nu$ values displayed by these latter species was ca. 8 cm^{-1} lower than that observed for the tetra-aryl dppe derivative **5a** (Table 1) and even lower than that showed by the corresponding fluorinated aryl diphosphine compounds. This feature supports that dialkyl diphosphine complexes display a lower Lewis acidity and that it decreases slightly with increasing steric bulkiness of the alkyl moieties, thus indicating that they are characterized by a similar Lewis acid character. As a consequence, it appears reasonable to ascribe the differences in the catalytic activity shown by this series of complexes mainly to the different steric properties of the diphosphines (see Fig. 14 above).

Looking for a different way to have a qualitative measure of the Lewis acidity some of us proposed recently an electrochemical method based on cyclic voltammetry (CV) technique, which gives information on the electronic properties of the complexes without introducing any other molecule that can modify the original catalyst. In fact, redox potential–structure relationships have already been recognized in coordination compounds and electrochemical parameters have been defined to measure the electron donor/acceptor properties of some types of metal centers and ligands [73].

Table 1
Summary of the IR data of the isocyanide complexes $[Pt(P\text{–}P)(CN\text{-}2,6\text{-}(CH_3)_2C_6H_3)Cl][BF_4]$ (**5a**–**l**) in CH_2Cl_2 solution.

P–P	Complex	$\Delta\tilde{\nu}(cm^{-1})$
dppe	**5a**	85
2Fdppe	**5b**	89
3Fdppe	**5c**	91
4Fdppe	**5d**	93
dfppe	**5e**	99
dmpe	**5f**	80
depe	**5g**	77
dippe	**5h**	76
dtbpe	**5i**	74
dcype	**5l**	76

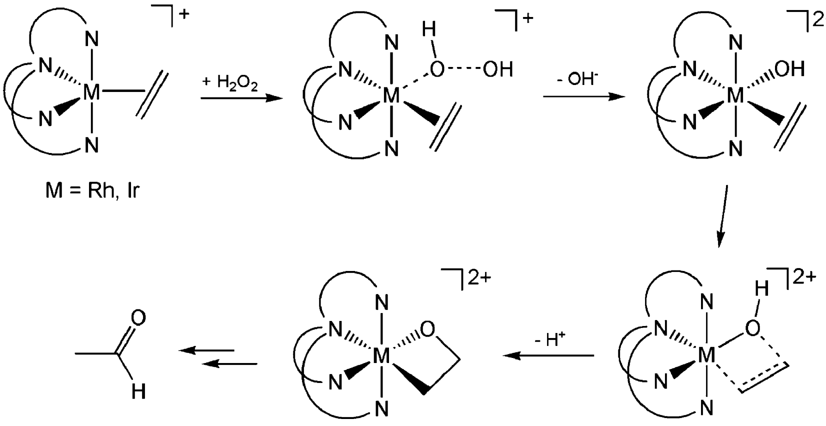


Fig. 21. Proposed mechanism for ethene oxidation by H_2O_2 in Rh^I and Ir^I complexes.

Table 2
Summary of the catalytic data for the oxidation of 2-methylcyclohexanone with hydrogen peroxide catalyzed by $[Pt(\mu\text{-}OH)(P\text{–}P)]_2[BF_4]_2$ (**2a**–**d**) at 50 °C and their CV.

P–P	Complex	$^1E_p^{red}$	Init. rate (M/s)
dppe	**2a**	−1.23	1.4×10^5
2Fdppe	**2b**	−1.14	4.1×10^5
4Fdppe	**2c**	−0.92	5.2×10^5
dfppe	**2d**	−0.79	14×10^5

CV was applied to study the homogeneous series of partially fluorinated Pt^{II} complexes previously used in the BV oxidation of 2-methyl cyclohexanone [74]. The reduction potential of the complexes reflected the electron-donor character of the phosphine ligand and thus the Lewis acidity of the metal centre, as corroborated by the overall relations of that potential with the number of fluorine atoms in the diphosphine and with the $\nu C{\equiv}N$ coordination shift using the isocyanide molecular probe (Table 2).

This suggests the possible application of the reduction potential to probe the reactivity of the Pt^{II} compounds that also depends on the Lewis acid character of the metal centre, namely the catalytic activity for the BV reaction. However, one should remember that the reduction potentials are not the thermodynamic ones (in view of the irreversible character of the reduction waves) and thus they are also dependent on kinetic factors. In addition, steric effects, apart from the electronic ones, can play a relevant role in some cases, namely on the values of the above parameters and on the chemical reactivity.

3.4. *Oxidation catalysis with other d^8 transition metal complexes*

Many years ago, after the first evidence of catalytic activity of Pt^{II} complexes in oxidation reactions with hydrogen peroxide, some of us thought to develop this chemistry with other d^8 transition metals, since they have a similar square-planar coordination geometry. Among them the most interesting were Rh^I and Ir^I, since they have been used in a wide range of reactions [51a] such as asymmetric hydrogenation [75] and isomerization [76], carbonylation and hydroformylation [77].

The easy reversibility of the redox couples Rh^I/Rh^{III} and Ir^I/Ir^{III} and the relative stability of the higher oxidation states is one of the reasons of such a wide range of catalyzed reactions since in various catalytic cycles oxidative addition steps are involved, leading to octahedral M^{III} complexes. However, there are no examples in the literature of rhodium and iridium-based Baeyer–Villiger catalysts, although some oxidation chemistry based on these metals can be found. In 1997 de Bruin et al. [78] obtained the first unambiguous rhodium catalyzed oxidation of a coordinated ethene molecule by hydrogen peroxide, and later this chemistry was extended to iridium [79].

In 2004, Budzelaar and Blok [80] proposed a mechanism for the oxidation of alkenes to aldehydes, involving the cleavage of the peroxide bond of H_2O_2, leading to $M^{III}(OH)(ethene)^{2+}$ (M = Rh, Ir) species via oxidative addition. After cyclization and deprotonation, a metallaoxetane is formed which does not convert to the desired epoxide by reductive elimination but rather to the aldehyde by β-hydride elimination (Fig. 21), overall a hydroxymetallation as the key step like in Wacker chemistry.

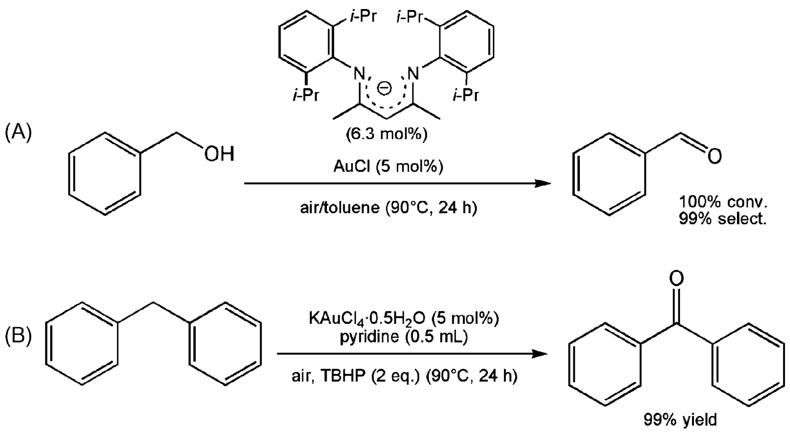


Fig. 22. Oxidation reactions catalyzed by Au^I, Au^{III} homogeneous complexes.

This mechanism is quite different from those proposed by us for the epoxidation of olefins catalyzed by Pt^{II} complexes [81] but also for the BV reaction, both involving the activation of the substrate and of hydrogen peroxide by metal coordination, without O–O bond breaking and without any change in the oxidation state of the metal centre.

Based on these considerations, Pt^{II} systems in the BV oxidation reactions appear to be quite peculiar and apparently the only possible choice among late transition metals. Anyhow, if we consider the general class of d^8 square-planar complexes, it would be interesting to study the properties of the homologous diphosphine complexes of Au^{III}.

In recent years gold is experiencing a real "golden era" and the number of papers dealing with its use in catalysis is constantly rising [82]. Among them, a few examples of selective oxidation reactions using homogeneous gold catalysts have been reported by Shi and coworkers [83]. A soluble Au^{I} catalyst was successfully used for the oxidation of benzyl alcohol to benzaldehyde (Fig. 22A) and a Au^{III} catalyst for the oxidation of a series of benzyl derivatives to the corresponding carbonyl compounds, such as diphenylmethane to benzophenone (Fig. 22B).

In both cases the structures of the actual catalytic species were not elucidated.

Considering the Baeyer–Villiger oxidation of ketones, the main reason for a possible application of Au^{III} diphosphine complexes is the larger positive charge of the metal center, that would increase its Lewis acidity. The success of such approach will depend on the possibility to synthesize a series of complexes, stable in the oxidizing reaction medium and characterized by easily accessible coordination sites.

4. Conclusions

This review has concentrated mainly on Pt complexes and has demonstrated that this metal can be profitably used as catalyst for accomplishing BV oxidation reactions with hydrogen peroxide as oxidant and is a much better catalysts for these reactions with respect to Pd or even Rh and Ir complexes. This is somehow surprising and in contrast to chemical common sense and decades of fundamental studies in organometallic chemistry and homogeneous catalysis that would indicate platinum as merely the slow brother of palladium.

Oxidation catalysis is a complicated job in which one has to face challenges such as the ability to preserve the catalyst in a highly oxidizing environment, the generally low selectivity as a consequence of the variety of easily accessible heterolytic and homolytic reaction pathways involving the oxidant, the variety of elementary steps generally exhibited by the otherwise very successful late transition metals that multiplies the number of possible reaction products, the sensitivity to water of most transition metal complexes when using the highly desirable, environmentally safe hydrogen peroxide as the oxidant.

Platinum does all that. Its relative inertness ensures its complexes a sufficiently long lifetime in a strongly oxidizing environment even using the easily oxidizable phosphines as ancillary ligands, turning what is generally considered as a limitation into an advantage. This acceptable stability is witnessed by the observation that platinum is one of the few metals that has allowed the isolation of stable hydroperoxo complexes [84] by direct reaction with hydrogen peroxide. The possibility to use phosphines as ancillary ligands has opened the way to the fine tuning of the electronic and steric properties of the catalyst because phosphines are the most successful class of ancillary ligands in homogeneous catalysis including an extreme variety of mono and bidentate and even chiral species. In a field in which for a complex being catalytically active or inactive may be a matter of a few kcals this is a formidable advantage.

Phosphines on Pt^{II} inhibit oxidative addition reducing the number of possible oxidant activation pathways contributing to avoiding undesired side reactions. Here again the relative inertness of platinum reveals as an advantage making β-hydride elimination more difficult thereby allowing the oxidation of olefins to epoxides (no Wacker chemistry) and ketones into esters. Of the many elementary steps that make the catalytic chemistry of Rh^{I}, Ir^{I}, Pd^{II} so rich and versatile (ligand association, oxidative addition, β-hydride elimination, etc.) only ligand association is used by Pt^{II} in the oxidation reactions here examined. Furthermore, having no easily accessible one-electron redox couples, it does not lead to radical type hydroperoxide decomposition. In its overall behavior Pt^{II} closely resembles d^0 early transition metal Lewis acid centers involved with Halcon chemistry, albeit with a notable difference. While the latter activate the peroxidic oxidant giving rise to electrophilic oxidation (Fig. 4), Pt^{II} activates the substrate leading to nucleophilic oxidation, in both cases, however, the metals behave as a simple Lewis acids.

The BV oxidation here examined has the merit to have revealed this point very clearly with an unequivocal correlation between catalytic activity and Lewis acid character, introducing the concept of soft Lewis acidity and the possibility to use catalysts developed for the BV reaction also for other acid catalyzed processes. Finally, the soft character of Pt^{II} complexes makes them inert to water allowing the efficient use of the "green" hydrogen peroxide oxidant and also opening the way to the use of aqueous reaction media and catalyst recycling, a chance that is generally precluded to ordinary Lewis acids.

Acknowledgements

The authors thank Università Ca' Foscari di Venezia, Università degli Studi di Padova, MIUR and Consorzio INSTM for support. A special acknowledgement is dedicated to the numerous students and collaborators that contributed with their enthusiasm and skills to this topic. This review is dedicated to Professor Fausto Calderazzo a paragon for generations of researchers both as a scientist and as a man.

References

[1] A. Baeyer, V. Villiger, Berichte 32 (1899) 3625.
[2] (a) C.H. Hassall, Org. React. 9 (1957) 73;
(b) J.E. Leffler, Chem. Rev. 45 (1949) 385;
(c) J.B. Lee, B.C. Uff, Quart. Rev. 21 (1967) 429;
(d) H.O. House, Modern Synthetic Reactions, Benjamin, New York, 1972;
(e) B. Plesnicar, in: W.S. Trahanovsky (Ed.), Oxidation in Organic Chemistry Part C, Academic Press, New York, 1978;
(f) G.C. Krow, Org. React. 43 (1993) 251.
[3] R. Criegee, Justus Liebigs Ann. Chem. 560 (1948) 127.
[4] (a) P.A. Grieco, Y. Yokoyama, S. Gilman, Y. Ohfune, Chem. Commun. (1977) 870;
(b) L. Syper, Synthesis (1989) 167;
(c) L. Syper, J. Mlochowski, Tetrahedron 43 (1987) 207;
(d) L. Syper, Tetrahedron 43 (1987) 2853.
[5] S.E. Jacobson, F. Mares, P.M. Zambri, J. Am. Chem. Soc. 101 (1979) 6938.
[6] (a) S.-I. Murahashi, Y. Oda, T. Naota, Tetrahedron Lett. 33 (1992) 7557;
(b) S.-I. Murahashi, Angew. Chem. Int. Ed. 34 (1995) 2443;
(c) C. Bolm, G. Schlingloff, K. Weickardt, Tetrahedron Lett. 34 (1993) 3408;
(d) M. Hamamoto, K. Nakayama, Y. Nishiyama, Y. Ishii, J. Org. Chem. 58 (1993) 6421;
(e) R. Giannandrea, P. Mastrorilli, C.F. Nobile, G.P. Suranna, J. Mol. Catal. 94 (1994) 27;
(f) C. Bolm, C. Palazzi, G. Francio, W. Leitner, Chem. Commun. (2002) 1588.
[7] (a) S.E. Jacobson, R. Tang, F. Mares, J. Chem. Soc. Chem. Commun. (1978) 888;
(b) S.E. Jacobson, R. Tang, F. Mares, Inorg. Chem. 17 (1978) 3055.
[8] (a) S. Campestrini, F. Di Furia, J. Mol. Catal. 79 (1993) 13;
(b) F. Di Furia, G. Modena, Pure Appl. Chem. 54 (1982) 1853.
[9] (a) M. Del Todesco Frisone, F. Pinna, G. Strukul, Stud. Surf. Sci. Catal. 66 (1991) 405;
(b) M. Del Todesco Frisone, F. Pinna, G. Strukul, Organometallics 12 (1993) 148.

[10] See for example:
(a) L. Vaska, Science 140 (1963) 809;
(b) G. Wilke, H. Schott, P. Heimbach, Angew. Chem. 79 (1967) 62;
(c) P.J. Hayward, D.M. Blake, G. Wilkinson, C.J. Nyman, J. Am. Chem. Soc. 92 (1970) 5873.
[11] (a) R. Ugo, F. Conti, S. Cenini, R. Mason, Chem. Commun. (1968) 1948;
(b) R. Ugo, G.M. Zanderighi, A. Fusi, D. Carreri, J. Am. Chem. Soc. 102 (1980) 3745.
[12] (a) W.A. Herrmann, R.W. Fischer, J.D.G. Correia, J. Mol. Catal. 94 (1994) 213;
(b) A.M. Faisca Phillips, C. Romão, EurJOC (1999) 1797;
(c) R. Bernini, E. Mincione, M. Cortese, G. Allotta, A. Oliva, R. Saladino, Tetrahedron Lett. 42 (2001) 5401.
[13] (a) C. Bolm, O. Beckmann, C. Palazzi, Can. J. Chem. 79 (2001) 1593;
(b) C. Bolm, O. Beckmann, A. Cosp, A. Palazzi, Synlett 9 (2001) 1461.
[14] A. Watanabe, T. Uchida, K. Ito, T. Katsuki, Tetrahedron Lett. 43 (2002) 4481;
(b) K. Ito, A. Ishii, T. Kuroda, T. Katsuki, Synlett (2003) 643.
[15] (a) A. Corma, L.T. Nemeth, M. Renz, S. Valencia, Nature 412 (2001) 423;
(b) M. Renz, T. Blasco, A. Corma, V. Fornes, R. Jensen, L.T. Nemeth, Chem. Eur. J. 8 (2002) 4708.
[16] (a) A. Corma, M.T. Navarro, L.T. Nemeth, M. Renz, Chem. Commun. (2001) 2190;
(b) A. Corma, M.T. Navarro, M. Renz, J. Catal. 219 (2003) 242.
[17] U.R. Pillai, E. Sahle-Demessiè, J. Mol. Catal. A: Chem. 191 (2003) 93.
[18] (a) C. Bolm, O. Beckmann, in: E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis, Springer Verlag, Berlin, 1999, p. 803;
(b) C. Bolm, C. Palazzi, O. Beckmann, in: M. Beller, C. Bolm (Eds.), Transition Metals For Organic Chemistry: Building Blocks and Fine Chemicals, vol. 2, 2nd ed., Wiley-VCH, Weinheim, 2004, p. 267;
(c) G. Strukul, Angew. Chem. Int. Ed. 37 (1998) 1198;
(d) G.-J. ten Brink, I.W.C.E. Arends, R.A. Sheldon, Chem. Rev. 104 (2004) 4105;
(e) M. Renz, B. Meunnier, Eur. J. Org. Chem. (1999) 737.
[19] (a) G. Strukul, A. Varagnolo, F. Pinna, J. Mol. Catal. A: Chem. 117 (1997) 413;
(b) R. Gavagnin, M. Cataldo, F. Pinna, G. Strukul, Organometallics 17 (1998) 661.
[20] A. Gusso, C. Baccin, F. Pinna, G. Strukul, Organometallics 13 (1994) 3442.
[21] A. Brunetta, G. Strukul, Eur. J. Inorg. Chem. (2004) 1030.
[22] A. Brunetta, P. Sgarbossa, G. Strukul, Catal. Today 99 (2005) 227.
[23] C. Bolm, G. Schlingloff, K. Weickardt, Angew. Chem. Int. Ed. 33 (1994) 1848.
[24] (a) R.A. Michelin, E. Pizzo, P. Sgarbossa, A. Scarso, G. Strukul, A. Tassan, Organometallics 24 (2005) 1012;
(b) V. Conte, B. Floris, P. Galloni, V. Mirruzzo, D. Sordi, A. Scarso, G. Strukul, Green Chem. 7 (2005) 262;
(c) P. Sgarbossa, A. Scarso, E. Pizzo, S. Mazzega Sbovata, R.A. Michelin, G. Strukul, M. Mozzon, F. Benetollo, J. Mol. Catal. A 261 (2006) 202;
(d) P. Sgarbossa, A. Scarso, R.A. Michelin, G. Strukul, Organometallics 26 (2007) 2714;
(e) G. Greggio, P. Sgarbossa, A. Scarso, R.A. Michelin, G. Strukul, Inorg. Chim. Acta 361 (2008) 3230.
[25] Y. Peng, X. Feng, K. Yu, Z. Li, Y. Jiang, C.-H. Yeung, J. Organomet. Chem. 619 (2001) 204.
[26] (a) S. Xu, Z. Wang, X. Zhang, X. Zhang, K. Ding, Angew. Chem. Int. Ed. 47 (2008) 2840;
(b) B. Wang, Y.-M. Shen, Y. Shi, J. Org. Chem. 71 (2006) 9519;
(c) S.-I. Murahashi, S. Ono, Y. Imada, Angew. Chem. Int. Ed. 41 (2002) 2366.
[27] G. Peris, S. Miller, Org. Lett. 10 (2008) 3049.
[28] T. Uchida, T. Katsuki, Tetrahedron Lett. 42 (2001) 6911.
[29] C. Bolm, T.K. Khanh Luong, G. Schlingloff, Synlett (1997) 1151.
[30] (a) K. Ito, A. Ishii, T. Kuroda, T. Katsuki, Synlett (2003) 643;
(b) A.V. Malkov, F. Friscourt, M. Bell, M.E. Swarbrick, P. Kocovský, J. Org. Chem. 73 (2008) 3996.
[31] C. Paneghetti, R. Gavagnin, F. Pinna, G. Strukul, Organometallics 18 (1999) 5057.
[32] (a) A. Watanabe, T. Uchida, R. Irie, T. Katsuki, Proc. Natl. Acad. Sci U.S.A. 101 (2004) 5737;
(b) A. Watanabe, T. Uchida, K. Ito, T. Katsuki, Tetrahedron Lett. 43 (2002) 4481;
(c) C. Bolm, O. Beckmann, Chirality 12 (2000) 523.
[33] K. Matsumoto, A. Watanabe, T. Uchida, K. Ogi, T. Katsuki, Tetrahedron Lett. 45 (2004) 2385.
[34] (a) C. Bolm, J.-C. Frison, Y. Zhang, W.D. Wulff, Synlett 9 (2004) 1619;
(b) J.-C. Frison, C. Palazzi, C. Bolm, Tetrahedron 62 (2006) 6700;
(c) C. Bolm, O. Beckmann, T. Kühn, C. Palazzi, W. Adam, P. Bheema Rao, C.R. Saha-Möller, Tetrahedron Asymm. 12 (2001) 2441.
[35] J.D. Stewart, Curr. Org. Chem. 2 (1998) 195.
[36] (a) S. Colonna, N. Gaggero, P. Pasta, G. Ottolina, Chem. Commun. (1996) 2303;
(b) S.M. Roberts, P.W.H. Wan, J. Mol. Catal. B 4 (1998) 111;
(c) J.D. Stewart, K.W. Reed, C.A. Martinez, J. Zhu, G. Chen, M.M. Kayser, J. Am. Chem. Soc. 120 (1998) 3541;
(d) G. Ottolina, S. Bianchi, B. Belloni, G. Carrea, B. Danieli, Tetrahedron Lett. 40 (1999) 8483;
(e) M.D. Mihovilovic, G. Chen, S. Wang, B. Kyte, F. Rochon, M.M. Kayser, J.D. Stewart, J. Org. Chem. 66 (2001) 733;
(f) M.D. Mihovilovic, B. Müller, P. Stanetty, Eur. J. Org. Chem. (2002) 3711;
(g) N.M. Kamerbeek, D.B. Janssen, W.J.H. van Berkel, M.W. Fraaije, Adv. Synth. Catal. 345 (2003) 667;
(h) G. Ottolina, G. de Ponzalo, G. Carrea, B. Danieli, Adv. Synth. Catal. 347 (2005) 1035;
(i) M.D. Mihovilovic, G. Chen, S. Wang, B. Kyte, F. Rochon, M.M. Kayser, J.D. Stewart, J. Org. Chem. 66 (2001) 733;
(j) B.G. Kyte, P. Rouvière, Q. Cheng, J.D. Stewart, J. Org. Chem. 69 (2004) 12;
(k) R. Snajdrova, I. Braun, T. Bach, K. Mereiter, M.D. Mihovilovic, J. Org. Chem. 72 (2007) 9597;
(l) M.D. Mihovilovic, F. Rudroff, A. Winninger, T. Schneider, F. Schulz, M.T. Reetz, Org. Lett. 8 (2006) 1221;
(m) M.T. Reetz, B. Brunner, T. Schneider, F. Schulz, C.M. Clouthier, M.M. Kayser, Angew. Chem. Int. Ed. 43 (2004) 4075;
(n) M.Y. Ríos, E. Salazar, H.F. Olivo, Green Chem. 9 (2007) 459.
[37] A. Cavarzan, G. Bianchini, P. Sgarbossa, L. Lefort, S. Gladiali, A. Scarso, G. Strukul, Chem. Eur. J. 15 (2009) 7930.
[38] M. Del Todesco Frisone, R. Giovanetti, F. Pinna, G. Strukul, Stud. Surf. Sci. Catal. 66 (1991) 405.
[39] G. Bianchini, A. Cavarzan, A. Scarso, G. Strukul, Green Chem. (2009) doi:10.1039/b916262n.
[40] E. Pizzo, P. Sgarbossa, A. Scarso, R.A. Michelin, G. Strukul, Organometallics 25 (2006) 3056.
[41] (a) U.M. Lindström, Angew. Chem. Int. Ed. 45 (2006) 548;
(b) M.C. Pirrung, Chem. Eur. J. 12 (2006) 1312;
(c) W. Blokzijl, J.B.F.N. Engberts, Angew. Chem. Int. Ed. 32 (1993) 1545.
[42] A. Scarso, G. Strukul, Adv. Synth. Catal. 347 (2005) 1227.
[43] M. Colladon, A. Scarso, G. Strukul, Adv. Synth. Catal. 349 (2007) 797.
[44] (a) M. Cataldo, E. Nieddu, R. Gavagnin, F. Pinna, G. Strukul, J. Mol. Catal. A: Chem. 142 (1999) 305;
(b) E. Nieddu, M. Cataldo, F. Pinna, G. Strukul, Tetrahedron Lett. 40 (1999) 6987;
(c) L. Battaglia, F. Pinna, G. Strukul, Can. J. Chem. 79 (2001) 621.
[45] K. Pignat, J. Vallotto, F. Pinna, G. Strukul, Organometallics 19 (2000) 5160.
[46] A. Scarso, M. Colladon, P. Sgarbossa, C. Santo, R.A. Michelin, G. Strukul, (manuscript in preparation).
[47] S. Oi, K. Kashiwagi, Y. Inoue, Tetrahedron Lett. 39 (1998) 6253.
[48] (a) C.H. Suresh, N. Koga, J. Phys. Chem. A 105 (2001) 5940;
(b) G.C. Bond, J. Mol. Catal. A-Chem. 156 (2000).
[49] For some example of homologous diphosphine complexes structural data, see:
(a) A.F. Maddox, A.L. Rheingold, J.A. Golen, W.S. Kassel, C. Nataro, Inorg. Chim. Acta 361 (2008) 3283;
(b) B.L. Ghent, S.L. Martinak, L.A. Sites, J.A. Golen, A.L. Rheingold, C. Nataro, J. Organomet. Chem. 692 (2007) 2365.
[50] (a) J.-L. Malleron, J.-C. Fiaud, J.-Y. Legros, Handbook of Palladium-Catalyzed Organic Reactions, Academic Press, 1997, p. 232;
(b) A.R. Chianese, S.J. Lee, M. Gagné, Angew. Chem. Int. Ed. 46 (2007) 4042;
(c) M.L. Clarke, Polyhedron 20 (2001) 151.
[51] (a) P.W.N.M. van Leeuwen, Homog. Catal. (2004);
(b) J.A. Keith, R.J. Nielsen, J. Oxgaard, W.A. Goddard III, P.M. Henry, Organometallics 28 (2009), 1618 and references therein.
[52] (a) C.H. Langford, H.B. Gray, Ligand Substitution Processes, W.A. Benjamin, Inc., 1965, p. 18, Chapter 2;
(b) G.K. Anderson, R.J. Cross, Chem. Soc. Rev. 9 (1980) 185.
[53] (a) T.G. Appleton, H.C. Clark, L.E. Manzer, Coord. Chem. Rev. 10 (1973) 335;
(b) Z. Chval, M. Sip, J.V. Burda, J. Comput. Chem. 29 (2008) 2370.
[54] M. Roussel, H. Mimoun, J. Org. Chem. 45 (1980) 5387.
[55] F. Basolo, R.G. Pearson, Mechanisms of Inorganic Reactions, John Wiley & Sons, Inc., 1958, p. 172.
[56] (a) Z. Chval, M. Sip, J.V. Burda, J. Comput. Chem. 29 (2008) 2370;
(b) J.E. Huheey, E.A. Keiter, R.L. Keiter, Inorganic Chemistry: Principles of Structure and Reactivity, 4th ed., HarperCollins College Pub, New York, 1993;
(c) J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Application of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987;
(d) F. Basolo, R.G. Pearson, Prog. Inorg. Chem. 4 (1962) 381;
(e) F. Basolo, R.G. Pearson, J. Chatt, H.B. Gray, B.L. Shaw, J. Chem. Soc. (1961) 2207.
[57] R.H. Crabtree, The Organometallic Chemistry of the Transition Metals, John Wiley & Sons, New York, 2001.
[58] J. Klosin, C.R. Landis, Acc. Chem. Res. 40 (2007) 1251.
[59] (a) I. del Rio, C. Claver, P.W.N.M. van Leeuwen, Eur. J. Inorg. Chem. (2001) 2719;
(b) F. Bertoux, E. Monflier, Y. Castanet, A. Mortreux, J. Mol. Catal. 143 (1999) 11.
[60] (a) T.V. RajanBabu, A.L. Casalnuovo, J. Am. Chem. Soc. 118 (1996) 6325;
(b) A.L. Casalnuovo, T.V. RajanBabu, T.A. Ayers, T.H. Warrens, J. Am. Chem. Soc. 116 (1994) 9869.
[61] (a) X.-L. Fu, L.-L. Wu, H.-Y. Fu, H. Chen, R.-X. Li, Eur. J. Org. Chem. (2009) 2051;
(b) R. Martin, S.L. Buchwald, Acc. Chem. Res. 41 (2008) 1461;
(c) L.R. Moore, E.C. Western, R. Craciun, J.M. Spruell, D.A. Dixon, K.P. O'Halloran, K.H. Shaughnessy, Organometallics 27 (2008) 576;
(d) J.P. Genet, M. Savignac, J. Organomet. Chem. 576 (1999) 305;
(e) G.P.F. van Strijdonck, M.D.K. Boele, P.C.J. Kamer, J.G. de Vries, P.W.N.M. van Leeuwen, Eur. J. Inorg. Chem. (1999) 1073.
[62] P.W.N.M. van Leeuwen, Appl. Catal. A-Gen. 212 (2001) 61.
[63] (a) K.T. Aye, J.J. Vittal, R.J. Puddephatt, J. Chem. Soc., Dalton Trans. (1993) 1835;
(b) G.B. Deacon, E.T. Lawarenz, T.W. Hambley, S. Rainone, L.K. Webster, J. Organomet. Chem. 493 (1995) 205;
(c) M. Rashidi, M. Nabavizadeh, R. Hakimelahi, S. Jamali, J. Chem. Soc., Dalton Trans. (2001) 3430.
[64] See for instance:
(a) J.-H. Xie, Q.-L. Zhou, Acc. Chem. Res. 41 (2008) 581;
(b) H. Shimizu, I. Nagasaki, T. Saito, Tetrahedron 61 (2005) 5405;
(c) R. Noyori, H. Takaya, Acc. Chem. Res. 23 (1990) 345.
[65] R.F. Childs, D.L. Mulholland, A. Nixon, Can. J. Chem. 60 (1982) 801.

[66] (a) M.A. Beckett, D.S. Brassington, M.E. Light, M.B. Hursthouse, J. Chem. Soc., Dalton Trans. (2001) 1768;
(b) M.A. Beckett, D.S. Brassington, S.J. Coles, M.B. Hursthouse, Inorg. Chem. Commun. 3 (2000) 530;
(c) M.A. Beckett, G.C. Strickland, J.R. Holland, K.S. Varma, Polym. Commun. 37 (1996) 4629.
[67] (a) V. Gutmann, Coord. Chem. Rev. 18 (1976) 225;
(b) U. Mayer, V. Gutmann, W. Gerger, Monatsh. Chem. 106 (1975) 1235.
[68] (a) L. Dadci, H. Elias, U. Frey, A. Hörnig, U. Koelle, A.E. Merbach, H. Paulus, J.S. Schneider, Inorg. Chem. 34 (1995) 306;
(b) A. Hofmann, D. Jaganyi, O.Q. Munro, G. Liehr, R. van Eldik, Inorg. Chem. 42 (2003) 1688.
[69] S. Fukuzumi, K. Ohkubo, J. Am. Chem. Soc. 124 (2002) 10270.
[70] (a) S. Fukuzumi, K. Ohkubo, Chem. Eur. J. 6 (2000) 4532;
(b) K. Ohkubo, S.C. Menon, A. Orita, S. Fukuzumi, J. Org. Chem. 68 (2003) 4720.
[71] M. Gasperini, F. Ragaini, Organometallics 23 (2004) 995.
[72] (a) R.A. Michelin, M.F.C. Guedes da Silva, A.J.L. Pombeiro, Coord. Chem. Rev. 218 (2001) 75;
(b) U. Belluco, R.A. Michelin, P. Uguagliati, B.J. Crociani, Organomet. Chem. 250 (1983) 565.
[73] (a) A.J.L. Pombeiro, Encyclopedia of Electrochemistry, in: A.J. Bard, M. Stratmann, F. Scholz, C.J. Pickett (Eds.), Inorganic Chemistry, vol. 7A, Wiley-VCH, 2006, p. 77, Chapter 3;
(b) A.J.L. Pombeiro, J. Organometal. Chem. 690 (2005) 6021;
(c) A.B.P. Lever, Comprehensive Coordination Chemistry II, vol. 2, Elsevier Science, 2003, p. 251;
(d) A.B.P. Lever, Y. Ma, in: A.J.L. Pombeiro, C. Amatore (Eds.), New Trends in Molecular Electrochemistry, FontisMedia (and Marcel Dekker), Lausanne, Switzerland, 2004, p. 99;
(e) A.B.P. Lever, Inorg. Chem. 29 (1990) 1271;
(f) M.P. López-Alberca, M.J. Mancheño, I. Fernández, M. Gómez-Gallego, M.A. Sierra, R. Torres, Chem. Eur. J. 15 (2009) 3595.
[74] P. Sgarbossa, M.F.C. Guedes da Silva, A. Scarso, R.A. Michelin, A.J.L. Pombeiro, Inorg. Chim. Acta 361 (2008) 3247.
[75] See for instance:
(a) G. Erre, S. Enthaler, K. Junge, S. Gladiali, M. Beller, Coord. Chem. Rev. 252 (2008) 471;
(b) T.L. Church, P.G. Andersson, Coord. Chem. Rev. 252 (2008) 513;
(c) A.J. Minnaard, B.L. Feringa, L. Lefort, J.G. de Vries, Acc. Chem. Res. 40 (2007) 1267.
[76] See for instance:
(a) N. Kuznik, S. Krompiec, Coord. Chem. Rev 251 (2007) 222;
(b) K. Tani, Y. Yamagata, Y. Tatsuno, Y. Yamagata, K. Tomita, S. Agutagawa, H. Kumobayashi, S. Otsuka, Angew. Chem. Int. Ed. Engl 24 (1985) 217.
[77] See for instance:
(a) M. Sparta, K.J. Børve, V.R. Jensen, J. Am. Chem. Soc. 129 (2007) 8487;
(b) J.J. Carbò, F. Maseras, C. Bo, P.W.N.M. van, Leeuwen, J. Am. Chem. Soc. 123 (2001) 7630;
(c) M. Beller, B. Cornils, C.D. Frohning, C.W. Kohlpaintner, J. Mol. Cat. A-Chem 104 (1995) 17.
[78] B. de Bruin, M.J. Boerakker, J.J.J.M. Donners, B.E.C. Christiaans, P.P.J. Schlebos, R. de Gelder, J.M.M. Smiths, A.L. Spek, A.W. Gal, Angew. Chem. Int. Ed. Engl. 36 (1997) 2064.
[79] T.C. Flood, M. Iimura, J.M. Perotti, A.L. Rheingold, T.E. Concolino, Chem. Commun. (2000) 1681.
[80] P.H.M. Budzelaar, A.N.J. Blok, Eur. J. Inorg. Chem. (2004) 2385.
[81] M. Colladon, A. Scarso, P. Sgarbossa, R.A. Michelin, G. Strukul, J. Am. Chem. Soc. 129 (2007) 7680.
[82] (a) A.S.K. Hashmi, Angew. Chem. Int. Ed. 47 (2008) 6754;
(b) A.S.K. Hashmi, Chem. Rev. 107 (2007) 3180;
(c) A.S.K. Hashmi, G.J. Hutchings, Angew. Chem. Int. Ed. 45 (2006) 7896.
[83] (a) H. Li, Z. Li, Z. Shi, Tetrahedron 65 (2009) 1856;
(b) H. Li, B. Guan, W. Wang, D. Xing, Z. Fang, X. Wan, L. Yang, Z. Shi, Tetrahedron 63 (2007) 8430;
(c) B. Guan, D. Xing, G. Cai, X. Wan, N. Yu, Z. Fang, L. Yang, Z. Shi, J. Am. Chem. Soc. 127 (2005) 18004.
[84] G. Strukul, R. Ros, R.A. Michelin, Inorg. Chem. 21 (1982) 495.