■ **Photooxidation** |*Hot Paper*|

Metallacarboranes as Photoredox Catalysts in Water

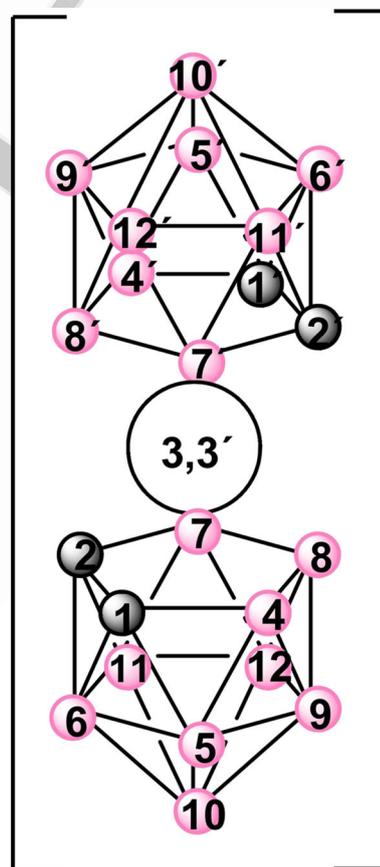Isabel Guerrero,[a, b] Zsolt Kelemen,[a] Clara Viñas,[a] Isabel Romero,*[b] and Francesc Teixidor*[a]

Abstract: ■■Please give authors' academic titles■■ Metallacarboranes with the shape of the Greek letter θ, such as [Co(C$_2$B$_9$H$_{11}$)$_2$]$^-$, were tested, for the first time, as efficient photoredox catalysts in the oxidation of aromatic and aliphatic alcohols in water. Their efficiency is linked to their high solubility in water, their high oxidizing power (Co$^{4+/3+}$), and their absence of fluorescence on excitation, among others. In most of the studied examples, using a catalyst load of 0.4 mol% gave high yields of 90–95% with selectivity greater than 99%. By reducing the catalyst load to 0.01 mol%, quantitative conversion of reactants to products was achieved, in some cases with greater than 99% yield, high catalyst efficiency reaching a turnover number of 10000, and a higher yield with a 45 times lower concentration of catalyst. The metallacarboranes can be recovered easily by precipitation on addition of [NMe$_4$]Cl. A pathway for the photoredox-catalyzed oxidation of alcohols is proposed.

Introduction

Due to the steric and electronic properties of anionic carborane clusters, they have been used as ligands for formation of metallacarborane complexes, which have been tested as catalysts in synthetic processes such as hydrogenation, hydroformylation, hydrosilylation, carbonylation, amination, alkylation, sulfonylation, the Kharasch reaction, polymerization, and ring-opening metathesis polymerization.[1] Cobaltabisdicarbollide [3,3'-Co(1,2-C$_2$B$_9$H$_{11}$)$_2$]$^-$ (Scheme 1), in which the two C$_c$ carbon atoms of the cluster occupy adjacent positions, is the best representative example of metallabisdicarbollides, in which a metal ion is sandwiched between two [C$_2$B$_9$H$_{11}$]$^{2-}$ units. The reasons why [3,3'-Co(1,2-C$_2$B$_9$H$_{11}$)$_2$]$^-$ is the most studied are diverse but doubtless lie in its thermal and chemical stability and simple synthesis. Cobaltabisdicarbollide is a highly compact θ-shaped molecule ready for stepwise substitutions at B that sequentially modify its redox potentials and keep them reversible.[2] Other properties of [3,3'-Co(1,2-C$_2$B$_9$H$_{11}$)$_2$]$^-$ that are relevant to the findings in this work are its nonlocalized negative charge spread all over the molecule,[3] its many possibilities to form hydrogen bonds such as C$_c$−H···O and C$_c$−H···H−B dihydrogen bonds, which have been proven to participate in their self-assembly,[4] water solubility,[5] micelle and vesicle for-

[a] *I. Guerrero, Z. Kelemen, C. Viñas, F. Teixidor*
    Institut de Ciencia de Materials de Barcelona, ICMAB-CSIC
    Campus UAB, 08193 Bellaterra (Spain)
    E-mail: teixidor@icmab.es

[b] *I. Guerrero, I. Romero*
    Departament de Química i Serveis Tècnics de Recerca
    Universitat de Girona, C/ M. Aurèlia Campmany, 69
    17003 Girona (Spain)
    E-mail: marisa.romero@udg.edu

🖥 *Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:*
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Scheme 1. Anionic icosahedral cobaltabisdicarbollide [3,3'-Co(1,2-C$_2$B$_9$H$_{11}$)$_2$]$^-$ with vertex numbering. Gray circles correspond to the C$_c$−H bonds, pink circles to the B−H bonds, and the Co atom is located at the 3,3'-position.

mation,[6] and derivatization capacity similar or superior to that of organic compounds.[3a, 7] The interactions in a supramolecular approach seem to be significant in the processes of elec-

tron transfer and therefore in the effectiveness of photocatalytic systems.[8]

The redox potentials are $+1.21$ V for the $[Co(C_2B_9H_{11})_2]^{0/1-}$, -1.75 V for $[Co(C_2B_9H_{11})_2]^{-/2-}$, and -2.64 V for $[Co(C_2B_9H_{11})_2]^{2-/3-}$ [all vs. ferrocenium/ferrocene (Fc$^{+/0}$)].[9] Some of these values match very well with these found for $[Ru(bpy)_3]Cl_2$ (bpy $=2,2'$-bipyridine), perhaps the archetype of molecular photoredox catalysts, which exhibits a reductive and oxidative quenching cycle in which $[Ru(bpy)_3]^+$, a strong reducing agent (-1.76 V vs. Fc$^{+/0}$ in CH$_3$CN), and $[Ru(bpy)_3]^{3+}$, a strong oxidant ($+0.85$ V vs. Fc$^{+/0}$ in CH$_3$CN), are produced, respectively.[10] The similar potentials of the two reducing agents near -1.75 V and the stronger oxidizing character of the oxidant in $[Co(C_2B_9H_{11})_2]^{0/-}$ compared with $[Ru(bpy)_3]^{3+/2+}$ led us to hypothesize that we could have at hand a promising photoredox system that is not based on noble metals. It just had to absorb light intensively and not show any photoluminescent properties. We are aware that we were making a great simplification comparing ground-state redox potentials when we should compare redox potentials of the electronically excited states, but we considered that it is an acceptable approach subject to the experimental results.

Considering further similarities, both $[Ru(bpy)_3]^{2+}$ and $[3,3'$-Co(1,2-C$_2$B$_9$H$_{11})_2]^-$ have octahedral geometry and participate in electron transfer through an outer-sphere mechanism. Considering that we wished to convert the maximum number of photons to chemical energy, $[3,3'$-Co(1,2-C$_2$B$_9$H$_{11})_2]^-$ could even be a better model than $[Ru(bpy)_3]^{2+}$, as we have not observed that excitation produces fluorescence. Due to its characteristics, $[3,3'$-Co(1,2-C$_2$B$_9$H$_{11})_2]^-$ could be an essential part of a photoredox catalytic system for the oxidation of organic substrates in which the solvent is water, the metal in the catalyst is an earth-abundant transition metal, the ligands are inorganic, the photoredox catalyst is redox-tunable, the excitation source is light, and the only organic component should be the substrate.

All these considerations motivated us to study whether $[3,3'$-Co(1,2-C$_2$B$_9$H$_{11})_2]^-$ could perform as a photoredox catalyst operating under UVA thanks to the bands at 293 or 345 nm. In contrast to typical coordination (e.g., $[Ru(bpy)_3]^{2+}$) or organometallic ($[Fe(C_5H_5)_2]$) octahedral complexes, the differences in electronegativity between the metal and the coordinating atoms of the ligands, (e.g., $X_{Ru}-X_N=-0.84$, $X_{Fe}-X_C=-0.72$) are much more negative than $X_{Co}-X_B=-0.16$ in $[Co(C_2B_9H_{11})_2]^-$. In the latter case, this may result in a better overlap of orbitals of the metal and ligands, so that these orbitals in the frontier orbital region of $[3,3'$-Co(1,2-C$_2$B$_9$H$_{11})_2]^-$ are less metal-based. Furthermore, the ligands have double negative electric charge, and $[3,3'$-Co(1,2-C$_2$B$_9$H$_{11})_2]^-$ itself is also negatively charged, which results in occupied molecular orbitals with relatively high energy level and with ligandlike character. In this regard, TD-DFT calculations of Bühl and co-workers[11] showed that the bands at 293 and 345 nm correspond mainly to HOMO$-1\rightarrow$LUMO$+1$ and HOMO$-3\rightarrow$LUMO transitions. It was mentioned therein that the excitations take place from the high-lying boron skeleton towards LUMO and LUMO$+1$ of $[3,3'$-Co(1,2-C$_2$B$_9$H$_{11})_2]^-$, but the charge-transfer character of these excitations was not investigated.

To test the photoredox capacity of cobaltabisdicarbollide we sought a system of interest that is well studied in terms of catalysis and in which photoredox catalysis had been done. We chose alcohols because their oxidation [Eq. (1)][12–14] had been demonstrated with visible-light-driven oxidation performed by using a Ru^{II} polypyridyl complex[15] and, more recently, by a using chromophore–catalyst dyad of ruthenium complexes,[16–19] one of which performs as a photosensitizer and the other as a catalyst, and because it involves a two-electron–two-proton coupled process.[20] This process has practical importance in hydrogen-based energy technologies, because the anodic liberation of protons and electrons can be coupled on a cathode for hydrogen fuel production in an integrated photoelectrochemical cell.

$$RCH(OH)R' \rightarrow RC(=O)R' + 2H^+ + 2e^- \qquad (1)$$
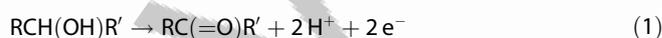
Further, the conversion of alcohols to aldehydes or ketones is of great relevance, as shown by the numerous publications. Due to the significance of using ambient air for oxidation, only some representative examples in which it is used are mentioned.[21–24]

Given that our expectations of the photoredox catalyst ability of cobaltabisdicarbollide were real, we planned this research at two levels, one by performing the catalytic studies under the catalytic conditions commonly used in the literature (usually 0.4–1% mol of catalyst vs. substrate, 0.08–0.2 mM of catalyst) and the other under more dilute conditions (0.01–0.1% mol of catalyst vs. substrate, 2–20 μM of catalyst).

On the other hand, the concept of decreasing the absolute difference in electronegativity $|\Delta X|$ of possible photoredox catalysts has not been discussed before, nor have metallabisdicarbollides as part of a photocatalytic system. Important for this work is that $[3,3'$-Co(1,2-C$_2$B$_9$H$_{11})_2]^-$, despite being a purely inorganic molecule, offers the possibility to tune its properties by substitutability comparable or superior to that of organic frameworks,[7] which is an important aspect that contributes new and interesting innovative features in photocatalysis.

We describe herein the photocatalytic behavior of $[Na\cdot2.5H_2O][3,3'$-Co(1,2-C$_2$B$_9$H$_{11})_2]$ (**Na[1]**), dichloro derivative $[Na\cdot2.5H_2O][3,3'$-Co(8-Cl-1,2-C$_2$B$_9$H$_{10})_2]$ (**Na[Cl$_2$-1]**), and hexachloro derivative $[Na\cdot2.5H_2O][3,3'$-Co(8,9,12-Cl$_3$-1,2-C$_2$B$_9$H$_8)_2]^-$ (**Na[Cl$_6$-1]**) (Figure 1 A), produced by dehydrohalogenation of the pristine $[3,3'$-Co(1,2-C$_2$B$_9$H$_{11})_2]^-$ anion, in the oxidation of alcohols in water. Remarkably, the metallabisdicarbollide performs two roles at once: photosensitizer and catalyst. As oxidizing agents we used Na$_2$S$_2$O$_8$ and air, showing that both are suitable to oxidize the alcohol. We used sodium as counterion due to the high solubility of the corresponding metallabisdicarbollide in water (1500 mM).[5] In addition, we show how matching the lamp frequency and the absorption maximum of the photoredox catalyst enhances the yield of the reaction. The photoredox catalyst can be easily recovered after performing the catalysis.
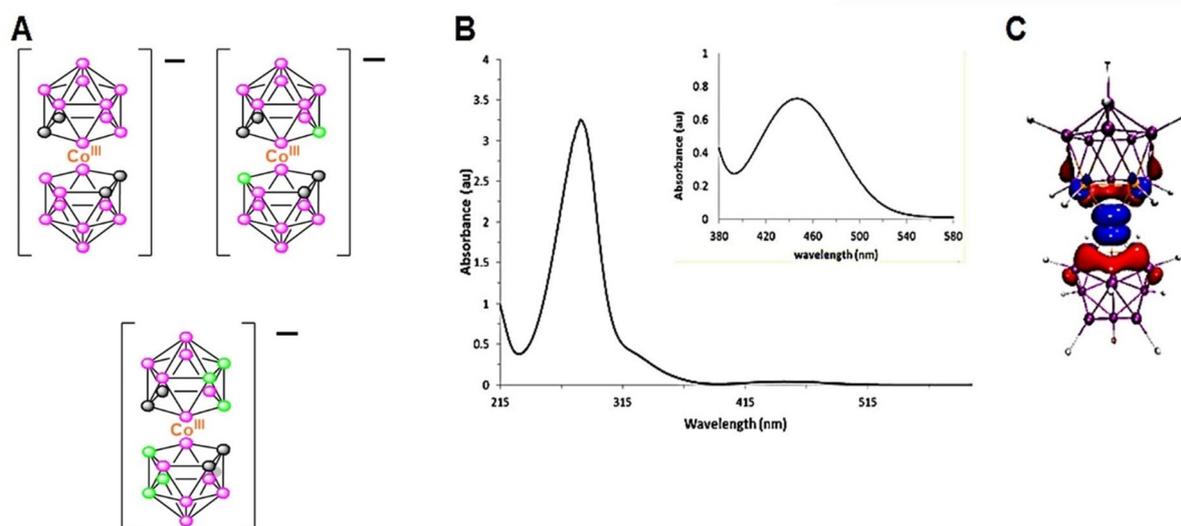
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Figure 1. A) Metallabisdicarbollides used in this work: $[3,3'-Co(1,2-C_2B_9H_{11})_2]^-$ ([**1**]$^-$, only the *trans* rotamer is shown) and its dichloro and hexachloro derivatives $[3,3'-Co(8-Cl-1,2-C_2B_9H_{10})_2]^-$ and $[3,3'-Co(8,9,12-Cl_3-1,2-C_2B_9H_8)_2]^-$, respectively. The green circles represent BCl units and the pink circles BH units. B) UV/Vis spectra of **Na[1]** in phosphate buffer solution, 1.3×10^{-4} M at pH 7.2. Inset: Magnification of the visible region of **Na[1]** in phosphate buffer, 2×10^{-3} M at pH 7.2. C) Charge-density difference map of the transition at 293 nm in case of the *transoid* structure. (The blue and red parts correspond to the regions in which electron density is increased and decreased after electron excitation, respectively. Isosurface value: 0.003.

Results and Discussion

General strategy

Our main goal was to demonstrate that a metallacarborane, namely $[3,3'-Co(1,2-C_2B_9H_{11})_2]^-$, with a nonconventional structure compared with existing photoredox catalysts can perform as such, with its own definite characteristics, which have been outlined in the introduction. To do so, the first thing to do was to demonstrate that the reaction could be done under homogeneous conditions in water. Thus, **Na[1]** was prepared from water-insoluble **Cs[1]** by using a cation-exchange resin[25] and its dichloro (**Na[Cl₂-1]**) and hexachloro (**Na[Cl₆-1]**) derivatives were prepared similarly.[26] All three Na$^+$ salts are soluble in water, as required by the catalysis conditions.

Likewise, we wanted to show that the cobaltabisdicarbollide anion could be tuned both to alter the $E°$ value of $[3,3'-Co(1,2-C_2B_9H_{11})_2]^{0/-1}$, to produce a more oxidizing molecule, for example, $[3,3'-Co(1,2-C_2B_9H_{11})_2]^0$, and to shift the absorption maximum to the visible region. By having two or six chloro substituents on the anion, we shifted the absorption maximum towards the visible range. By using lamps with the closest emission to the absorption maximum of the photoredox catalyst, we sought to improve the yield of the reaction in the shortest possible exposure time. The UV/Vis spectrum of **Na[1]** (Figure 1 B) shows one strong absorption band at 293 nm and two weaker ones at 345 and 445 nm, in agreement with the literature,[27] and the visible spectrum was interpreted on the basis of ligand-field theory.[28] The UV/Vis spectra of **Na[Cl₂-1]** and **Na[Cl₆-1]** show bands at 320 nm ($\varepsilon = 26\,000$ M^{-1} cm^{-1}) and 384 nm ($\varepsilon = 3700$ M^{-1} cm^{-1}) and at 327 nm ($\varepsilon = 29\,000$ M^{-1} cm^{-1}) and 393 nm ($\varepsilon = 3500$ M^{-1} cm^{-1}), respectively (see Supporting Information)

Computational study

To get more detailed insight into the character of the electron transitions of $[3,3'-Co(1,2-C_2B_9H_{11})_2]^-$, TD-DFT calculations were performed at the B3LYP/6–311+G** level of theory (for more computational details, see Supporting Information). The stabilities of the *cisoid*, *gauche*, and *transoid* rotamers (Figure S1 in the Supporting Information) are similar, but the stability depends on their interactions with the environment. Remarkably, their relative stability depends on whether the environment is vacuum, water, or the solid state.[29] Hence the three rotamers were computationally investigated in vacuum, and they exhibit practically identical electronic properties (more details in the Supporting Information), which were in good agreement with the previously published results.[11] We studied in more detail the excitation at 293 nm, which is the most intensive band in the spectrum. Since there are no dominant MO transitions, which makes it difficult to analyze the nature of the excitation, we generated and analyzed the natural transition orbitals (NTOs) corresponding to the proper transitions (Table S2 in the Supporting Information) and also generated charge-density difference maps (Figure S2 and Table S4 in the Supporting Information). The NTOs (Table S2 in the Supporting Information) show that the electron transfer can be regarded as a transition from the boron skeleton towards the metal center, and the charge-density difference map (Figure 1 C) clearly demonstrates that the electron density shifted from the ligand towards the metal center (and a little bit towards the carbon atoms as well) during excitation at 293 nm, and this indicates charge transfer from the ligand framework towards the metal center (LMCT) during the transition. This is in full agreement with the double negative charge of the carborane ligands, which increases the energy level of these occupied orbitals ($\varepsilon_{HOMO}([3,3'-Co(1,2-C_2B_9H_{11})_2]^-)$ is between -4.00 and -4.03 eV depending on the

rotamer, whereas $\varepsilon_{HOMO}([Ru(bpy)_3]^{2+}) = -11{,}17$ eV at the B3LYP/6-311+G** level of theory) and the ligands make significant contributions to HOMO−1 and HOMO−3. Thus, on irradiation electrons are promoted mainly from the orbitals with ligand-like character to the rather metal-based LUMO and LUMO+1. This is opposite to the electron path in $[Ru(bpy)_3]^{2+}$, from the metal to the ligand, and is a first indication of a possible distinct behavior in electron transfer as a consequence of the difference in electronegativity among the elements participating in the bonding, the negative charge of the carboranyl ligands, and the overall negative charge of $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$.

Photocatalytic oxidations under common conditions (0.4 mol% catalyst versus substrate, 0.08 mM)

There are few photoredox catalytic systems based on earth-abundant metals for organic transformations. Due to its relevance, we chose the oxidation of alcohols to test the photoredox properties of **Na[1]**. The first photocatalytic oxidation experiments, mostly with **Na[1]**, were all performed by exposing quartz reaction vials to UV irradiation (2.2 W, $\lambda = 253.7$ nm) at room temperature and atmospheric pressure for different times. The samples were made from 5 mL of water (phosphate buffer, pH 7.2) and a mixture of **Na[1]** (0.08 mM), substrate (20 mM), and $Na_2S_2O_8$ (40 mM) as oxidizing agent. Following irradiation for a specified time (see Table 1), the reaction products were extracted with dichloromethane three times, dried with Na_2SO_4, quantified by ^1H NMR spectroscopy (Figure 2 and Figures S4–S7 in the Supporting Information), and confirmed by GC-MS analysis (Figure S8 in the Supporting Information).

1-Phenylethanol was taken as the reference compound to find the optimal reaction conditions. Then, preliminary catalytic oxidation studies at different concentrations of **Na[1]** as photoredox catalyst were performed for 3 h (Table S6 in the Support-
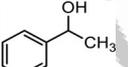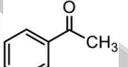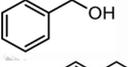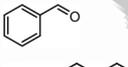
ing Information) while maintaining constant concentrations of substrate (1-phenylethanol) and $Na_2S_2O_8$; the results showed that an increased amount of acetophenone is produced at higher catalyst loadings. However, as shown in Table S6 in the Supporting Information, a sixfold increase in catalyst concentration results only in a 1.7-fold increase in yield. Therefore, lower concentrations of catalyst seem 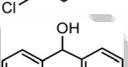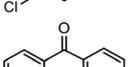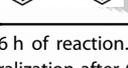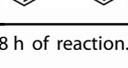to be more effective. Thus, we took the lowest tested concentration of $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ (0.08 mM) as optimal for extending the study to other alcohols. Also, different reaction times were tested with 1-phenylethanol as substrate (Figure S3 in the Supporting Information). We chose 8 h as optimal time to perform the catalytic experiments, but we also studied the performance of the catalyst after 6 h of reaction.

Blank controls showed that after 8 h of reaction in the dark with all reagents in the reaction pot, no significant oxidation of alcohol occurred ($< 2\%$). With all components and light, with no exception, aldehyde or ketone was detected as only product of the oxidation reaction, and the selectivity was greater than 99%.

Table 1 lists the results obtained in the catalytic oxidation of different alcohols with **Na[1]** in phosphate buffer solution at pH 7.2 after 6 and 8 h of reaction. These results show moderate to high yields of aldehydes or ketones. Oxidation of the secondary alcohol 1-phenylethanol (Table 1, entry 1) leads to the corresponding ketone with slightly lower conversion than in the case of benzyl alcohol (Table 1, entry 2); however, oxidation of the secondary alcohol diphenylmethanol to benzophenone gave the highest yield (Table 1, entry 5). The conversion is enhanced by the presence of electron-donating substituents on the aromatic ring of benzyl alcohol (Table 1, entry 3) but decreased by the presence of electron-withdrawing substituents such as chloro (Table 1, entry 4). In all cases it was observed that the initial neutral pH of the system decreases from 7.2 to 5–6 after 6 h of irradiation. To investigate the role of pH, the reaction mixture of 1-phenylethanol (Table 1, entry 1) was neutralized (pH 7) after 6 h of reaction by addition of dilute NaOH and further irradiated until 8 h. The yield of the oxidation product increased from 48 to 62%. These results reveal that increasing acidity of the catalytic solution deactivates the system and prove that H^+ is eliminated in the mechanism. This prompted us to use NEt_3 to corroborate our hypothesis (see below). The MALDI-TOF mass spectrum of a solution of **Na[1]** after the catalytic experiments showed that most of the catalyst remained unchanged after the catalysis, and only 10% was hydroxylated[30] (Figure 3). According to the computational studies the hydroxylated derivative maintains the photoredox capacity, so its formation should not affect the conversion (see Table S5 in the Supporting Information).

The LMCT mode suggested by the DFT calculations and the electrochemistry of **Na[1]** evidence that $[Co^{IV}]$ is a strong oxidizing agent that can be obtained both electrochemically and in a photoinduced manner. The reaction pathway postulated in Figure 4

Table 1. Oxidation tests performed with **Na[1]**. Conditions: **Na[1]** (0.08 mM), substrate (20 mM), $Na_2S_2O_8$ (40 mM), 5 mL 0.1 M phosphate buffer solution at pH 7.2 light irradiation (2.2 W, $\lambda = 253{,}7$ nm) for 6 and 8 h. Yield values in the absence or in the presence of 40 mM NEt_3.

	Substrate	Product	Yield [%] (no NEt₃)	Yield [%] (with NEt₃)
1	![1-phenylethanol, OH CH₃]	![acetophenone, O CH₃]	48[a], 54[b] 62[c]	91[b]
2	![benzyl alcohol, OH]	![benzaldehyde, O]	53[a] 63[b]	92[b]
3	![4-methylbenzyl alcohol, H₃C OH]	![4-methylbenzaldehyde, H₃C O]	63[a] 67[b]	94[b]
4	![4-chlorobenzyl alcohol, Cl OH]	![4-chlorobenzaldehyde, Cl O]	50[a] 59[b]	75[b]
5	![diphenylmethanol, OH]	![benzophenone, O]	78[a] 85[b]	94[b]
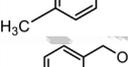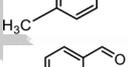
[a] After 6 h of reaction. [b] After 8 h of reaction. [c] After 8 h of reaction, with previous neutralization after 6 h.
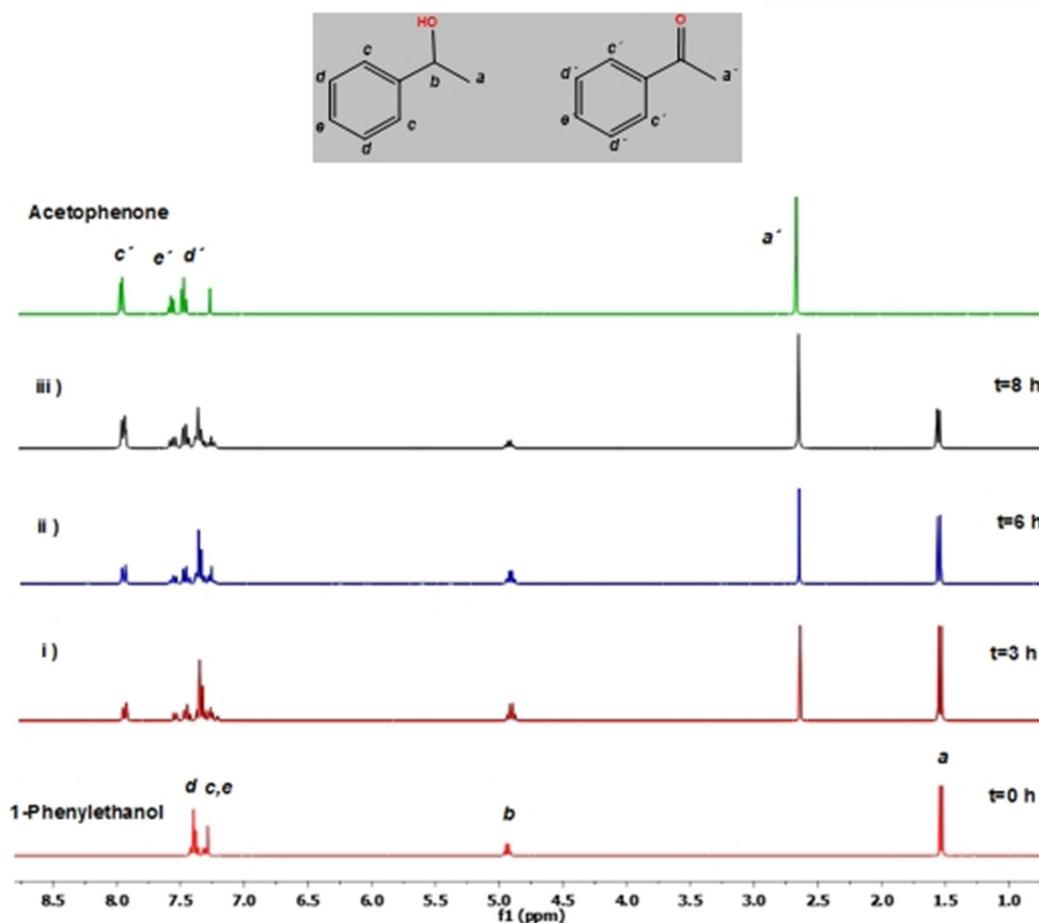
Figure 2. Representative ^{1}H NMR spectra of the reaction mixtures of the substrate (1-phenylethanol) and the corresponding oxidation product (acetophenone), dissolved in CDCl$_3$ at room temperature. The mixtures were obtained by photoirradiation ($\lambda = 253.7$ nm) of 1-phenylethanol at different times with **Na[1]** as catalyst. i) 3 h after irradiation, ii) 6 h after irradiation, 48% yield, iii) 8 h after irradiation after pH neutralization, 62% yield. The ^{1}H NMR spectra of 1-phenylethanol and acetophenone are included as control at the bottom and the top, respectively.
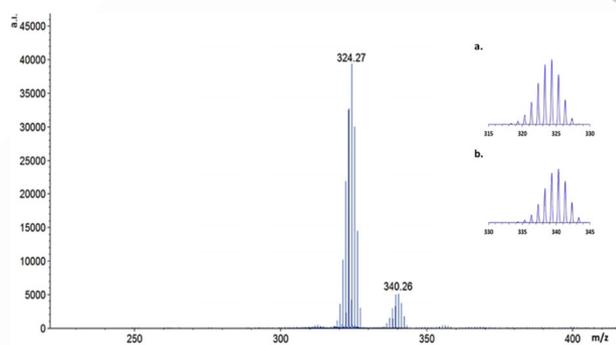

Figure 3. Experimental MALDI mass spectrum of **Na[1]** after the photocatalytic oxidation of 1-phenylethanol. The peak at m/z 324 corresponds to [3,3′-Co(1,2-C$_2$B$_9$H$_{11}$)$_2$]$^-$, and that on the right to [3,3′Co(1,2-C$_2$B$_9$H$_{11}$)(1,2-C$_2$B$_9$H$_{11}$O)]$^-$. Simulated spectra for a) [3,3′-Co(1,2-C$_2$B$_9$H$_{11}$)$_2$]$^-$ = 324.28 (m/z) and b) [3,3′Co(1,2-C$_2$B$_9$H$_{11}$)(1,2-C$_2$B$_9$H$_{11}$O)]$^-$ = 340.28 (m/z).

Figure 4. Postulated pathway for alcohol oxidation with **Na[1]** on UV irradiation.

accounts for the observed photoredox-catalyzed oxidation of alcohols by **Na[1]**. Incident photons are absorbed by photoredox catalyst [3,3′-Co^{III}(1,2-C$_2$B$_9$H$_{11}$)$_2$]$^-$, which undergoes excitation to form [3,3′-Co^{III}(1,2-C$_2$B$_9$H$_{11}$)$_2$]*$^-$, which undergoes oxida-

tive quenching by S$_2$O$_8$$^{2-}$ (oxidizing agent) to generate two strong oxidizing agents: [3,3′-Co^{IV}(1,2-C$_2$B$_9$H$_{11}$)$_2$] and SO$_4$$^{•-}$. The

formation of $SO_4^{\bullet-}$ is well documented and is normal in the oxidation of Fe^{II} or Ag^I by $S_2O_8^{2-}$ to Fe^{III} or Ag^{II}, respectively.[31] The photogenerated strong oxidant Co^{IV} is able to oxidize the alcohol to the corresponding alcohol radical, which in the presence of the $SO_4^{\bullet-}$ radical leads to the corresponding aldehyde or ketone.
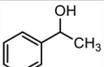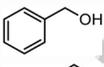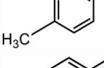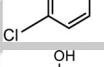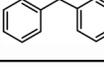
With the postulated pathway proposed in Figure 4, the exchange of two electrons and two protons takes place in the oxidation of alcohols, with associated increase of the acidity in the reaction medium, as we have also evidenced after the catalytic tests. The increased acidity could be responsible for the moderate yield observed in the absence of base (Table 1).

To support the postulated pathway a weak base was added to the system. For convenience and availability, we added 0.2 mmol of NEt_3 for 0.1 mmol of substrate. For 1-phenylethanol as substrate, base addition resulted in a significant increase in the amount of ketone to 91% [turnover number (TON) = 227] after 8 h (See Table 1, entry 1). We extended our study to the other alcohols, to evaluate the catalytic activity in presence of NEt_3 (Table 1). In all experiments (see last column in Table 1) the degree of conversion improved remarkably, in most cases to greater than 90%, while still maintaining selectivity greater than 99%. This, along with the fact that the cobaltabisdicarbollide remains practically unchanged after the catalytic oxidation reaction (only 10% is hydroxylated) is consistent with the proposed pathway. Just after irradiation and before extraction, on addition of $[Me_4N]Cl$ the salt $[Me_4N][3,3'-Co(1,2-C_2B_9H_{11})_2]$ precipitates. After filtration, solubilization with acetonitrile, and addition of water, the solution was passed to a cationic exchange resin loaded with Na^+ to regenerate **Na[1]**. The resulting catalyst has been tested in a second catalytic reaction with 1-phenylethanol as substrate, in the presence of NEt_3, which produced 89% of the corresponding ketone, which is similar to the yield observed in the first run. Nevertheless, in the vast majority of studies, we skipped this step and proceeded directly after irradiation to extraction with dichloromethane. Cobaltabisdicarbollide $[1]^-$ is a platform with many sites for the substitution of BH by BCl, which results in the formation of chlorinated derivatives $[Cl_x-1]^-$, successive substitutions of which modulate the redox potential.[32] It has been observed that a simple substitution produces a shift of the redox potential of approximately 0.1 V to more anodic voltages. Consequently, this results in a decrease in the energy gap of the frontier orbitals, which leads to longer wavelengths with respect to unsubstituted $[1]^-$. This behavior allows the absorption maximum of the UV/Vis spectrum to be shifted towards the visible region. Among these chlorinated compounds, $[Cl_2-1]^-$ and the $[Cl_6-1]^-$ were chosen to explore their behavior as catalysts in the oxidation of alcohols. The photocatalytic oxidation experiments were all performed by exposing the quartz reaction vials to UV irradiation ($\lambda = 253.7$ or 352 nm) for different reaction times under the same conditions as listed in Table 1 for **Na[1]**. The results shown in Table 2 indicate high yields, in some cases total conversion, after 6 h of irradiation when the wavelength of the lamp was 352 nm, near to the absorption maximum in the UV/Vis spectra of these derivatives (see Supporting Information). As expected, the performance of the catalysts was lower when the irradiation of the samples was done with a lamp of wavelength 253 nm, far from their absorption maxima. In all cases, the selectivity for the corresponding aldehydes or ketones was greater than 99%. Under the studied conditions, **Na[Cl$_6$-1]** generally shows slightly higher activity than **Na[Cl$_2$-1]**, probably due to the enhanced oxidizing capacity of Co^{IV} in the former, as a consequence of the presence of more electron-withdrawing substituents on the metallacarborane platform.

With the aim to lower even further the requirements of these metallacarboranes, we tested the behavior of the three catalysts in the photoredox oxidation of diphenylmethanol using only water, no buffer, and NEt_3 or K_2CO_3 as base. In the case of catalyst **Na[1]**, the wavelength of the lamp used was 300 nm, closer to the absorption maximum of observed in the UV/Vis spectrum (293 nm). The results listed in Table 3 reveal that the three catalysts show high performance in water in the

Table 2. Oxidation tests performed with chlorinated cobaltabisdicarbollide complexes **Na[Cl$_2$-1]** and **Na[Cl$_6$-1]**. Conditions: catalyst (0,08 mM), substrate (20 mM), $Na_2S_2O_8$ (40 mM), NEt_3(40 mM), 5 mL 0.1 M phosphate buffer solution at pH 7.2, light irradiation for 4, 6, and 8 h. Percentage yields.[a]

| Substrate | 8 h, $\lambda = 253.7$ nm | | 4 h, $\lambda = 352$ nm | | 6 h, $\lambda = 352$ nm | |
	Na[Cl$_6$-1]	Na[Cl$_2$-1]	Na[Cl$_6$-1]	Na[Cl$_2$-1]	Na[Cl$_6$-1]	Na[Cl$_2$-1]
OH / CH₃ (phenyl)	40	50	60	53	92	86
phenyl-CH₂-OH	22	32	61	63	90	81
H₃C-phenyl-CH₂-OH	45	40	67	46	>99	85
Cl-phenyl-CH₂-OH	21	30	82	60	85	77
diphenyl-CH-OH	68	89	93	90	>99	93

[a] Yields of products were determined by NMR spectroscopy (see Supporting Information).

◣◣ These are not the final page numbers!

Table 3. Oxidation tests on diphenylmethanol performed with **Na[1]**, **Na[Cl₂-1]**, and **Na[Cl₆-1⁻]**. Conditions: catalyst (0,08 mM), substrate (20 mM), Na₂S₂O₈ (40 mM), 5 mL of an aqueous solution containing 40 mM of NEt₃ or K₂CO₃. Light irradiation for 6 h.

Catalyst	Yield [%] (water/NEt₃)	Yield [%] (water/K₂CO₃)
Na[1], $\lambda = 300$ nm	96	> 99
Na[Cl₂-1], $\lambda = 352$ nm	89	89
Na[Cl₆-1], $\lambda = 352$ nm	93	94

absence of phosphate buffer, and their activities are slightly enhanced in all cases when organic base NEt₃ is replaced by inorganic base K₂CO₃. The results shown by catalyst [1]⁻ in these two media, (NEt₃ or K₂CO₃) after 6 h of reaction with a 300 nm lamp are noteworthy. The yields achieved were slightly higher (96 and > 99 %, respectively) than those obtained in phosphate buffer after 8 h (94 %; see Table 1, entry 5).

Considering the good results shown above, one step further was the replacement of Na₂S₂O₈ by air. In a preliminary study, we performed the oxidation of diphenylmethanol in water/K₂CO₃ using [1]⁻ as a reference catalyst and an air stream during 6 h of irradiation ($\lambda = 300$ nm). We observed 98 % yield with total formation of benzophenone. This preliminary and promising result, which is a step towards the development of practical processes with inorganic catalyst systems based on boron compounds, is unprecedented in the literature. More studies are being carried out in this regard.

To learn whether water was a key reaction medium, we tested the oxidation of diphenylmethanol in acetonitrile with NEt₃ as base and an air stream as oxidant. After 6 h of irradiation, practically no conversion was observed. Then the reaction medium was changed to acetonitrile/water in 9/1 and 8/2 ratio with K₂CO₃, and after 6 h of irradiation conversions of 26 and 34 % were obtained, respectively, with exclusive formation of benzophenone. This result may indicate that the acetonitrile in water/acetonitrile mixtures displaces the necessary water molecules for the catalysis to occur from the vicinity of [3,3′-Co(1,2-C₂B₉H₁₁)]⁻ and thus prevents electron transfer, which is in agreement with experimental values reported earlier.[33] These results indicate that water is a key participant for these systems to work efficiently as catalysts in the photoredox oxidation processes. The fact that an all-inorganic catalyst system consisting of water as solvent, K₂CO₃ as base, a metallabisdicarbollide photoredox catalyst with fully inorganic ligands and an earth-abundant transition metal, and air as oxidizing agent can oxidize alcohols to aldehydes or ketones indicates the feasibility of all-inorganic catalytic processes with earth-abundant transition metals.

Photocatalytic oxidations under uncommon conditions (0.01–0.1 mol % of catalyst (0.002 mM to 0.02 mM catalyst)
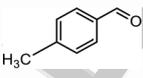
As mentioned above, a sixfold increase in catalyst concentration from 0.4 mol % (0.08 mM) to 2.5 mol % (0.5 mM) of [1]⁻ results only in a 1.7-fold increase in conversion, whereas the UV/Vis absorption spectrum increases according to the increase in concentration. This seems to indicate that lower concentrations of catalyst are more effective. Hence, we kept the concentrations of substrate and oxidizing agents constant, as in the earlier described experiments, but we reduced the catalyst loading to 0.1 mol % (0.02 mM) and 0.01 mol % (0.002 mM) as opposed to the original 0.4 mol % (0.08 mM), corresponding to catalyst:substrate:oxidizing agent ratios of 1:1000:2000 and 1:10000:20000, all in homogeneous phase. For these experiments, we used K₂CO₃ as base, a total irradiation time of 8 h, and pH 7, with readjustment at $t = 4$ h. Control experiments revealed that no reaction occurred in the absence of photocatalyst **Na[1]** or light. Table 4 lists the results corresponding to the photooxidation of different alcohols, including aliphatic alcohols. In general primary and secondary aromatic alcohols with different substituents were found to be effective in the photooxidation process, and the primary aromatic alcohols were slightly less reactive than the secondary ones. The yields observed for 1-phenylethanol (**1**) and diphenylmethanol (**5**) were remarkable, greater than 99 % in both cases for 0.01 mol % catalyst loading (0.002 mM). To the best of our knowledge these are among the highest turnover numbers (TON = 10000) achieved in alcohol photoredox oxidation under homogeneous conditions. With the same catalyst loading of 0.01 mol % (0.002 mM), **Na[1]** shows high efficiency towards primary and secondary aliphatic alcohols, with yields greater than 90 % and selectivities greater than 99 %. Cyclohexanol was converted to **6** in 93 % yield, and 1-butanol and 2-ethoxyethanol were converted to the corresponding acids in yields of 90 % (**7**) and 95 % (**8**), respectively. The observed quantitative conversion with 1-phenylethanol and diphenylethanol is in support of the pathway shown in Figure 4. If 1 mol of S₂O₈²⁻ is needed for each mole of alcohol to perform the oxidation reaction, on lowering the fraction of oxidizing agent the conversion should be decreased if the ratio of oxidizing agent to substrate is smaller than 1:1. Under the same conditions as in Table 4, but with reduced amount of oxidizing agent (ratio 1:10000:10000), the degree of conversion should still be close to 100 %, although it could be a bit lower due to the kinetics of the reaction; we found 91 %, and if the ratio is lowered to 1:10000:5000, the maximum yield would be 50 %, and we found 43 %. This is fully consistent with the pathway shown in Figure 4.Further studies on the application of these cobaltabisdicarbollides as photoredox catalysts to other substrates are underway.

Conclusion

It has been demonstrated for the first time that [3,3′-Co(1,2-C₂B₉H₁₁)₂]⁻ and its chloro derivatives [3,3′-Co(8-Cl-1,2-C₂B₉H₁₀)₂]⁻ and [3,3′-Co(8,9,12-Cl₃-1,2-C₂B₉H₈)₂]⁻ are efficient tunable photoredox catalysts for the oxidation of alcohols in water, including aliphatic alcohols, through single-electron-transfer processes. This behavior is possible thanks to properties of metallacarboranes, such as their high solubility in water, their lack of photoluminescence, easy modification of the HOMO–LUMO gap, and high oxidizing power of the Co⁴⁺/³⁺ couple.

Table 4. Substrate scope of photooxidation of alcohols by **Na[1]**.[a]

$>99\%$, TON = 1000 (0.1 mol%)
$>99\%$, TON = 10 000 (0.01 mol%)

$>96\%$, TON = 9600 (0.1 mol%)

$>97\%$, TON = 9600 (0.1 mol%)
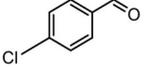
$>94\%$, TON = 9400 (0.01 mol%)
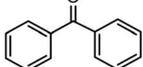
$>99\%$, TON = 1000 (0.1 mol%)
$>99\%$, TON = 10 000 (0.01 mol%)

93 %, TON = 9300 (0.01 mol%)
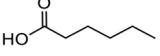
91 %, TON = 9100 (0.01 mol%)
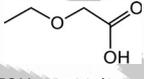
97 %, TON = 9700 (0.01 mol%)

[a] Conditions: **Na[1]** (0.002 or 0.02 mM), substrate (20 mM), $Na_2S_2O_8$ (40 mM), 5 mL potassium carbonate solution at pH 7; light irradiation for 8 h by using a lamp with $\lambda = 300$ nm; yields and TONs obtained are shown together with loading of **Na[1]** in parentheses.

Computational studies showed that LMCT takes place on excitation at 293 nm, probably due to the difference in electronegativity between Co and B (-0.16) and evidence that a strong Co^{IV} oxidizing agent can be obtained in a photoinduced manner, which seems to be responsible for the good performance of the catalysts.

$[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$ and derivatives showed high conversions and selectivities in the photooxidation of alcohols, with yields of 90–95 % at catalyst loadings of 0.4 mol% (0.08 mM) in neutral media. Further, the catalyst can be recovered easily by precipitation on addition of [NMe$_4$]Cl. A promising result is the high conversion (98 %) obtained in the photooxidation of diphenylmethanol by $[1]^-$ with an air stream as oxidizing agent. This is a step towards the development of practical processes with inorganic catalyst systems based on boron compounds.

The more striking fact was that, on reducing the catalyst load to 0.01 mol% (0.002 mM), the high performance of **Na[1]** in the oxidation of alcohols, including aliphatic alcohols, is maintained. High yields of the corresponding aldehyde or ketone were achieved, greater than 99 % in the case of 1-phenylethanol, and diphenylmethanol, with a TON of 10 000. This value is among the highest TONs achieved in the alcohol photoredox oxidation under homogeneous conditions. A possible pathway is also proposed.

In summary, we have shown that $[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]^-$ and its chloro derivatives are efficient compounds acting both as catalysts and photosensitizers for the photooxidation of alcohols. They operate in a catalyst system in which the solvent is water, the metal in the catalyst is an earth-abundant transition metal, the ligand is inorganic, the base is an inorganic salt, the oxidizing agent is an inorganic salt or air, and the excitation source is light. The only organic compound in the mixture is the substrate. This work opens wide opportunities for inorganic catalysts to work under ideal catalytic conditions.

Experimental Section

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 deionized water was obtained by passing distilled water through a Milli-Q water purification system. $Na[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]$ (**Na[1]**) was synthesized from commercial $Cs[3,3'\text{-Co}(1,2\text{-}C_2B_9H_{11})_2]$ (**Cs[1]**, Katchem Spol.sr.o), by following a method described in the literature,[25] similar to dichloro $(Na[3,3'\text{-Co}(8\text{-}Cl\text{-}1,2\text{-}C_2B_9H_{10})_2])$ and hexachloro $(Na[3,3'\text{-Co}(8,9,12\text{-}Cl_3\text{-}1,2\text{-}C_2B_9H_8)_2])$ derivatives.[26] The elemental analysis and NMR and IR spectra of all compounds compare well with those already reported in the literature.

UV/Vis spectroscopy was performed with a Cary 50 Scan (Varian) UV/Vis spectrophotometer with 1 cm quartz cells or with an immersion probe of 5 mm path length. NMR spectra were recorded with a Bruker ARX 300 instrument; ^{1}H NMR spectra were recorded in CDCl$_3$. Chemical shifts were referenced to SiMe$_4$. Mass spectra were recorded in negative-ion mode with a Bruker Biflex MALDI-TOF [N$_2$ laser; $\lambda_{exc} = 337$ nm (0.5 ns pulses); voltage ion source 20 000 kV (Uis1) and 17 500 kV(Uis2)] without matrix. The intensity of the laser was fixed at 30 %.

Computational details

All calculations were carried out with the Gaussian 09 program package[34] at the B3LYP/6-311+G** level of theory. For Ru the Def2TZVP basis set was used. Full geometry optimization calculations were performed and harmonic vibrational frequencies were calculated to establish the nature of the stationary points obtained, as characterized by no one negative eigenvalue of the Hessian for minima structures. The NTOs, electron and hole distributions, and charge-density difference maps were calculated with the Multiwfn program.[35] For the visualization the MOLDEN[36] and VMD programs[37] were used.

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Photocatalytic oxidation studies

A quartz tube containing an aqueous solution (5 mL) at pH 7.2 (phosphate buffer) with **Na[1]**, **Na[Cl$_2$-1]**, or **Na[Cl$_6$-1]** as catalyst, alcohol as substrate, and Na$_2$S$_2$O$_8$ or an air stream as sacrificial acceptor was exposed to UV light (2.2 W, $\lambda = 253.7$, 300, or 352 nm) for different times. The complex:substrate:sacrificial oxidant ratios used (1:250:500, 1:1000:2000, 1:10000:20000, 1:10000:10000, and 1:10000:5000 corresponding to concentrations of 0.08:20:40 mm, 0.02:20:40 mm, and 0.002:20:40 mm), were varied according to the study. For each experiment, light illumination was supplied by a light reactor with twelve lamps that produce UVA light at room temperature. The resulting solutions were extracted with CH$_2$Cl$_2$ three times in the case of aromatic alcohols and with diethyl ether in the case of aliphatic alcohols. The solution was dried with anhydrous sodium sulfate and the solvent was evaporated under reduced pressure. To check the reproducibility of the reactions all the experiments were carried out three times. The reaction products were quantified and characterized by ^{1}H NMR spectroscopy. For comparison with NMR measurements, the oxidation products were also determined by gas chromatography. In a second set of experiments, NEt$_3$ or K$_2$CO$_3$ was added to water as a base.

Gas chromatography studies

Gas chromatography was performed with a GC-2010 Gas Chromatograph from Shimadzu, equipped with an Astec CHIRALDEX G-TA column, 30 m × 0.25 mm (i.d); FID detector, 250 °C; injection: 250 °C; carrier gas: helium; rate: 1.57 mL min^{-1}; area normalization. All products and their corresponding substrates of catalysis were detected under the following conditions: column temperature: 80 °C for 5 min, raised to 170 °C at a rate of 10 °C min^{-1}, held at 170 °C for 2 min. The product analyses in the catalytic experiments with 1-phenylethanol, benzyl alcohol, and 4-methylbenzyl alcohol were performed by GC with biphenyl as internal standard. In the case of the product analysis in the catalytic experiment with 4-chlorobenzyl alcohol, naphthalene was used as internal standard.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

Keywords: carboranes · cobalt · homogeneous catalysis · oxidation · photochemistry

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FULL PAPER

Catalyst and photosensitizer: Cobalta-bisdicarbollide $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ and its chloro derivatives are both efficient catalysts and photosensitizers for the photooxidation of alcohols in water through single-electron-transfer processes. This behavior is due to their high solubility in water, lack of photoluminescence, easy modification of the HOMO–LUMO gap, and high oxidizing power for the $Co^{4+/3+}$ couple, among others. High performance is achieved with a catalyst loading of only 0.01 mol%.
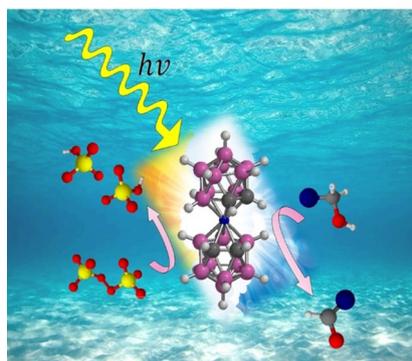
■ **Photooxidation**

I. Guerrero, Z. Kelemen, C. Viñas,
I. Romero,* F. Teixidor*

■■ – ■■

Metallacarboranes as Photoredox Catalysts in Water

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Isabel Guerrero
Zsolt Kelemen
Clara Viñas http://orcid.org/0000-0001-5000-0277
Isabel Romero http://orcid.org/0000-0003-4805-8394
Francesc Teixidor http://orcid.org/0000-0002-3010-2417

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