

Review

Metal Complexes Bearing Sulfur-Containing Ligands as Catalysts in the Reaction of CO₂ with Epoxides

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Abstract: Coupling of CO₂ with epoxides is a green emerging alternative for the synthesis of cyclic organic carbonates (COC) and aliphatic polycarbonates (APC). The scope of this work is to provide a comprehensive overview of metal complexes having sulfur-containing ligands as homogeneous catalytic systems able to efficiently promote this transformation with a concise discussion of the most significant results. The crucial role of sulfur as the hemilabile ligand and its influence on the catalytic activity are highlighted as well.

Keywords: homogeneous catalysis; sulfur; carbon dioxide; epoxides; cyclic carbonates; polycarbonates

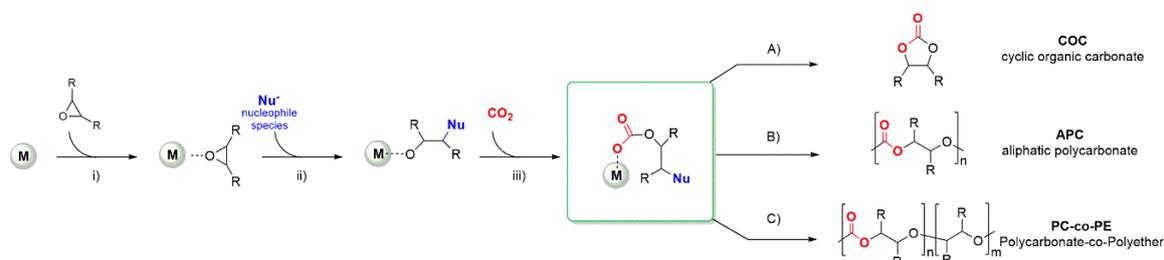
1. Introduction

Homogeneous catalysis is one of the most fast-developing areas of chemistry because of the possibility to finely tune the course of a given reaction by rational design of the catalyst architecture. Indeed, compared to heterogeneous catalysis, mechanisms governing the activity and selectivity are easier to be understood and therefore the overall performances can be consequentially greatly improved. In particular, the use of soluble transition-metal complexes in catalysis opened unprecedented possibilities to control the product features by a judicious modification of the electronic and steric properties of the ancillary ligand. Inspired by this simple concept, chemists have unfolded countless stereoselective reactions encompassing all families of chemical transformations (oxidations, cross-coupling reactions, polymerizations, etc.) [1–3].

Parallel to this trend, in the last two decades, the use of renewable feedstocks has gained momentum because of the growing demand for more sustainable chemical processes. In particular, carbon dioxide utilization (CDU) has emerged as an important tool for the transition to a carbon-neutral society because of the possibility to close, through the use of renewable energies, an anthropogenic carbon cycle avoiding net emission of greenhouse gases. Besides, CO₂ displays evident advantages in terms of toxicity, flammability, and the possibility of storage with respect to other C₁ feedstocks (such as phosgene and carbon monoxide) that render the implementation of industrial processes based on this molecule quite promising [4–9].

Among the possible products obtainable from CO₂, cyclic organic carbonates (COCs) and aliphatic polycarbonates (APCs) have received considerable attention because of their wide range of application and straightforward synthetic pathway starting from the corresponding epoxides [10–19]. The coupling between CO₂ and an epoxide can result in the formation of the cyclic product or of the polymeric one depending on many factors such as the nature of the substrate, the reaction conditions, and the catalytic system. Notwithstanding the efforts to develop efficient metal-free catalysts, most of the active systems are based on the combination of a metal complex activated by a suitable nucleophile, often added as ammonium or phosphonium salt. The basic reaction mechanism can be exemplified following the steps depicted in Scheme 1: (i) The coordination of the epoxide to the metal center; (ii) the ring-opening

of the activated epoxide by the nucleophilic attack and the formation of the metal-alkoxo bond; (iii) the insertion of CO₂. At this stage, the intermediate can give an intramolecular ring-closing with the formation of the COC (path A) or the alternating insertion of epoxide and CO₂ with the formation of the APC (path B). Since two consecutive insertions of the epoxide are possible as well (path C), often the resulting polymer also contains some polyether linkages [20].



Scheme 1. Mechanism of the coupling of CO₂ with epoxides [20].

The metal complexes successfully employed as catalysts in this reaction can be based both on main group metals such as Al, Mg, Ca [21–23] and on transition metals such as Ti, Cr, Fe, Co, Nb, La, and Zn [17,18,20,24–28]. Some examples of highly active catalysts for the formation of cyclic carbonates are given in Figure 1 [22,25,29,30].

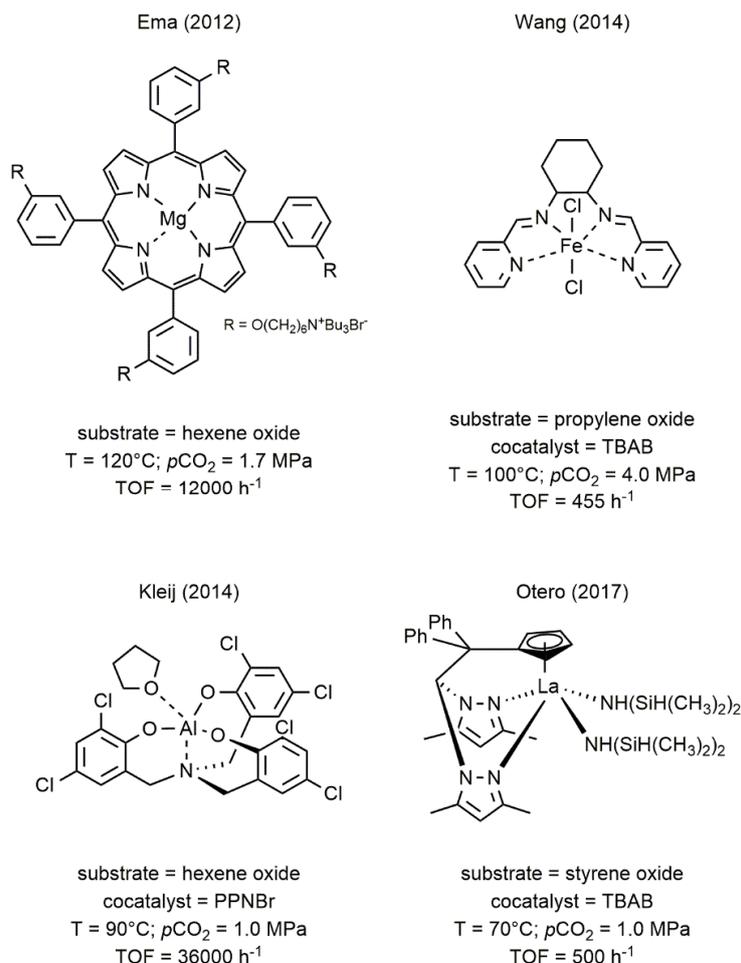


Figure 1. Selected catalytic systems for the synthesis of cyclic organic carbonates (COC) from CO₂ and epoxides [22,25,29,30].

As for other metal-mediated catalytic transformations, also in this case the Lewis acidic metal center requires to be wrapped by a suitable ligand environment in order to reach good performances in terms of activity and selectivity. Indeed, the most active catalysts developed for the alternating copolymerization of CO₂ with epoxides bear well-known structural motifs as the ligand framework, modified, in some cases, to allow obtaining binuclear complexes [31–37]. Some of the most efficient systems are reported in Figure 2.

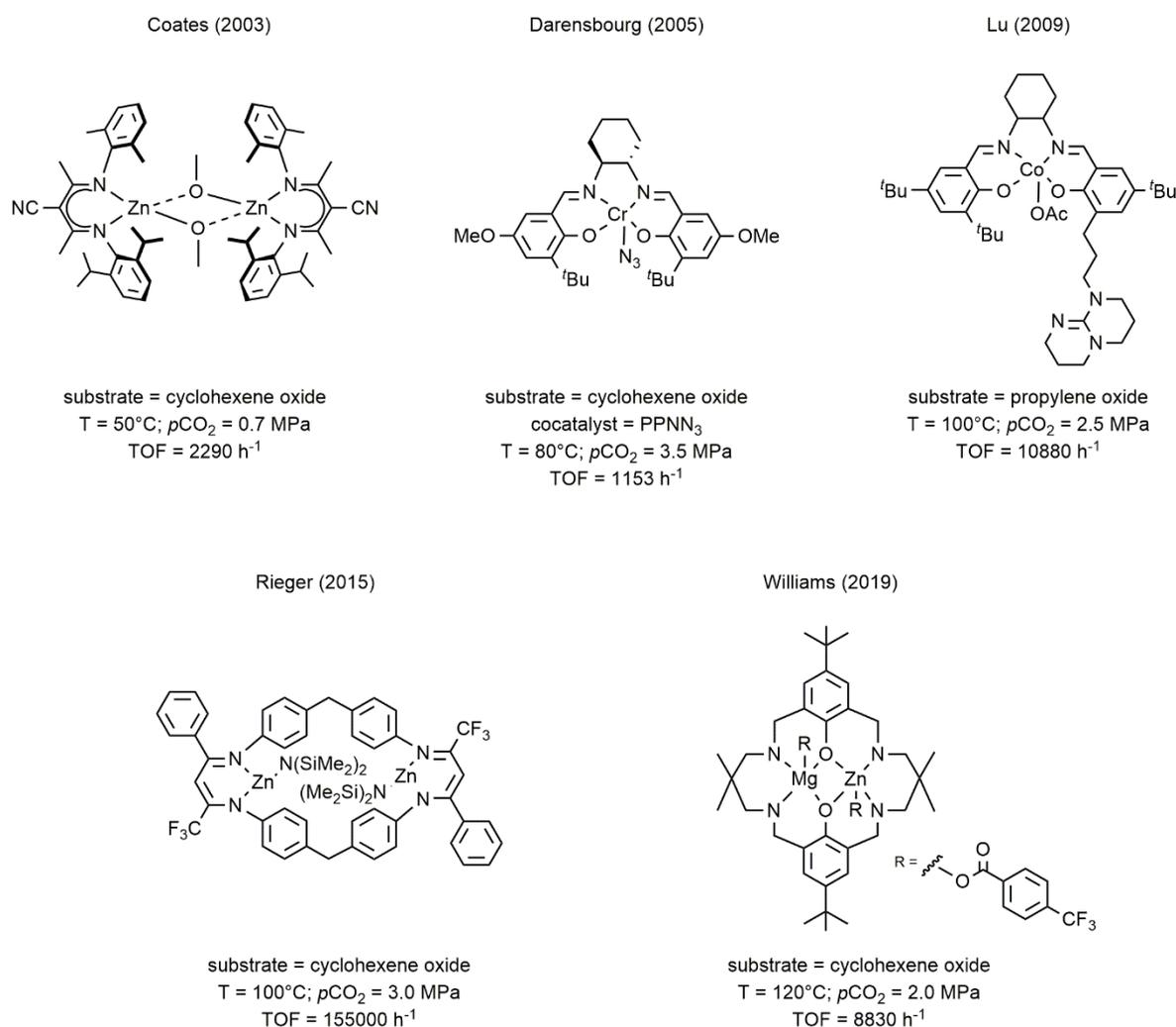


Figure 2. Representative catalytic systems for the synthesis of aliphatic polycarbonates (APC) from CO₂ and epoxides [33–37].

At first glance, it is evident that the nitrogen-based macrocycles, multidentate nitrogen framework, and Salen-type ligands, or in general, combination of phenoxo units with neutral nitrogen donors have played the main role in this kind of catalysis. In most cases, these ligands had been already developed to promote other catalytic transformations (polymerizations, oxidations, etc.) and therefore offer the possibility to be easily synthesized and modified. Salen ligands, for example, represent one of the most successful examples, owing to the possibility to finely tune the steric and electronic properties of the aromatic substituents and modify the bridge between the two imino nitrogen atoms. This also provided the opportunity to obtain chiral, enantiopure ligands for asymmetric transformations (Figure 3) [38].

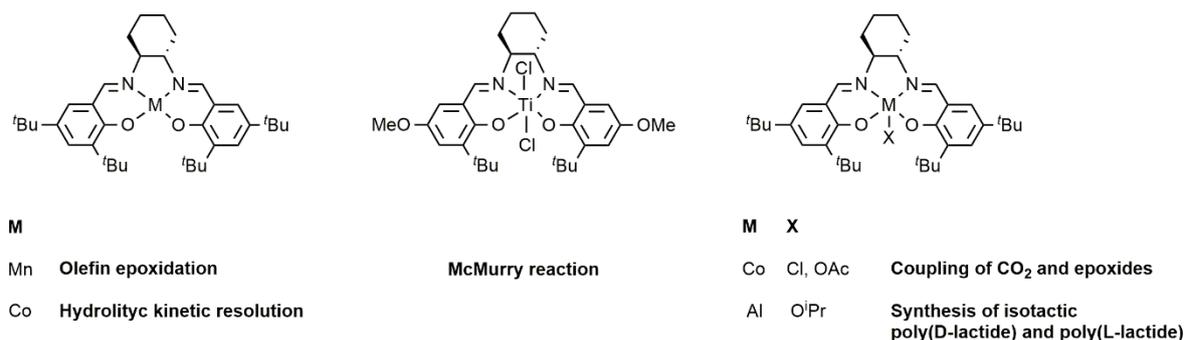


Figure 3. Selected examples of metal complexes containing a chiral Salen ligand and their applications [38].

However, in these species, the strength of the interaction between the metal center and the donor atoms can be scarcely modulated because of the hard nature of nitrogen as a Lewis base. On this basis, it was thought that the introduction in the ligand of a soft donor, such as sulfur, can be advantageous because of the possibility to tune the Lewis acidity of the metal center by using the weaker metal–donor interaction. Indeed, many successful examples of catalysts having sulfur-containing ligands have been reported to date in the field of olefin polymerization [39–46], ring-opening polymerization of cyclic esters [47–49], hydroamination [50] and hydrosilylation [51] with various metal centers (Figure 4). In this context, theoretical and experimental studies have shown the crucial role of the hemilabile sulfur atom in determining the catalytic activity and selectivity [52,53].

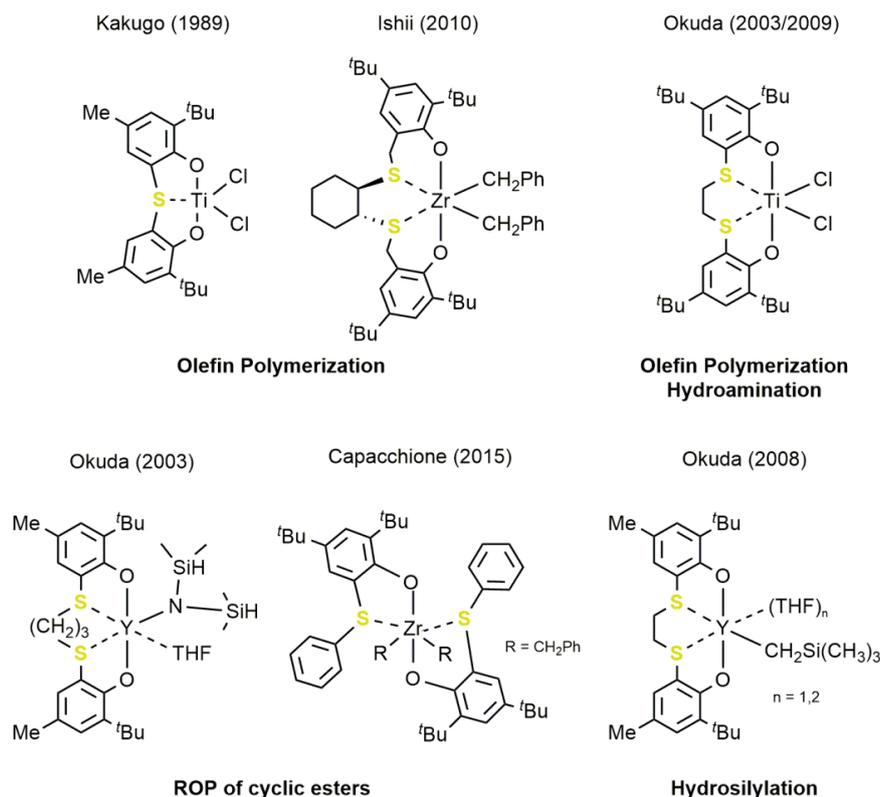


Figure 4. Representative examples of complexes bearing [OSO], [OSSO], or [OS]-ligands [39,41,43,47,49–51].

Despite these findings, the use of sulfur-based ligands in the CO₂/epoxide coupling has been neglected until recently. In this review, we cover the recent progress in the use of the corresponding metal complexes in the cycloaddition and copolymerization of CO₂ and epoxides, evidencing the fundamental role played by the ligand framework in modulating the catalytic efficiency.

2. Metal Complexes Bearing Sulfur-Containing Ligands Active in the Coupling of CO₂ and Epoxides

2.1. Chromium-Based Systems

Chromium Salen complexes are among the most studied coordination compounds in catalysis. Indeed, in the last years, their chemistry had been deeply investigated because of their unique properties in the oxidation, even in the enantioselective version, of various substrates [38]. The easy synthesis and the possibility to design chiral metal species sparked the interest in using these complexes also in the CO₂/epoxide coupling. In this context, Darensbourg and Nguyen separately reported the use of chromium Salen complexes for the coupling of cyclohexene oxide (CHO) or propylene oxide (PO) with CO₂ for the formation of polycyclohexene carbonate (PCHC) and propylene carbonate (PC), respectively (Figure 5) [54,55].

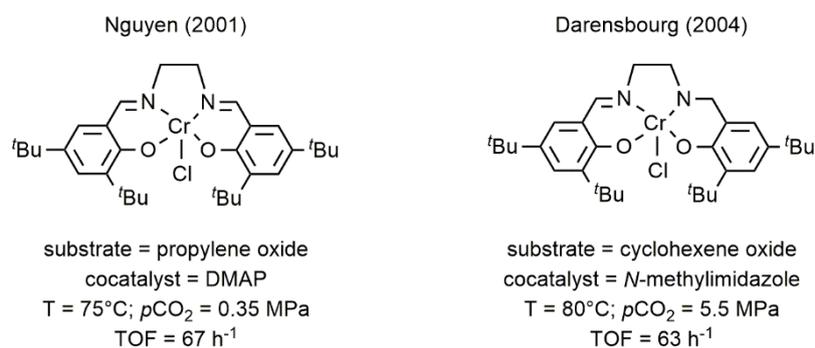


Figure 5. Chromium(III) Salen complexes for the reaction of CO₂ with CHO or propylene oxide (PO) [54,55].

After these first reports, many mononuclear and dinuclear chromium Salen complexes have been developed for the copolymerization of epoxides with CO₂ allowing the synthesis, with high activity, of new copolymer microstructures (Figure 6) [56,57].

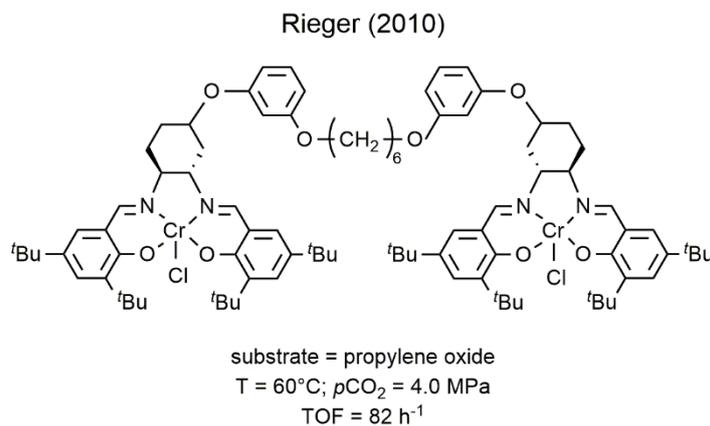
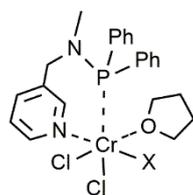


Figure 6. Bimetallic chromium(III) Salen complex developed by Rieger for the coupling of CO₂ with PO [56].

In the search of alternative ligands for the CO₂/epoxide chemistry, the first example of chromium catalysts bearing a soft donor atom in the ligand skeleton was reported by Duchateau and coworkers only in 2014 and regarded the utilization of two chromium(III) complexes having an aminophosphine bidentate ligand (Figure 7) [58]. These catalysts showed moderate catalytic activity in the copolymerization of CO₂ with CHO affording low molecular weight PCHC (M_n up to 1930 g mol⁻¹).

Duchateau (2014)



substrate = cyclohexene oxide
 cocatalyst = DMAP (X = Cl); PPNCI (X = CH₃)
 T = 80 °C; $p\text{CO}_2 = 5.0 \text{ MPa}$
 TOF = 25 h⁻¹ (X = Cl); 21 h⁻¹ (X = CH₃)

Figure 7. Chromium(III)-Aminophosphine complexes developed by Duchateau for the coupling of CO₂ with CHO [58].

In this field, the choice of sulfur as the soft Lewis base is even more recent. In 2015, the tetradentate [OSSO]-type chromium complexes (1–4) were developed by Liu and coworkers for the copolymerization of various epoxides with phthalic anhydride and subsequently used for the copolymerization of CO₂ with vinylcyclohexeneoxide (VCHO) (Figure 8) [59].

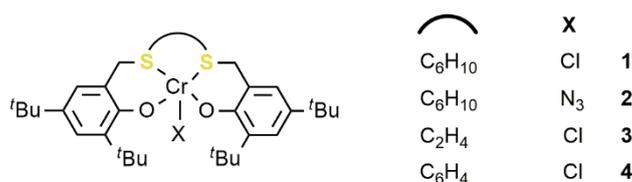


Figure 8. Chromium(III)-[OSSO] catalysts 1–4 [59].

Complexes 1–4, activated by bis(triphenylphosphoranylidene) ammonium chloride (PPNCI) are all active catalysts in the CO₂/VCHO coupling by using a [VCHO]/[[OSSO]CrX]/[PPNCI] ratio of 1000/1/2 at 90 °C and high pressure ($p\text{CO}_2 = 3.0 \text{ MPa}$). Activity and chemoselectivity toward the APC vis a vis COC depended on the catalyst structure. Indeed, the complexes 1–3 with a cyclohexyl or an ethyl carbon bridge showed better performances compared to the phenylene analogue 4. Selected results are reported in Table 1.

Table 1. Complexes 1–4 in the copolymerization of vinylcyclohexeneoxide (VCHO) and CO₂ [59].

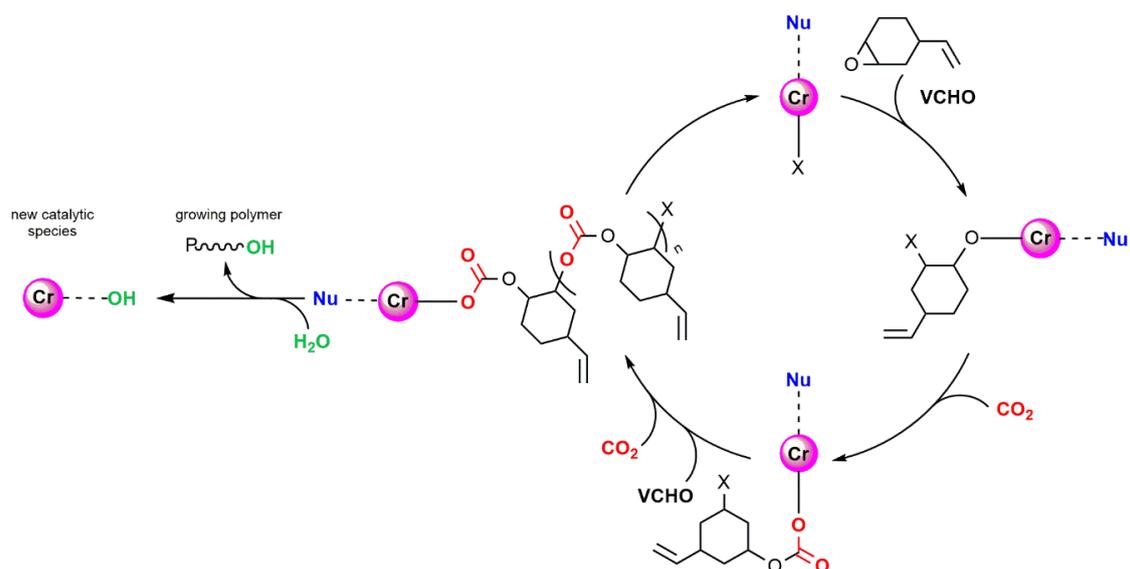
Complex	TOF ^a (h ⁻¹)	Selectivity ^b (%) (Polymer-Carbonate Linkages)	M_n ^c (KDa)	\bar{D} ^c
1	74	73–97.5	15	1.30
2	82	68–98.0	20	1.35
3	78	71–99.0	19	1.27
4	13	44–95.5	6	1.26

Reaction conditions: [VCHO]/[[OSSO]CrX]/[PPNCI] = 1000/1/2; T = 90 °C, $p\text{CO}_2 = 3.0 \text{ MPa}$; time = 6 h. ^a Turnover frequency (TOF) for the copolymer calculated as mole of VCHO consumed per mole of catalyst per hour. ^b Selectivity of PVCHC estimated by IR spectroscopy; selectivity toward polycarbonate linkages calculated through ¹H NMR spectroscopy. ^c Determined by GPC.

In addition, 4 also produced a low molecular weight polymer, in comparison to the other complexes, albeit with a narrow dispersity ($\bar{D} = 1.24$ – 1.49). For the most active catalyst 1, the authors also explored the use of different co-catalysts, such as bis(triphenylphosphoranylidene)ammonium azide, (PPNN₃), tetrabutylammonium chloride (TBAC), and 4-dimethylaminopyridine (DMAP) obtaining the best compromise between activity and selectivity toward the polymeric product by using 2 equivalents, with respect to the metal, of PPNCI. Notably, by adjusting the [VCHO]/[1]/[PPNCI] ratio to 500/1/2,

the activity reached the value of 134 h^{-1} with 76% of selectivity for the polymeric product at 90°C and with a CO_2 pressure of 3.0 MPa. ^{13}C NMR analysis showed that the resulting polymer is atactic in all cases. The reaction of terminal epoxides such as PO or epichlorohydrine (EPC) invariably resulted in the formation of the corresponding COC.

Starting from the observation that 2 equivalents of cocatalyst (PPNCl or PPNN_3) are needed to reach the best catalytic performances, the authors speculated about interaction of the onium salt with the metal center enhancing the catalytic performance. This idea was supported by IR experiments that revealed an interaction between the N_3^- anion or DMAP with the metal center that leads to the formation of a six-coordinated chromium atom. Based on these experiments, it was proposed a mechanism in which the true catalytic species was formed by the interaction of the nucleophile with the precatalyst. The presence of a protic compound such H_2O lead to a chain transfer with the formation of hydroxyl-terminated polymeric chains that were observed in the ^1H NMR spectrum (Scheme 2).



Scheme 2. Proposed mechanism for the copolymerization of VCHO and CO_2 . $\text{X} = \text{Cl}^-$, N_3^- [59].

Almost simultaneously, Darensbourg and coworkers reported the synthesis of four new imine-thioether-bridged bis(phenolate) [ONSO]-type chromium(III) complexes **5–8** and their use as catalysts for the CO_2/CHO copolymerization (Figure 9) [60].

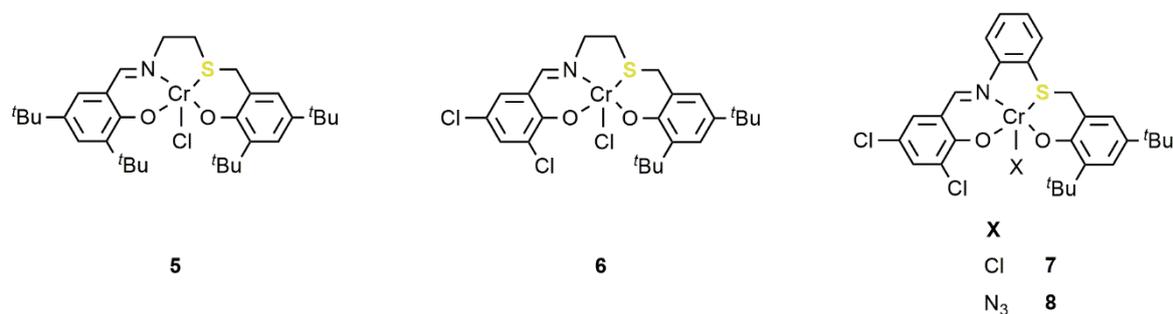


Figure 9. Chromium(III)-[ONSO] catalysts **5–8** [60].

Also in this case, in analogy with the abovementioned [OSSO]-type chromium complexes reported by Liu, the best cocatalysts are PPNCl and PPNN_3 in a 2/1 molar ratio with respect to the chromium complex. These nucleophile sources performed better than the more hygroscopic TBAC giving the polymeric product with good selectivity (72–77%) at 80°C and with a CO_2 pressure of 3.0 MPa. Complexes **7** and **8** bearing a phenylene-bridged ligand were the most active catalysts reaching a TOF

up to 71 h^{-1} with the azide-derivative **8** slightly better performing with respect to the chloro-derivative **7**. The PCHC obtained was atactic in nature under all the reaction conditions explored and displayed narrow dispersity ($D = 1.23\text{--}1.28$). As expected, the selectivity toward the polymer is negatively affected by an increase of the reaction temperature although the catalytic activity increased (TOF up to 100 h^{-1} at $110 \text{ }^\circ\text{C}$). An in situ IR spectroscopy study showed that, in the early stages, only the COC was formed by complexes **5** and **6**, whereas the production of the APC started after 50 min. These results were rationalized proposing a mechanism in which the backbiting reaction initially predominated, leading to the COC. However, once the alternating CHO/CO₂ insertion began, the backbiting of the alkyl carbonate became less favored with respect to the polymerization process. Differently, by using the less electron-rich Cr(III) complex **7** the production of the polymer immediately started.

Liu and Darensbourg both explained the observed lower activity and selectivity for the formation of the polymeric product of the sulfur-containing Cr(III) complexes when compared to the corresponding Salan analogues by the fact that the electron-releasing sulfur atoms in the ligand skeleton render the chromium atom more electron-rich, thus favoring the displacement of the growing polymeric chain from the metal center and the formation of the cyclic product.

Recently, our group reported the synthesis of the new [OSSO]-type Cr(III) complex **9** (Figure 10) [61]. This complex contained the ligand developed by Okuda and coworkers for group 4-based complexes which differed from the ligands used for the foregoing complexes **1–8** for the absence of the methylene spacer between the sulfur atoms and the aromatic rings. It was expected that this design would render the sulfur atoms electron poorer, weakening their electron-releasing character and consequently enhancing the Lewis acidity of the metal center. When activated by TBAC, complex **9** under 1.0 MPa of CO₂ pressure produced a mixture of polymeric and cyclic products by using PO as the substrate ([PO]/[**9**]/[TBAC] ratio of 1000/1/1). The selectivity strongly depends on the reaction temperature with a maximum (45%) for the polypropylene carbonate (PPC) at $45 \text{ }^\circ\text{C}$ and with the almost exclusive formation of the PC at higher temperatures ($80 \text{ }^\circ\text{C}$) (Figure 10).

Changing the onium salt to PPNCl, reducing the [**9**]/[PPNCl] ratio to 1/0.5, and increasing the CO₂ pressure to 2.0 MPa, both the activity and the selectivity increased, reaching a TOF of 35 h^{-1} and a selectivity of 93% for the polymer. The PPC produced was atactic but highly regioregular (up to 90% of head to tail enchainment) with no polyether linkages detectable. The molecular weight was high (M_n up to 36 kDa) with a bimodal distribution due to the presence of traces of water that acted as a chain transfer agent. The same system also promoted the copolymerization of CO₂ with CHO, 1-hexene oxide (HO) and styrene oxide (SO). In the case of CHO, activity was lower to those observed by using PO (TOF up to 19 h^{-1}) but the selectivity reached the value of 99%. Notably, HO was copolymerized with good selectivity (up to 92%) albeit with low activity (TOF up to 16 h^{-1}). Moreover even SO that, because of its electronic features, it is usually less prone to copolymerize, giving 32% of polystyrene carbonate (PSC).

The high versatility of complex **9** in promoting the copolymerization of CO₂ with various epoxides was further confirmed by the obtaining of PO/CHO/CO₂ and PO/HO/CO₂ terpolymers. The resulting polycarbonates had high content of carbonate linkages (87–93%) and narrow dispersity ($D = 1.16\text{--}1.27$) with thermal and ¹³C NMR analyses suggesting a block microstructure for these materials.

DFT calculation, carried out for the coupling involving PO as the substrate, displayed that the activation energies for cyclization and copolymerization are quite close in value (Scheme 3). This was coherent with the experimental observation that the course of the reaction can be driven to the formation of PC or PPC by a proper choice of the reaction conditions.

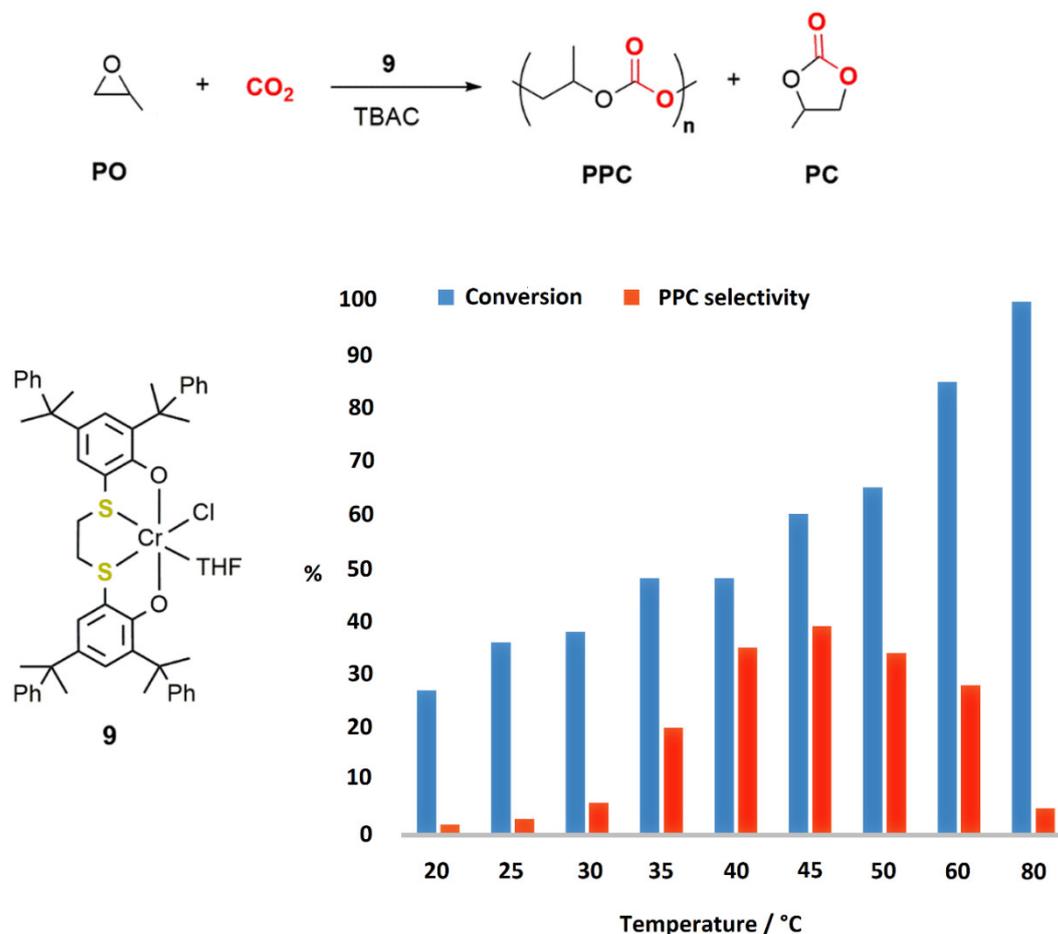
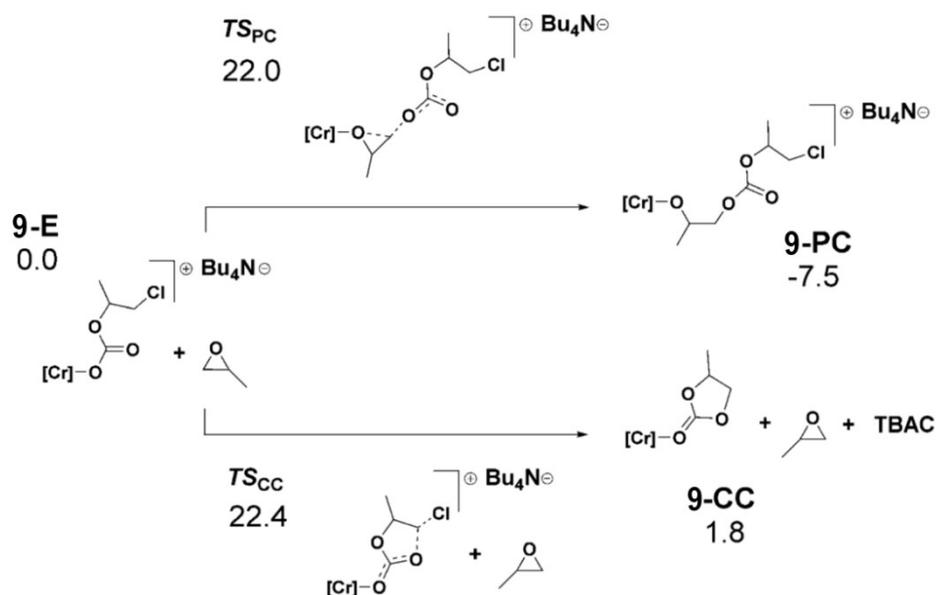


Figure 10. Coupling of PO and CO₂ catalyzed by the chromium(III)-[OSSO] catalyst 9 [61]. Reprinted with permission from ref. 61. Copyright (2020) John Wiley and Sons.



Scheme 3. Free energy profile evaluating the cyclization versus polymerization paths for the coupling of PO and CO₂ promoted by complex 9 [61]. Reprinted with permission from ref. 61. Copyright (2020) John Wiley and Sons.

2.2. Iron-Based Systems

Despite the abundance of this metal on the Earth-crust, the use of iron in homogeneous catalysis has been longtime neglected and only in the last two decades emerged as a viable alternative to catalysts based on rare/precious metals. In this trend, the development of iron catalysts for the reaction of CO₂ with epoxides was not an exception, with only few examples of complexes that showed significant activity in the cycloaddition of CO₂ to epoxide or in the alternating copolymerization [18,62–65]. As for other metals, the structural motifs of choice were based on macrocyclic or polydentate ligands having oxygen and nitrogen as donor atoms. In particular, the complexes developed by Williams and Nozaki [62,63], depicted in Figure 11, were the first examples of iron catalysts able to promote the copolymerization of CO₂ with CHO and PO, respectively. The iron complexes developed by Kleij [64,65] (Figure 11), efficiently produced cyclic carbonates from a variety of terminal and internal epoxides.

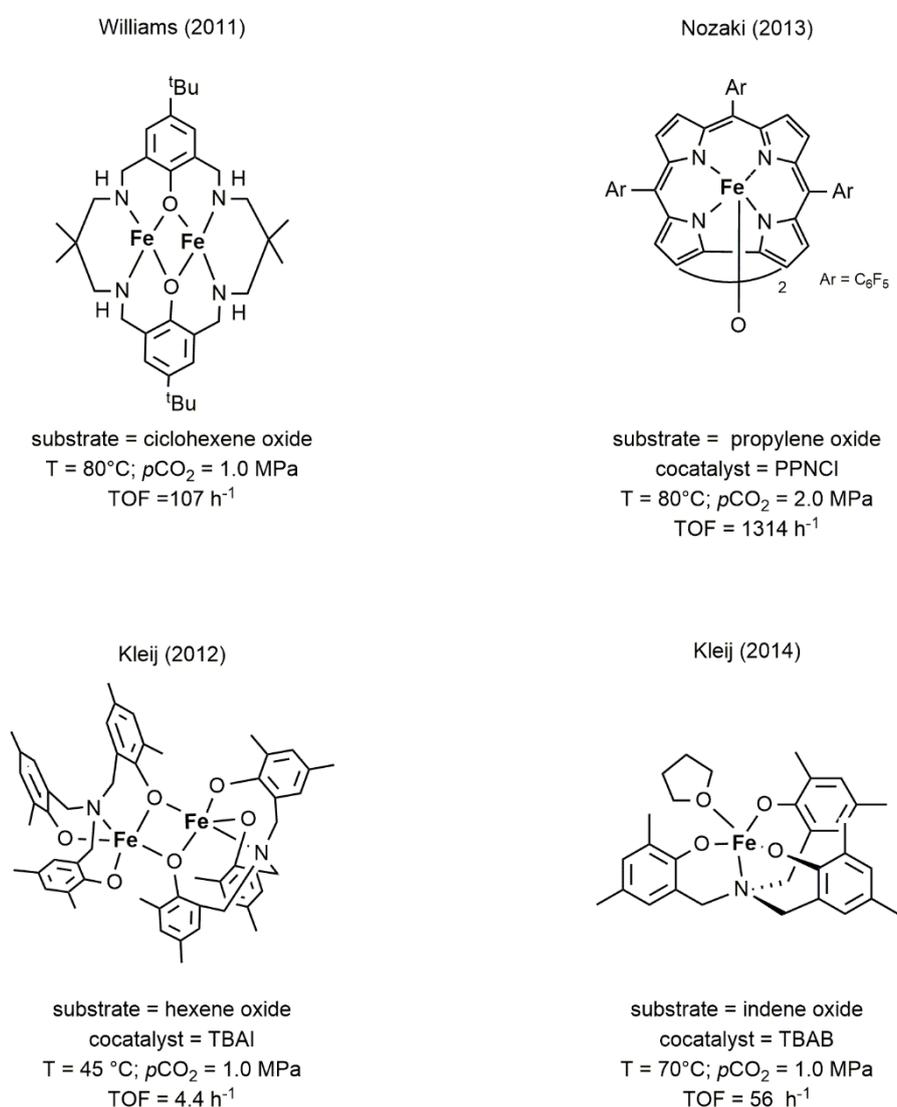


Figure 11. Representative examples of iron-based complexes active in the coupling of CO₂ with epoxides [18,62–65].

The first example of sulfur-containing ligand for iron complexes active in the reaction of CO₂ with epoxides was reported by Abu-Surrah and coworkers in 2013 (10, Figure 12) [66]. This thiophenaldimine Fe(II) complex, activated by TBAB, at 130 °C and 0.5 MPa of CO₂ pressure, promoted the formation of styrene carbonate (SC) with low activity (TON = 799; TOF = 33.3 h⁻¹).

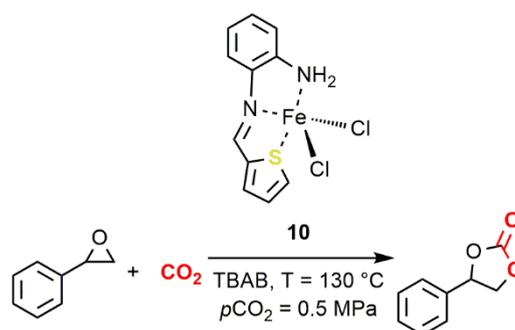


Figure 12. Coupling of styrene oxide (SO) and CO₂ promoted by the iron(II) thiophenaldimine complex **10** [66].

In 2015, our group reported on the synthesis of a new air-stable dinuclear iron(III) complex (**11**, Figure 13) bearing a bis-thioether-triphenolate ligand [67–69]. These complexes were stable in solution, and when activated by TBAB (**11**/TBAB = 1/2), were able to promote the transformation of various terminal or internal epoxides to the corresponding COCs with good activity and selectivity. In particular, PO was converted to PC reaching a TOF of 580 h⁻¹ at 100 °C with a CO₂ pressure of 2.0 MPa, and with a [PO]/[**11**]/[TBAB] ratio of 4000/1/5. Furthermore, this catalyst showed to be also highly stereoselective affording exclusively the *cis*-COC by using CHO as the substrate regardless the TBAB/[**11**] ratio. Moreover, by using the enantiopure SO as the epoxide (*ee* = 94%) the corresponding SC was gained with a good degree of stereoretention (*ee* = 74%).

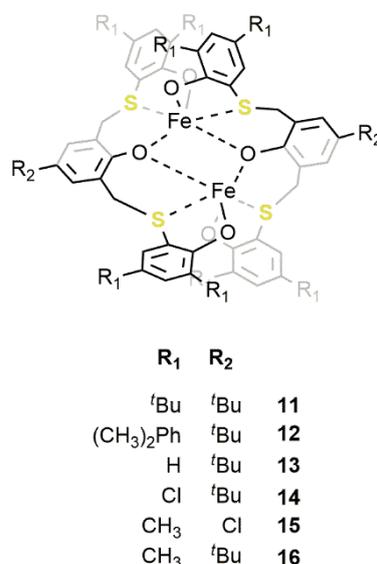


Figure 13. Dinuclear iron(III) complexes **11–16** containing a bis-thioether-triphenolate ligand [67,68].

An enlargement of the catalysts' family and an optimization of the reaction conditions led to a further improvement of the catalytic activity. In particular, complex **16**, bearing methyl substituents on the phenol ring, displayed the highest activity so far reported for an iron catalyst with a TOF of 5200 and 7000 h⁻¹ in the conversion of PO and EPC, respectively, in the corresponding COCs at 120 °C with a CO₂ pressure of 2.0 MPa and a [PO]/[**16**]/[TBAB] ratio of 10000/1/10. Conversely, the introduction of bulkier substituents in catalyst **12** and electron-withdrawing groups in catalyst **14** resulted in a lowering of the catalyst activity.

In order to shed more light on the reaction mechanism, DFT calculations were performed and highlighted three important features regarding the formation of COCs promoted by these catalysts: (i) The coordination of the epoxide to the iron(III) center requires the detachment of a sulfur atom from

the coordination sphere; (ii) the insertion of CO₂ is not mediated by the second iron center; (iii) the ring-closure of the COCs is the rate-limiting step (Figure 14). As a matter of fact, the hemilability of the sulfur atoms plays a fundamental role in determining the catalytic activity. This was also confirmed by the worse performances of catalyst **14**, which were reasonably caused by a stronger sulfur-iron interaction which, in turn, was caused by the presence of electron-withdrawing substituents on the phenoxo rings.

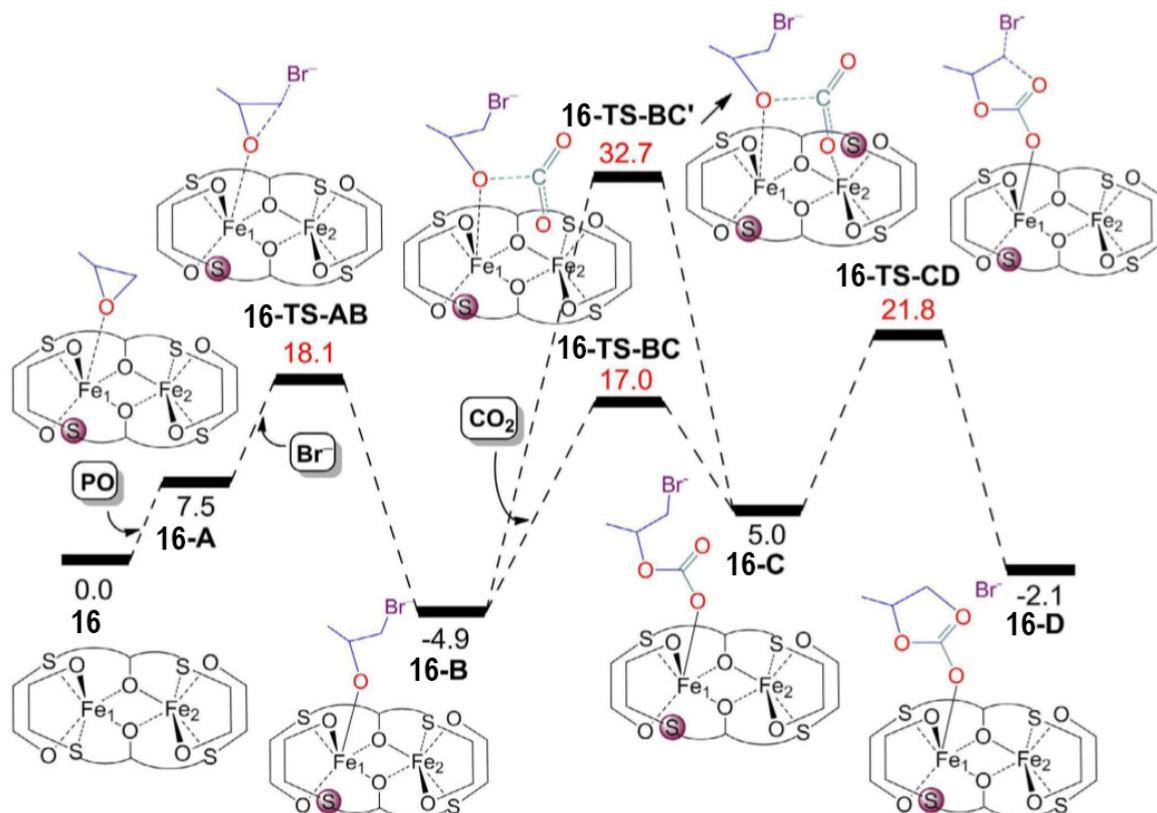


Figure 14. Free energy profile for the coupling of PO and CO₂ promoted by complex **16** [68]. Reprinted with permission from ref. 68. Copyright (2020) John Wiley and Sons.

Later on, we moved to the development of iron(III) mononuclear complexes bearing [OSSO]-type ligands **17–20** (Figure 15) [52].

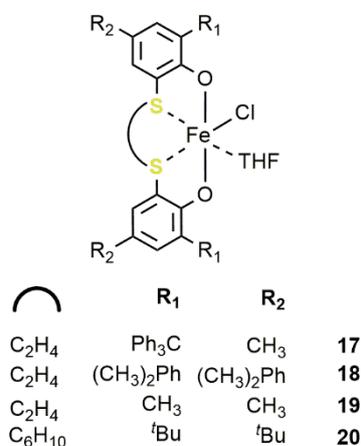


Figure 15. Iron(III)-[OSSO] complexes **17–20** [52].

Notably, when activated by TBAB, these catalysts efficiently performed in the cycloaddition of CO₂ to terminal and internal epoxides giving the corresponding COC under mild reaction conditions (35 °C; *p*CO₂ = 0.1 MPa) and, by using catalyst **20**, reaching a TOF of 290 h⁻¹ in the case of PO with a [PO]/[**20**]/[TBAB] ratio of 1000/1/5. Substituents on the ligand framework had a negligible influence on the catalytic activity. In analogy with the bis-thioether-triphenolate complexes **11–16**, the reaction occurred with a high degree of stereoretention (98%) in the case of internal epoxides such as 2-buteneoxide. More importantly, when the substrate was CHO, only the alternating PCHC was observed. In this case, the best cocatalyst was TBAC and the activity order was **18** > **20** ≈ **17** > **19**.

A thorough kinetic investigation of the formation of PC was performed by means of ATR-IR spectroscopy. This study evidenced that reaction followed a second-order dependence in **20**. Furthermore, this behavior was observed exclusively when 2 equivalents of TBAB were used, suggesting that only under these conditions the true catalytic species was formed. As a further confirmation, UV-vis spectra detected the formation of a new ferrate species when an excess of TBAB was added to the catalyst's solution. These findings were rationalized by DFT calculations showing that the rate-limiting step was the ring-opening of the epoxide that took place in the presence of two iron centers: one acted as the Lewis acid and the other one, as metallate, furnished the nucleophile (Figure 16).

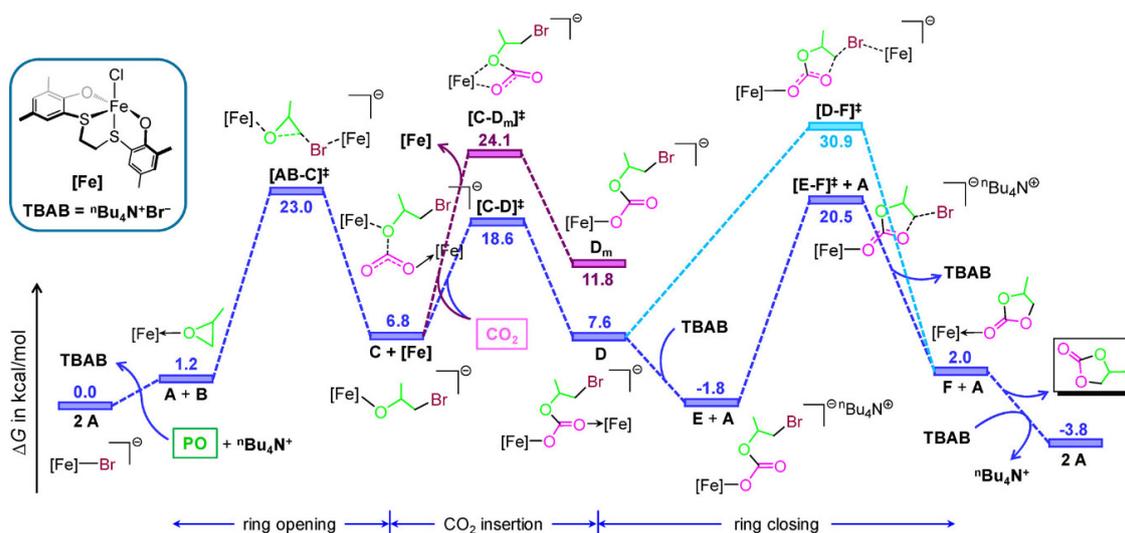


Figure 16. Free energy profile for the coupling of PO and CO₂ promoted by complex **20** [52]. Reprinted with permission from ref. 52. Copyright (2020) American Chemical Society.

The ferrate species **21** was also isolated and characterized both starting from the chloro-derivative **20** and the bromo-derivative **22** by reaction with two and one equivalent of TBAB, respectively (Figure 17) [70]. Complex **21** was used as single-component catalyst in couplings of various terminal and internal epoxides showing good performances under mild reaction conditions (35 °C; *p*CO₂ = 0.1 MPa, [PO]/[**21**] = 100) and reached a TOF of 54 h⁻¹.

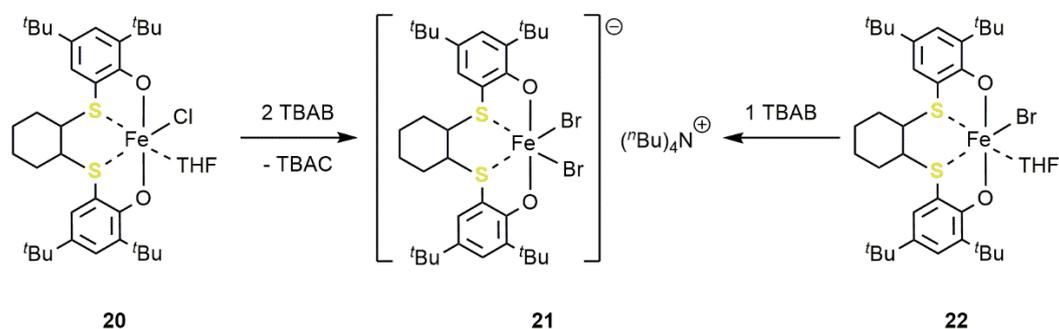


Figure 17. Synthesis of the ferrate species **21** from complexes **20** or **22** through reaction with two or one equivalents of TBAB, respectively [70].

Lately, we also developed a new family of tridentate bithioether phenolate ligands that supported both Fe(II) and Fe(III) centers [71]. It is worth noting that the both Fe(II) and Fe(III) complexes existed in solution as mononuclear or dinuclear species depending on the steric bulk of the ligand (Figure 18).

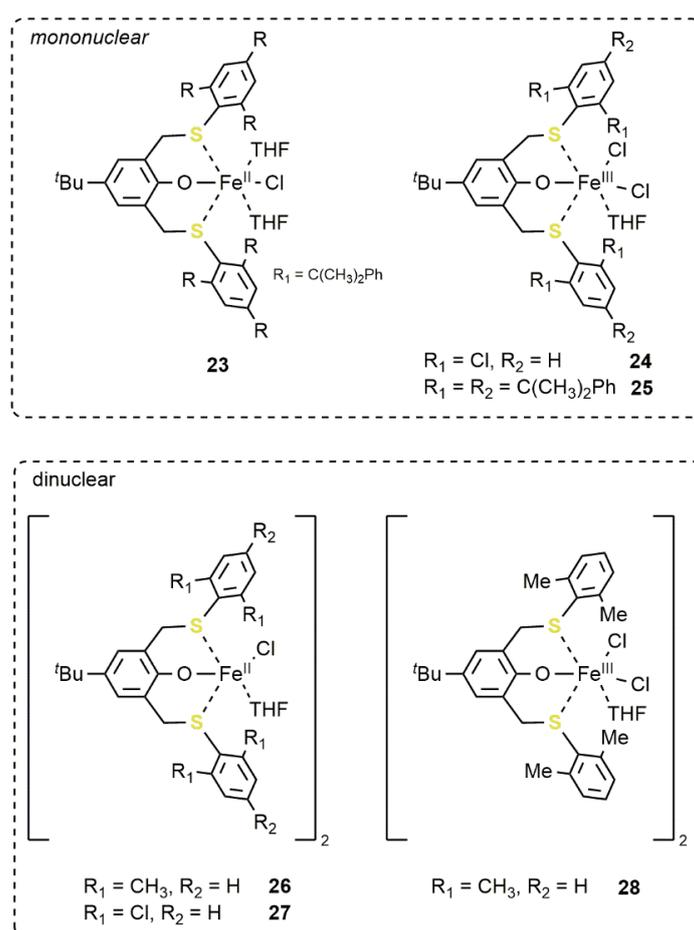


Figure 18. Bisthioether phenolate Fe(II) and Fe(III) complexes **23–28** [71].

The cycloaddition reaction of CO₂ to HO was used as the benchmark reaction to test the catalytic activity of these complexes: on one hand, for the Fe(II) complexes the activity depended on the complex structure, with **26** being the most active (TOF = 36 h⁻¹), on the other hand all the Fe(III) species showed comparable activities (TOF = 32 h⁻¹). This different behavior was explained by supposing that the Fe(III) complexes reacted with TBAB forming the corresponding ferrate, in analogy to what was observed for the [OSSO]-type Fe(III) complexes. In contrast, the formation of such anionic species

does not occur in the case of the Fe(II) complexes. This mechanistic picture was supported by UV-vis experiments treating the precatalysts with an excess of TBAB.

More recently, Jones and coworkers reported on the synthesis of a wide family of imine-thioether-bridged bis(phenolate) ([ONSO]-type) Fe(III) complexes **29–34** (Figure 19) [72].

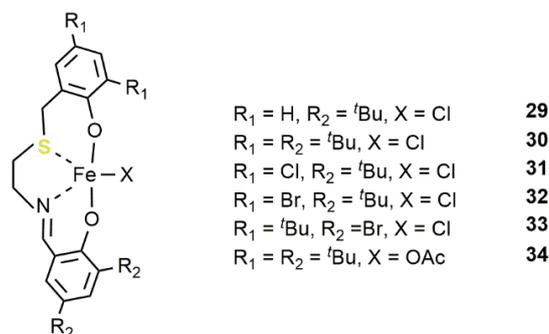


Figure 19. ([ONSO]-type) Fe(III) complexes **29–34** [72].

These complexes, when activated by TBAC at 80 °C, with a CO₂ pressure of 1.0 MPa and a [CHO]/[Fe]/[TBAB] ratio of 1250/1/8 performed as active catalysts (TOF = 22–31 h⁻¹) for the cycloaddition of CO₂ to CHO with excellent selectivity toward the formation of *cis*-CHC (>99%). The most active catalytic system, complex **33**, could reach a TOF of 156 h⁻¹ by increasing the temperature to 120 °C. However, under this condition, a lower selectivity was detected, because of the simultaneous production of the polyether product. A reduction of the [TBAC]/[**33**] ratio down to 2, resulted in a lower selectivity as well, with the formation of polycyclohexeneoxide (PCHO) and, in lower amounts, of the *trans*-CHC. In this publication, the use of other terminal epoxides was also explored. By using PO, a higher activity with respect to the case of CHO was detected (TOFs of 42 h⁻¹ versus 31 h⁻¹). As a matter of fact, Thiolen Fe(III) compounds showed to be more active if compared to the corresponding Salen Fe(III) complexes demonstrating, once again, the beneficial effect of sulfur on catalytic activity.

2.3. Bismuth-Based Systems

Among the possible Lewis acidic metal centers in catalysis, the last two decades have witnessed a rising interest in the use of bismuth. Indeed, bismuth is cheap and low-toxic and therefore the implementation of catalytic processes based on this metal are an active task of research in green chemistry [73–76].

Actually, the use in CO₂/epoxide reactions was barely explored and only recently received more attention [77,78]. In this field, one of the most efficient catalytic systems was developed by Shimada e Yin in 2009 [79]. In this study, the synthesis of Bi(III) compounds **35** and **36**, bearing a sulfur bridged bis(phenolate) ligand, was reported (Figure 20).

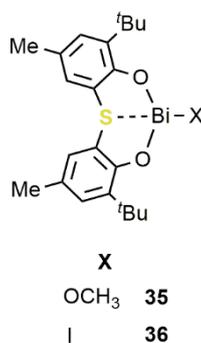


Figure 20. Bi(III) complexes **35–36** containing an [OSO]-bisphenolate ligand [79].

In the presence of iodide as the nucleophile, by using sources such as Ph_3PI , tetrabutylammonium iodide (TBAI), NaI or LiI, these compounds were found to be active catalysts for the conversion of PO to PC under mild reaction conditions (RT; $p\text{CO}_2 = 0.1 \text{ MPa}$; $[\text{PO}]/[\text{Bi}]/[\text{I}^-] = 820/1/4$) reaching a TOF of 34 h^{-1} . More recently, Wong, Au, and coworkers reported that the dinuclear sulfide-bridged complexes **37–40** (Figure 21) performed as active catalysts for the conversion of EPC to the corresponding carbonate at $140 \text{ }^\circ\text{C}$ and a CO_2 pressure of 3.0 MPa ($[\text{EPC}]/[\text{Bi}]/[\text{TBAI}] = 200/1/0.2$) reaching TOFs up to 25 h^{-1} [80]. Complexes **37–39** are also among the few air-stable organobismuth compounds reported so far.

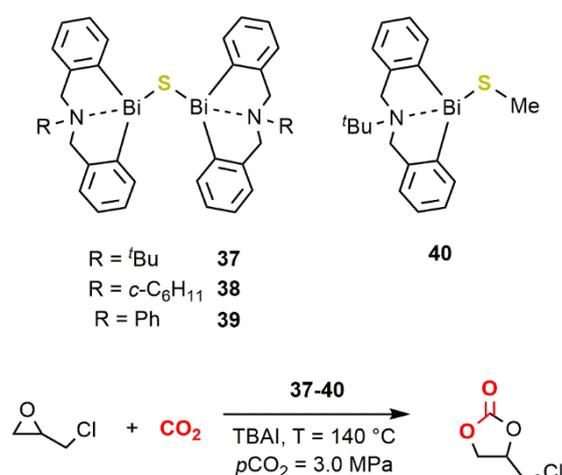


Figure 21. Dinuclear sulfide-bridged complexes **37–40** [80].

3. Conclusions

The use of sulfur-containing ligands to support metal ions in the reaction between CO_2 and epoxides has attracted an increasing interest in the past years. In many cases, the presence of sulfur in the ligand backbone imparts unique properties in terms of activity, selectivity, and stability of the catalyst precursor. Furthermore, both cyclic carbonates and polycarbonates were obtained with good activity and selectivity for a wide range of substrates showing a high potential for further development. In particular, the use of these ligands can be extended to a major variety of metal centers, allowing an increase in the catalytic performances and expanding the portfolio of possible products. Finally, the design and the synthesis of new structural motifs containing sulfur atoms in the ligand backbone is another important objective for a possible expansion of the catalytic applications.

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