Green Chemistry

Cutting-edge research for a greener sustainable future

rsc.li/greenchem

Volume 20
Number 9
7 May 2018
Pages 1919-2160

ISSN 1463-9262

ROYAL SOCIETY OF CHEMISTRY

PAPER
Paul T. Anastas et al.
The Green ChemisTREE: 20 years after taking root with the 12 principles

ROYAL SOCIETY OF CHEMISTRY

rsc.li/greenchem

A Stand-Alone Cobalt bis(dicarbollide) Photoredox Catalyst Epoxidates Alkenes in Water at Extremely Low Catalyst Load

Isabel Guerrero,[a,b] Clara Viñas,[a] Isabel Romero,[b]* Francesc Teixidor[a]*

[a]Institut de Ciència de Materials de Barcelona, ICMAB-CSIC, Campus UAB, E-08193 Bellaterra, Spain.

[b]Departament de Química and Serveis Tècnics de Recerca, Universitat de Girona, C/ M. Aurèlia Campmany, 69, E-17003 Girona, Spain.

*Correspondence to: teixidor@icmab.es; marisa.romero@udg.edu

Abstract

The cobalt bis(dicarbollide) complex, $Na[3,3'-Co(\eta^5-1,2-C_2B_9H_{11})$ (**Na[1]**) is an effective photoredox catalyst for alkene oxidation to epoxides in water. Advantageous features of **Na[1]** include its lack of photoluminescence, high solubility and surfactant behavior in aqueous media, as well as the donor ability of the carborane ligand and high oxidizing power of the $Co^{4+/3+}$ couple.

These features differentiate it from the well-known and widely used photosensitizer tris (2,2′-bipyridine) ruthenium(II) ($[Ru(bpy)_3]^{2+}$), which also participates in electron transfer through an outer sphere mechanism. A comparison of the catalytic performance of $[Ru(bpy)_3]^{2+}$ with **Na[1]** for alkene photo-oxidation is fully in favor of **1**, as the former shows very low or null efficiency.

With a catalyst load of 0,1 mol % conversions between 65-97% have been obtained in short reaction times, 15 minutes, with moderate selectivity for the corresponding epoxide, due to the formation of side products as diols. But when the catalyst load is reduced to 0.01 mol %, the selectivity for the corresponding epoxide increased considerably, being the only compound formed after 15 minutes of reaction (selectivity >99%). High TON values have been obtained (TON=8500) for the epoxidation of aromatic and aliphatic alkenes in water. We have verified that $Na[3,3'-Co(\eta^5-1,2-C_2B_9H_{11})_2]$, acts as a photocatalyst in both the epoxidation of alkenes and in their hydroxylation in aqueous medium with a higher rate for epoxidation than for hydroxylation.

Preliminary photooxidation tests using methyl oleate as substrate, led to the selective epoxidation of the double bond. These results represent a promising starting point for the development of practical methods for the processing of unsaturated fatty acids, such as the valorisation of animal fat waste by using this sustainable photoredox catalyst.

Green Chemistry Accepted Manuscript

1. Introduction

Our century is characterized by an exponential growth in energy consumption based on fossil fuels, which have a significant environmental impact causing climate change, which threatens the questioning the sustainability of human development.[1] Environmentally friendly methodologies which take advantage of renewable energy sources are thus needed to reduce emission of polluting gases, reduce waste generation, and increase energy efficiency. Photoredox catalysis[2] is emerging as an excellent and promising alternative in chemical synthesis, because it provides a direct means of accessing the chemistry of reactive intermediates that often cannot be easily generated using other non-photochemical strategies, and because it does so using clean energy sources, such as sunlight. Light combined with water, are alternative energy sources for the development of non-fossil fuels, as well as other processes.

Olefin epoxidation has received considerable interest from both academics and industry. Epoxides constitute an important and versatile class of intermediates and building blocks to obtain more elaborated chemical products both in organic synthesis and in industrial production of bulk and fine chemicals.[3,4] Epoxides can be transformed into a variety of functionalized products. For example reductions, rearrangements or ring-opening reactions with various nucleophiles give diols, aminoalcohols, allylic alcohols, ketones, etc.[5-8] Starting from alkenes four general methods are available: the Jacobsen-Katsuki epoxidation that uses a Mn-salen catalyst and NaOCl or variations of these,[9,10] the Prilezhaev reaction uses commercially available m-CPBA,[11,12] the Sharpless epoxidation that uses *tert*-butyl hydroperoxide and is catalyzed by Ti(O*i*Pr)$_4$,[13,14] and the Shi epoxidation that uses oxone and a ketone as a catalyst to generate dioxirane.[15,16] Most of these processes have been studied by chemical catalysis in organic media by some of us.[17,18,19] A common characteristic is that all these reactions are carried out in organic solvents. On the other hand, the products derived from oils and fats (oleochemicals) represent one of the cheapest and readily available sources of potential feedstock for replacing petroleum-derived products and for the chemical industry. Moreover, the enormous amounts of fat waste generated, need to be treated or recycled to give them some added value, since this waste contribute to environmental contamination with high economic cost to the industry. One of the main applications of the animal fat by-products is the production of biodiesel through transesterification reactions. However, other functional compounds such as lubricants, plasticizers, polymer stabilizers and other olefinic compounds can be obtained through oxidation processes. Recently, the epoxidation reaction of oils, has been catalyzed by metallic complexes such as manganese,[20] ruthenium[21] or peroxopolyoxometalates (PPOMs),[22] under mild conditions using hydrogen peroxide as a green oxidant.

Currently, photochemical systems studied for the oxidation of substrates involve a photocatalyst[23] or a photocatalyst combined with a transition metal catalyst based on polypyridyl compounds.[24,25,26,27,28,29] In these, one compound acts as the light-harvesting antenna and the second metal complex is used as catalyst to activate a water molecule or an organic substrate by a proton coupled electron transfer mechanism (PCET). However, few examples of photochemical epoxidation of alkenes have been carried out with earth abundant metals.[30,31] Recently there are scattered examples in which these oxidations are performed using only a photocatalyst such as methylene blue[32] or Ru(bpy)$_3$Cl$_2$.[33] For the methylene blue example, 2.5% mol % of catalyst, 2 eq of K$_2$S$_2$O$_8$, 2 eq of K$_2$CO$_3$ and water as a solvent under illumination were utilized. This is the case most similar to our experiments, although in our case we use 0.01% catalyst (250 times less), and 1.3 eqs of K$_2$S$_2$O$_8$ and at pH=7. Althoughit is hard to compare epoxidation (in our case) with epoxyacylation (methylene blue) the time required (15 min, our case, vs 12 h) may be indicative of the relative speed of these catalysts.

Metallacarborane complexes have been tested as catalysts in different synthetic processes such as: hydrogenation, hydroformylation, hydrosilylation, carbonylation, amination, alkylation and

sulfonylation, Kharasch reaction, polymerization and ring-opening metathesis polymerization, among others.[34,35,36,37,38,39,40,41,42,43,44,45] Manganese and cobalt compounds all containing the carboranylcarboxylate ligand, [1-CH$_3$-2-CO$_2$-1,2-*closo*-C$_2$B$_{10}$H$_{10}$]$^-$, have been tested in the epoxidation of aliphatic and aromatic alkenes using peracetic acid as oxidant.[46] The catalytic results highlight the role of the carboranylcarboxylate ligand in the selectivity of the processes; it was found that coordination of the carboranylcarboxylate ligand to the metal ions is key to their catalytic performance. On the other hand, it is well known that some boron clusters interact with light[47,48,49] and that they have been studied as catalysts in different processes. The most well-known metallacarborane is the anionic cobaltabis(dicarbollide)[50] that can be synthesized in high yield by a fast and environmentally-friendly solid state reaction.[51] The cobaltabis(dicarbollide) sandwich compound Na[Co(1,2-C$_2$B$_9$H$_{11}$)$_2$], **Na[1]**, is a particular boron cluster that has many possibilities to form hydrogen bonds, e.g. C$_c$-H···O or C$_c$-H···X (X= halogen) as well as dihydrogen bonding C$_c$-H···H-B and B-H···H-N (C$_c$ stands for the cluster carbon atoms).[52,53,54] Compound **Na[1]** is highly stable in water, but even at low concentration it forms aggregates (vesicles and micelles).[55,56,57] Dihydrogen interactions participate in the self-assembling formation.[57] These supramolecular interactions appear to be significant in electron transfer processes and therefore in the performance and efficiency of photocatalytic systems.

Recently, we have shown that **Na[1]**, and its chloro derivatives, act both as catalyst and photosensitizer, being highly efficient in the photooxidation of alcohols in water, through single electron transfer processes (SET),[58] and via proton-coupled electron transfer (PCET).[59] High performance of **Na[1]** in the photooxidation of alcohols is observed, using catalyst load to 0.01 mol % and reaching TON= 10000, in some cases. We have also supported the metallabis(dicarbollide) catalyst on silica-coated magnetite nanoparticles.[60] This system has proven to be a green and sustainable heterogeneous catalytic system, highly efficient and easily reusable for the photooxidation of alcohols in water.

Given the characteristics and the demonstrated high activity performance of these systems, [Co(C$_2$B$_9$H$_{11}$)$_2$]$^-$ could be a photoredox catalytic system for the oxidation of alkenes in water. We envisage that its absence of fluorescence, surfactant behavior and water solubility, along with its high oxidizing power (Co$^{III/IV}$) could lead to an efficient system for the photoxidation of alkenes, and consequently to a sustainable and green photocatalysis.

Herein we report the photo-oxidation of alkenes catalysed by **Na[1]** in water using peroxysulfate as a sacrificial acceptor. Moreover, we establish a comparison between Na[1] and conventional photoredox catalyst, Ru(bpy)$_3^{2+}$ widely studied in the literature.[61,62,63]
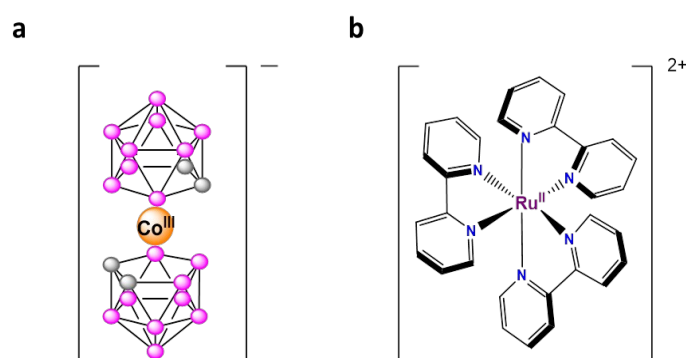
Figure 1. Drawing of the a) metallabis(dicarbollide) used in this work, [Co(C$_2$B$_9$H$_{11}$)$_2$]$^-$, **[1]**$^-$. The pink circles indicate B-H units; b) tris(2,2'-bipyridyl)ruthemium(II), [Ru(bpy)$_3$]$^{2+}$.

2. Results and discussion

2. 1. Photocatalytic alkene oxidations

The water soluble **Na[1]** was prepared by cationic exchange resin from the water insoluble **Cs[1]** as described in the literature.[64]

The first photocatalytic alkene oxidation experiments using **Na[1]** as catalyst were all performed by exposing the reaction quartz vials to UV irradiation (2.2 W, λ ˷ 300 nm, 12 lamps in the walls of a box), at room temperature and atmospheric pressure, and using styrene as substrate; this was the reference compound used to find the optimal reaction conditions. The samples were made of 5 mL of water (0.4 μM in K_2CO_3 pH=7) with a mixture of **Na[1]** (0.02 mM), styrene (20 mM) and $Na_2S_2O_8$ (26 mM) as oxidizing agent, ratios 1:1000:1300. Then, different reaction times were tested to assess the conversion and yields as a function of time. Following irradiation for a specified time, see Figure S1, the reaction products were extracted with dichloromethane six times, dried with Na_2SO_4 and quantified by means of GC-MS analysis. As can be observed in Figure S1, after 30 minutes of reaction practically all the styrene was converted, and different products of oxidation were obtained, in function of the reaction time. The evolution of yields with the reaction time and the evolution of the molar fractions of the styrene together with those of the oxidation products are displayed in Figure 2 a, b. Figure 2a shows that after 5 minutes of reaction the amount of epoxide obtained is greater (37%) with respect to the other generated products (diol, benzaldehyde and benzoic acid); however, after 15 minutes, the amount of diol increases (35% diol vs 27% epoxide) and finally after 30 minutes the amount of epoxide is maintained whereas the diol increases (50% diol vs 25% epoxide). Throughout this time, benzaldehyde and benzoic acid have been formed but in less proportion. Moreover, as is shown in Figure 2, increased reaction time is accompanied by a decrease in yield and selectivity values for epoxide formation. Therefore, we have chosen 15 minutes as the time to perform the catalytic experiments, though in some cases, we have also studied the performance of the catalyst after 30 minutes of reaction.

Blank experiments after 30 minutes of reaction, in the absence of catalyst, light or oxidizing agent, showed that no significant conversion of styrene occurred.

The effect of pH on the photocatalytic oxidation of styrene has also been examined. Figure S2 shows that the optimal TON value for the epoxidation of styrene to styrene oxide after 15 minutes of reaction is obtained at pH=7 (TON=270) since this value decreases at lower (pH=5, TON=200) and higher (pH=8, TON=250 and pH=10, TON=180) values of pH. The lower value observed at pH=5, probably is due to the easy epoxy ring opening in acidic medium.[65]
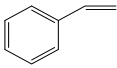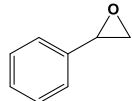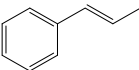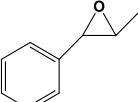
5

a)
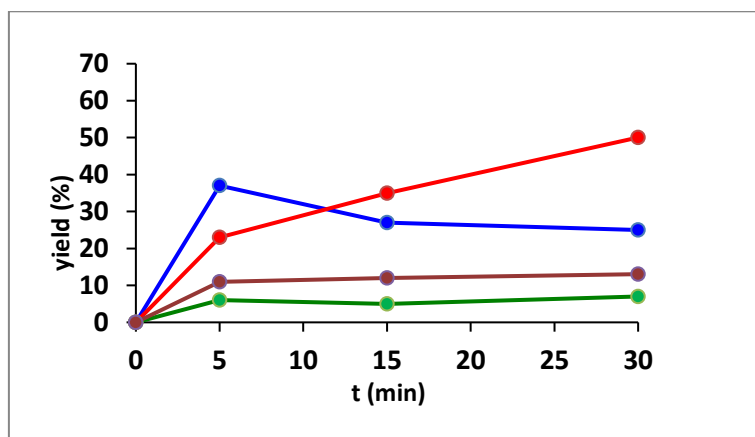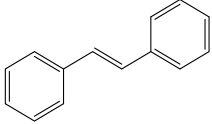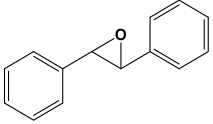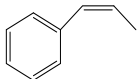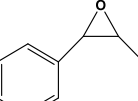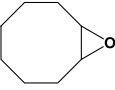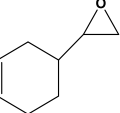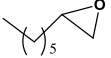
b)
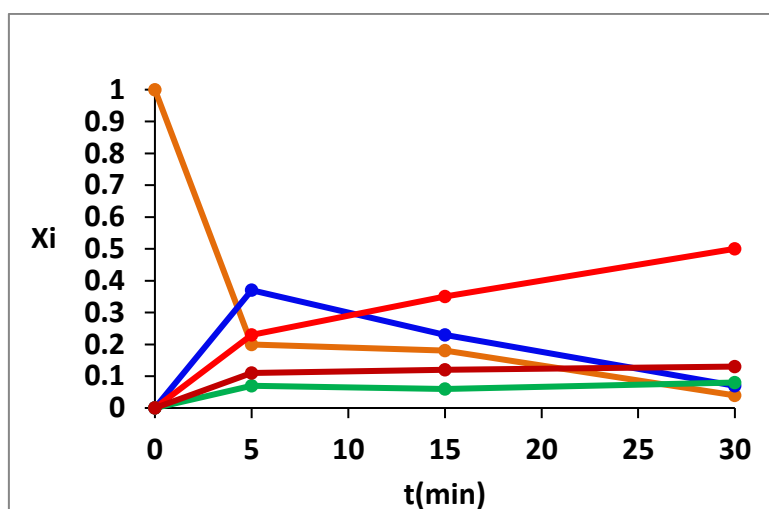
Figure 2. Plot of a) yield and b) molar fractions (X_M) *versus* time for the photoredox catalysis of styrene. Blue: styrene oxide; red: 1-phenyl-1,2-ethanediol; green: benzaldehyde; brown: benzoic acid; orange: styrene. Conditions: Na[3,3'-Co(1,2-$C_2B_9H_{11}$)$_2$] (0.02 mM), styrene (20 mM), Na$_2$S$_2$O$_8$ (26 mM), 5 ml K$_2$CO$_3$ solution at pH=7, light irradiation (2.2 W, λ ~300 nm).

Table 1. Photooxidation tests performed with **Na[1]** complex.

Entry	substrate	Conv.%	product	TON	Selectivity %
1		78[a] 80[b] 96[c]		370[a] 270[b] 250[c]	47 34 26
2		85[b] 91[c]		440[b] 200[c]	52 22
3		66[b] 95[c]		390[b] 290[c]	44 41
4		92[b] ≥99[c]		750(97%,cis)[b] 330(48%,cis)[c]	82 33
5		91[b] ≥99[c]		470[b] 380[c]	47 42
6		97[b] ≥99[c]		700[b] 370[c]	72 37
7		81[b] ≥99[c]		580[b] 160[c]	72 16

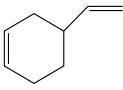Conditions: **Na[1]** (0.02 mM), substrate (20 mM), $Na_2S_2O_8$ (26 mM), 5 mL potassium carbonate solution at pH=7. Ratio 1:1000:1300: [a] 5 min of reaction [b] 15 min of reaction. [c] 30 min of reaction.

Green Chemistry Accepted Manuscript

2. 2. Photocatalytic oxidations using catalyst load of 0,1 mol %.

Once the catalytic conditions were optimized, we moved on to study the photocatalytic oxidation of other alkenes using **Na[1]** as photoredox catalyst. Table 1 and Table S1 display the performance of the photocatalyst after 5, 15 and 30 minutes of reaction. In general it can be observed that high conversion values were achieved after 15 minutes of reaction with, in many cases, ttotal conversion after 30 minutes. However, moderate epoxide selectivity decreases whith reaction time, along with the TON values. This happens simultaneously with an increase in the amount of the corresponding diol for most of the substrates studied (see Table S1).

The photoepoxidation of *trans*-β-methylstyrene (entry 2), *trans*-stilbene (entry 3) and *cis*-β-methylstyrene (entry 4), led to the formation of the corresponding isomer without isomerization in the first 15 minutes; however in the case of *cis*-β-methylstyrene, the stereoselectivity towards the formation of the *cis*-epoxide isomer decreases, up to half, after 30 minutes of reaction. This could be due to formation of a more long-lived free radical from the substrate that leads to rotacion of the C-C bond during the oxygen-transfer process, and consequently to the isomerization of *cis* to *trans* isomer.[66]

For the aromatic alkenes, conversion is enhanced by the presence of electron-donating substituents on the double bond (entry 2 and 4) but   decrease in the presence of electron withdrawing substituents (entry 3).

Oxidation of aliphatic alkenes has also been tested, with linear 1-octene (entry 7) slightly less efficient than cyclooctene (entry 5) and 4-vinyl-1-cyclohexene (entry 6). The photooxidation of this last substrate, occurs on the external double bond, indicatingthat this reaction is regiospecific.

On the other hand, the highly studied octahedral tris(2,2′-bipyridine)ruthenium(II) ([Ru(bpy)$_3$]$^{2+}$),[61] participates in electron transfer through an outer sphere mechanism, with no major structural modification occurring upon ET. To the best our knowledge this compound has never been studied as photocatalyst for the epoxidation of alkenes in water medium. Then for the purpose of comparison, we also studied the performance of this compound in the photoredox oxidation of *trans*-stilbene, *cis*-β-methylstyrene, cyclooctene and 1-octene, under the conditions described in Table 1 and after 30 minutes of reaction (see Table S3). As can be observed in Table S3, epoxide products were only observed after 30 minutes foractivated *trans*-stilbene (10%) and *cis*-β-methylstyrene (3 %). No reaction occurred with thealiphatic alkenes. Based on these results, we can conclude that, unlike the photosensitizer [Ru(bpy)$_3$]$^{2+}$, the cobalt based **Na[1],** acts both as an efficient photosensitizer and a redox catalyst for the epoxidation of alkenes in water.

It is important to remark that just after irradiation and before extraction, upon addition of [Me$_4$N]Cl to the solution, the [Me$_4$N][Co(C$_2$B$_9$H$_{11}$)$_2$] catalyst precipitates. This was filtered. The material produced from various catalytic processes was solubilized in acetonitrile and upon addition of water, the solution is passed to a cationic exchange resin loaded with Na$^+$ to generate again the **Na[1]**, which purity was proven either by ^{1}H- and ^{11}B-NMR spectra and by MALDI-TOF_MS**.** Once confirmed the stability of the catalyst after its recovery we confirmed that its catalytic activity remained. This recovered catalyst was tested for a second catalytic reaction using *trans*-β-methylstyrene, producing 80% of the epoxide, similar value to the observed in the first catalysis.

Based on the above results, we have proposed a mechanism, displayed in the Figure 3, for the photoepoxidation of alkenes carried out by **Na[1]**. In the mechanism, the absorption of light by the

photoredox catalyst $[Co^{III}(C_2B_9H_{11})_2]^-$ in the presence of water and $S_2O_8^{2-}$ (oxidizing agent) generates the oxidized $[Co^{IV}(C_2B_9H_{11})_2]$ compound together with hydroxyl radical (OH·), protons (H^+) and sulfate anion (SO_4^{2-}). The subsequentoxidation of the alkene by $[Co^{IV}(C_2B_9H_{11})_2]$ and the addition of hydroxyl radical (OH·) to the double bond, lead to the formation of the corresponding epoxide.
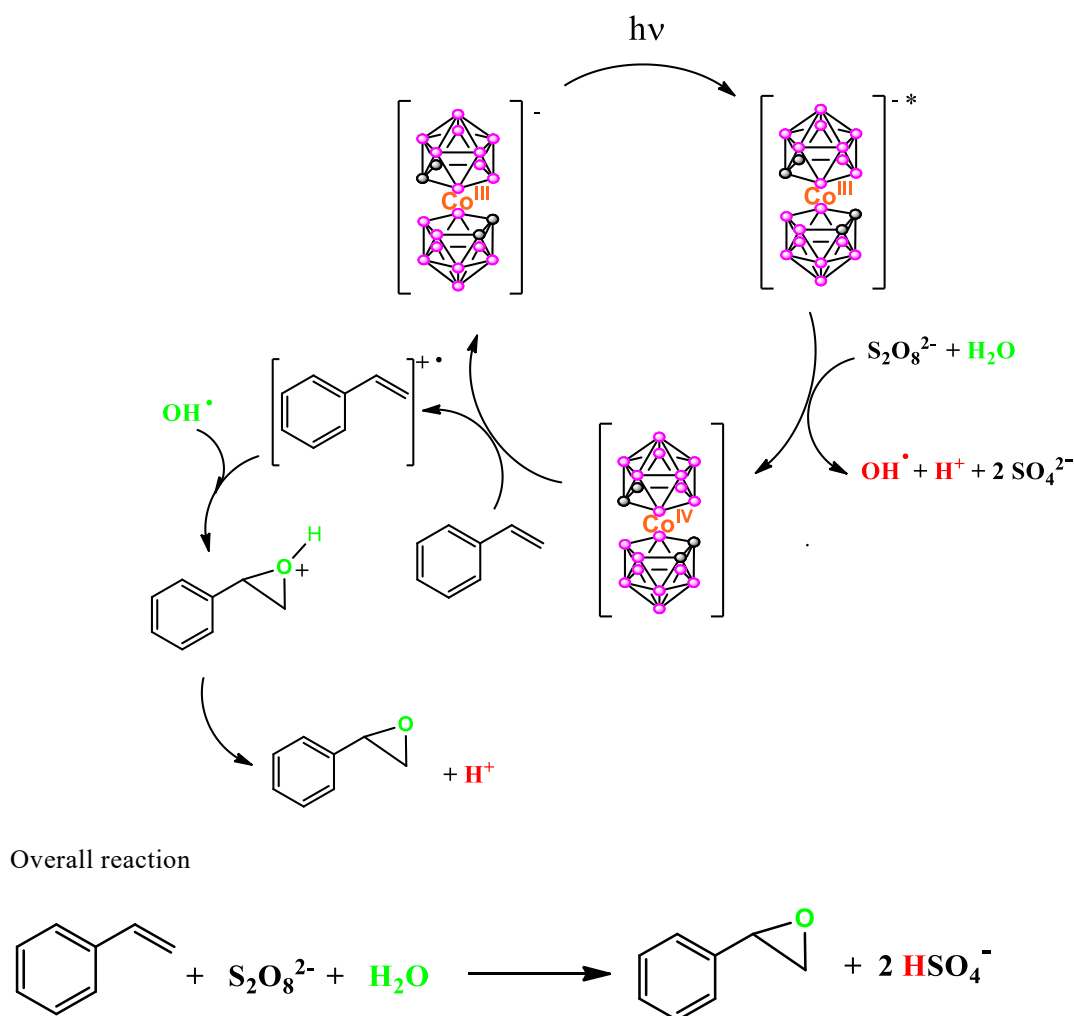
Figure 3. Proposed mechanism for the alkene epoxidation in water, with **Na[1]** as photoredox catalyst upon UV light irradiation.

Earlier we indicated that the selectivity towards the epoxide decreased with reaction time. The study of the graphs shown in Figure 2 reflects that when the epoxide decreases, the diol increases, which proves that this is a consequence of the evolution of the epoxide in aqueous media. It should be noted that ring opening of epoxides is a promising process to produce 1,2-diols, an important functional group to produce surfactants, pharmaceuticals or their intermediates.[65,67]
It is known that in an aqueous medium an opening of the epoxide ring occurs, but in our case, we wanted to know if this opening was due solely to water or if **Na[1]** catalysed the process. Then

different experiments were performed by exposing the sealed reaction quartz vials to UV irradiation (2.2 W, λ 300 nm, 12 lamps), at room temperature and atmospheric pressure, for 15 and 30 minutes, using three different epoxides, 1,2-epoxyoctane, styrene oxide and *trans*-stilbene oxide.
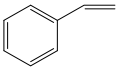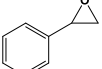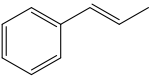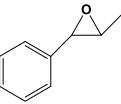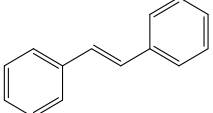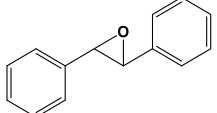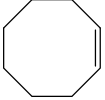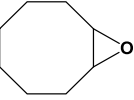
The samples were made of 5 mL of water (K_2CO_3 pH=7) with a mixture of **Na[1]** (0.02 mM), epoxide (20 mM) and $Na_2S_2O_8$ (26mM) as oxidizing agent, following irradiation for a specified time, see Table S2. Previously, a set of different blank experiments were run at 15 and 30 minutes. These results show that formation of the corresponding diols in water takes place if the photocatalyst is present, since their absence in the reaction medium caused a low or nonexistent yield of diols in the short times of reaction that we have studied. Therefore, we can conclude that **Na[1]** acts as a photocatalyst in both processes, in the epoxidation of alkenes and in their hydroxylation in aqueous medium.

2. 3. Photocatalytic oxidations under lower catalyst load.

As described in previous work, **[1]**[-] performs as a surfactant and at concentrations between 10^{-3}-10^{-2}M, vesicles, free molecules, and micelles coexist, but at lower concentrations the ratio of molecules is higher.[68,69] Based on the non-parallel conversion of substrate *vs* the amount of catalyst observed in the oxidation of alcohols,[58] we assumed that free molecules were more efficient, in terms of catalytic activity, than vesicles or micelles and we wanted to know if this also occurred in the photooxidation reaction of alkenes. Therefore, we kept the concentrations of substrate and oxidizing agents constant and reduced the catalyst load to 0.01 mol % *vs* the original 0.1 mol%, corresponding to ratios of 1:10000:16000 of catalyst: substrate:oxidizing agent. The corresponding results are displayed in Table 2. We can observe that the conversion values were remarkable, higher than 90% in most cases, after 30 minutes of reaction, with high TON in the photoepoxidation of alkenes, that to the best of our knowledge corresponds to one of the highest turnover numbers achieved in alkene photoredox oxidation in homogeneous conditions. It is worth noting that in most of the substrates studied with the exception of styrene, the selectivity for the corresponding epoxide is $\geq$ 99% after 15 minutes of reaction. This value decreases after 30 minutes for four of the tested substrates, d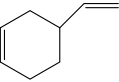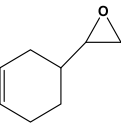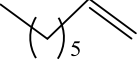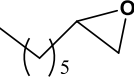ue to the increase in the amount of the corresponding diol. For styrene, we also observed aldehyde and carboxylic acid formation.

Under these conditions of reaction, we have done a preliminary photooxidation test using methyl oleate, the ester of oleic acid, as substrate (see Scheme 1). Natural fats and oils are known to be a valuable source of saturated and unsaturated hydrocarbons for the chemical industry. In many cases, their successful application as renewable raw materials depends on the efficiency of oxidative transformation of their alkyl chain. It was found that after 60 minutes of reaction and after the organic phase was analysed by HPLC/ESI-MS, the oxidation took place exclusively on the double bond C=C, detecting the presence of epoxide (see Figure S3). These preliminary studies show the high potential of this compound as photocatalyst to produce high added value products from animal fats.

Table 2. Photooxidation tests performed with **Na[1]** complex in very low catalyst loading conditions.

Entry	substrate	Conv.%	product	TON	Selectivity%
1		68[a] 98[b]		3600 [a] 2000 [b]	53 20
2		85[a] 93[b]		8500[a] 9300[b]	≥99 ≥99
3		75[a] 95[b]		7500[a] 6400[b]	≥99 75
4		76[b]		7600 [b]	≥99
5		78[a] 90[b]		7800[a] 3900[b]	≥99 43
6		85[a] ≥99[b]		8500[a] 5000[b]	≥99 50

Conditions: **Na[1]** (0.002 mM), substrate (20 mM), $Na_2S_2O_8$ (26 mM), 5 mL potassium carbonate solution at pH=7. Ratio 1:10000:13000: [a] 15 min of reaction. [b] 30 min of reaction.
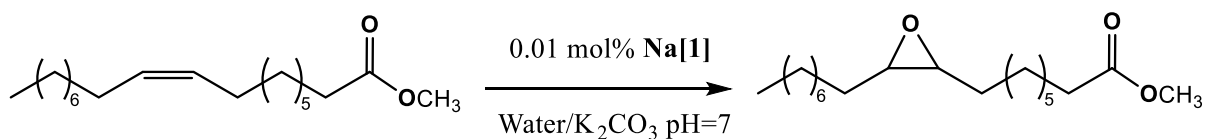
Scheme1. Oxidation of methyl oleate by **Na[1]**

3. Conclusions

It has been demonstrated that the water soluble cobalt bis(dicarbollide), **Na[1]**, is an efficient photoredox catalyst for the epoxidation of aromatic and aliphatic alkenes in water, requiring short reaction times (15-30 min), operating through single electron transfer processes (SET). This compound acts both as a catalyst and a photosensitizer. It is concluded that this behaviour is possible thanks to the properties of **Na[1]**, as their high solubility in water, its molecular compactness, the donor ability of the boron unit ligand, their lack of photoluminescence, the high oxidizing power for the couple $Co^{4+/3+}$ and probably extremely relevant, their surfactant behaviour in aqueous media. These characteristics make the difference with the well-known and widely used photosensitizer tris (2,2′-bipyridine) ruthenium(II) ($[Ru(bpy)_3]^{2+}$), which also participates in electron transfer through an outer sphere mechanism. We have compared the $[Ru(bpy)_3]^{2+}$ performance in the photo oxidation of alkenes in water following the procedures described earlier for **Na[1]**, and the comparative epoxidation tests have been strongly supportive of **Na[1]**, showing for $[Ru(bpy)_3]^{2+}$ a very low or null efficiency.

The catalyst can be recovered easily by precipitation upon the addition of $[NMe_4]Cl$, and re-utilized. In general, under catalyst loads of 0,1 mol % high conversion values can be found with only 15 minutes of reaction, being in most of the cases the conversion total after 30 minutes. The major product after 15 minutes is the epoxide that gradually upon reaction with water converts into the dihydroxide. This reaction prevents a high throughput of the epoxide. This is in agreement with the increase in the amount of the corresponding diol for most of the substrates studied. We have also proven that **Na[1]**, acts as a photocatalyst/catalyst in both processes, in the epoxidation of alkenes and in their hydroxylation in aqueous medium. The question was whether the catalyst was faster for epoxidation than for hydroxylation. If this was the case it would enable the epoxide ratio to be improved in a short time reaction operation. And indeed it was so.

When **Na[1]** was added in a very low ratio 0,01%, it was observed an extremely good performance for the epoxidation of alkenes in short times of reaction, with less ratio of the diol, proving our hypothesis.

We have taken advantage of the surfactant capacity of $[1]^-$ to treat in water highly water insoluble molecules such as methyl oleate. Thus, preliminary photooxidation tests using methyl oleate as substrate have shown the selective epoxidation on the double bond C=C. This can represent a milestone towards the development of practical processes as the valorization of animal fat waste using **Na[1]**, as to promote circular economy. Perhaps the combination of both surfactant and high photoredox capacities are the prime concepts that make this metallacarborane $[1]^-$ catalyst highly innovative.

4. Experimental

4. 1. Materials and methods

All reagents used in the present work were obtained from Aldrich Chemical Co and were used without further purification. Reagent grade organic solvents were obtained from SDS and high purity de-ionized water was obtained by passing distilled water through a nano-pure Mili-Q water purification system. $Na[Co(\eta^5\text{-}1,2\text{-}C_2B_9H_{11})_2]$, **Na[1]** was synthesized from commercial $Cs[Co(1,2\text{-}C_2B_9H_{11})_2]$, **Cs[1]**, (Katchem Spol.sr.o), following a method described in the literature.[64]

4. 2. Gas chromatography studies

Gas chromatography was performed with a GC-2010 gas chromatograph from Shimadzu, equipped with as Astec CHIRALDEX G-TA column, 30 m x 0.25 mm (i.d); FID detector, 250 °C; carrier gas: He, rate: 1.57 mL min^{-1}. The quantification was achieved from calibration curves. All the products and their corresponding substrates of catalysis were detected under the following conditions. Styrene and derivatives: column temperature, 80°C for 5 minutes, raising to 170°C in a rate of 10°C/min, holding 170°C for 6 minutes. *Trans*-β-methyl-styrene, *cis*-β-methyl-styrene, *cis*-cyclooctene and derivatives: column temperature, 40°C for 5 minutes, raising to 170°C in a rate of 5°C/min, holding 170°C for 2 minutes. 4-vinyl-1-cyclohexene and derivatives: column temperature, 40°C for 5 minutes, raising to 170°C in a rate of 10°C/min, holding 170°C for 2 minutes. 1-octene and derivatives: column temperature, 30°C for 5 minutes, raising to 170°C in a rate of 10°C/min, holding 170°C for 3 minutes. *Trans*-stilbene and derivatives: column temperature, 50°C for 1 minutes, raising to 150°C in a rate of 15°C/min, holding 150°C for 2 minutes, then raising to 170°C in a rate of 4°C/min, holding 170°C for 12 minutes. The products analyses in the catalytic experiments were performed by GC with biphenyl as internal Standard.

4. 3. HPLC/ESI-MS chromatography studies

An Agilent LC 1200 series HPLC system equipped with a UV-Vis detector was used to analyze samples. Separation of products was achieved on an Eclipse XDB-C18 column (150x4.6 nm,5μm) from Agilent Technologies. The column was thermostatically controlled at 25∘C. The flow rate was set to 1 mL/min, and the injection volume was 100 μL. The mobile phase consisted of two solvents: methanol (A, 100%) and Milli-Q water (B,100%). The system worked in isocratic mode and the volume ratios was as follows: 85% A, 15% B. The ultraviolet (UV) absorbance values of the peaks were collected at 242 nm. An Ion Trap mass spectrometer (Bruker Squire 6000 system from Agilent Technologies) equipped with an Orthogonal electrospray ionization (ESI) source was used to identify the derivatives. Positive mode was selected for data collection. The products were qualitatively identified according mass spectra peaks and matching with mass spectra with the software Bruker Compass DataAnalysis 4.0.

4. 4. Photocatalytic oxidation studies

A quartz tube containing an aqueous solution (5 mL) at pH 7 (0.4 μM in K_2CO_3) with **Na[1]** or [Ru(bpy)$_3$]Cl$_2$ as catalyst, alkene as substrate, and $Na_2S_2O_8$ as sacrificial acceptor was exposed to UV light (2.2 W, λ=300 nm for different times. The complex: substrate: sacrificial oxidant ratios used were varied according to the study, (1:1000:1300 and 1:10000:13000 corresponding to concentrations of 0.02: 20: 26 mM and 0.002: 20: 26 mM, respectively). For each experiment, a light reactor supplied light illumination with twelve lamps that produce UVA light at room temperature. The resulting solutions were extracted with CH_2Cl_2 six times. *(We focused our attention on the synthetic/catalytic process that was environmentally friendly and not so much on using an analytical method that met the requirements. We tried ethyl ether but did not observe a clear phase separation, so we turned to DCM, which facilitated the extraction).* The solution was dried with anhydrous sodium sulfate and the solvent was reduced to a minimum volume under reduced pressure, then 100 μL of biphenyl 100 mM as internal standard was added to the resulting solution, 2mM in the resulting 5 mL solution. To check the reproducibility of the reactions all the experiments were carried by triplicate and analyzed by gas chromatography.

For methyl oleate: a quartz tube containing an aqueous solution (5 mL) at pH 7 (0.4 μM in K_2CO_3) with **Na[1]** was sonicated for 10 min. The complex: substrate: sacrificial oxidant ratios used were, 1:10000:13000 corresponding to concentrations of 0.002: 20: 26 mM, respectively. The samples were exposed to UVA light at room temperature during 60 min and the resulting solutions were extracted

with CH_2Cl_2 six times. This solution was dried with anhydrous sodium sulfate and the solvent was reduced to 2 ml. The organic phase was analized by HPLC/ESI-MS.

Conflicts of interest

There are no conflicts to declare

Acknowledgements

Green Chemistry Accepted Manuscript

Notes and References

1 R. H. Crabtree, *Energy Production and Storage – Inorganic Chemical Strategies for a Warming World*. *Encyclopedia of Inorganic Chemistry*, ed., John Wiley & Sons, Inc., 2nd ed, 2010, 73–87.

2 J. Twilton, C. Le, P. Zhang, M. H. Shaw, R. W. Evans and D. W. C. MacMillan, *Nat. Rev. Chem.* 2017, **1**, 1-19.

3 S. D. H. F. Gagnon, *Encyclopedia of Polymer Science and Engineering*, 2nd ed., Eds. H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges, J. I. Kroschwitz, John Wiley & Sons: New York, 1985, Vol. **6**, pp 273-307.

4 G. de Faveri, G. Ilyashenko and M. Watkinson, *Chem. Soc. Rev.,* 2011, **40**, 1722-1760.

5 J. G. Smith, *Synthesis,* 1984, 629-656.

6 E. N. Jacobsen, *Acc. Chem. Res*., 2000, **33**, 421-431.

7 E. J. de Vries and D. B. Janssen, *Curr. Opin. Biotechnol*., 2003, **14**, 414-420.

8 J. Muzart, *Eur. J. Org. Chem*., 2011, 4717-4741.

9 E. N. Jacobsen, W. Zhang, A. R. Muci, J. R. Ecker, and L. Deng, *J. Am. Chem. Soc.*, 1991, **113**, 7063-7064.

10 O. Cussó, I. Garcia-Bosch, X. Ribas, J. Lloret-Fillol, and M. Costas, *J. Am. Chem. Soc.*, 2013, **135,** 14871-14878.

11 N. K. Jana, and J. G. Verkade, *Org. Lett.,* 2003, **5**, 3787-3790.

12 H. Hussain, A. Al-Harrasi, I. R. Green, I. Ahmed, G. Abbasa and N. Ur Rehmana, *RSC Adv.,* 2014, **4**, 12882-12917.

13 S.-J. Jeon, H. Li, and P. J. Walsh, *J. Am. Chem. Soc.*, 2005, **127**, 16416-16425.

14 S. K. Sartori, I. L. Miranda, M. A. N. Diaz and G. Diaz-Munoz, *Mini Rev. Org. Chem.* 2021, **18**, 606-620.

15 Z.-X. Wang, Y. Tu, M. Frohn, J.-R. Zhang, and Y. Shi, *J. Am. Chem. Soc.*, 1997, **119**, 11224-11235.

16 H. Tian, X. She, L. Shu, H. Yu and Y. Shi, *J. Am. Chem. Soc.*, 2000, **122**, 11551-11552.

17 I. Serrano, M. I. López, I. Ferrer, A. Poater, T. Parella, X. Fontrodona, M. Solà, A. Llobet, M. Rodríguez and I. Romero, *Inorg. Chem*., 2011, **50**, 6044-6054.

18 E. Manrique, X. Fontrodona, A. Poater, M. Sola, M. Rodríguez and I. Romero, *Dalton Trans*., 2015, **44**, 17529-17543.

19 I. Ferrer, X. Fontrodona, A. Roig, M. Rodríguez and I. Romero, *Chem. Eur. J.,* 2017, **23**, 4096-4107.

20 J. Chen, M. de Liedekerke Beaufort, L. Gyurik, J. Dorresteijn, M. Otte and R. J. M. Klein Gebbink, *Green Chem,* 2019, **21**, 2436-2447.

21 J. Vondran, J. Pela, D. Palczewski, M. Skiborowski and T. Seidensticker, *ACS Sustainable Chem, Eng.* 2021, **9**, 11469-11478.

22 J. C. de la Garza, K. de Oliveira Vigier, G. Chatel and A. Moores, *Green Chem,* 2017, **19**, 2855-2862.

23 F. Glasser, and O. S. Wenger, *Coord. Chem. Rev.,* 2020, **405**, 213-129.

24 W. Chen, F. N. Rein and R. C. Rocha, *Angew. Chem., Int. Ed.,* 2009, **48**, 9672-9675.

25 W. Chen, F. N. Rein, B. L. Scott and R. C. Rocha, *Chem. Eur. J.,* 2011, **17**, 5595-5604.

26 A. J. J. Lennox, S. Fischer, M. Jurrat, S. P. Luo, N. Rockstroh, H. Junge, R. Ludwig and M. Beller, *Chem. Eur. J.,* 2016, **22**, 1233-1238.

27 P. Farràs, S. Maji, J. Benet-Buchholz and A. Llobet, *Chem. Eur. J.,* 2013, **19**, 7162-7172.

28 X. Lang, J. Zhao and X. Chen, *Chem. Soc. Rev.,* 2016, **45**, 3026-3038.

29 B. M. Hockin, C. Li, N. Robertson and E. Zysman-Colman, *Catal. Sci. Technol*., 2019, **9**, 889-915.

30 S. Fukuzumi, T. Kishi, H. Kotani, Y. M. Lee and W. Nam, *Nat. Chem*., 2011, **3**, 38-41.

31 G. Chen, L. Chen, L. Ma, H.-K. Kwonga and T.-C. Lau, *Chem. Commun.,* 2016, **52**, 9271-9274.

32 G. F. P. de Souza, J. A. Bonacin, and A. G. Jr. Salles, *J. Org. Chem.*, 2018, **83**, 8331-8340.

33 J. Li, and D. Z. Wang, *Org. Lett.*, 2015, **17**, 5260-5263.

34 P. E. Behnken, D. C. Busby, M. S. Delaney, R. E. King III, C. W. Kreimendahl, T. B. Marder, J. J. Wilczynski and M. F. Hawthorne, *J. Am. Chem. Soc.,* 1984, **106** (24), 7444-7450.

35 P. E. Behnken, J. A. Belmont, D. C. Busby, M. S. Delaney, R. E. King III, C. W. Kreimendahl, T. B. Marder, J. J. Wilczynski and M. F. Hawthorne, *J. Am. Chem. Soc.* 1984, **106**, 3011-3025.

36 R. T. Baker, M. S. Delaney, R. E. King III, C. B. Knobler, J. A. Long, T. B. Marder, T. E. Paxson, R. G. Teller and M. F. Hawthorne, *J. Am. Chem. Soc.* 1984, **106**, 2965-2978.

37 J. A. Long, T. B. Marder, P. E. Behnken and M. F. Hawthorne, *J. Am. Chem. Soc.* 1984, **106**, 2979-2989.

38 J. A. Long, T. B. Marder and M. F. Hawthorne, *J. Am. Chem. Soc.* 1984, **106**, 3004-3010.

39 J. D. Hewes, C. W. Kreimendahl, T. B. Marder and M. F. Hawthorne, *J. Am. Chem. Soc.* 1984, **106**, 5757-5759.

40 H. Shen and Z. Xie, Boron Science, New Technologies and Applications, chapter 21, ed. N. S. Hosmane, CRC Press: Boca Raton, FL, USA, 2012, pp 517-528.

41 S. Bauer and E. Hey-Hawkins, Boron Science, New Technologies and Applications, chapter 22, ed. N. S. Hosmane, CRC Press: Boca Raton, FL, USA, 2012, pp 529-579.

Green Chemistry Accepted Manuscript

42 Handbook of Boron Chemistry in Organometallics, Catalysis, Materials and Medicine, Volume 2: Boron in Catalysis, ed. N. S. Hosmane, World Science Publishers, New Jersey 2018.

43 Z.W. Xie, Coord. *Chem. Rev*., 2006, **250**(1-2), 259-272.

44 H. Ying-Feng and J. Guo-Xin, *Acc. Chem. Res*., 2014, **47**(12), 3571-3579.

45 S. P. Fisher, A. W. Tomich, S. O. Lovera, J. F. Kleinsasser, J. Guo, M. J. Asay, H. M. Nelson and V. Lavallo, *Chem. Rev*., 2019, **119**(14), 8262-8290.

46 M. Fontanet, M. Rodriguez, C. Vinas, F. Teixidor and I. Romero, *Eur. J. Inorg. Chem.,* 2017, 4425-4429.

47 R. Núñez, M. Tarrés, A. Ferrer-Ugalde, F. Fabrizi di Biani and F. Teixidor, *Chem. Rev.,* 2016, **116**, 14307-14378.

48 S. Mukherjee and P. Thilagar, *Chem. Commun.,* 2016, **52**, 1070-1093.

49 O. Junki, T. Kazuo and C. Yoshiki, *Angew. Chem. Int. Ed.,* 2020, **59** (25), 9841-9855.

50 M. F. Hawthorne, D. C. Young, P. M. Garret, D. A. Owen, S. G. Schwerin, F. N. Tebbe and P. M. Wegner, *J. Am. Chem. Soc*. 1968, **90**, 862-868.

51 I. Bennour, A. M. Cioran, F. Teixidor and C. Viñas, *Green Chem.,* 2019, **21**, 1925-1928.

52 A.-I. Stoica, C. Viñas and F. Teixidor, *Chem. Commun*. 2008, 6492-6494.

53 A.-I. Stoica, C. Viñas, F. Teixidor, *Chem. Commun.* 2009, 4988-4990.

54 I. Fuentes, J. Pujols, C. Viñas, S. Ventura and F. Teixidor, *Chem. Eur. J.,* **2019**, *25*, 12820-12829.

55 P. Bauduin, S. Prevost, P. Farràs, F. Teixidor, O. Diat and T. Zemb, *Angew. Chemie Int. Ed.,* 2011, **50**, 5298-5300.

56 M. Uchman, V. Ďorďovič, Z. Tošner and P. Matějíček, *Angew. Chemie Int. Ed.,* 2015, **54**, 14113-14117.

57 A. Zaulet, F. Teixidor, P. Bauduin, O. Diat, P. Hirva, A. Ofori and C. Viñas. *J. Organomet. Chem*., 2018, **865**, 214-225.

58 I. Guerrero, Z. Kelemen, C. Viñas, I. Romero and F. Teixidor, *Chem. Eur. J.,* 2020, **26**, 5027-5036.

59 I. Guerrero, X. Fontrodona, C. Viñas, I. Romero and F. Teixidor, *Inorg. Chem.,* 2021, **60**, 8898-8907.

60 I. Guerrero, A. Saha, J. A. M. Xavier, C. Viñas, I. Romero and F. Teixidor, *ACS Appl. Mater. Interfaces,* 2020, **12** (50) 56372-56384.

61 C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.,* 2013, **113**, 5322-5363.

62 J. Du, K. L. Skubi, D. M. Schultz and T. P. Yoon, *Science,* 2014, **344**, 392-396.

63 J. W. Beatty, J. J. Douglas, K. P. Cole, C. R. J. Stephenson, *Nature Commun*., 2015, **6**, 7919.

64 I. Fuentes, A. Andrio, F. Teixidor, C. Viñas and V. Compañ, *Phys. Chem. Chem. Phys.,* 2017, **19**, 15177-15186.

65 S. M. Danov, O. A. Kazantsev, A. L. Esipovich, A. S. Belousov, A. E. Rogozhin and E. A. Kanakov, *Catal. Sci. Technol.,* 2017, **7**, 3659-3675.

66 M. Palucki, M. S. Finney, P. J. Pospisil, M. L. Güler, T. Ishida and E. N. Jacobsen, *J. Am. Chem. Soc.,* 1998, **120**, 948-954**.**

67 A. Behr, *Chem. Eng. Technol.,* 2008, **31**, 700-714.

68 D. Brusselle, P. Bauduin, L. Girard, A. Zaulet, C. Viñas, F.; Teixidor, I. Ly and O. Diat, *Angew. Chem. Int. Ed.,* 2013, **52** (46) 12194-12194.

69 P. Matejicek, P. Cigler, K. Prochazka and V. Kral, *Langmuir,* 2006, **22**, 575-581.