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COMMUNICATION

Carboranycarboxylate complexes as efficient catalysts in epoxidation reactions

Mònica Fontanet, [a] Montserrat Rodríguez, [a] Clara Viñas, [b] Francesc Teixidor*[b] and Isabel Romero*[a]

Dedicated to Prof. Evamarie Hey-Hawkins for her high contribution to the Boron and Phosphorous chemistries on the occasion of her 60th birthday.

Abstract: This work presents the first examples of carboranylcarboxylate complexes as precatalysts in epoxidation reactions using peracetic acid as oxidant. The manganese complexes $[Mn(\mu\text{-}H_2O)(1\text{-}CH_3\text{-}2\text{-}CO_2\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10})_2]_n\cdot(H_2O)_n$, **1**, $[Mn_2(1\text{-}CH_3\text{-}2\text{-}CO_2\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10})_4(bpy)_2]$, **2**, $[Mn(1\text{-}CH_3\text{-}2\text{-}CO_2\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10})_2(bpm)]_n$, **3,** $[Mn(1\text{-}CH_3\text{-}2\text{-}CO_2\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10})_2(bpy)_2]$, **4**, the cobalt complex $[Co_2(\mu\text{-}H_2O)(1\text{-}CH_3\text{-}2\text{-}CO_2\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10})_4(THF)_4]$, **6**, all containing the carboranylcarboxylic ligand, $1\text{-}CH_3\text{-}2\text{-}CO_2H\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}$ **(LH),** together with $Mn_3(OAc)_6(bpy)_2$ **5**, display good performance with high conversion and selectivity values in short reaction times, in most cases. The work highlights that the coordination of the carboranylcarboxylic ligand LH to the metal ions is crucial in the performance of the complexes as catalysts.

Introduction

Metal-catalyzed oxidation reactions are one of the most significant electron transfer reactions in chemistry and biology.[1] Selective olefin epoxidation has received considerable interest from both academics and industry since epoxides play an important role as intermediates and buildings blocks in organic chemistry and materials science.[2] Few manganese complexes containing carboxylate ligands have been reported as catalysts in oxidation reactions; among them, the trinuclear manganese complex $[Mn_3(OAc)_6(2,2'\text{-}bpy)_2]$ has proved to be a highly efficient catalyst in the epoxidation of alkenes using peracetic acid as oxidant.[3] In the case of cobalt, to the best of our knowledge, no carboxylate cobalt compound has been evaluated as epoxidation catalyst using this oxidant. The 1,2-dicarba-*closo*-dodecaborane cluster, *ortho*-$C_2B_{10}H_{12}$, and its derivatives are clusters with uncommon characteristics such as low nucleophilicity, chemical inertness,[4] thermal stability,[5] electron-withdrawing properties,[6] stability and low toxicity in biological systems[7] that have stimulated the development of a

wide range of potential applications based on a molecular approach for the preparation of materials.[8] Although a large number of half- and mixed sandwich metalladicarbollide complexes have been reported as active catalysts[9] in organic transformations such as olefin cyclopropanation,[10] alkene hydroformylation,[11] Kharasch addition to olefins,[12] asymmetric hydrogenation of enamides,[13] hydrogenation of alkenes[14] as well as in polymerization reactions,[15] complexes containing *closo*-carboranylcarboxylate ligands have never been tested in metal-catalyzed oxidation reactions. Consequently, the use of metalla-*closo*-*o*-carboranes as catalysts in oxidation reactions is a field to be explored for their particular characteristics that shall induce unconventional properties in the studied oxidation processes. Previously, we have studied the coordination of $1\text{-}CH_3\text{-}2\text{-}CO_2H\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}$ ligand to Mn^{II} and Co^{II} ions together with their physical and chemical properties.[16],[17] In this work we study the reactivity of some of the previously reported manganese and cobalt complexes (Scheme 1) towards the epoxidation of some aromatic and aliphatic alkenes using peracetic acid as the oxidant. For purpose of comparison, we have also studied the performance of the trinuclear acetate manganese (II) complex $[Mn_3(OAc)_6(2,2'\text{-}bpy)_2]$ in the epoxidation reactions; besides, the role of the carboranylcarboxylic ligand $1\text{-}CH_3\text{-}2\text{-}CO_2H\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}$ in these processes has been evaluated. These systems constitute the first examples of carboranylcarboxylate manganese and cobalt complexes described in the literature that have been tested in the epoxidation of alkenes.

Results and Discussion

The catalytic activity of the manganese complexes $[Mn(\mu\text{-}H_2O)(1\text{-}CH_3\text{-}2\text{-}CO_2\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10})_2]_n\cdot(H_2O)_n$, **1,** $[Mn_2(1\text{-}CH_3\text{-}2\text{-}CO_2\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10})_4(2,2'\text{-}bpy)_2]$ **2**, $[Mn(1\text{-}CH_3\text{-}2\text{-}CO_2\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10})_2(bpm)]_n$ **3**, $[Mn(1\text{-}CH_3\text{-}2\text{-}CO_2\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10})_2(2,2'\text{-}bpy)_2]$ **4**, and $[Mn_3(OAc)_6(2,2'\text{-}bpy)_2]$ **5**, as well as the cobalt complex $[Co_2(\mu\text{-}H_2O)(1\text{-}CH_3\text{-}2\text{-}CO_2\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10})_4(THF)_4]$, **6** and the $1\text{-}CH_3\text{-}2\text{-}CO_2H\text{-}1,2\text{-}closo\text{-}C_2B_{10}H_{10}$ ligand (**L**H) (Scheme 1), were investigated in the epoxidation of alkenes in CH_2Cl_2 using commercial peracetic acid (32%) as oxidant. In the absence of catalyst and in presence of Mn^{II} or Co^{II} salts, no significant epoxidation of olefin occurred, with conversion values below 3%. In all cases, benzaldehyde was detected as a side product of the oxidation reaction. Preliminary catalytic studies using styrene as substrate (see Table1) showed total conversion of styrene in 4 minutes for all the manganese complexes tested, with the polymeric complexes **1** and **3**

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displaying the highest selectivity values. However, in the case of the cobalt complex (entries 7-8) moderate conversions and selectivity values are observed. [Mn$_3$(OAc)$_6$(2,2'-bpy)$_2$] (entry 6) displays similar high conversion values that our compounds, with a slight increase of selectivity values with regard to **2** and **4**, however with lower selectivity values than the displayed by our polymeric compounds **1** and **3**. In the case of using LH as catalyst, no epoxide was observed after 4 minutes.

1-CH$_3$-2-COOH-1,2-*closo*-C$_2$B$_{10}$H$_{10}$ (LH)
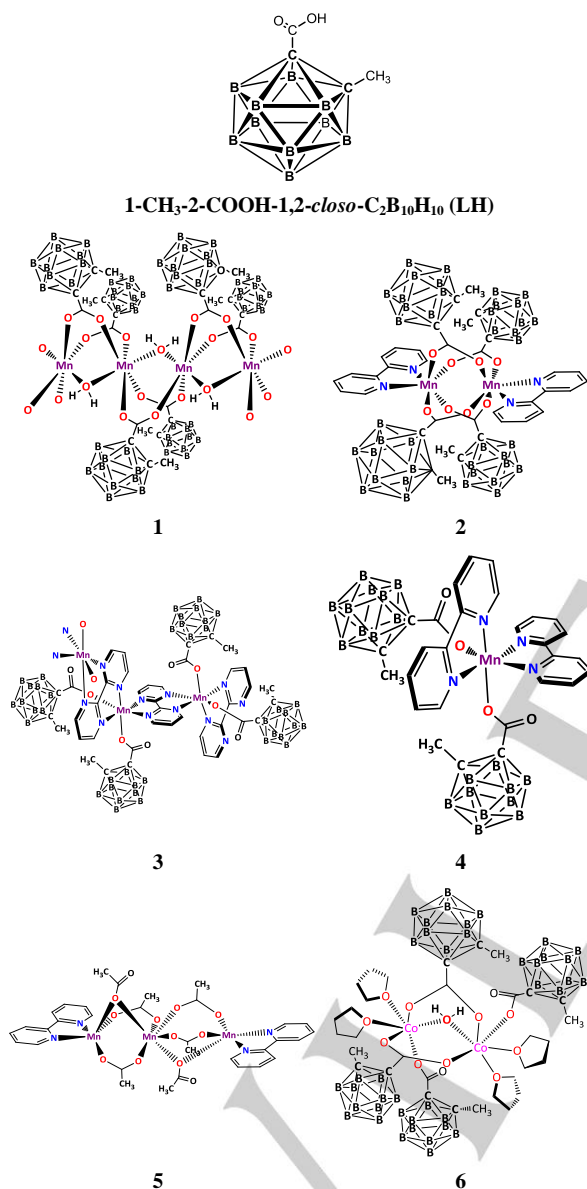
Scheme 1. Schematic representation of the ligand and the metal complexes utilized in the present work.

The results observed with these manganese complexes are promising since it is well known that the epoxidation reactions of aromatic olefins are sluggish, leading to significant amounts of secondary products, in some cases.[18] A study of the stability of the ligand in peracetic acid 32% was carried out by NMR and IR spectroscopies (see SI). The ^{11}B{^{1}H} NMR spectrum resonances

appeared in the same region, from δ -1.0 to -10.0 ppm, and showing the same 2:2:6 pattern characteristic of a *closo* cluster as the just synthesised **L**H. No signals of *nido*-shaped [7, 8-C$_2$B$_9$H$_{10}$]$^-$ or [7,8-C$_2$B$_9$H$_9$]$^{2-}$ anions or B(OCH$_3$)$_3$ has been observed in NMR spectra after reaction with the acid. In addition, each resonance splits in the ^{11}B NMR spectrum which confirms that all of the hydrogen atoms bonded *exo*-cluster of the **L**H has not been substituted as Xie and co-workers have recently reported.[19] The IR spectra of the **L**H after being for 1 hour in peracetic acid at the ratios (1:1) and (1:200) were recorded and compared with the pure **L**H ligand (see S. I.). No changes were observed neither in the typical υ(B-H) absorption at frequencies above 2590 cm^{-1}, characteristic of *closo* carborane derivatives,[20] nor above 1270 and 1720 cm^{-1}, that correspond to the frequencies of the symmetric and antisymmetric stretches of the carboxylate groups of the **L**H ligand. These evidences lead us to conclude that the carboranylcarboxylate ligand **L**H remains unaltered after reaction with peracetic acid 32%.

Table 1. Catalytic oxidation of styrene by Mn(II) and Co(II) complexes and LH using CH$_3$CO$_3$H as oxidant. Conditions: catalyst (2.6 µmol), substrate (260 µmol), peracetic acid 32% (520 µmol), CH$_2$Cl$_2$ (2.5 mL). Oxidant added at 0ºC, then reaction at room temperature for the time indicated. % yields are determinated by GC.

Entry	Cat	Conv (%)	Epoxide yield (%)	Sel (%)[a]	Time (min)
1	1	96	58	61	4
2	1	100	77	77	30
3	2	100	44	44	4
4	3	100	76	76	4
5	4	100	44	44	4
6	5	99	58	58	4
7	6	21	12	56	4
8	6	39	9	23	30
9	LH	10	0	0	4
10	LH	25	6	23	30
11	LH	29	16	55	120

[a] Calculated as [epoxide yield/substrate conversion] x 100

We have also studied the complexes as catalysts in the epoxidation of other olefins maintaining 4 minutes as reaction time. Table 2 displays the performed epoxidation tests using the manganese complexes **1-5** on different substrates. As can be observed, high conversion (in some cases are close to 100%) and moderate to high selectivity values have been achieved in most cases. When 4-vinyl-1-cyclohexene is used as substrate (entry 2), it is noticeable that the reaction is regiospecific, with all catalysts leading solely to the epoxidation of the ring alkene

position. This suggests that an electrophilic active species could be responsible for the attack at the more electron-rich alkene in the ring of substrate.[21]

Regarding the epoxidation of *cis-β*-methylstyrene (entry 3), it is remarkable the high stereoselectivity towards the formation of the *cis*-epoxide in all the compounds containing the carboranylcarboxylate ligand with regard to the trinuclear complex [Mn$_3$(OAc)$_6$(2,2'-bpy)$_2$], **5**, that generates 67% of *cis*-epoxide as consequence of the isomerization to a 33% of *trans*. The *cis→trans* isomerization in epoxidation processes involving *cis* alkenes is a common phenomenon due to the higher thermodynamic stability of the *trans* epoxides. These results suggest that a relatively long-lived free radical is formed from the substrate and during the subsequent oxygen transfer process the C-C bond rotation, leading to *cis/trans* isomerization, occurs at a rate faster than the ring closing. [22] However, the radical intermediate species formed for complexes **1-4**, containing the carboranylcarboxylate ligand, must be short-lived than those of complex **5** thus improving the stereoselectivity of the reaction. These results suggest that a lower barrier for the closure of the *cis* epoxide than for the isomerisation step takes place when the carboranylcarboxylate is present. Therefore, it is clear that the carborane cluster must have a distinctive electronic and/or structural influence in the stabilization of the intermediate species formed, with respect to acetate ligand and consequently in the *cis/trans* selectivity values observed.

Table 2. Epoxidation tests performed with manganese complexes 1-5. Conditions: catalyst (2.6 μmol), substrate (260 μmol), CH$_2$Cl$_2$ (2.5 mL). Peracetic acid 32% (520 μmol) added at 0ºC, then reaction at RT. % yields are determinated by Gas Chromatography (GC).
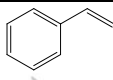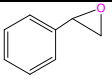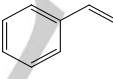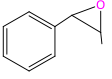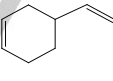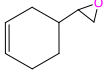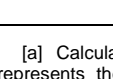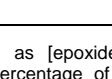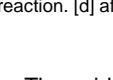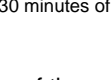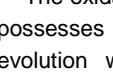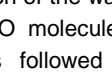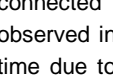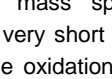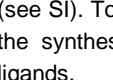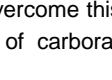
Complex	1		2		3		4		5	
Substrate	Conv (%)	Sel (%)[a]	Conv (%)	Sel (%)[a]	Conv (%)	Sel (%)[a]	Conv (%)	Sel (%)[a]	Conv (%)	Sel (%)[a]
1	96	61	100	44	100	76	100	44	99	58
2	70	91	89	40[c]	100	55	100	45	97	68
3	90	75 (*79*)[b]	99	80 (*88*)[b]	100	66 (*94*)[b]	98	82 (*87*)[b]	75	75 (*67*)[b]
4	95	80	100	97	100	95	100	88	100	100
5	61	72	95	41	98	46	83	54	83	56
6	86	70	100	63	100	74	100	48	100	83

[a] Calculated as [epoxide yield/substrate conversion] x 100. [b] In parentheses, the percentage of *cis* isomer obtained.

The catalytic activity was also tested with the aliphatic substrate 1-octene (entry 5). The compounds provide good conversion values and moderate selectivity in the epoxidation of this substrate, being remarkable the selectivity displayed by the polymer **1**, which improves the results shown by other catalysts reported in the literature, where modest performance is generally observed toward inactivated monosubstituted alkenes.[23]

The catalytic activity of [Co$_2$(μ-H$_2$O)(1-CH$_3$-2-CO$_2$-1,2-*closo*-C$_2$B$_{10}$H$_{10}$)$_4$(THF)$_4$], **6**, has been also tested and the results obtained are gathered in Table 3. The catalyst shows only moderate performance for all the substrates tested. The conversion values improve after 30 minutes of reaction but a decrease in the selectivity is also observed except for the 4-vinyl-1-cyclohexene substrate. The epoxidation of *cis-β*-methylstyrene with **6** results in moderate stereoselectivity value which evidences a long-lived radical intermediate species in this case. Finally, catalyst **6** leads specifically to the epoxidation of the ring alkene position at the 4-vinyl-1-cyclohexene substrate.

Table 3. Epoxidation tests performed with cobalt complex **6**. Conditions: catalyst (2.6 μmol), substrate (260 μmol), CH$_2$Cl$_2$ (2.5 mL). Peracetic acid 32% (520 μmol) added at 0ºC, then reaction at RT. % yields are determinated by GC.

Substrate	Product	Conv. (%)	Select. (%) [a]
		21 [c]	56 [c]
		39 [d]	23 [d]
		16 [c]	46 [c] *c/t*=49% [b]
		42 [d]	45[d] *c/t*=62% [b]
		41 [c]	55 [c]
		67 [d]	70 [d]

[a] Calculated as [epoxide yield/substrate conversion] x 100. [b] c/t represents the percentage of *cis* isomer obtained. [c] after 4 minutes of reaction. [d] after 30 minutes of reaction

The oxidation of the water was tested by using polymer **1** that possesses H$_2$O molecules bridging two Mn metals. The gas evolution was followed by means of gas chromatography connected to mass spectrometer and O$_2$ formation was observed in a very short time but this evolution decreases with time due to the oxidation of the carboxylic group of the ligand (see SI). To overcome this difficulty, we are currently working on the synthesis of carboranylphosphinic acids, purely inorganic ligands.

Conclusions

The catalytic activity of manganese and cobalt compounds containing all the carboranylcarboxylate ligand, 1-CH$_3$-2-CO$_2$-1,2-*closo*-C$_2$B$_{10}$H$_{10}$ **LH**, have been tested in the epoxidation of aliphatic and aromatic alkenes using peracetic acid as oxidant. Manganese complexes have proven to be active in the epoxidation of alkenes after 4 minutes of reaction, showing total conversion and high selectivity values, in most of the cases, whereas the cobalt complex displays less activity. The catalytic results highlight the role of the carboranylcarboxylate ligand in the selectivity of the processes, where the carborane cluster seems to have a distinctive electronic and/or structural influence in the stabilization of the intermediate species formed with respect to acetate. It is found that the coordination of the carboranylcarboxylate ligand LH to the metal ion is crucial in the performance of the compounds as catalysts.

Experimental Section.

Materials and preparations: 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. 1-CH$_3$-1,2-*closo*-C$_2$B$_{10}$H$_{11}$ was purchased from Katchem. 1-CH$_3$-2-CO$_2$H-1,2-*closo*-C$_2$B$_{10}$H$_{10}$ [24] carboranylcarboxylate complexes tested **1**[16a] **2-4**[16b] **6** [17] and [Mn$_3$(OAc)$_6$(2,2'-bpy)$_2$][3] complex were prepared according to literature procedures. All the oxidation manipulations were performed under inert atmosphere.

Instrumentation and Measurements: GC measurements were taken in a Shimadzu GC-2010 gas chromatography apparatus equipped with an Astec CHIRALDEX G-TA column and a FID detector. FT-IR spectra were taken in a Mattson-Galaxy Satellite FT-IR spectrophotometer containing a MKII Golden Gate Single Reflection ATR System. NMR spectra were recorded with a Bruker ARX 300 or a DPX 400 instrument equipped with the appropriate decoupling accessories. ^{1}H and ^{1}H{^{11}B} NMR (300.13/400.13 MHz), ^{13}C{^{1}H} NMR (75.47/100.62 MHz) and ^{11}B and ^{11}B{^{1}H} NMR (96.29/128.37 MHz) spectra were recorded in d$_6$-acetone, CD$_2$Cl$_2$ and D$_2$O . Chemical shift values for ^{11}B NMR spectra were referenced to external BF$_3$←OEt$_2$ and those for ^{1}H, ^{1}H{^{11}B} and ^{13}C{^{1}H} NMR spectra were referenced to Si(CH$_3$)$_4$. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants in Hz.

Catalytic epoxidation: a CH$_2$Cl$_2$ (2.5 mL) solution of alkene (260 μmol), catalyst (2.6 μmol) and biphenyl (250 μmol, internal standard) was prepared in a 5 mL flask and cooled in an ice bath. Afterwards, 32 % peracetic acid (520 μmol) was slowly added via syringe under stirring at 0ºC. The reaction vessel was then taken out of the ice bath and allowed to progressively warm to room temperature. Each aliquot of the reaction taken for analysis was filtered through a basic alumina plug and was analysed in a Shimadzu GC-2010 gas chromatography apparatus equipped with an Astec CHIRALDEX G-TA column and a FID detector. Quantification was achieved from calibration curves.[21]

Catalytic water oxidation: the water oxidation measurements were carried out by GC-MS. To a flask containing 112 mg (0.204 mmols) of Ce(NH$_4$)$_2$(NO$_3$)$_6$ under stirring and inert atmosphere, were added 2 mL of an aqueous solution of CF$_3$SO$_3$H (pH 1.0). Once the Ce^{IV} was dissolved, 0.51 mL of a solution 2mM of catalyst **1** in water was injected to the above solution under stirring and under nitrogen atmosphere. Immediately, measurements of the evolution of O$_2$ vs time were recorded.

Acknowledgements

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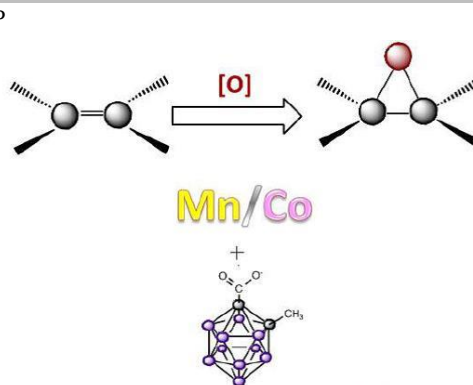
Oxidation catalysis*
Mònica Fontanet, [a]
Montserrat Rodríguez, [a]
Clara Viñas, [b] Francesc
Teixidor* [b] and Isabel
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