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# Salphen-Co(III) complexes catalyzed copolymerization of epoxides with $\mathrm{CO}_{2}$ 

Zdeněk Hošt'álek, Robert Mundil, Ivana Císařová, Olga Trhlíková, Etienne Grau, Frederic Peruch, Henri Cramail, Jan Merna


#### Abstract

The series of novel symmetric and asymmetric salphen cobalt (III) complexes with different counteranions (trichloroacetate, dinitrophenolate, pentafluorobenzoate and acetate) was synthesized and used as catalysts in copolymerization of $\mathrm{CO}_{2}$ with propylene oxide (PO) and cyclohexene oxide ( CHO ). Hexacoordinated structure of complexes adducts was found in solid phase. The effect of catalyst structure, temperature, $\mathrm{CO}_{2}$ pressure, catalyst/cocatalyst ratio on overall activity and selectivity was investigated. Synthesized salphen-Co (III) complexes were effective for both $\mathrm{PO} / \mathrm{CO}_{2}$ and $\mathrm{CHO} / \mathrm{CO}_{2}$ highly alternating copolymerization. Substitution of phenylene framework of salphen ligand by chlorine atom led to decrease of activity in $\mathrm{PO} / \mathrm{CO}_{2}$ copolymerization. Complexes with trichloroacetate counteranion were shown to be the most active and selective in $\mathrm{PO} / \mathrm{CO}_{2}$ copolymerization leading to poly(propylenecarbonate) with highest molar mass. On contrary, catalytic performance of salphen Co (III) complexes in $\mathrm{CHO} / \mathrm{CO}_{2}$ copolymerization was almost independent on ligand structure and counteranion. Excellent selectivity to poly(cyclohexenecarbonate) was achieved even at 0.1 MPa $\mathrm{CO}_{2}$. MALDI-TOF analysis of polycarbonates was used to investigate the initiation step of the copolymerization.


## 1. Introduction

The use of $\mathrm{CO}_{2}$ as a C 1 feedstock in chemical synthesis became an attractive research target, since it is abundant, renewable and nontoxic gas [1], [2]. Beside classical large scale industrial processes like urea manufacture, $\mathrm{CO}_{2}$ could find an application also as a substrate for synthetic polymer production, thus reducing the dependence of their production on crude-oil. A great interest was devoted especially to copolymerization of epoxides with $\mathrm{CO}_{2}$, which represent a new, phosgene free, route towards aliphatic polycarbonates. The versatility of this synthetic approach lies in possibility to prepare polyesters with very different properties by variation of the epoxide structure.

Although the first catalytic system used for copolymerization of epoxides with $\mathrm{CO}_{2}$ (heterogeneous $\mathrm{ZnEt}_{2} / \mathrm{H}_{2} \mathrm{O}$ ) was reported already in 1969 [3], the significant progress in field of $\mathrm{CO}_{2}$ polymer chemistry was achieved in last decade, when new types of homogenous catalytic systems were discovered [4], [5]. Variety of metal complexes of zinc [6], [7], [8], cobalt [9], [10], chromium [11], [12], [13], magnesium [14], manganese [15], aluminium [16], iron [17], [18] and rare-earth metals [19], [20], [21] proved to be effective for epoxide/CO2 copolymerization. Prominent among these catalysts are $\beta$-diminate zinc complexes [8] and metal salen complexes [22], which show high activity, selectivity to polycarbonate, good stereoselectivity and in some cases enhanced
enantioselectivity [23], [24], [25] at mild conditions. So far, a large number of salen catalysts was prepared by complexation of salen ligands mostly with $\mathrm{Al}, \mathrm{Cr}$ and Co precursors. These complexes efficiently catalyzed coupling of epoxides with $\mathrm{CO}_{2}$ to produce cyclic carbonates or polycarbonates. The most effective catalysts for epoxide $/ \mathrm{CO}_{2}$ copolymerization proved to be chiral salen Co (III) complexes in combination with strong Lewis acids and nucleophilic cocatalysts [22].

Since 2003, when Coates first reported salen Co(III) complex [10] which showed an excellent selectivity to poly(propylenecarbonate) (PPC) formation ( $99 \%$ vs. cyclic carbonate) with $99 \%$ of carbonate linkages, a significant effort was devoted to the synthesis of more efficient salen Co complexes as well as mechanistic studies, which contributed to better understanding of reaction mechanism [24], [26], [27]. Based on the number of metal atoms involved in the catalytic cycle, monometallic or bimetallic mechanisms have been described [28]. A detailed study of salen Co (III) complexes with various ligand substitutions, initiating groups and cocatalysts was performed by Lu and coworkers [23]. It was concluded, that ideal catalytic system for epoxide $/ \mathrm{CO}_{2}$ copolymerization is chiral ( $\mathrm{R}, \mathrm{R}^{\prime}$ )-Salen Co (III) complex with tert-butyl substituents in ortho and para positions of aryl rings in salen ligand. Further, low nucleophilicity of initiating group is crucial for high catalyst activity as well as the use of cocatalyst (ionic salt with bulky cation) with poor leaving group [23], [29]. Significant increase in activity was achieved when novel types of single component salen Co(III) catalyst with covalently attached cocatalyst groups (ammonium) were synthesized [30], [31]. These complexes show very high activities up to $26,000 \mathrm{~h}^{-1}$ at low catalyst loadings $(1: 100,000)$ and elevated temperatures $\left(80^{\circ} \mathrm{C}\right)$ compared to activity in order of $10^{2} \mathrm{~h}^{-1}$ displayed by simple salen complexes [23], [32]. Similarly, Co complex with 1,5,7triazabicyclo $4,4,0$ ] dec-5-ene (TBD) side arm showed very high TOF $10,800 \mathrm{~h}^{-1}$ and high molar mass up to $100 \mathrm{~kg} \mathrm{~mol}^{-1}$ [33]. However, high catalytic activity of these complexes is paid by a tedious multistep procedure of their preparation.

For the synthesis of stereoregular polycarbonates catalytic systems with enhanced stereoselectivity were developed [34], [35]. Beside simple already discussed chiral salen Co complexes, which can afford enantioenriched polycarbonates (kinetic resolution of epoxide enantiomers with $k_{\text {rel }}$ up to 9.7) [24], the significantly higher $k_{\text {rel }}$ value (or enantiomeric excess) was achieved with multichiral [36], [37] and bimetallic bridged [38] salen Co(III) complexes to produce more enantioenriched PPC and poly(cyclohexenecarbonate) (PCHC) respectively. Enantioselectivity of salen complexes in copolymerization of propylene oxide (PO) with $\mathrm{CO}_{2}$ was investigated in detail and related to the bimetallic or binary mechanism of copolymerization [39].

An extensive research was devoted to $\mathrm{CO}_{2}$ with epoxide copolymerizations catalyzed by salen complexes with chiral ( $R, R^{\prime}$ ) cyclohexylene backbone [22] while only few publication was devoted to its salphen analogues containing phenylene ligand backbone (Fig. 1). Compared to salen analogues salphen ligands are more costeffective, their substitution is more feasible and their rigid geometry allows to efficiently influence the Lewis acidity of the metal center and subsequently the reactivity of the corresponding complex [40]. Indeed, some salphen complexes proved to be effective catalysts for various types of substrates (carbonylation, epoxidation,
epoxide and lactones ROP) and, in some cases, they exceeded their salen analogues [11], [41], [42], [43], [44], [45]. First copolymerization of PO with $\mathrm{CO}_{2}$ catalyzed by salphen chromium complex in combination with 4-dimethylaminopyridine (DMAP) cocatalyst was performed by Rieger in 2003 [11] resulting in a mixture of cyclic propylenecarbonate (CPC) and PPC with $M_{n}$ of $15 \mathrm{~kg} \mathrm{~mol}^{-1}$. A series of aluminium salphen complexes was also used for copolymerization of cyclohexene oxide ( CHO ) with $\mathrm{CO}_{2}$ to produce polycarbonates with $M_{\mathrm{n}}$ up to $10 \mathrm{~kg} \mathrm{~mol}^{-1}$ and carbonate linkage up to $97 \%$ [42]. Copolymerization of PO with $\mathrm{CO}_{2}$ was investigated using salphen $\mathrm{Co}(\mathrm{III}) \mathrm{Br}$ complex without any cocatalyst resulting in high selectivity to PPC (99\%) but poor activity $\left(23 \mathrm{~h}^{-1}\right)$ [24]. The same complex was reported as inactive for $\mathrm{CHO} / \mathrm{CO}_{2}$ copolymerization [46]. A monometallic and bimetallic flexibly linked salphen chromium complexes were used in $\mathrm{CO}_{2} /$ epoxide copolymerization producing selectively PPC with moderate TOF $50-90 \mathrm{~h}^{-1}$ containing $40-90 \%$ carbonate linkage and $M_{\mathrm{n}}$ up to $32 \mathrm{~kg} \mathrm{~mol}^{-1}$ [47]. Kinetic investigation proved the action of bimetallic mechanism (without cocatalyst) and binary (or monometallic) mechanism (with cocatalyst). Very recently the new salphen Ti(III) complex was used for production of $100 \%$ alternating PCHC ( $M_{\mathrm{n}} \approx 5 \mathrm{~kg} \mathrm{~mol}^{-1}$ ) with TOF up to $570 \mathrm{~h}^{-1}[48]$.


Fig. 1. Structure of chiral ( $R, R^{\prime}$ ) salen complexes $\mathbf{1 a} \mathbf{- c}$ and prepared salphen complexes ( $\mathbf{2 a} \mathbf{a} \mathbf{c}, \mathbf{3 a} \mathbf{a} \mathbf{d}$ ).
Herein, we describe the synthesis of novel symmetric and asymmetric salphen cobalt (III) complexes with different counteranions, and their reactivity in copolymerization of $\mathrm{CO}_{2}$ with PO and CHO in presence of bis(triphenylphosphine)iminium chloride (PPNCI) as a cocatalyst. The effect of catalyst structure as well as of temperature, catalyst and cocatalyst loading on catalyst activity and selectivity was investigated.

## 2. Results and discussion

### 2.1. Preparation and characterization of Salphen $\mathrm{Co}($ III ) complexes

We synthetized a series of novel salphen $\mathrm{Co}($ III $)$ complexes with trichloroacetate $\left(\mathrm{OOCCCl}_{3}\right)$, dinitrophenolate (DNP), pentafluorobenzoate ( $\mathrm{OBzF}_{5}$ ) and acetate ( OAc ) counterions based on published procedure [23], by reacting ligands $\mathbf{L 2}$ ( $\mathrm{N}, \mathrm{N}$ '-Bis(3,5-di-tert-butylsalicylidene)-1,2-phenylenediamine) and $\mathbf{L 3}$ ( $\mathrm{N}, \mathrm{N}$ '-Bis(3,5-di-tert-butylsalicylidene)-4-chloro-1,2-phenylenediamine) with cobalt acetate and subsequent oxidation by oxygen in presence of nucleophile.

Prepared complexes were obtained in most of cases as microcrystalline dark red powders, unsuitable for solid state structure characterization. Crystals of $\mathrm{Co}(\mathrm{III})$ salphen complexes bearing $\mathrm{N}, \mathrm{N}$ '-Bis( 3,5 -di-tert-butylsalicylidene)-1,2-phenylenediamine ligand $\mathbf{L 2}$ and $\mathrm{OBzF}_{5}$ counteranion obtained by crystallization from $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ /hexane were suitable for X -ray analysis. Surprisingly the solid state structure shows that the complex is not an expected pentacoordinated complex with one $\mathrm{OBzF}_{5}$ counteranion but a hexacoordinated octahedral complex bearing one $\mathrm{OBzF}_{5}$ anion and another coordinated $\mathrm{HOBzF}_{5}$ molecule (complex 2c, Fig. 2). Although the other complexes could not be analyzed by X-Ray diffraction, we can deduce structure of complexes from elemental analysis (Table 1). Elemental composition of complexes $\mathbf{2 b}$ and $\mathbf{3 d}$ shows better agreement with structure calculated for salphenCo(III) complex with one attached Y group, whereas complexes $\mathbf{2 a}$, $\mathbf{2 b}$ and 3a have probably hexacoordinated structure of YH adduct. Additional elemental analysis of hexacoordinated complex 2c also confirms the presence two $\mathrm{OBzF}_{5}$ groups. Non-integer values of average number of Y molecules coordinated to Co center shows that they are rather a mixture of pentacoordinated complexes and hexacoordinated YH adducts.


Fig. 2. View on the molecular structure of complex $\mathbf{2 c}$ with atom numbering. The displacement ellipsoids are drawn on $30 \%$ probability level. The geometry is stabilized by short hydrogen bond: $\mathrm{O}(1)-\mathrm{H}(1) \ldots$ O(6) 2.4418 (19) Á, angle at $\mathrm{H}(1) 165^{\circ}$.

Table 1. Elemental analysis of complexes $\mathbf{2 a - c}$ and $\mathbf{2 a , b}, \mathbf{d}$.

| Complex |  | $\mathbf{2 a}$ | $\mathbf{2 b}$ | $\mathbf{2 c}$ | 3a | 3b | 3d |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| FOUND | C | 53.93 | 65.53 | 60.00 | 50.01 | 58.40 | 65.43 |
|  | H | 5.37 | 6.76 | 5.32 | 5.13 | 5.75 | 7.25 |
| Calculated for optimum | N | 3.28 | 6.28 | 2.89 | 2.81 | 6.37 | 4.18 |
|  | C | 53.80 | 65.53 | 59.93 | 49.91 | 58.45 | 65.40 |
|  | H | 7.76 | 6.50 | 4.79 | 4.70 | 5.28 | 6.95 |
| Optimum | N | 3.18 | 6.88 | 2.90 | 2.90 | 8.16 | 3.95 |
|  |  | 1.75 eq. | 0.85 eq. | 1.75 eq. | 2.05 eq. | 1.80 eq. | 1.30 eq. |

NMR, FT-IR, HR-MS spectroscopy and elemental analysis were used for structural characterization of complexes. Both Salphen $\mathrm{Co}(\mathrm{III})^{+}$cation and $\mathrm{Y}^{-}$counteranion were detected for complexes $\mathbf{2 b}, \mathbf{2 c}$ and also $\mathbf{3 b}$ by HR-MS in positive and negative mode, respectively. Complexes $\mathbf{2 a}$, $\mathbf{3 a}$ and $\mathbf{3 d}$ were characterized only in HR-MS positive mode. Trichloroacetate group of complexes $\mathbf{2 a}$ and $\mathbf{3 a}$ attached to Co was confirmed by ATR-IR spectroscopy by observing typical vibration of $\mathrm{C}=0$ group at $\approx 1700 \mathrm{~cm}^{-1}$. Detailed COSY, HSQC and HMBC experiments were used to fully assign the ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra of new asymmetric salphen cobalt complex 3. (See Fig. S4-8 in Supp. information).

### 2.2. Alternating copolymerization of propylene oxide and $\mathrm{CO}_{2}$ with (salphen)CoY complexes

Basic salphen complex 2a was used to optimize polymerization conditions (Table 2). PPNCI, the most frequent and efficient cocatalyst for salen complexes [23], [24], [32], [49] was used at 1:1 ratio to Co. At 1 MPa and ambient temperature $\mathbf{2 a} / \mathrm{PPNCl}$ affords a high molar mass polycarbonate with $M_{\mathrm{n}} 25 \mathrm{~kg}$.mol ${ }^{-1}$. However, the selectivity to polymer formation and TOF of $\mathbf{2 a} /$ PPNCl are much lower compared to 1a/PPNCl [23]. Lower activity of salphen complex 2a compared to salen complex 1a can be explained by stronger interaction of nucleophile $Y$ group or growing polymer chain with Co center as a result of higher Lewis acidity of $\pi$-conjugated salphen complex. This limits ring-opening of activated epoxide molecules (during initiation and propagation step) by nucleophile which has to be released from Co center (in case nucleophile does not come from the cocatalyst). We could further expect that higher Lewis acidity of salphen complex should lead to better selectivity to polycarbonate vs. cyclic carbonate as was observed in the case of salphen Cr (III) complex compared to its salen analogue [11] However, in our case, the selectivity of salphen Co (III) complex 2a to polycarbonate formation is lower at all conditions than in the case of benchmark salen complex 1a. This shows on the complexity of the copolymerization reactions where many parameters play role and can work in opposite manner. Enhanced activity was observed at elevated temperature $50^{\circ} \mathrm{C}$ and even at $75^{\circ} \mathrm{C}$. An optimal polymerization temperature of $\mathbf{2} \mathbf{a}$ from point of view of both high TOF and selectivity to PPC ( $80 \%$ ) was $50^{\circ} \mathrm{C}$. Decrease of selectivity to PPC
observed at higher temperatures is a general phenomenon of these catalytic systems due to higher activation energy for the formation of CPC than for the formation of PPC [29]. Decrease of pressure resulted in decrease of activity, molar mass and at 0.1 MPa also to significant decrease of selectivity to PPC (Exp. 3, 4, Table 2). However, even at 0.1 MPa polymer consists of more than $99 \%$ of carbonate linkage suggesting the insertion of $\mathrm{CO}_{2}$ into metal-alkoxy bond is sufficiently fast.

Table 2. The effect of temperature and reaction pressure to $\mathrm{racPO} / \mathrm{CO}_{2}$ copolymerization catalyzed by salphen Co complex 2a/PPNCI.

| Exp. | Cat. | $T\left({ }^{\circ} \mathrm{C}\right)$ | $p(\mathrm{MPa})$ | $t_{p}(\mathrm{~h})$ | $\begin{aligned} & Y_{w} \\ & \text { PoL }^{\text {a }}(\%) \end{aligned}$ | TOF PoL $^{\text {b }}\left(\mathrm{h}^{-1}\right)$ | $\mathrm{TOF}_{\text {cFC }}{ }^{\text {c }}\left(\mathbf{h}^{-1}\right)$ | $M^{\text {n }}{ }^{\text {d,e }}$ (MALLS) $\left(\mathrm{kg} \mathrm{mol}^{-1}\right)$ | $\boldsymbol{D}^{\text {d, }}$ | Selectivity ${ }^{\dagger}$ (\% PPC) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Ref [23] | $1 \mathrm{a}^{\mathrm{g}}$ | 25 | 1.5 | 1.5 | - | 568 | - | $30.9{ }^{\text {h }}$ | $1.20^{\text {h }}$ | 99 |
| 1 | 2a | 25 | 1 | 4 | 36.9 | 190 | 27 | 25.0(34 + 18) | 1.09 | 88 |
| 2 | 2a | 50 | 1 | 2 | 42.9 | 456 | 110 | $34.4(48+25)$ | 1.16 | 81 |
| 3 | 2a | 50 | 0.2 | 2 | 20.4 | 206 | 51 | 18.1(27 + 14) | 1.13 | 80 |
| 4 | 2a | 50 | 0.1 | 2 | 9.5 | 98 | 94 | 11.8(13 + 7) | 1.24 | 51 |
| 5 | 2a | 75 | 1 | 1 | 27.1 | 560 | 391 | 26.5(43 + 21) | 1.25 | 59 |

Polymerizations run in neat epoxide, $[\mathrm{PO}] /[\mathrm{Co}] /[\mathrm{PPNCl}]=2000: 1: 1 ; V_{\mathrm{PO}}=1.5-2 \mathrm{~mL}$; Carbonate linkage of all polymers were $>99 \%$ as determined by ${ }^{1} \mathrm{H}$ NMR spectroscopy. a Based on isolated polymer yield. b Turnover frequency to polycarbonate. c Turnover frequency to cyclic carbonate; (For details see experimental part). d Determined by SEC-MALLS in THF. e All polymers exhibit bimodal distributions (values in brackets correspond to $M_{p}$ ). f Selectivity to PPC over cyclic carbonate. g Ref. [23]: Chiral ( $\mathrm{R}, \mathrm{R}^{\prime}$ )SalenCo-OOCCCl $\mathrm{I}_{3}$ complex (Fig. 1). h Literature data, $M_{\mathrm{n}}$ and $Đ$ determined by SEC with PS standard calibration in THF.

Influence of catalyst/cocatalyst ratio on activity and selectivity to PPC was further investigated with 2a combined with PPNCI (Fig. 3). Complex 2a without PPNCl cocatalyst was almost completely inactive and produced only trace amount of $\mathrm{CPC}\left(\mathrm{TOF}_{\mathrm{CPC}} \approx 2 \mathrm{~h}^{-1}\right.$ ) showing the crucial role of nucleophilic cocatalyst, which helps to ring opening of the epoxide as the rate determining step of the copolymerization. The highest activity, molar mass and maximum selectivity was observed at equimolar ratio of catalyst and cocatalyst. Further increase of cocatalyst loading (above 1:1 ratio) resulted in significant decrease of activity, selectivity and decrease of molar mass. This is due to the displacement of growing polymer chain from active metal center by nucleophilic cocatalyst moieties promoted at higher cocatalyst concentration resulting in increased back-biting of free polymer chains leading to CPC formation. Additionally, PPNCI alone was tested as a catalyst. At identical conditions, only trace amount of cyclic carbonate ( $\mathrm{TOF}_{\mathrm{CPC}} \approx 3 \mathrm{~h}^{-1}$ ) was detected in ${ }^{1} \mathrm{H}$ NMR spectrum of reaction mixture.


Fig. 3. The effect of $\mathbf{2 a} / \mathrm{PPNCl}$ loading to racPO/CO2 copolymerization at 1 MPa and $50^{\circ} \mathrm{C}$ ([PO]/[Co] = 2000:1, $t_{\mathrm{p}}=2 \mathrm{~h}$ ).

Using reaction conditions optimized for $\mathbf{2 a} / \mathrm{PPNCI}$ system ( $50^{\circ} \mathrm{C}, 1 \mathrm{MPaCO}, \mathrm{Co} /$ PPNCI $=1: 1$ ) a screening of polymerization behavior was performed for the series of salphen complexes $\mathbf{2 a}$-c with phenylene backbone and complexes 3a,b,d with 3-chlorophenylene backbone bearing different Y nucleophile groups. (Table 3) The results were compared with those published for analogous salen complex 1a [23]. Complex 2a with weakest nucleophile - trichloroacetate ( $p \mathrm{Ka}$ of conjugated acid 0.65 ) proved to be the most effective for $\mathrm{PO} / \mathrm{CO}_{2}$ copolymerization to produce PPC with highest activity, molar mass and selectivity up to $80 \%$ towards polymer. Complexes bearing stronger nucleophiles, such as $\mathbf{2 c}$ with pentafluorobenzoate ( $p K a=1.60$ ) and $\mathbf{2 b}$ with 2,4 -dinitrophenolate ( $p K a=4.11$ ) exhibit lower activity, molar mass and also selectivity was decreased to $60 \%$. The decrease of catalyst activity with increase of $Y$ nucleophilicity is caused by the fact that the stronger nucleophile dissociates from metal center more slowly and thus the coordination and subsequent epoxide activation is slower. Similarly, higher affinity of more nucleophilic Y group to metal center leads to higher concentration of uncoordinated polymer chains which undergo the back-biting reaction to CPC which leads to decreased selectivity.

Table 3. Copolymerization of $\mathrm{racPO} / \mathrm{CO}_{2}$ catalyzed with salphen Co complexes $\mathbf{2 a} \mathbf{a} \mathbf{c}$ and $\mathbf{3 a -}$ d compared with chiral ( $R, R^{\prime}$ ) salen Co complex (1a).

| Exp. | Catalyst | $\begin{aligned} & \boldsymbol{Y}_{\mathrm{w}} \\ & \text { PoL }^{\mathrm{a}} \text { (\%) } \end{aligned}$ | TOF PoL $^{\text {b }}\left(\mathrm{h}^{-1}\right)$ | $\mathrm{TOF}_{\text {cPC }}{ }^{\text {c }}\left(\mathbf{h}^{-1}\right)$ | $\begin{aligned} & M_{\mathrm{n}}^{\mathrm{d}, \mathrm{e}} \text { (MALLS) }(\mathrm{kg} \\ & \left.\mathrm{mol}^{-1}\right) \end{aligned}$ | $\boldsymbol{m}^{\text {d, }}$ | Selectivity ${ }^{f}$ (\% PPC) | HT <br> linkage ${ }^{\mathrm{g}}$ (\%) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Ref [23] | $1 a^{\text {h }}$ | - | 568 | - | $30.9{ }^{\text {i }}$ | $1.20^{\circ}$ | 99 | 96 |
| 6 | 2 | 0 | 0 | 243 | - | - | 0 | - |
| 2 | 2a | 42.9 | 456 | 110 | $34.4(48+25)$ | 1.16 | 81 | 92 |
| 7 | 2b | 38.0 | 391 | 251 | 21.3(40 + 21) | 1.30 | 61 | - |
| 8 | 2c | 36.7 | 374 | 228 | 25.0(41 + 21) | 1.28 | 62 | - |
| 9 | 3a | 37.7 | 386 | 72 | $29.4(43+23)$ | 1.13 | 84 | 95 |
| 10 | 3b | 33.2 | 340 | 87 | 14.8(23 + 11) | 1.10 | 80 | - |
| 11 | 3d | 12.5 | 124 | 184 | 10.3(10 + 9) | 1.05 | 40 | - |

Polymerizations run in neat epoxide, $[\mathrm{PO}] /[\mathrm{Co}] /[\mathrm{PPNCl}]=2000: 1: 1 ; V_{\mathrm{PO}}=1.5-2 \mathrm{~mL} ; T=50^{\circ} \mathrm{C}, t_{\mathrm{p}}=2 \mathrm{~h}, p_{\mathrm{CO} 2}=1 \mathrm{MPa}$, Carbonate linkage of all polymers were $\mathbf{> 9 9 \%}$ as determined by ${ }^{1} \mathrm{HNMR}$ spectroscopy. a Based on isolated polymer yield. b Turnover frequency to polycarbonate. c Turnover frequency to cyclic carbonate; (For details see experimental part). d Determined by SEC-MALLS in THF. e All polymers exhibit bimodal distributions (values in brackets correspond to $M_{p}$ ). f Selectivity to PPC over cyclic carbonate. g Head-to-tail linkage determined by ${ }^{13} \mathrm{C}$ NMR spectroscopy. h Ref. [23]: Chiral (R,R')SalenCo-OOCCCl ${ }_{3}$ complex (Fig. 1), $T=25{ }^{\circ} \mathrm{C}, t_{\mathrm{p}}=1.5 \mathrm{~h}, p_{\mathrm{co2}}=1.5 \mathrm{MPa}$. I Literature data, $M_{\mathrm{n}}$ and $Đ$ determined by SEC with PS standard calibration in THF.

The substitution of phenylene backbone by Cl atom was further investigated as analogous Cr complex was found to be highly active in similar catalytic ROP of $\beta$-butyrolactone [44]. However, in case of $\mathrm{CO}_{2} / \mathrm{PO}$ copolymerization, the activity of chloro substituted $\mathbf{C o}$ complexes $\mathbf{3 a}$ and $\mathbf{3} \mathbf{b}$ was lower compared to unsubstituted derivatives $\mathbf{2 a}$ and $\mathbf{2 b}$ (Table 3, runs 9 and 10 vs. 2 and 7). This can be explained by increased Lewis acidity of Co metal center in $\mathbf{3 a}$ and $\mathbf{3 b}$ which lowers the activity of salphen complexes due to the stronger interaction of nucleophile and metal which slows down PO coordination and its attack by nucleophile in initiation and propagation step. As expected, complex 3d combining chloro substitution on phenylene backbone and the strongest $Y$ nucleophile (acetate group, $p K a=4.76$ ) displayed the lowest activity and selectivity in $\mathrm{CO}_{2} / \mathrm{PO}$ copolymerization.

Investigation of temperature dependence of catalytic behavior of complexes shows that 2a continuously increases its activity up to $75^{\circ} \mathrm{C}$ upon while the selectivity simultaneously decreases. Complex 3 a reaches the maximum activity and selectivity at $50^{\circ} \mathrm{C}$ (Fig. 4). This shows the importance of optimization of reaction conditions for each of the catalyst to achieve its best catalytic performance. In addition, asymmetric salphen complex 3a exhibited slightly higher regioselectivity (expressed as head-to-tail linkage \%) compared to corresponding symmetric complex 2a (Table 3, exp. 2 vs. 9).


Fig. 4. The effect of catalyst and temperature to overall activity and selectivity of $\mathrm{racPO} / \mathrm{CO}_{2}$ copolymerization catalyzed by salphen Co complexes $\mathbf{2 a} / \mathrm{PPNCl}$ and $3 \mathrm{a} / \mathrm{PPNCl}$ at 1 MPa ([M]/[CAT] = 2000:1).

All prepared polypropylene carbonates displayed bimodal molar mass distribution as already observed for other salen complexes earlier [42], [50]. $M_{n}$ value of the higher-molar-mass peak was twice as large as that of the lower-molar-mass one in all prepared polycarbonates. This was previously described and explained due to the presence of contaminant water, which works as a bifunctional initiating group to give a telechelic polymers [42], [47], [50]. This indicate, that copolymerization can be initiated by several different active species such as axial Y group of catalyst and a chlorine anion which is a part of PPNCI cocatalyst or also by contaminant water.

To clear up the mechanism of activation, the MALDI-TOF analysis of prepared polycarbonates was used to determine end-groups of final polymer (Fig. 5). Probably due to poor ionization of polycarbonate samples and their fragmentation, only low molar mass fractions of polymers up to $3 \mathrm{~kg} \cdot \mathrm{~mol}^{-1}$ were detected. Obtained spectra for PPC prepared by $\mathbf{3 b} /$ PPNCI revealed presence of DNP ( $\alpha$ end group) and catalyst adduct ( $\omega$ end group). Catalyst $\omega$ end group can be attached either to ether or carbonate oxygen (Fig. 5).


Fig. 5. MALDI-TOF spectrum of PPC prepared by 3b/PPNCI (exp. 10).

For peak 1 we detected molar mass corresponding to initiation by DNP $^{-}$and termination by adduct $3-\mathrm{MeOH}$ attached to carbonate oxygen (see Fig. 5): $M_{\text {Peak1 }}(2096.2)=M_{\text {DNP }}(183.1)+M_{\text {Na+ }}(23)+12 x M_{\text {C4H603 }}(1225.1)+M_{3-}$ Меон $(664.2)=2095.4 \mathrm{~g} \mathrm{~mol}^{-1}$. Peak 2 correspond to initiation by $\mathrm{DNP}^{-}$and termination by adduct $\mathbf{3 - M e O H}$ attached to ether oxygen: $M_{\text {peak2 }}(2052.2)=M_{\text {DNP }}(183.1)+M_{\text {Na+ }}(23)+11 \times M_{\text {C4H603 }}(1123)+M_{\text {C3H60 }}(58)+M_{3-}$ Меон (664.2) $=2051.3 \mathrm{~g} \mathrm{~mol}^{-1}$. Peak 3 was attributed to structure where DNP $^{-}$and $3-\mathrm{H}_{2} \mathrm{O}$ adduct attached to ether oxygen are presented as end groups of polycarbonate: $\quad M_{\text {Peak3 }}(2038.2)=M_{\text {DNP }}(183.1)+$ $M_{\text {Na+ }}(23)+11 \times M_{\text {C4H6O3 }}(1123)+M_{\text {C3H6O }}(58)+M_{3-\text {-H2O }}(650.2)=2037.3 \mathrm{~g} \mathrm{~mol}^{-1}$
For comparison reasons we also used (salphen) Co (II) complex 2 for rac- $\mathrm{PO} / \mathrm{CO}_{2}$ copolymerization (Table 3, exp. 6). In combination with PPNCI the complex 2 was able to catalyze the cyclization reaction to CPC at much higher TOF ( $243 \mathrm{~h}^{-1}$ ) than PPNCl alone ( $3 \mathrm{~h}^{-1}$ ).

### 2.3. Alternating copolymerization of cyclohexene oxide with $\mathrm{CO}_{2}$ in presence of (salphen)CoY complexes

Salphen Co (III) complexes were further tested for copolymerization of CHO with $\mathrm{CO}_{2}$ which leads to polycarbonates with higher $T_{\mathrm{g}}$ (Table 4). Copolymerization conditions were optimized with salphen complex 3d, founding $[\mathrm{Co}] /[\mathrm{PPNCI}]=1: 1$ at $[\mathrm{CHO}] /[\mathrm{Co}]=1000-2000: 1,1 \mathrm{MPa}$ and $75^{\circ} \mathrm{C}$ affording PCHC with molar mass around $20 \mathrm{~kg} \mathrm{~mol}^{-1}$ and TOF 260-290 $\mathrm{h}^{-1}$ (Table 4, exp. 13, 14). A $100 \%$ selectivity to copolymer with no production of cyclohexene carbonate byproduct during $\mathrm{CHO} / \mathrm{CO}_{2}$ copolymerization is attributed to high ( $86 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ) difference of activation barriers for cyclic carbonate formation compared to the formation of PCHC [29]. Decrease of reaction temperature from $75^{\circ} \mathrm{C}$ to $50^{\circ} \mathrm{C}$ or decrease of pressure from 1 MPa to 0.1 MPa resulted in $50 \%$ decrease of polycarbonate formed molar mass and 2-5 times polymerization rate reduction (Table 4, exp. 13 vs. 12 and 16).

Table 4. Copolymerization of CHO with $\mathrm{CO}_{2}$ with salphen Co complex $\mathbf{3 d}$ compared to literature data obtained with Salen complexes $\mathbf{1 b}$ and $\mathbf{1 c}$.

| Exp. | Catalyst | $T\left({ }^{\circ} \mathrm{C}\right)$ | $p(\mathrm{MPa})$ | [CHO]/[Co]/[PPNCI] | $\boldsymbol{Y}_{\mathrm{wPOL}}{ }^{\text {a }}$ (\%) | TOF $_{\text {POL }}{ }^{\text {b }}\left(\mathbf{h}^{-1}\right)$ |  | $\underbrace{\text { c,d }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Ref [23] | $1 b^{\text {e }}$ | 40 | 1.5 | 1000:1:1 | - | 298 | $18.3^{\text {g }}$ | $1.20^{8}$ |
| Ref [46] | $1 c^{\text {f }}$ | 70 | 0.7 | 1000:1:1 | 44 | 440 | $11.9^{8}$ | $1.23{ }^{\text {g }}$ |
| 12 | 3d | 50 | 1 | 1000:1:1 | 27.8 | 133 | 13.8(18 + 10) | 1.08 |
| 13 | 3d | 75 | 1 | 1000:1:1 | 45.8 | 263 | 21.5(30 + 16) | 1.12 |
| 14 | 3d | 75 | 1 | 2000:1:1 | 29.4 | 287 | 23.1(29 + 16) | 1.08 |
| $15^{\text {h }}$ | 3d | 75 | 1 | 1000:1:0.5 | 45.3 | 161 | 23.8(36 + 19) | 1.15 |
| 16 | 3d | 75 | 0.1 | 1000:1:1 | 12.9 | 64 | 8.9 | 1.07 |

Polymerizations run in neat epoxide; $\mathrm{V}_{\text {сно }}=1.5-2 \mathrm{~mL}, t_{\mathrm{p}}=2 \mathrm{~h}$; Selectivity to polycarbonate as determined by ${ }^{1} \mathrm{H}$ NMR spectroscopy was $>99 \%$ in all cases; All poly(cyclohexene carbonate)s have $>99 \%$ carbonate linkages as determined by ${ }^{1} \mathrm{H}$ NMR spectroscopy. a Based on isolated polymer yield. $b$ Turnover frequency to polycarbonate. c Determined by SEC-MALLS in THF. d All polymers exhibit bimodal distributions (values in brackets correspond to $M_{p}$ ). e Catalyzed with chiral ( $R, R^{\prime}$ )SalenCo-DNP complex (Fig. 1). f Catalyzed with chiral ( $R, R^{\prime}$ )Salen Co$\mathrm{OBzF}_{5}$ complex (Fig. 1). g Literature data, $M_{\mathrm{n}}$ and $\doteq$ determined by SEC on PS standards calibration in THF. $\mathrm{h} t_{\mathrm{p}}=3 \mathrm{~h}$.

The variation of $Y$ nucleophile (Table 5) has only a little effect to Co complexes activity and molar mass of resulted polycarbonates, except of complex 2a, which was significantly less active compared to other complexes $\mathbf{2 b}, \mathbf{c}$ and $\mathbf{3 a - d}$. Surprisingly the complexes $\mathbf{2 a}$ and $\mathbf{3 a}$ containing the same nucleophile show considerable different activity which is not possible to ascribe to the ligand substitution by Cl atom in $\mathbf{3 a}$ as the same ligands in $\mathbf{2 b}$ and $\mathbf{3 b}$ have no effect on their activity. All complexes produced PCHC with $100 \%$ selectivity to polymer (no formation of cyclic carbonate) and $>99 \%$ of carbonate linkage at $75^{\circ} \mathrm{C}$ and 1 MPa . Number average molar mass values of PCHC prepared by $\mathbf{2 b}, \mathbf{c}$ and $\mathbf{3 a - d}$ were in the range of $15-23 \mathrm{~kg} \mathrm{~mol}^{-1}$, again displaying a bimodal molar mass distribution as in the case of polypropylene carbonates described above.

Table 5. Copolymerization of cyclohexene oxide with $\mathrm{CO}_{2}$ with salphen Co complexes $\mathbf{2 a - c}$ and $\mathbf{3 a - d}$.

| Exp. | Catalyst | $Y_{\text {w PoL }}{ }^{\text {a }}$ (\%) | TOF $_{\text {PoL }}{ }^{\text {b }}\left(\mathrm{h}^{-1}\right)$ | $\boldsymbol{M}_{\mathrm{n}}(\mathrm{MALLs})^{\mathrm{c}, \mathrm{d}}\left(\mathrm{kg} \mathrm{mol}^{-1}\right)$ | $\mathrm{D}^{\text {c,d }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 17 | 2a | 20.6 | 106 | $8.7(14+7)$ | 1.41 |
| 18 | 2b | 46.0 | 222 | 20.0(29 + 15) | 1.14 |
| 19 | 2c | 46.5 | 236 | 21.0(30 + 16) | 1.22 |
| 20 | 3a | 42.4 | 276 | 18.4(30 + 15) | 1.27 |
| 21 | 3b | 45.3 | 230 | 17.3(26 + 13) | 1.10 |
| 13 | 3d | 45.8 | 263 | $23.0(29+15)$ | 1.09 |

Polymerizations run in neat epoxide; $V_{\text {сно }}=1.5-2 \mathrm{~mL}, T=75^{\circ} \mathrm{C}, t_{\mathrm{p}}=2 \mathrm{~h}, p_{\mathrm{co2}}=1 \mathrm{MPa} \quad[\mathrm{CHO}] /[\mathrm{Co}] /[\mathrm{PPNCI}]=1000: 1: 1$; In all cases cyclohexene carbonate byproduct is not observed and all poly(cyclohexene carbonate)s have $>99 \%$ carbonate linkages as determined by ${ }^{1} \mathrm{H}$ NMR spectroscopy. a Based on isolated polymer yield. b Turnover frequency to polycarbonate. c Determined by SEC-MALLS in THF. d All polymers exhibit bimodal distributions (values in brackets correspond to $M_{p}$ ).

The $M_{n}$ and $M_{p}$ values of PCHC prepared with catalytic system $\mathbf{2 a}$ /PPNCl increased linearly in proportion to conversion in the range of $0-30 \%$ (Fig. 6) while dispersity remained relatively low ( $\left(\begin{array}{l}\text { ( }\end{array}\right.$ 1.1-1.4) indicating controlled manner of these catalytic polymerizations [51].


Fig. 6. Linear increase of PCHC molar mass with conversion (catalytic system 2a/PPNCI, $[\mathrm{PO}] /[\mathrm{Co}] /[\mathrm{PPNCl}]=1000: 1: 1, t_{\mathrm{p}}=0.5,2$ and $\left.4 \mathrm{~h}, T=75^{\circ} \mathrm{C}, p=1 \mathrm{MPa}\right)$.

MALDI-TOF analysis of synthesized PCHC prepared by 2a/PPNCI (Fig. 7) confirmed the presence of OOCCCl $3^{-}$and $\mathrm{Cl}^{-}$anions ( $\alpha$ end groups) and PPN ${ }^{+}$and (Salphen)Co.MeOH ( $\omega$ end groups) respectively. In contrast to PPC polymer, (Salphen) $\mathrm{Co}^{+}$and $\mathrm{PPN}^{+} \omega$ end groups are attached solely to carbonate oxygen showing that the last monomer unit comes from $\mathrm{CO}_{2}$ insertion, probably due to higher steric hindrance of CHO units compared to PO .




Fig. 7. MALDI-TOF spectrum of PCHC prepared by $\mathbf{2 a}$ /PPNCI (exp. 17).
Peak was attributed to polycarbonate with $100 C C C l_{3}{ }^{-}$and $\mathrm{PPN}^{+}$end groups: $M_{\text {Peak1 }}(2146.1)=M_{\text {OосСС13 }}(162.4)+M_{\text {Na+ }}(23)+10 \times M_{\text {C7H1003 }}(1421.5)+M_{\text {PPN+ }}(538.6)=2145.5 \mathrm{~g} \mathrm{~mol}^{-1}$. Peak 3 was attributed to polycarbonate with $\mathrm{Cl}^{-}(\alpha$ end groups) and $2-\mathrm{MeOH}$ adduct ( $\omega$ end group): $M_{\text {Peak3 }}(2110.0)=M_{\text {cl- }}(35.5)+M_{\text {Na+ }}(23)+10 x M_{\text {C7H1003 }}(1421.5)+M_{2}$ меон $(629.8)=2109.8 \mathrm{~g} \mathrm{~mol}^{-1}$ (Fig. 7). Peak 2 could be composed of same $\alpha$ and $\omega$ end groups as peak 3 with one more water attached to Co metal: $M_{\text {Peak2 }}(2128.1)=M_{\text {Cl }}(35.5)+M_{\text {Nat }}(23)+10 \times M_{\text {C7H1003 }}(1421.5)+M_{2}$ МеОн $(629.8)+$ МНго $^{\text {(18) }}=2127.8 \mathrm{~g} \mathrm{~mol}^{-1}$.

MALDI TOF spectra of PCHC shows that both nucleophiles $\left(\mathrm{OOCCCl}_{3}{ }^{-}, \mathrm{Cl}^{-}\right)$initiate the growth of polycarbonate chain and both countercations can be connected as the $\omega$ end group.

## 3. Conclusions

Herein, we reported a series of novel salphen $\mathrm{Co}(\mathrm{III})-\mathrm{Y}$ complexes, which were effective for both $\mathrm{PO} / \mathrm{CO}_{2}$ and $\mathrm{CHO} / \mathrm{CO}_{2}$ copolymerization leading to polycarbonates ( $>99 \%$ carbonate linkage) with molar mass 15$30 \mathrm{~kg} \mathrm{~mol}^{-1}$ and narrow dispersity. Substitution of phenylene framework of salphen ligand by chlorine atom led to decrease of activity in $\mathrm{PO} / \mathrm{CO}_{2}$ copolymerization. Variation of Y counteranions on $\mathrm{PO} / \mathrm{CO}_{2}$ copolymerization showed significant differences in activity, selectivity and molar mass, the best results were obtained with complexes bearing the weakest nucleophile trichloroacetate. $\mathrm{PO} / \mathrm{CO}_{2}$ copolymerization catalyzed by salphen Co complexes was accompanied by formation of cyclic carbonate (20-60\%). Activity and selectivity of all salphen Co (III) complexes in $\mathrm{CHO} / \mathrm{CO}_{2}$ copolymerization was almost independent on ligand structure and counteranion. No cyclic carbonate was formed in $\mathrm{CHO} / \mathrm{CO}_{2}$ copolymerization even at low $\mathrm{CO}_{2}$ pressures.

## 4. Experimental part

### 4.1. General information

All manipulation involving water or air sensitive compounds were carried out using standard Schlenk techniques under dry nitrogen. Propylene oxide (Aldrich) and cyclohexene oxide (Aldrich) were dried under $\mathrm{CaH}_{2}$ and distilled under vacuum or $\mathrm{N}_{2}$ atmosphere. $\operatorname{PPNCI}(\mathrm{ABCR})$ was purified by precipitation of its dry dichloromethane solution in dry diethylether. 1,2-phenylenediamine, 4-chloro-1,2-phenylenediamine, 3,5-ditert-butyl-2hydroxybenzaldehyde, cobalt(II)acetate tetrahydrate (all Aldrich), pentafluorobenzoic acid and trichloroacetic acid (both Alfa Aesar) were used as received. 2,4-dinitrophenol (Aldrich, stabilized with $15 \% \mathrm{H}_{2} \mathrm{O}$ ) was dried under high vacuum to remove water prior to use. Dichloromethane, diethylether and hexane were dried over $\mathrm{CaH}_{2}$ and distilled under $\mathrm{N}_{2}$ atmosphere. Water content of monomers and solvents was determined by Karl Fischer titration. Nitrogen (5.0, SIAD) was purified by passing through deoxygenating and drying columns. $\mathrm{CO}_{2}$ (4.8, SIAD) was used without further purification.

### 4.2. Synthesis of complexes

$\mathrm{N}, \mathrm{N}^{\prime}-\mathrm{Bis}\left(3,5-\right.$ di-tert-butylsalicylidene)-1,2-phenylenediamine (L2) and $\mathrm{N}, \mathrm{N}^{\prime}$-Bis(3,5-di-tert-butylsalicylidene)-4-chloro-1,2-phenylenediamine (L3) were synthesized according to literature [44].
4.2.1. (N,N'-Bis(3,5-di-tert-butylsalicylidene)-1,2-phenylenediamine)Cobalt(II) (2)

It was synthesized according to modified literature procedure [52]. Degassed ethanol ( 150 mL ) was added to a flask charged with ligand (L2) ( 3.5 mmol ). Suspension was heated to $50^{\circ} \mathrm{C}$ until complete ligand dissolution. Then cobalt(II) acetate tetrahydrate ( $0.7 \mathrm{~g}, 2.9 \mathrm{mmol}$ ) was dissolved in 30 mL of degassed EtOH and immediately added dropwise to solution of $\mathbf{L 2}$. The flask was heated to $80^{\circ} \mathrm{C}$ for 30 min and then slowly cooled to room temperature. Final suspension was concentrated to cca 70 mL , filtered under nitrogen atmosphere and washed with cold $\left(-20^{\circ} \mathrm{C}\right)$ dried methanol. The dark red/brown powder was recrystallized by dissolving it in dry methylene chloride $(30 \mathrm{~mL})$ and layered with dry hexane $(700 \mathrm{~mL})$. Solution was let few days to recrystallize in the fridge and then filtered under nitrogen atmosphere and dried 24 h under high vacuum. $Y_{w}=80 \%$.

MS-ESI ${ }^{+}\left(m / z, \mathrm{M}^{+}\right)=597.2888 ;$ Calcd. For: $\left[\mathrm{C}_{36} \mathrm{H}_{46} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{Co}^{+}\right.$: 597.2886.
IR (ATR, $\mathrm{cm}^{-1}$ ): 2954, 2902, 2866, 1613, 1574, 1543, 1519, 1489, 1463, 1424, 1386, 1355, 1323, 1249, 1198, 1178, 1161, 1131, 930, 918, 785, 740, 638.
4.2.2. (N,N'-Bis(3,5-di-tert-butylsalicylidene)-4-chloro-1,2-phenylenediamine)Cobalt(II) (3)

It was synthesized as 2. $Y_{w}=90 \%$.
${ }^{1} \mathrm{H}$ NMR (DMSO-d6, 500 MHz ): $\delta 1.33\left(18 \mathrm{H},-\mathrm{CH}_{3}(\mathbf{b})\right), 1.69\left(\mathrm{~s}, 18 \mathrm{H},-\mathrm{CCH}_{3}(\mathrm{a})\right), 7.39(2 \mathrm{H},=\mathrm{CH}-(\mathrm{g})) ; 7.47(2 \mathrm{H}, \mathrm{ArH}$ (i)), $7.50(1 \mathrm{H}, \operatorname{ArH}(\mathbf{o})), 8.47(1 \mathrm{H}, \operatorname{ArH}(\mathbf{p})), 8.61(1 \mathrm{H}, \operatorname{ArH}(\mathbf{m})), 8.71\left(1 \mathrm{H},-\mathrm{N}=\mathrm{CH}-\left(\mathbf{k}^{\prime}\right)\right), 8.77(1 \mathrm{H},-\mathrm{N}=\mathrm{CH}-(\mathbf{k}))$;
${ }^{13} \mathrm{H}$ NMR (DMSO-d6, 500 MHz$): 30.09\left(-\mathrm{CH}_{3}(\mathrm{a})\right), 31.24\left(-\mathrm{CH}_{3}(\mathrm{c})\right), 33.61\left(-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}(\mathrm{~d})\right), 35.84\left(-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}(\mathrm{~b})\right), 116.10$ (=CH-Ar, (m)), 116.91 (=CH- Ar, (p)), 117.76 (=C- Ar, (j)), 125.90 (=C-Ar, (o)), 129.13 (=CH- Ar, (i)), 129.57 (=CH$\operatorname{Ar},(\mathrm{g})$ ), 131.09 (=CCl-Ar (n)), 134.59 (=C-Ar (f)), 141.63 (=C-Ar (h)), 145.31(=C-Ar, (q)), 147.35(=C-Ar, (I)), 159.97 $\left(-\mathrm{N}=\mathrm{CH}-, \quad\left(\mathrm{k}^{\prime}\right)\right), \quad 160.48 \quad(-\mathrm{N}=\mathrm{CH}-, \quad(\mathrm{k})), \quad 166.06 \quad\left(=\mathrm{C}-\mathrm{O} \quad \operatorname{Ar} \quad\left(\mathrm{e}^{\prime}\right)\right), \quad 166.46 \quad(=\mathrm{C}-\mathrm{O} \quad \mathrm{Ar} \quad(\mathrm{e}))$.


MS-ESI ${ }^{+}\left(m / z, \mathrm{M}^{+}\right)=631.2499$; Calcd. For: $\left[\mathrm{C}_{36} \mathrm{H}_{45} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{ClCo}\right]^{+}$: 631.2496.
IR (ATR, $\mathrm{cm}^{-1}$ ): 2953, 2904, 2867, 1607, 1574, 1543, 1519, 1484, 1463, 1425, 1387, 1358, 1334, 1261, 1197, 1170, 1161, 1131, 1122, 1090, 935, 910, 785, 806, 748.

Complexes 2a-c and 3a,b,d were synthesized according to the literature method [23], [52].

### 4.2.3. Synthesis of complex 2a

To a stirred mixture of $2(0.6040 \mathrm{~g}, 1 \mathrm{mmol})$ in dry $\mathrm{CH}_{2} \mathrm{Cl}_{2}(20 \mathrm{~mL})$ was added trichloroacetic acid $(0.1840 \mathrm{~g}$, $1 \mathrm{mmol}, 1$ equiv.) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ( 15 mL ). The solution was stirred under dry oxygen atmosphere at room temperature for 90 min . The solvents were removed in vacuo and dark red/brown solid was dried under high vacuum. Crude product was washed $3 x$ with 20 mL of dry hexane and dried 24 h under high vacuum. $Y_{\mathrm{w}}=78 \%$. (Complex is mixture of complex with one $\mathrm{Y}^{-}$group and complex with one $\mathrm{Y}^{-}$group and coordinated YH molecule)

MS-ESI ${ }^{+/-}\left(\mathrm{m} / \mathrm{z}, \mathrm{M}^{+}\right)=597.2883 ;$ Calcd. For: $\left[\mathrm{C}_{36} \mathrm{H}_{46} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{Co}\right]^{+}$: 597.2886.
IR (ATR, $\mathrm{cm}^{-1}$ ): 2959, 2905, 2868, 1718, 1704 ( $\mathrm{C}=\mathrm{O}$ vibrations of $\mathrm{CCl}_{3} \mathrm{COO}^{-}$), 1612, 1578, 1546, 1519, 1486, $1461,1418,1387,1358,1330,1288\left(\mathrm{C}-\mathrm{O}\right.$ vibration of $\mathrm{CCl}_{3} \mathrm{COO}^{-}$), 1199, 1182, 1167, 1133, 1110, 883 (C-Cl vibration of $\left.\mathrm{CCl}_{3} \mathrm{COO}^{-}\right), 753,676$.

EA calculated for [ $\left.\mathrm{C}_{36} \mathrm{H}_{46} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{Co}\left(\mathrm{C}_{2} \mathrm{Cl}_{3} \mathrm{O}_{2}\right)_{1.75}\right]$ (\%): $\mathrm{C} 53.80 ; \mathrm{H} 7.76$; N 3.18 ; Found: C 53.93 ; H 5.37 ; N 3.28 .

### 4.2.4. Synthesis of complex $2 b$

It was synthesized as a similar procedure of the complex 2a. Crude product was washed 3 x with 20 mL of mixture hexane/ethyl acetate (dry) (50/50) and dried 24 h under high vacuum. $Y_{\mathrm{w}}=61 \%$.
$\mathrm{MS}-\mathrm{ESI}^{+/-}\left(\mathrm{m} / \mathrm{z}, \mathrm{M}^{+}\right)=597.2888$; Calcd. For: $\left[\mathrm{C}_{36} \mathrm{H}_{46} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{Co}^{+}\right.$: 597.2886; ( $\mathrm{m} / \mathrm{z}, \mathrm{M}^{-}$): 183.0041; Calcd. for $\left[\mathrm{C}_{6} \mathrm{H}_{3} \mathrm{~N}_{2} \mathrm{O}_{5}\right]^{-}, 183.0036$.

IR (ATR, $\mathrm{cm}^{-1}$ ): 2952, 2904, 2867, 1610, 1576 ( $\mathrm{N}=\mathrm{O}$ vibration of DNP), 1519, 1519, 1489, 1462, 1428, 1389, 1358, 1319 ( $\mathrm{N}=\mathrm{O}$ vibration of DNP), 1267, 1248, 1197, 1174, 1130, 936, 919, 833, 784, 743.
${ }^{1} \mathrm{H}$ NMR (DMSO-d6, 500 MHz ): $\delta 1.35\left(18 \mathrm{H},-\mathrm{CH}_{3}(\mathrm{~b})\right), 1.78$ (s, 18H, $\left.-\mathrm{CCH}_{3}(\mathrm{a})\right), 6.42$ (1H, ArH (DNP)), 7.56 (4H, $\operatorname{ArH}(\mathrm{i}, \mathrm{g})), 7.65(2 \mathrm{H}, \operatorname{ArH}(\mathrm{n})), 7.84(1 \mathrm{H}, \operatorname{ArH}(\mathrm{DNP})), 8.63(3 \mathrm{H}, \mathrm{ArH}(\mathrm{m}+\mathrm{DNP})), 8.93(2 \mathrm{H},-\mathrm{N}=\mathrm{CH}-(\mathrm{k}))$. EA calculated for [ $\mathrm{C}_{36} \mathrm{H}_{46} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{Co}\left(\mathrm{C}_{6} \mathrm{~N}_{2} \mathrm{O}_{5}\right)_{0.85}$ ] (\%): C 65.53; H 6.50; N 6.88 ; Found: C 65.53 ; H 6.76; N 6.28 .

### 4.2.5. Synthesis of complex 2c

It was synthesized by a similar procedure as the complex 2a. $Y_{w}=53 \%$. Crystals suitable for $X$-ray analysis were prepared by layering technique (solvent diffusion). Cca 10 mg of complex $\mathbf{2 c}$ was placed into dry clean NMR tube under nitrogen and dissolved in (cca 0.3 mL of dry $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. Solution was then layered by slow dribbling of dry hexane ( $2.5-3 \mathrm{~mL}$ ). The NMR tube was then carefully placed in a quiet place for $2-3$ weeks until dark red blockshaped crystals occurred.
$\mathrm{MS}-\mathrm{ESI}^{+}\left(\mathrm{m} / \mathrm{z}, \mathrm{M}^{+}\right)=597.2893$; Calcd. For: $\left[\mathrm{C}_{36} \mathrm{H}_{46} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{Co}^{+}\right]^{+}$597.2886; ( $\mathrm{m} / \mathrm{z}, \mathrm{M}^{-}$): 166.9932; Calcd. for [ $\left.\mathrm{C}_{6} \mathrm{~F}_{5}\right]^{-}$, 166.9926; and; ( $\mathrm{m} / \mathrm{z}, \mathrm{M}^{-}$): 210.9817; Calcd. for $\left[\mathrm{C}_{7} \mathrm{~F}_{5} \mathrm{O}_{2}\right]^{-}, 210.9824$.

IR (ATR, $\mathrm{cm}^{-1}$ ): 2955, 2906, 2869, 1734, 1666, 1651 ( $\mathrm{C}=\mathrm{O}$ vibrations of $\mathrm{OBzF}_{5}{ }^{-}$), 1612, 1592, 1581, 1520, 1485, 1463, 1423, $1387\left(\mathrm{C}-\mathrm{F}\right.$ vibration of $\mathrm{OBzF}_{5}^{-}$) , 1356, 1331, 1274, 1241, 1197, 1170, 1133, 1112, 995 (C-F vibration of $\mathrm{OBzF}_{5}^{-}$), 761, 749.
${ }^{1} \mathrm{H}$ NMR (DMSO-d6, 500 MHz ): $\delta 1.35\left(18 \mathrm{H},-\mathrm{CH}_{3}(\mathrm{~b})\right), 1.78\left(\mathrm{~s}, 18 \mathrm{H},-\mathrm{CCH}_{3}(\mathrm{a})\right), 7.40(2 \mathrm{H},=\mathrm{CH}-(\mathrm{g})) ; 7.46(2 \mathrm{H}, \mathrm{ArH}$ (i)), $7.56(2 \mathrm{H}, \mathrm{ArH}(\mathrm{m})), 8.64(2 \mathrm{H}, \mathrm{ArH}(\mathrm{m})), 8.95(2 \mathrm{H},-\mathrm{N}=\mathrm{CH}-(\mathrm{k}))$
${ }^{19}$ F NMR ( 500 MHz , DMSO-d6): -138.96, -143.73, -154.57, -157.57, -162.28.
EA calculated for [ $\left.\mathrm{C}_{36} \mathrm{H}_{46} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{Co}\left(\mathrm{C}_{7} \mathrm{~F}_{5} \mathrm{O}_{2}\right)_{1.75}\right](\%): \mathrm{C} 59.93 ; \mathrm{H} 4.79 ; \mathrm{N} 2.90$; Found: $\mathrm{C} 60.00 ; \mathrm{H} 5.32 ; \mathrm{N} 2.89$.

### 4.2.6. Synthesis of complex 3a

It was synthesized by a similar procedure as the complex 2a using precursor 3. $Y_{w}=52 \%$.
MS-ESI ${ }^{+/-}\left(m / z, \mathrm{M}^{+}\right)=631.2497$; Calcd. For: $\left[\mathrm{C}_{36} \mathrm{H}_{45} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{ClCo}\right]^{+}$: 631.2496.
IR (ATR, $\mathrm{cm}^{-1}$ ): 2958, 2907, 2869, 1761, 1697 ( $\mathrm{C}=\mathrm{O}$ vibrations of $\mathrm{CCl}_{3} \mathrm{COO}^{-}$), 1603, 1580, 1522, 1483, 1418, 1383, 1359, 1307, 1254 ( $\mathrm{C}-\mathrm{O}$ vibration of $\mathrm{CCl}_{3} \mathrm{COO}^{-}$), 1197, 1167, 1126, 1092, $937,836(\mathrm{C}-\mathrm{Cl}$ vibration of $\left.\mathrm{CCl}_{3} \mathrm{COO}^{-}\right), 755,683$.

EA calculated for [ $\mathrm{C}_{36} \mathrm{H}_{45} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{ClCo}\left(\mathrm{C}_{2} \mathrm{Cl}_{3} \mathrm{O}_{2}\right)_{2.05}$ ] (\%): $\mathrm{C} 49.91 ; \mathrm{H} 4.70 ; \mathrm{N} 2.90$; Found: $\mathrm{C} 50.01 ; \mathrm{H} 5.13 ; \mathrm{N} 2.81$.

### 4.2.7. Synthesis of complex 3b

It was synthesized by a similar procedure as the complex 3a. Crude product was washed $3 x$ with 20 mL of mixture hexane/ethyl acetate (dry) (50/50) and dried 24 h under high vacuum. $Y_{\mathrm{w}}=65 \%$.

MS-ESI ${ }^{+/-}\left(m / z, \mathrm{M}^{+}\right)=631.2499$; Calcd. For: $\left[\mathrm{C}_{36} \mathrm{H}_{45} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{ClCo}\right]^{+}: 631.2496 ;\left(\mathrm{m} / \mathrm{z}, \mathrm{M}^{-}\right): 183.0055$; Calcd. for $\left[\mathrm{C}_{6} \mathrm{H}_{3} \mathrm{~N}_{2} \mathrm{O}_{5}\right]^{-}: 183.0047$.

IR (ATR $\mathrm{cm}^{-1}$ ): 2952, 2904, 2867, 1600, 1573, 1545, 1519, 1483, 1462, 1424, 1389, 1357, 1327 ( $\mathrm{N}=\mathrm{O}$ vibration of DNP), 1262, 1196, 1174, 1131, 1122, 934, 912, 835, 783, 744.
${ }^{1} \mathrm{H}$ NMR (DMSO-d6, 500 MHz ): $\delta 1.35$ ( $18 \mathrm{H},-\mathrm{CH}_{3}(\mathrm{c})$ ), 1.78 (s, $18 \mathrm{H},-\mathrm{CCH}_{3}(\mathrm{a})$ ), 6.99 ( $1 \mathrm{H}, \mathrm{ArH}(\mathrm{DNP})$ ), 7.40 $(2 \mathrm{H},=\mathrm{CH}-(\mathrm{g})) ; 7.51(2 \mathrm{H}, \operatorname{ArH}(\mathrm{i})), 7.56(1 \mathrm{H}, \operatorname{ArH}(\mathrm{o})), 8.20(1 \mathrm{H}, \operatorname{ArH}(\mathrm{DNP})), 8.57(1 \mathrm{H}, \operatorname{ArH}(\mathrm{p})), 8.70(1 \mathrm{H}, \operatorname{ArH}$ $(\mathrm{m}+\mathrm{DNP})), 8.93(1 \mathrm{H},-\mathrm{N}=\mathrm{CH}-(\mathrm{k})), 8.97\left(1 \mathrm{H},-\mathrm{N}=\mathrm{CH}-\left(\mathrm{k}^{\prime}\right)\right)$.

EA calculated for $\left[\mathrm{C}_{36} \mathrm{H}_{45} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{ClCo}\left(\mathrm{C}_{6} \mathrm{~N}_{2} \mathrm{O}_{5}\right)_{1.80}\right]$ (\%): C 58.45; H 5.28; N 8.16; Found: C 58.40; H 5.75; N 6.37.

### 4.2.8. Synthesis of complex 3d

It was synthesized according to the literature [52]. $Y_{w}=99 \%$.
MS-ESI ${ }^{+}\left(\mathrm{m} / \mathrm{z}, \mathrm{M}^{+}\right)=631.2484$; Calcd. For: $\left[\mathrm{C}_{36} \mathrm{H}_{45} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{ClCo}\right]^{+}$: 631.2496 .
IR (ATR, $\mathrm{cm}^{-1}$ ): 2950, 2904, 2867, 1603, 1572, 1543, 1519, 1484, 1462, 1424, 1357, 1263, 1197, 1173, 1159, 1121, 934.

EA calculated for $\left[\mathrm{C}_{36} \mathrm{H}_{45} \mathrm{~N}_{2} \mathrm{O}_{2} \mathrm{ClCo}\left(\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right)_{1.30}\right]$ (\%): C 65.40; H 6.95; N 3.95 ; Found: C 65.43; H 7.25; N 4.18 .

### 4.3. Copolymerization of PO and CHO with $\mathrm{CO}_{2}$

A 100 mL Fischer-Porter bottle was heated to $100^{\circ} \mathrm{C}$ in an oven for 60 min . Immediately after removing from an oven, the Fischer-Porter bottle was screwed to the pressure pipe and purified by few vacuum $/ \mathrm{N}_{2}$ cycles. The reactor was then shortly opened to air. Solid catalyst and cocatalyst were introduced rapidly and bottle was closed and purified by vacuum $/ \mathrm{CO}_{2}$ cycles. The epoxide ( $1.5-2 \mathrm{~mL}$ ) was then introduced via syringe through the ball valve against flow of $\mathrm{CO}_{2}$. Fischer Porter bottle was pressurized to 1 MPa and heated to desired temperature using an oil bath. After desired polymerization time, the reaction mixture was cooled to $-78{ }^{\circ} \mathrm{C}$, excess of pressure was carefully vented of and polymerization vessel was disassembled. A small aliquot of reaction mixture was removed from the reactor for ${ }^{1} \mathrm{H}$ NMR analysis. A viscous reaction mixture was then dissolved in small amount of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and precipitated into excess of MeOH . Final polymer was separated by filtration and dried 24 h under high vacuum at $60^{\circ} \mathrm{C}$.

### 4.4. Analysis

${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra of ligands, complexes, reaction mixtures and polymers were recorded on Bruker 500 Avance III using $\mathrm{CDCl}_{3}$ or DMSO-d6 at room temperature. Elemental analysis of complexes was measured on El III instrument, from Elementar Vario. The resulting values are average values of two analyses. Mass spectra were recorded on spectrometer Orbitrap Velos (Thermo, USA). Samples were dissolved $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and then transferred into MeOH . The isocratic methanol was used as mobile phase. FT-IR spectra were recorded on spectrometer Nicolet 6700 by ATR technique. Crystallographic data for complex 2c were collected on Nonius KappaCCD diffractometer equipped with Bruker APEX-II CCD detector by monochromatized MoK a radiation ( $\lambda=0.71073 \AA$ ) at the temperature of 150 K .

MALDI-TOF MS mass spectra were acquired with an UltrafleXtreme (Bruker Daltonics, Bremen, Germany) in the positive ion reflectron mode. The spectra were the sum of 25,000 shots with a DPSS, Nd: YAG laser ( 355 nm , 1000 Hz ). Delayed extraction and external calibration was used. The samples were prepared by the dried droplet method: solutions of polycarbonate sample ( $10 \mathrm{mg} \mathrm{mL}^{-1}$ ), DCTB (trans-2-[3-(4-t-butyl-phenyl)-2-methyl-2propenylidene]malonitrile; $10 \mathrm{mg} \mathrm{mL}^{-1}$ ) as a matrix and sodium trifluoroacetate $\left(\mathrm{CF}_{3} \mathrm{COONa}^{2} 10 \mathrm{mg} \mathrm{mL}^{-1}\right.$ ) as a cationization agent in DMF were mixed in the volume ratio 4:20:1. 1 mL of the mixture was deposited on the ground-steel target plate. Drop was dried at ambient atmosphere.

Absolute molar masses were determined using a chromatograph Waters Breeze with RI detector operating at wavelength 880 nm and with MALLS detector miniDawn TREOS (Wyatt). Detector operated at wavelength of 658 nm . Both methods (absolute and PS calibration) were used for determination of molar mass and subsequently correlated. Absolute molar masses of polypropylene carbonates were determined using $\mathrm{dn} / \mathrm{dc}$ increment $0.050 \pm 0.003 \mathrm{~mL} \mathrm{~g}^{-1}$. Analyzed PPC's were on average $12 \%$ superior compared to PS calibration values (Figure S1a in Supp. information). Absolute molar masses of analyzed PCHC were calculated with dn/dc increment $0.087 \pm 0.002 \mathrm{~mL} \mathrm{~g}^{-1}$ and they are by $29 \%$ higher compared to $M_{\mathrm{n}}$ 's obtained from PS calibration method (Figure S1b in Supp. information).

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## SUPPORTING INFORMATION

## Salphen-Co(III) complexes catalyzed copolymerization of epoxides with $\mathrm{CO}_{2}$

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Content:

1. Evaluation of $\mathrm{Y}_{\mathrm{w}}$, TOF to polymer and TOF to cyclic carbonate ..... S1
2. Corelation of molar masses obtained with SEC-MALLS and SEC-PS calibration method ..... S2
3. SEC chromatograms of poly(propylene carbonate) polymers ..... S2
4. NMR characterization of complex 3 ..... S3
5. Characterization of complex 2 a ..... S7
6. Characterization of complex $2 b$ ..... S8
7. Characterization of complex 2 c ..... S10
8. Characterization of complex 3a ..... S12
9. Characterization of complex 3b ..... S14
10. Characterization of complex 3d ..... S16
11. Crystal data of complex 2c ..... S16

## 1. Evaluation of $Y_{w}$, TOF to polymer and TOF to cyclic carbonate

Yield was calculated by using equation (1),
(1) $Y_{w}=m_{\text {POLYMER }} \times \frac{M_{\text {EPOXIDE }}}{M_{R U}} / m_{\text {EPOXIDE }}$
where $m_{\text {POLYMER }}$ and $m_{\text {EPOXIDE }}$ is mass of isolated polymer and epoxide in feed, respectively, $M_{\text {EPOXIDE }}$ is molar mass of monomer unit and $M_{R U}$ corresponds to molar mass of repeating (carbonate) unit in polymer.
Turnover frequency to polymer was calculated using formula (2):
(2) TOF $_{P O L}=\frac{m_{\text {POLYMER }}}{M_{R U} \times n_{C A T} \times t_{p}}$;

Where $n_{\text {CAT }}$ is molar amount of catalyst and $t_{\mathrm{p}}$ is time of polymerization.

Turnover frequency to cyclic carbonate (CC) was calculated from equation (3):
(3) $T O F_{c C}=\frac{m_{C C}}{M_{C C} \times n_{C A T} \times t_{p}}$
where $m_{\mathrm{cc}}$ is mass of cyclic carbonate calculated according to (4):
(4) $m_{C C}=\left(m_{\text {EPOXXD }}-\left(m_{\text {EPOXIDE }} \times Y_{W P O L}\right)\right) \times \frac{I_{C H}(C C)}{I_{C H}(C C)+I_{C H}(E P O X I D E)}$
where $I_{C H}(C C)$ and $I_{C H}(E P O X I D E)$, are integrals of ${ }^{1} \mathrm{H}$ NMR signals of methine groups present in cyclic carbonate and epoxide respectively.
2. Corelation of molar masses obtained with SEC-MALLS and SEC-PS calibration method


Figure S1: Correlation of molar masses of PPC (a) and PCHC (b) obtained by SEC-MALLS and PS calibration method
3. SEC chromatograms of poly(propylene carbonate) polymers


Figure S2: SEC chromatograms (RI-detection) of poly(propylenecarbonate)s obtained with catalyst 2a (exp. 2-blue) and 2b (exp. 7 - grey)


Figure S3: SEC chromatograms (RI-detection) of poly(propylenecarbonate) (a) and poly(cyclohexenecarbonate) (b) before hydrolysis (red line) and after hydrolysis in $1 \mathrm{M} \mathrm{HCl} \mathrm{DCM}_{\text {sol. }}$ (blue line)

## 4. NMR characterization of complex 3



Figure S4: ${ }^{1} \mathrm{H}$ NMR of complex $\mathbf{3}$ in DMSO
${ }^{1} \mathrm{H}$ NMR (DMSO-d6, 500 MHz ): $\delta 1.33\left(18 \mathrm{H},-\mathrm{CH}_{3}(\mathrm{~b})\right), 1.69\left(\mathrm{~s}, 18 \mathrm{H},-\mathrm{CCH}_{3}(\mathrm{a})\right), 7.39(2 \mathrm{H},=\mathrm{CH}-(\mathrm{g})) ; 7.47(2 \mathrm{H}, \mathrm{ArH}(\mathrm{i})), 7.50(1 \mathrm{H}, \mathrm{ArH}$ (o)), $8.47(1 \mathrm{H}, \mathrm{ArH}(\mathbf{p})), 8.61(1 \mathrm{H}, \mathrm{ArH}(\mathbf{m})), 8.71\left(1 \mathrm{H},-\mathrm{N}=\mathrm{CH}-\left(\mathbf{k}^{\prime}\right)\right), 8.77(1 \mathrm{H},-\mathrm{N}=\mathrm{CH}-(\mathbf{k}))$.


Figure S5: ${ }^{13} \mathrm{C}$ APT NMR of complex $\mathbf{3}$ in DMSO
${ }^{13} \mathrm{H}$ NMR (DMSO-d6, 500 MHz$)$ : $30.09\left(-\mathrm{CH}_{3}(\mathrm{a})\right), 31.24\left(-\mathrm{CH}_{3}(\mathrm{c})\right)$, $33.61\left(-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}(\mathrm{~d})\right), 35.84\left(-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}(\mathrm{~b})\right), 116.10(=\mathrm{CH}-\mathrm{Ar},(\mathrm{m}))$, 116.91 (=CH-Ar, (p)), 117.76 (=C-Ar, (j)), 125.90 (=C-Ar, (o)), 129.13 (=CH-Ar, (i)), 129.57 (=CH-Ar, (g)), 131.09 (=CCl-Ar (n)), 134.59 (=C-Ar (f)), 141.63 (=C-Ar (h)), 145.31(=C-Ar, (q)), 147.35(=C-Ar, (I)), 159.97 (-N=CH-, (k')), 160.48 (-N=CH-, (k)), 166.06 (=C-O $\left.\operatorname{Ar}\left(e^{\prime}\right)\right), 166.46$ (=C-O $\left.\operatorname{Ar}(e)\right)$.


Figure S6: ${ }^{1} \mathrm{H}$ COSY NMR of complex $\mathbf{3}$ (aromatic region) in DMSO

## Complex 3.esp



Figure S7: ${ }^{1} \mathrm{H}-{ }^{13} \mathrm{C}$ NMR of complex $\mathbf{3}$ in DMSO


Complex 3.esp


Figure S8 (a) HMBC NMR of complex 3, (b) expansion of region $6.5 \mathrm{ppm}-9.5 \mathrm{ppm}$

## 5. Characterization of complex 2a

1 Hostalek ZH 438 1 \#49-60 ${ }^{-} \mathrm{RT}^{-}{ }^{-} 0.73-0.89^{-} \mathrm{AV}^{-} 12^{-} \mathrm{NL}^{-} 8.63 \mathrm{E} 6$


Figure S9: HRMS-ESI ${ }^{+}$spectrum of complex $\mathbf{2 a}$


Figure S10: HRMS-ESI spectrum of complex 2a


Figure S11: FT-IR spectra of complexes $\mathbf{2}$ and $\mathbf{2 a}$

## 6. Characterization of complex $\mathbf{2 b}$



Figure S12: ${ }^{1} \mathrm{H}$ NMR of complex $\mathbf{2 b}$ in DMSO
${ }^{1} \mathrm{H}$ NMR (DMSO-d6, 500 MHz$)$ : $\delta 1.35\left(18 \mathrm{H},-\mathrm{CH}_{3}(\mathrm{c})\right), 1.78\left(\mathrm{~s}, 18 \mathrm{H},-\mathrm{CCH}_{3}(\mathrm{a})\right), 6.42(1 \mathrm{H}, \mathrm{ArH}(\mathrm{DNP})), 7.56(4 \mathrm{H}, \operatorname{ArH}(\mathrm{i}, \mathrm{g})), 7.65(2 \mathrm{H}$, $\operatorname{ArH}(\mathrm{n})), 7.84(1 \mathrm{H}, \mathrm{ArH}(\mathrm{DNP})), 8.63(3 \mathrm{H}, \mathrm{ArH}(\mathrm{m}+\mathrm{DNP})), 8.93(2 \mathrm{H},-\mathrm{N}=\mathrm{CH}-(\mathrm{k}))$.


Figure S13: HRMS-ESI ${ }^{+}$spectrum of complex 2b


Figure S14: HRMS-ESI spectrum of complex 2b


Figure S15: FT-IR spectra of complexes $\mathbf{2}$ and $\mathbf{2 b}$

## 7. Characterization of complex 2c



Figure S16: HRMS-ESI spectrum of complex 2c


Figure S17: HRMS-ESI- spectrum of complex 2c


Figure S18: FT-IR spectra of complexes $\mathbf{2}$ and $\mathbf{2 c}$


Figure S19: ${ }^{19}$ F NMR of complex 2c

## 8. Characterization of complex 3a



Figure S20: HRMS-ESI ${ }^{+}$spectrum of complex 3a


Figure S21: HRMS-ESI spectrum of complex 3a


Figure S22: FT-IR spectra of complexes $\mathbf{3}$ and $\mathbf{3 a}$

## 9. Characterization of complex 3b

Complex 3b.esp





Figure S23: ${ }^{1} \mathrm{H}$ NMR of complex 3b in DMSO
${ }^{1} \mathrm{H}$ NMR (DMSO-d6, 500 MHz$): \delta 1.35\left(18 \mathrm{H},-\mathrm{CH}_{3}(\mathrm{~b})\right), 1.78\left(\mathrm{~s}, 18 \mathrm{H},-\mathrm{CCH}_{3}(\mathrm{a})\right), 6.99(1 \mathrm{H}, \mathrm{ArH}(\mathrm{DNP})), 7.40(2 \mathrm{H},=\mathrm{CH}-(\mathrm{g})) ; 7.51(2 \mathrm{H}$, $\operatorname{ArH}(\mathrm{i})), 7.56(1 \mathrm{H}, \operatorname{ArH}(\mathrm{o})), 8.20(1 \mathrm{H}, \operatorname{ArH}(\mathrm{DNP})), 8.55(1 \mathrm{H}, \operatorname{ArH}(\mathrm{p})), 8.70(1 \mathrm{H}, \mathrm{ArH}(\mathrm{m}+\mathrm{DNP})), 8.93(1 \mathrm{H},-\mathrm{N}=\mathrm{CH}-(\mathrm{k})), 8.97(1 \mathrm{H},-$ $\left.\mathrm{N}=\mathrm{CH}-\left(\mathrm{k}^{\prime}\right)\right)$.


Figure S24: HRMS-ESI ${ }^{+}$spectrum of complex 3b


Figure S25: HRMS-ESI' spectrum of complex $\mathbf{3 b}$


Figure S26: FT-IR spectra of complexes $\mathbf{3}$ and $\mathbf{3 b}$

## 10. Characterization of complex 3d



Figure S27: HRMS-ESI ${ }^{+}$spectrum of complex 3d

## 11. Crystal data of complex 2c

Crystal data for complex 2c: $\mathrm{C}_{50} \mathrm{H}_{47} \mathrm{CoF}_{10} \mathrm{~N}_{2} \mathrm{O}_{6}, M_{\mathrm{r}}=1020.83$, triclinic, $P-1$ (No 2), $a=13.6323$ (6) $\AA, b=14.3118$ (6) $\AA$, $c=14.4602(6) \AA, \alpha=76.884(2)^{\circ}, \quad b=85.260(2)^{\circ}, y=65.678(2)^{\circ} ; Z=2, D_{x}=1.354 \mathrm{Mg} . \mathrm{m}^{-3}$, dark red crystal of dimensions $0.40 \times$ $0.31 \times 0.18 \mathrm{~mm}$, the multi-scan absorption correction was applied was $\left(\mu=0.43 \mathrm{~mm}^{-1}\right), T_{\min }=0.846, T_{\max }=0.925 ; 31019$ diffraction collected ( $\theta_{\max }=27^{\circ}$ ), 10924 independent ( $R_{\text {int }}=0.032$ ) and 8543 observed $(I>2 \sigma(I))$ ). The refinement converged $\left(\Delta / \sigma_{\max }=0.001\right)$ to $R=0.046$ for observed reflections and $w R\left(F^{2}\right)=0.127, G O F=1.08$ for 634 parameters and all 10924 reflections. The final difference map displayed no peaks of chemical significance ( $\Delta \rho_{\max }=0.79, \Delta \rho_{\min }-0.51 \mathrm{e} . \AA^{-3}$ )

## Crystal data

| $\mathrm{C}_{50} \mathrm{H}_{47} \mathrm{CoF}_{10} \mathrm{~N}_{2} \mathrm{O}_{6}$ | $Z=2$ |
| :--- | :--- |
| $M_{r}=1020.83$ | $F(000)=1052$ |
| Triclinic, $P^{-} 1$ | $D_{x}=1.354 \mathrm{Mg} \mathrm{m}$ |
| $a=13.6323(6) \AA$ | Mo Ka radiation, $\mathrm{I}=0.71073 \AA$ |
| $b=14.3118(6) \AA$ | Cell parameters from 9942 reflections |
| $c=14.4602(6) \AA$ | $\mathrm{q}=2.7-27.0^{\circ}$ |
| $\mathrm{a}=76.884(2)^{\circ}$ | $\mathrm{m}=0.43 \mathrm{~mm}^{-1}$ |
| $\mathrm{~b}=85.260(2)^{\circ}$ | $T=150 \mathrm{~K}$ |
| $\mathrm{~g}=65.678(2)^{\circ}$ | Prism, dark red |
| $V=2503.58(18) \AA^{3}$ | $0.40 \times 0.31 \times 0.18 \mathrm{~mm}$ |


| Bruker APEX-II CCD <br> diffractometer | 10924 independent reflections |
| :--- | :--- |
| Radiation source: fine-focus sealed tube | 8543 reflections with $I>2 \mathrm{~s}(I)$ |
| Graphite monochromator | $R_{\text {int }}=0.032$ |
| f and w scans | $\mathrm{q}_{\max }=27.0^{\circ}, \mathrm{q}_{\text {min }}=1.5^{\circ}$ |
| Absorption correction: multi-scan <br> SADABS V2012 $/ 1$ (Bruker AXS Inc.) | $h=-17^{\circledR} 16$ |
| $T_{\min }=0.846, T_{\max }=0.925$ | $k=-18^{\circledR} 13$ |
| 31019 measured reflections | $I=-18^{\circledR} 18$ |

## Refinement

| Refinement on $F^{2}$ | Primary atom site location: structure-invariant <br> direct methods |
| :--- | :--- |
| Least-squares matrix: full | Secondary atom site location: difference <br> Fourier map |
| $R\left[F^{2}>2 \mathrm{~s}\left(F^{2}\right)\right]=0.046$ | Hydrogen site location: inferred from <br> neighbouring sites |
| $w R\left(F^{2}\right)=0.127$ | H atoms treated by a mixture of independent <br> and constrained refinement |
| $S=1.08$ | $w=1 /\left[s^{2}\left(F_{\mathrm{o}}^{2}\right)+(0.0703 P)^{2}+0.2024 P\right]$ <br> where $P=\left(F_{o}^{2}+2 F_{\mathrm{c}}^{2}\right) / 3$ |
| 10924 reflections | $(\mathrm{D} / \mathrm{s})_{\max }=0.001$ |
| 634 parameters | $\mathrm{D} \rho_{\max }=0.79 \mathrm{e} \AA^{-3}$ |
| 0 restraints | $\mathrm{D} \rho_{\min }=-0.51 \mathrm{e} \AA^{-3}$ |

## Special details

Geometry. All esds (except the esd in the dihedral angle between two I.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of $F^{2}$ against ALL reflections. The weighted R-factor wR and goodness of fit $S$ are based on $F^{2}$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^{2}$. The threshold expression of $F^{2}>2 \operatorname{sigma}\left(F^{2}\right)$ is used only for calculating $R$-factors $(g t)$ etc. and is not relevant to the choice of reflections for refinement. R-factors based on $F^{2}$ are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

## Geometric parameters (Å, o) for 2c

| $\mathrm{Co1}-\mathrm{O} 2$ | $1.8607(12)$ | $\mathrm{C} 21-\mathrm{H} 21 \mathrm{C}$ | 0.9800 |
| :--- | :--- | :--- | :--- |
| $\mathrm{Co1-N2}$ | $1.8626(15)$ | $\mathrm{C} 22-\mathrm{C} 23$ | $1.416(3)$ |
| $\mathrm{Co1-O3}$ | $1.8807(13)$ | $\mathrm{C} 22-\mathrm{H} 22$ | 0.9500 |
| $\mathrm{Co1-N1}$ | $1.9106(15)$ | $\mathrm{C} 23-\mathrm{C} 28$ | $1.414(3)$ |
| $\mathrm{Co1-O1}$ | $1.9612(13)$ | $\mathrm{C} 23-\mathrm{C} 24$ | $1.427(3)$ |
| $\mathrm{Co1-O5}$ | $1.9681(13)$ | $\mathrm{C} 24-\mathrm{C} 25$ | $1.367(3)$ |


| N1-C7 | 1.293 (2) | C24-H24 | 0.9500 |
| :---: | :---: | :---: | :---: |
| N1-C1 | 1.418 (2) | C25-C26 | 1.402 (3) |
| N2-C22 | 1.307 (2) | C25-C33 | 1.532 (3) |
| N2-C6 | 1.417 (2) | C26-C27 | 1.383 (3) |
| O1-C9 | 1.386 (2) | C26-H26 | 0.9500 |
| O1-H1 | 0.9638 | C27-C28 | 1.432 (3) |
| O2-C28 | 1.320 (2) | C27-C29 | 1.528 (3) |
| O3-C37 | 1.231 (2) | C29-C32 | 1.533 (3) |
| O5-C44 | 1.242 (2) | C29-C30 | 1.535 (3) |
| O6-C44 | 1.251 (2) | C29-C31 | 1.541 (3) |
| O4-C37 | 1.220 (2) | C30-H30A | 0.9800 |
| C1-C2 | 1.394 (3) | C30-H30B | 0.9800 |
| C1-C6 | 1.399 (3) | C30-H30C | 0.9800 |
| C2-C3 | 1.373 (3) | C31-H31A | 0.9800 |
| C2-H2 | 0.9500 | C31-H31B | 0.9800 |
| C3-C4 | 1.395 (3) | C31-H31C | 0.9800 |
| C3-H3 | 0.9500 | C32-H32A | 0.9800 |
| C4-C5 | 1.386 (3) | C32-H32B | 0.9800 |
| C4-H4 | 0.9500 | C32-H32C | 0.9800 |
| C5-C6 | 1.390 (3) | C33-C35 | 1.521 (3) |
| C5-H5 | 0.9500 | C33-C36 | 1.524 (3) |
| C7-C8 | 1.437 (3) | C33-C34 | 1.533 (3) |
| C7-H7 | 0.9500 | C34-H34A | 0.9800 |
| C8-C9 | 1.405 (3) | C34-H34B | 0.9800 |
| C8-C13 | 1.408 (3) | C34-H34C | 0.9800 |
| C9-C10 | 1.390 (3) | C35-H35A | 0.9800 |
| C10-C11 | 1.402 (3) | C35-H35B | 0.9800 |
| C10-C18 | 1.544 (3) | C35-H35C | 0.9800 |
| C11-C12 | 1.398 (3) | C36-H36A | 0.9800 |
| C11-H11 | 0.9500 | C36-H36B | 0.9800 |
| C12-C13 | 1.371 (3) | C36-H36C | 0.9800 |
| C12-C14 | 1.536 (2) | C37-C38 | 1.549 (3) |
| C13-H13 | 0.9500 | C38-C43 | 1.388 (3) |
| C14-C15 | 1.519 (3) | C38-C39 | 1.393 (3) |
| C14-C16 | 1.532 (3) | C39-F1 | 1.332 (2) |
| C14-C17 | 1.536 (3) | C39-C40 | 1.373 (3) |
| C15-H15A | 0.9800 | C40-F2 | 1.341 (3) |
| C15-H15B | 0.9800 | C40-C41 | 1.356 (3) |
| C15-H15C | 0.9800 | C41-F3 | 1.342 (3) |
| C16-H16A | 0.9800 | C41-C42 | 1.367 (4) |
| C16-H16B | 0.9800 | C42-F4 | 1.345 (3) |
| C16-H16C | 0.9800 | C42-C43 | 1.376 (4) |


| C17-H17A | 0.9800 | C43-F5 | 1.330 (3) |
| :---: | :---: | :---: | :---: |
| C17-H17B | 0.9800 | C44-C45 | 1.511 (3) |
| C17-H17C | 0.9800 | C45-C50 | 1.379 (3) |
| C18-C21 | 1.527 (3) | C45-C46 | 1.388 (3) |
| C18-C19 | 1.537 (3) | C46-F6 | 1.330 (2) |
| C18-C20 | 1.544 (3) | C46-C47 | 1.382 (3) |
| C19-H19A | 0.9800 | C47-F7 | 1.343 (3) |
| C19-H19B | 0.9800 | C47-C48 | 1.371 (3) |
| C19-H19C | 0.9800 | C48-F8 | 1.339 (3) |
| C20-H2OA | 0.9800 | C48-C49 | 1.383 (3) |
| C20-H2OB | 0.9800 | C49-F9 | 1.337 (3) |
| C20-H20C | 0.9800 | C49-C50 | 1.373 (3) |
| C21-H21A | 0.9800 | C50-F10 | 1.347 (2) |
| C21-H21B | 0.9800 |  |  |
| O2-Co1-N2 | 96.24 (6) | H21B-C21-H21C | 109.5 |
| O2-Co1-O3 | 93.27 (6) | N2-C22-C23 | 125.94 (18) |
| N2-Co1-O3 | 97.50 (7) | N2-C22-H22 | 117.0 |
| O2-Co1-N1 | 178.40 (6) | C23-C22-H22 | 117.0 |
| N2-Co1-N1 | 85.28 (6) | C28-C23-C22 | 123.10 (17) |
| O3-Co1-N1 | 86.03 (6) | C28-C23-C24 | 120.71 (17) |
| O2-Co1-O1 | 85.97 (5) | C22-C23-C24 | 116.16 (18) |
| N2-Co1-O1 | 176.27 (6) | C25-C24-C23 | 121.50 (19) |
| O3-Co1-O1 | 85.35 (6) | C25-C24-H24 | 119.2 |
| N1-Co1-O1 | 92.54 (6) | C23-C24-H24 | 119.2 |
| O2-Co1-O5 | 88.09 (6) | C24-C25-C26 | 116.31 (17) |
| N2-Co1-O5 | 85.28 (6) | C24-C25-C33 | 123.40 (19) |
| O3-Co1-O5 | 176.75 (6) | C26-C25-C33 | 120.26 (17) |
| N1-Co1-O5 | 92.54 (6) | C27-C26-C25 | 125.60 (18) |
| O1-Co1-O5 | 91.81 (5) | C27-C26-H26 | 117.2 |
| C7-N1-C1 | 121.67 (16) | C25-C26-H26 | 117.2 |
| C7-N1-Co1 | 125.03 (13) | C26-C27-C28 | 117.46 (18) |
| C1-N1-Co1 | 112.67 (11) | C26-C27-C29 | 121.87 (17) |
| C22-N2-C6 | 121.28 (16) | C28-C27-C29 | 120.67 (16) |
| C22-N2-Co1 | 123.47 (13) | O2-C28-C23 | 123.26 (16) |
| C6-N2-Co1 | 113.79 (12) | O2-C28-C27 | 118.91 (17) |
| C9-O1-Co1 | 125.48 (11) | C23-C28-C27 | 117.83 (16) |
| C9-O1-H1 | 106.9 | C27-C29-C32 | 109.69 (17) |
| Co1-O1-H1 | 101.6 | C27-C29-C30 | 111.58 (17) |
| C28-O2-Co1 | 125.55 (12) | C32-C29-C30 | 107.46 (19) |
| C37-O3-Co1 | 126.31 (13) | C27-C29-C31 | 110.37 (18) |
| C44-O5-Co1 | 126.20 (13) | C32-C29-C31 | 110.71 (18) |


| C2-C1-C6 | 119.99 (17) | C30-C29-C31 | 106.97 (17) |
| :---: | :---: | :---: | :---: |
| C2-C1-N1 | 126.42 (16) | C29-C30-H30A | 109.5 |
| C6-C1-N1 | 113.58 (16) | C29-C30-H30B | 109.5 |
| C3-C2-C1 | 119.58 (17) | H30A-C30-H30B | 109.5 |
| C3-C2-H2 | 120.2 | C29-C30-H30C | 109.5 |
| $\mathrm{C} 1-\mathrm{C} 2-\mathrm{H} 2$ | 120.2 | H30A-C30-H30C | 109.5 |
| C2-C3-C4 | 120.47 (18) | H30B-C30-H30C | 109.5 |
| C2-C3-H3 | 119.8 | C29-C31-H31A | 109.5 |
| C4-C3-H3 | 119.8 | C29-C31-H31B | 109.5 |
| C5-C4-C3 | 120.58 (19) | H31A-C31-H31B | 109.5 |
| C5-C4-H4 | 119.7 | C29-C31-H31C | 109.5 |
| C3-C4-H4 | 119.7 | H31A-C31-H31C | 109.5 |
| C4-C5-C6 | 119.07 (18) | H31B-C31-H31C | 109.5 |
| C4-C5-H5 | 120.5 | C29-C32-H32A | 109.5 |
| C6-C5-H5 | 120.5 | C29-C32-H32B | 109.5 |
| C5-C6-C1 | 120.21 (17) | H32A-C32-H32B | 109.5 |
| C5-C6-N2 | 125.32 (16) | C29-C32-H32C | 109.5 |
| C1-C6-N2 | 114.46 (16) | H32A-C32-H32C | 109.5 |
| N1-C7-C8 | 127.41 (17) | H32B-C32-H32C | 109.5 |
| N1-C7-H7 | 116.3 | C35-C33-C36 | 109.5 (2) |
| C8-C7-H7 | 116.3 | C35-C33-C25 | 111.53 (18) |
| C9-C8-C13 | 118.90 (17) | C36-C33-C25 | 108.03 (17) |
| C9-C8-C7 | 124.91 (16) | C35-C33-C34 | 107.33 (19) |
| C13-C8-C7 | 116.07 (16) | C36-C33-C34 | 108.7 (2) |
| O1-C9-C10 | 119.91 (16) | C25-C33-C34 | 111.67 (17) |
| O1-C9-C8 | 118.98 (16) | C33-C34-H34A | 109.5 |
| C10-C9-C8 | 121.10 (16) | C33-C34-H34B | 109.5 |
| C9-C10-C11 | 116.93 (17) | H34A-C34-H34B | 109.5 |
| C9-C10-C18 | 123.06 (16) | C33-C34-H34C | 109.5 |
| C11-C10-C18 | 119.99 (17) | H34A-C34-H34C | 109.5 |
| C12-C11-C10 | 124.08 (18) | H34B-C34-H34C | 109.5 |
| C12-C11-H11 | 118.0 | C33-C35-H35A | 109.5 |
| C10-C11-H11 | 118.0 | C33-C35-H35B | 109.5 |
| C13-C12-C11 | 116.90 (17) | H35A-C35-H35B | 109.5 |
| C13-C12-C14 | 121.33 (17) | C33-C35-H35C | 109.5 |
| C11-C12-C14 | 121.55 (17) | H35A-C35-H35C | 109.5 |
| C12-C13-C8 | 122.02 (17) | H35B-C35-H35C | 109.5 |
| C12-C13-H13 | 119.0 | C33-C36-H36A | 109.5 |
| C8-C13-H13 | 119.0 | C33-C36-H36B | 109.5 |
| C15-C14-C16 | 107.67 (17) | H36A-C36-H36B | 109.5 |
| C15-C14-C12 | 112.47 (16) | C33-C36-H36C | 109.5 |
| C16-C14-C12 | 110.87 (16) | H36A-C36-H36C | 109.5 |


| C15-C14-C17 | 109.65 (19) | H36B-C36-H36C | 109.5 |
| :---: | :---: | :---: | :---: |
| C16-C14-C17 | 109.28 (19) | O4-C37-O3 | 129.4 (2) |
| C12-C14-C17 | 106.88 (16) | O4-C37-C38 | 117.84 (19) |
| C14-C15-H15A | 109.5 | O3-C37-C38 | 112.80 (16) |
| C14-C15-H15B | 109.5 | C43-C38-C39 | 115.0 (2) |
| H15A-C15-H15B | 109.5 | C43-C38-C37 | 121.70 (19) |
| C14-C15-H15C | 109.5 | C39-C38-C37 | 123.28 (18) |
| H15A-C15-H15C | 109.5 | F1-C39-C40 | 115.30 (19) |
| H15B-C15-H15C | 109.5 | F1-C39-C38 | 122.01 (19) |
| C14-C16-H16A | 109.5 | C40-C39-C38 | 122.7 (2) |
| C14-C16-H16B | 109.5 | F2-C40-C41 | 119.4 (2) |
| H16A-C16-H16B | 109.5 | F2-C40-C39 | 120.3 (2) |
| C14-C16-H16C | 109.5 | C41-C40-C39 | 120.4 (2) |
| H16A-C16-H16C | 109.5 | F3-C41-C40 | 120.4 (2) |
| H16B-C16-H16C | 109.5 | F3-C41-C42 | 120.4 (2) |
| C14-C17-H17A | 109.5 | C40-C41-C42 | 119.2 (2) |
| C14-C17-H17B | 109.5 | F4-C42-C41 | 120.0 (2) |
| H17A-C17-H17B | 109.5 | F4-C42-C43 | 119.7 (2) |
| C14-C17-H17C | 109.5 | C41-C42-C43 | 120.3 (2) |
| H17A-C17-H17C | 109.5 | F5-C43-C42 | 116.4 (2) |
| H17B-C17-H17C | 109.5 | F5-C43-C38 | 121.2 (2) |
| C21-C18-C19 | 108.16 (19) | C42-C43-C38 | 122.4 (2) |
| C21-C18-C10 | 112.01 (16) | O5-C44-06 | 126.82 (18) |
| C19-C18-C10 | 108.82 (17) | O5-C44-C45 | 117.33 (17) |
| C21-C18-C20 | 106.71 (18) | O6-C44-C45 | 115.84 (17) |
| C19-C18-C20 | 110.42 (18) | C50-C45-C46 | 117.34 (19) |
| C10-C18-C20 | 110.69 (17) | C50-C45-C44 | 120.91 (18) |
| C18-C19-H19A | 109.5 | C46-C45-C44 | 121.66 (18) |
| C18-C19-H19B | 109.5 | F6-C46-C47 | 118.35 (19) |
| H19A-C19-H19B | 109.5 | F6-C46-C45 | 120.36 (18) |
| C18-C19-H19C | 109.5 | C47-C46-C45 | 121.3 (2) |
| H19A-C19-H19C | 109.5 | F7-C47-C48 | 120.2 (2) |
| H19B-C19-H19C | 109.5 | F7-C47-C46 | 119.9 (2) |
| C18-C20-H20A | 109.5 | C48-C47-C46 | 119.8 (2) |
| C18-C20-H20B | 109.5 | F8-C48-C47 | 120.0 (2) |
| H2OA - C20-H2OB | 109.5 | F8-C48-C49 | 120.0 (2) |
| C18-C20-H20C | 109.5 | C47-C48-C49 | 120.1 (2) |
| H2OA - C20-H2OC | 109.5 | F9-C49-C50 | 120.7 (2) |
| H20B-C20-H20C | 109.5 | F9-C49-C48 | 120.1 (2) |
| C18-C21-H21A | 109.5 | C50-C49-C48 | 119.2 (2) |
| C18-C21-H21B | 109.5 | F10-C50-C49 | 117.7 (2) |
| H21A-C21-H21B | 109.5 | F10-C50-C45 | 119.99 (18) |


| C18-C21-H21C | 109.5 | C49-C50-C45 | 122.3 (2) |
| :---: | :---: | :---: | :---: |
| H21A-C21-H21C | 109.5 |  |  |
| N2-Co1-N1-C7 | -169.60 (16) | C22-C23-C24-C25 | -178.53 (18) |
| O3-Co1-N1-C7 | -71.73 (16) | C23-C24-C25-C26 | -4.4 (3) |
| O1-Co1-N1-C7 | 13.43 (16) | C23-C24-C25-C33 | 173.57 (18) |
| O5-Co1-N1-C7 | 105.35 (16) | C24-C25-C26-C27 | 2.8 (3) |
| N2-Co1-N1-C1 | 1.35 (12) | C33-C25-C26-C27 | -175.24 (19) |
| O3-Co1-N1-C1 | 99.23 (12) | C25-C26-C27-C28 | 3.7 (3) |
| O1-Co1-N1-C1 | -175.62 (12) | C25-C26-C27-C29 | -176.90 (19) |
| O5-Co1-N1-C1 | -83.69 (12) | Co1-O2-C28-C23 | 7.2 (3) |
| O2-Co1-N2-C22 | 15.73 (16) | Co1-02-C28-C27 | -172.65 (13) |
| O3-Co1-N2-C22 | 109.87 (15) | C22-C23-C28-O2 | 5.1 (3) |
| N1-Co1-N2-C22 | -164.78 (16) | C24-C23-C28-O2 | -172.83 (17) |
| O5-Co1-N2-C22 | -71.82 (15) | C22-C23-C28-C27 | -175.09 (17) |
| O2-Co1-N2-C6 | -177.93 (12) | C24-C23-C28-C27 | 7.0 (3) |
| O3-Co1-N2-C6 | -83.79 (13) | C26-C27-C28-O2 | 171.47 (17) |
| N1-Co1-N2-C6 | 1.57 (12) | C29-C27-C28-02 | -7.9 (3) |
| O5-Co1-N2-C6 | 94.52 (12) | C26-C27-C28-C23 | -8.4 (3) |
| O2-Co1-O1-C9 | 152.85 (14) | C29-C27-C28-C23 | 172.23 (18) |
| O3-Co1-O1-C9 | 59.24 (14) | C26-C27-C29-C32 | 123.1 (2) |
| N1-Co1-O1-C9 | -26.57 (14) | C28-C27-C29-C32 | -57.5 (2) |
| O5-Co1-O1-C9 | -119.19 (14) | C26-C27-C29-C30 | 4.1 (3) |
| N2-Co1-O2-C28 | -15.10 (15) | C28-C27-C29-C30 | -176.49 (18) |
| O3-Co1-O2-C28 | -113.02 (15) | C26-C27-C29-C31 | -114.7 (2) |
| O1-Co1-O2-C28 | 161.89 (15) | C28-C27-C29-C31 | 64.7 (2) |
| O5-Co1-O2-C28 | 69.94 (14) | C24-C25-C33-C35 | 132.3 (2) |
| O2-Co1-O3-C37 | 38.60 (17) | C26-C25-C33-C35 | -49.9 (3) |
| N2-Co1-O3-C37 | -58.15 (17) | C24-C25-C33-C36 | -107.3 (2) |
| N1-Co1-O3-C37 | -142.85 (17) | C26-C25-C33-C36 | 70.5 (3) |
| O1-Co1-O3-C37 | 124.28 (17) | C24-C25-C33-C34 | 12.2 (3) |
| O2-Co1-O5-C44 | 73.86 (15) | C26-C25-C33-C34 | -169.98 (19) |
| N2-Co1-O5-C44 | 170.29 (15) | Co1-O3-C37-O4 | 14.5 (3) |
| N1-Co1-O5-C44 | -104.66 (15) | Co1-03-C37-C38 | -165.82 (12) |
| O1-Co1-O5-C44 | -12.04 (15) | O4-C37-C38-C43 | -1.3 (3) |
| C7-N1-C1-C2 | -11.7 (3) | O3-C37-C38-C43 | 178.9 (2) |
| $\mathrm{Co1}-\mathrm{N} 1-\mathrm{C} 1-\mathrm{C} 2$ | 177.03 (16) | O4-C37-C38-C39 | 176.9 (2) |
| C7-N1-C1-C6 | 167.26 (17) | O3-C37-C38-C39 | -2.9 (3) |
| Co1-N1-C1-C6 | -4.0 (2) | C43-C38-C39-F1 | 179.1 (2) |
| C6-C1-C2-C3 | -0.9 (3) | C37-C38-C39-F1 | 0.8 (4) |
| N1-C1-C2-C3 | 177.98 (18) | C43-C38-C39-C40 | -0.3 (4) |
| $\mathrm{C} 1-\mathrm{C} 2-\mathrm{C} 3-\mathrm{C} 4$ | -1.5 (3) | C37-C38-C39-C40 | -178.6 (2) |


| C2-C3-C4-C5 | 1.5 (3) | F1-C39-C40-F2 | 0.7 (4) |
| :---: | :---: | :---: | :---: |
| C3-C4-C5-C6 | 0.9 (3) | C38-C39-C40-F2 | -179.9 (2) |
| C4-C5-C6-C1 | -3.3 (3) | F1-C39-C40-C41 | -178.3 (3) |
| C4-C5-C6-N2 | 175.50 (18) | C38-C39-C40-C41 | 1.1 (4) |
| C2-C1-C6-C5 | 3.3 (3) | F2-C40-C41-F3 | -1.1 (4) |
| N1-C1-C6-C5 | -175.69 (17) | C39-C40-C41-F3 | 177.9 (3) |
| C2-C1-C6-N2 | -175.62 (16) | F2-C40-C41-C42 | -179.8 (3) |
| N1-C1-C6-N2 | 5.4 (2) | C39-C40-C41-C42 | -0.8(5) |
| C22-N2-C6-C5 | -16.5 (3) | F3-C41-C42-F4 | 1.0 (5) |
| Co1-N2-C6-C5 | 176.85 (16) | C40-C41-C42-F4 | 179.7 (3) |
| C22-N2-C6-C1 | 162.40 (17) | F3-C41-C42-C43 | -178.9 (3) |
| Co1-N2-C6-C1 | -4.3 (2) | C40-C41-C42-C43 | -0.3(5) |
| C1-N1-C7-C8 | -171.16 (18) | F4-C42-C43-F5 | 0.7 (5) |
| Co1-N1-C7-C8 | -1.0 (3) | C41-C42-C43-F5 | -179.3 (3) |
| N1-C7-C8-C9 | -5.9 (3) | F4-C42-C43-C38 | -178.9 (3) |
| N1-C7-C8-C13 | 170.04 (19) | C41-C42-C43-C38 | 1.1 (5) |
| Co1-O1-C9-C10 | -154.02 (14) | C39-C38-C43-F5 | 179.7 (3) |
| Co1-O1-C9-C8 | 26.6 (2) | C37-C38-C43-F5 | -2.0 (4) |
| C13-C8-C9-01 | 176.43 (16) | C39-C38-C43-C42 | -0.8 (4) |
| C7-C8-C9-01 | -7.7(3) | C37-C38-C43-C42 | 177.5 (3) |
| C13-C8-C9-C10 | -2.9 (3) | Co1-05-C44-06 | 13.7 (3) |
| C7-C8-C9-C10 | 172.95 (18) | Co1-05-C44-C45 | -166.30 (12) |
| O1-C9-C10-C11 | -176.71 (17) | O5-C44-C45-C50 | -125.8 (2) |
| C8-C9-C10-C11 | 2.6 (3) | O6-C44-C45-C50 | 54.2 (3) |
| O1-C9-C10-C18 | 5.2 (3) | O5-C44-C45-C46 | 57.8 (3) |
| C8-C9-C10-C18 | -175.50 (18) | O6-C44-C45-C46 | -122.2 (2) |
| C9-C10-C11-C12 | -1.0 (3) | C50-C45-C46-F6 | -179.03 (19) |
| C18-C10-C11-C12 | 177.15 (18) | C44-C45-C46-F6 | -2.5 (3) |
| C10-C11-C12-C13 | -0.3 (3) | C50-C45-C46-C47 | -0.5 (3) |
| C10-C11-C12-C14 | -174.89 (18) | C44-C45-C46-C47 | 175.95 (19) |
| C11-C12-C13-C8 | 0.0 (3) | F6-C46-C47-F7 | -0.5 (3) |
| C14-C12-C13-C8 | 174.64 (18) | C45-C46-C47-F7 | -179.0 (2) |
| C9-C8-C13-C12 | 1.5 (3) | F6-C46-C47-C48 | 178.5 (2) |
| C7-C8-C13-C12 | -174.69 (18) | C45-C46-C47-C48 | 0.0 (4) |
| C13-C12-C14-C15 | 164.47 (19) | F7-C47-C48-F8 | -0.5 (4) |
| C11-C12-C14-C15 | -21.2 (3) | C46-C47-C48-F8 | -179.4 (2) |
| C13-C12-C14-C16 | 43.9 (3) | F7-C47-C48-C49 | 179.7 (2) |
| C11-C12-C14-C16 | -141.8 (2) | C46-C47-C48-C49 | 0.8 (4) |
| C13-C12-C14-C17 | -75.1 (2) | F8-C48-C49-F9 | -0.1 (4) |
| C11-C12-C14-C17 | 99.2 (2) | C47-C48-C49-F9 | 179.7 (2) |
| C9-C10-C18-C21 | 177.2 (2) | F8-C48-C49-C50 | 179.3 (2) |
| C11-C10-C18-C21 | -0.8(3) | C47-C48-C49-C50 | -0.9 (4) |


| $\mathrm{C} 9-\mathrm{C} 10-\mathrm{C} 18-\mathrm{C} 19$ | $57.7(3)$ | $\mathrm{F} 9-\mathrm{C} 49-\mathrm{C} 50-\mathrm{F} 10$ | $-1.5(3)$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{C} 11-\mathrm{C} 10-\mathrm{C} 18-\mathrm{C} 19$ | $-120.3(2)$ | $\mathrm{C} 48-\mathrm{C} 49-\mathrm{C} 50-\mathrm{F} 10$ | $179.1(2)$ |
| $\mathrm{C} 9-\mathrm{C} 10-\mathrm{C} 18-\mathrm{C} 20$ | $-63.8(3)$ | $\mathrm{F} 9-\mathrm{C} 49-\mathrm{C} 50-\mathrm{C} 45$ | $179.7(2)$ |
| $\mathrm{C} 11-\mathrm{C} 10-\mathrm{C} 18-\mathrm{C} 20$ | $118.1(2)$ | $\mathrm{C} 48-\mathrm{C} 49-\mathrm{C} 50-\mathrm{C} 45$ | $0.3(4)$ |
| $\mathrm{C} 6-\mathrm{N} 2-\mathrm{C} 22-\mathrm{C} 23$ | $-174.40(17)$ | $\mathrm{C} 46-\mathrm{C} 45-\mathrm{C} 50-\mathrm{F} 10$ | $-178.40(18)$ |
| $\mathrm{C} 1-\mathrm{N} 2-\mathrm{C} 22-\mathrm{C} 23$ | $-9.0(3)$ | $\mathrm{C} 44-\mathrm{C} 45-\mathrm{C} 50-\mathrm{F} 10$ | $5.1(3)$ |
| $\mathrm{N} 2-\mathrm{C} 22-\mathrm{C} 23-\mathrm{C} 28$ | $-4.0(3)$ | $\mathrm{C} 46-\mathrm{C} 45-\mathrm{C} 50-\mathrm{C} 49$ | $0.4(3)$ |
| $\mathrm{N} 2-\mathrm{C} 22-\mathrm{C} 23-\mathrm{C} 24$ | $173.98(18)$ | $\mathrm{C} 44-\mathrm{C} 45-\mathrm{C} 50-\mathrm{C} 49$ | $-176.1(2)$ |
| $\mathrm{C} 28-\mathrm{C} 23-\mathrm{C} 24-\mathrm{C} 25$ | $-0.5(3)$ |  |  |

Hydrogen-bond geometry ( $(\AA$, , - ) for $\mathbf{2 c}$

| $D-\mathrm{H} \cdots A$ | $D-\mathrm{H}$ | $\mathrm{H} \cdots A$ | $D \cdots A$ | $D-\mathrm{H} \cdots A$ |
| :---: | :--- | :--- | :--- | :--- |
| $\mathrm{O} 1-\mathrm{H} 1 \cdots \mathrm{O} 6$ | 0.96 | 1.50 | $2.4418(19)$ | 165 |

Crystallographic data was collected on Nonius KappaCCD diffractometer equipped with Bruker APEX-II CCD detector by monochromatized MoKa radiation ( $\lambda=0.71073 \AA$ A) at the temperature of $150(2) \mathrm{K}$. The structure was solved by direct methods (SHELXS) ${ }^{1}$ and refined by full matrix least squares based on $F^{2}$ (SHELXL97) ${ }^{1}$. The hydrogen atoms on carbon were calculated into idealized positions and were refined as fixed (riding model) with assigned temperature factors $\mathrm{H}_{\text {iso }}(\mathrm{H})=1.2 \mathrm{U}_{\text {eq }}$ (pivot atom) or $1.5 \mathrm{U}_{\text {eq }}$ for methyl moiety.

The hydrogen in -OH moiety was found on difference Fourier map and fixed during refinement with assigned temperature factors Hiso(H) $=1.2 \mathrm{U}_{\text {eq }}(\mathrm{O}(6))$.

To improved the resolution of the complex PLATON ${ }^{2}$ / SQUEEZE procedure was used to correct the data for the presence of the disordered dichlormethane solvent. One potential solvent cavity with volume of $292 \AA^{3}$ was found at special position of inversion. 57 electrons worth of scattering were located in the void, highest peak corresponds to electron density $2.1 \mathrm{e} / \mathrm{A}^{3}$.

1. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122
2. Spek, A.L. (2009). Acta Cryst. D65, 148-155
