

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 carboranycarboxylate complexes as precatalysts in epoxidation reactions using peracetic acid as oxidant. The manganese complexes $[\text{Mn}(\mu\text{-H}_2\text{O})(1\text{-CH}_3\text{-2-CO}_2\text{-1,2-}i\text{closo-C}_2\text{B}_{10}\text{H}_{10})_2]_n \cdot (\text{H}_2\text{O})_n$, **1**, $[\text{Mn}_2(1\text{-CH}_3\text{-2-CO}_2\text{-1,2-}i\text{closo-C}_2\text{B}_{10}\text{H}_{10})_4(\text{bpy})_2]$, **2**, $[\text{Mn}(1\text{-CH}_3\text{-2-CO}_2\text{-1,2-}i\text{closo-C}_2\text{B}_{10}\text{H}_{10})_2(\text{bpm})]_n$, **3**, $[\text{Mn}(1\text{-CH}_3\text{-2-CO}_2\text{-1,2-}i\text{closo-C}_2\text{B}_{10}\text{H}_{10})_2(\text{bpy})_2]$, **4**, the cobalt complex $[\text{Co}_2(\mu\text{-H}_2\text{O})(1\text{-CH}_3\text{-2-CO}_2\text{-1,2-}i\text{closo-C}_2\text{B}_{10}\text{H}_{10})_4(\text{THF})_4]$, **6**, all containing the carboranycarboxylic ligand, 1-CH₃-2-CO₂H-1,2-*closo*-C₂B₁₀H₁₀ (**LH**), together with Mn₃(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 carboranycarboxylic 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 building 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 $[\text{Mn}_3(\text{OAc})_6(2,2'\text{-bpy})_2]$ 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*-C₂B₁₀H₁₂, 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 metalladicalcarbollide 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*-carboranycarboxylate 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-CH₃-2-CO₂H-1,2-*closo*-C₂B₁₀H₁₀ 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 $[\text{Mn}_3(\text{OAc})_6(2,2'\text{-bpy})_2]$ in the epoxidation reactions; besides, the role of the carboranycarboxylic ligand 1-CH₃-2-CO₂H-1,2-*closo*-C₂B₁₀H₁₀ in these processes has been evaluated. These systems constitute the first examples of carboranycarboxylate 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 $[\text{Mn}(\mu\text{-H}_2\text{O})(1\text{-CH}_3\text{-2-CO}_2\text{-1,2-}i\text{closo-C}_2\text{B}_{10}\text{H}_{10})_2]_n \cdot (\text{H}_2\text{O})_n$, **1**, $[\text{Mn}_2(1\text{-CH}_3\text{-2-CO}_2\text{-1,2-}i\text{closo-C}_2\text{B}_{10}\text{H}_{10})_4(2,2'\text{-bpy})_2]$, **2**, $[\text{Mn}(1\text{-CH}_3\text{-2-CO}_2\text{-1,2-}i\text{closo-C}_2\text{B}_{10}\text{H}_{10})_2(\text{bpm})]_n$, **3**, $[\text{Mn}(1\text{-CH}_3\text{-2-CO}_2\text{-1,2-}i\text{closo-C}_2\text{B}_{10}\text{H}_{10})_2(2,2'\text{-bpy})_2]$, **4**, and $[\text{Mn}_3(\text{OAc})_6(2,2'\text{-bpy})_2]$, **5**, as well as the cobalt complex $[\text{Co}_2(\mu\text{-H}_2\text{O})(1\text{-CH}_3\text{-2-CO}_2\text{-1,2-}i\text{closo-C}_2\text{B}_{10}\text{H}_{10})_4(\text{THF})_4]$, **6** and the 1-CH₃-2-CO₂H-1,2-*closo*-C₂B₁₀H₁₀ ligand (**LH**) (Scheme 1), were investigated in the epoxidation of alkenes in CH₂Cl₂ 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 Table 1) showed total conversion of styrene in 4 minutes for all the manganese complexes tested, with the polymeric complexes **1** and **3**

[a] Departament de Química
Universitat de Girona
Campus de Montilivi, E-17003 Girona, Spain.
E-mail: marisa.romero@udg.edu
<http://www.udg.edu/depa/>

[b] Institut de Ciència de Materials de Barcelona, ICMA-B-CSIC,
Campus UAB, E-08193 Bellaterra, Spain.
E-mail: teixidor@icmab.es
<http://www.icmab.es/lmi/>

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 $[\text{Mn}_3(\text{OAc})_6(2,2'\text{-bpy})_2]$, **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_2Cl_2 (2.5 mL). Peracetic acid 32% (520 μmol) added at 0°C, then reaction at RT. % yields are determined by Gas Chromatography (GC).

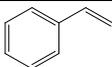
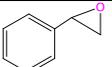
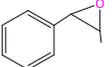
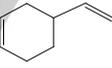
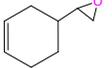
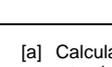
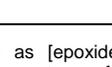
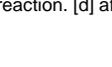
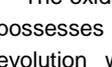
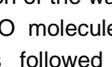
Complex	1		2		3		4		5	
	Conv (%)	Sel (%) ^a								
1	96	61	100	44	100	76	100	44	99	58
2	70	91	89	40 ^c	100	55	100	45	97	68
3	90	75 (79) ^b	99	80 (88) ^b	100	66 (94) ^b	98	82 (87) ^b	75	75 (67) ^b
4	95	80	100	97	100	95	100	88	100	100
5	61	72	95	41	98	46	83	54	83	56
6	86	70	100	63	100	74	100	48	100	83

[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 $[\text{Co}_2(\mu\text{-H}_2\text{O})(1\text{-CH}_3\text{-2-CO}_2\text{-1,2-}i\text{-}o\text{-C}_2\text{B}_{10}\text{H}_{10})_4(\text{THF})_4]$, **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_2Cl_2 (2.5 mL). Peracetic acid 32% (520 μmol) added at 0°C, then reaction at RT. % yields are determined 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_2O 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-CH₃-2-CO₂-1,2-*c/oso*-C₂B₁₀H₁₀ **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 Milli-Q water purification system. 1-CH₃-1,2-*c/oso*-C₂B₁₀H₁₁ was purchased from Katchem. 1-CH₃-2-CO₂H-1,2-*c/oso*-C₂B₁₀H₁₀ [24] carboranylcarboxylate complexes tested **1**^[16a] **2-4**^[16b] **6** [17] and [Mn₃(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. ¹H and ¹H{¹³C} NMR (300.13/400.13 MHz), ¹³C{¹H} NMR (75.47/100.62 MHz) and ¹¹B and ¹¹B{¹H} NMR (96.29/128.37 MHz) spectra were recorded in d₆-acetone, CD₂Cl₂ and D₂O. Chemical shift values for ¹¹B NMR spectra were referenced to external BF₃←OEt₂ and those for ¹H, ¹H{¹¹B} and ¹³C{¹H} NMR spectra were referenced to Si(CH₃)₄. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants in Hz.

Catalytic epoxidation: a CH₂Cl₂ (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 0°C. 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(NH₄)₂(NO₃)₆ under stirring and inert atmosphere, were added 2 mL of an aqueous solution of CF₃SO₃H (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 O₂ vs time were recorded.

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Keywords: carboranes • manganese • cobalt • oxidation • carboxylate

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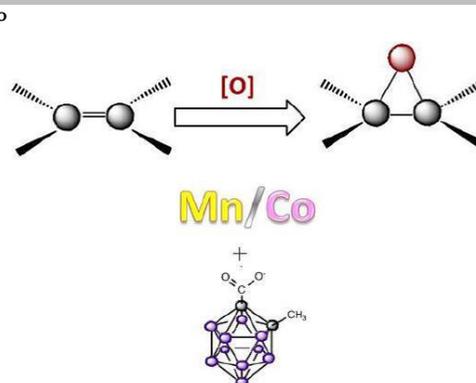
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First examples of carboranylcarboxylate complexes as precatalysts in epoxidation reactions display good performance with high conversion and selectivity values in short reaction times, in most cases; being crucial the coordination of the carboranylcarboxylate ligand to the metal ion in the performance of the compounds as catalysts.



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

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**Carboranylcarboxylate
 complexes as efficient
 catalysts in epoxidation
 reactions**

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