Group 9 open-shell organometallics: reactivity at the ligand
Dzik, W.I.

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Chapter 6

‘Carbene Radicals’ in Co\textsuperscript{II}(por)-Catalyzed Olefin Cyclopropanation*

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6.1 Introduction

Transition metal-catalyzed olefin cyclopropanation with diazo reagents is one of the most attractive methods to prepare functionalized cyclopropanes, which have found a myriad of fundamental and practical applications. Highly diastereo- and enantioselective catalytic systems, which are mainly based on diamagnetic Cu I and binuclear Rh 2-paddlewheel complexes, have been successfully developed to catalyze certain types of cyclopropanation reactions. While excellent results with styrenes and other electron-rich olefins have been obtained with these catalysts, their performance with electron-deficient olefins (e.g. acrylates) is, however, problematic due to the electrophilic nature of the metal-carbene intermediate.

Following the discovery that cobalt(II) complexes are capable of (stereo- and enantioselective) olefin cyclopropanation reactions, various cobalt-based catalytic systems have been developed. So far, the most successful cobalt-based catalysts are complexes with salen and porphyrin ligands developed by the groups of Katsuki and Zhang, respectively. Chiral cobalt-porphyrin cyclopropanation catalysts are unprecedented in their reactivity, stereocontrol, and their ability to affect cyclopropanation with (near) stoichiometric amounts of alkenes avoiding carbene dimer formation. Another intriguing feature of the cobalt(II) porphyrin systems is their effectiveness in cyclopropanation of electron-deficient olefins like methyl acrylate or acrylonitrile, while they perform rather poorly in the cyclopropanation of aliphatic alkenes (Scheme 1). This reactivity is remarkable, and suggests some nucleophilic character of the carbene transfer intermediate in these reactions. This is unexpected, because in analogy with Cu- and Rh-based systems one would expect the formation of electrophilic (Fischer-type) transition-metal carbene intermediates from diazo esters with relatively late transition metals like cobalt. This points to a very different character of the carbene transfer intermediate for CoII(por)-mediated ring-closing reactions compared to the generic late transition metal electrophilic (Fischer-type) carbene intermediate.

Understanding these reactions in terms of a detailed reaction mechanism, thus explaining the above-mentioned unique reactivities and exceptional selectivities, will be important for future developments in (stereo)selective cyclopropanation reactions, especially regarding the use of diazo compounds (such as diazomalonates and diazoacetoacetates) and alkene substrates, for which high selectivities have not yet been achieved. Detailed mechanistic insights in these reactions may eventually allow us to expand the scope to other CoII(por)-mediated ring-closing reactions (e.g. formation of five-membered rings from dienes and carbones).

The available mechanistic information so far from previously reported kinetic studies and spectroscopic investigations using CoII(salen) and CoII(por) systems is fragmented and susceptible to different mechanistic interpretations. Reported DFT studies are restricted to simplified models of CoII(salen) systems and provide only limited information about small substrate models (ethene and diazoacetaldehyde). As a result, questions regarding the (electronic) structures of the proposed cobalt carbene...
intermediates and transition states, as well as an estimate of the energy barriers on the basis of computational studies with realistic models, are unanswered. Especially, a rationale behind the remarkable activity of CoII(por) systems towards electron-deficient olefins is an important question to answer. Clearly, the mechanism of CoII-catalyzed cyclopropanation is poorly understood, and requires detailed attention.5

In this Chapter we address the above questions in a combined experimental and computational approach. EPR spectroscopic studies and complementary DFT-EPR-property calculations allowed us to detect and characterize the elusive carbene-transfer intermediate operating in CoII(por) systems, providing valuable new information about its unusual (electronic) structure. In addition, we performed a full mechanistic DFT study of the CoII(por)-catalyzed cyclopropanation of methyl acrylate, styrene and propene with methyl diazoacetate.

However, before we describe the details of our studies, let us first summarize the most relevant experimental mechanistic information available from previous reports in the next section (section 6.2).

6.2 Background and available experimental mechanistic information

Some kinetic and spectroscopic investigations of CoII(TPP) (TPP = tetraphenylporphyrin) catalyzed styrene cyclopropanation by ethyl diazoacetate (EDA) have been reported by Cenini and coworkers.7 This system performed relatively well in the cyclopropanation of styrenes, while its reactivity towards relatively electron-rich aliphatic alkenes was rather poor. The kinetic studies revealed a first order rate dependence on [catalyst], [EDA] and [styrene]8 concentrations.9 The authors claimed the IR and NMR spectroscopic observation of a relatively stable ‘carbene’ species CoII(TPP)(CHCOOEt), formed upon addition of EDA to CoII(TPP), in which the :CHCOOEt moiety ends up bridging between the metal and a pyrrole nitrogen atom.7 In general, carbene moieties can bind to transition metal porphyrin complexes in two ways: (1) classic coordination of the carbene carbon solely to the transition metal, where this ‘terminal carbene’ is generally thought to result in a metal-carbon double bond; and (2) as a ‘bridging carbene’ between the metal and a pyrrolato nitrogen of the porphyrin moiety, formed by insertion of the ‘terminal carbene’ into the M−N bond (see Figure 1).10-15

The IR detection of the ‘carbene’ species, CoII(TPP)(CHCOOEt) was independently reported by Yamada and coworkers,16 although with a different carbonyl stretch frequency (νCO = 1597 cm−1 in DCM) than the one reported by Cenini and coworkers7 (νCO = 1722 cm−1 in benzene). Yamada and coworkers assigned the IR signals to a ‘terminal carbene’ species, albeit with a cobalt-carbon single bond, and proposed that this species has substantial unpaired spin density delocalized over the carbene carbon

Figure 1. Possible coordination modes of carbenes to transition metal porphyrin complexes.

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and its neighboring carbonyl moiety, in analogy with the ‘terminal carbene’ species proposed to be formed from Co\textsuperscript{II}(salen) and methyl diazoacetate (based on IR spectroscopy and complementary DFT calculations).\textsuperscript{17} A similar mechanism was proposed by Zhang and coworkers in their original report on the discovery of Co\textsuperscript{II}(por)-catalyzed olefin cyclopropanation.\textsuperscript{4a} For Ir\textsuperscript{II} complexes, we demonstrated experimentally and computationally that carbene ligands generated from diazo esters like EDA at low-spin open-shell d\textsuperscript{7} group 8 transition metals indeed behave as so-called ‘redox non-innocent’ ligands.\textsuperscript{18,19} In analogy, the elusive ‘terminal carbene’ Co\textsuperscript{II}(por)(CHCOOEt) species are perhaps not true ‘carbenes’ in the classic sense, but rather carbon centered ‘carbene radicals’ (see Scheme 2). This clearly adds to the complexity of our understanding of the (electronic) structure of ‘carbene’ intermediates in Co\textsuperscript{II}(por)-mediated cyclopropanation reactions (\textit{vide infra}).

![Scheme 2. Redox non-innocent behavior of carbene ligands in open-shell d\textsuperscript{7} group 8 transition metal complexes.](image)

The proposed Co\textsuperscript{II}(por)(CHCOOEt) ‘carbene’ species could not be isolated, because a fast reaction with additional EDA immediately produced diethyl maleate and (at higher EDA concentrations) the catalytically inactive diamagnetic species Co\textsuperscript{III}(TPP)(CH\textsubscript{2}COOEt).\textsuperscript{7} The latter species was characterized by X-ray diffraction and must be formed from Co\textsuperscript{II}(TPP)(CHCOOEt) by hydrogen atom abstraction from EDA or the solvent, indeed pointing to a significant radical character of the ‘carbene’ species. In the presence of styrene, no intermediates could be detected at all, and EDA dimerization was suppressed. Addition of the radical scavenger TEMPO (TEMPO = 2,2,6,6-tetramethylpiperidine N-oxide) substantially slowed down the cyclopropanation reaction, but no irreversible reaction occurred between Co\textsuperscript{II}(TPP) and TEMPO.\textsuperscript{7,20-22} Hence, an intermediate with substantial unpaired spin density at one of the organic moieties must play an important role in the mechanism.

### 6.3 Results and discussion

#### 6.3.1 EPR spectroscopy and ESI-MS spectrometry

We decided to study the reaction of Co\textsuperscript{II}(por) species with ethyl diazoacetate (EDA) by EPR spectroscopy and ESI mass spectrometry in an attempt to detect and characterize the putative Co\textsuperscript{II}(por)(CHCOOR) ‘carbene’ species. Detection of this species with EPR spectroscopy in combination with complementary DFT calculations should allow us to characterize their electronic structure in detail. Quite remarkably, despite the proposed unusual carbene radical character of these Co\textsuperscript{II}(por)(CHCOOR) species,\textsuperscript{4a,16,17} their detection with EPR spectroscopy has not been reported.

Hence, in an attempt to investigate the electronic structure of the elusive carbene adducts, we investigated the reaction of the porphyrin complexes Co(TPP) and Co(3,5-Di'Bu-ChenPhyrin)\textsuperscript{b} (Figure 2) with EDA by EPR spectroscopy. Both these complexes are active catalysts for olefin cyclopropanation, but Co(3,5-Di'Bu-ChenPhyrin) was shown to be much more active and selective.\textsuperscript{4}
A solution of Co(TPP) in toluene at 40 K gave exactly the same EPR spectrum as reported previously by Van Doorslaer & Schweiger. Quite remarkably, addition of 4 eq. of EDA to the toluene solution at RT led to instant and complete disappearance of the EPR signals (measured in the range of 5–70 K). Although we cannot exclude that some diamagnetic material was being formed in this reaction (e.g. formation of CoIII(TPP)(CH2COOEt) by hydrogen atom abstraction), this does not seem to be the main reason for the EPR silence, considering the clear observation of [Co(TPP)(CHCOOEt)]+ species representing the dominant signals in the ESI-MS spectrum of the same batch (vide infra). This was confirmed by measuring 1H NMR spectra of Co(TPP) directly after addition of 4 equivalents of EDA in benzene-d6, which show only the presence of paramagnetically broadened Co(TPP)-derived signals, free EDA, diethyl maleate, and minute amounts of the diamagnetic species CoIII(TPP)(CH2COOEt), in agreement with previous observations. Hence it seems that the Co(TPP)(CHCOOEt) radical species (irrespective of its exact structure) is EPR silent. The EPR silence can perhaps be explained by the presence of one or more exited states with energies close to the ground state causing rapid electron spin relaxation, in analogy with arguments proposed to explain the EPR silence of IrII(por) species. However, the exact reason for the EPR silence of Co(TPP) samples in the presence of EDA is presently not clear and contrasts markedly with the results obtained with CoII(3,5-Di’Bu-ChenPhyrin) described below. Co(3,5-Di’Bu-ChenPhyrin) shows a quite complex EPR spectrum in toluene at 40 K (Figure 3), indicating the presence of 2-3 paramagnetic cobalt species. EPR parameters of cobalt porphyrins are highly influenced by their ligand surroundings, and it is known that Co(TPP) forms 1:1 and 1:2 adducts with toluene. The approx. gxy > 3 and gz < 2 and large ACo values observed for Co(3,5-Di’Bu-ChenPhyrin) in toluene are indicative of the expected square planar cobalt porphyrin complex, and agree qualitatively with the reported data for Co(TPP) in toluene.
Addition of 4 eq. of EDA to the toluene solution at RT resulted in a considerable change of the spectrum (measured at 40 K), and revealed full conversion from a 4-coordinate complex to a mixture of axially coordinated Co(3,5-Di'Bu-ChenPhyrin)(L) species. The spectrum could be simulated (Figures 3-5) as a mixture of three species I, II and III in a rough ratio of 5 to 1 to 0.8 (as derived from the spectral simulations). The simulated EPR parameters of these species are listed in Table 1.

The g and $A^{Co}$ values of species II are in the range of strong field carbon adducts (CO, isocyanides) of Co II porphyrins, whereas the signals of species I are indicative of coordination of a weak field ligand (comparable to H2O). Therefore, we assign the signals of species I to the EDA adduct Co II(3,5-Di'Bu-ChenPhyrin)(EDA), with EDA coordinated to cobalt either via its carbon, carbonyl or dinitrogen moiety. The signals of species II can be assigned to the ‘bridging carbene’ species Co II(3,5-Di'Bu-ChenPhyrin)(CHCOOEt) (Figure 1, right).

Remarkably, the EPR parameters of the third species III are indicative for an ‘organic radical’ (Figure 5, bottom), but the simulations also reveal resolved hyperfine couplings with cobalt and a proton. We therefore assign these signals to the ‘terminal carbene’ species Co II(3,5-Di'Bu-ChenPhyrin)(CHCOOEt), which we take as the first direct experimental evidence for its carbon-centered radical character (Figure 1, left). It thus seems that the ‘bridging carbene’ II and ‘terminal carbene’ III isomeric forms of Co II(3,5-Di'Bu-ChenPhyrin)(CHCOOEt) exist in dynamic equilibrium with each other in solution.

The EPR parameters of the ‘bridging carbene’ species Co II(por)(CHCOOEt) (II) and the ‘terminal carbene’ species Co II(por)(CHCOOMe) (III) were also calculated with DFT methods, using the non-substituted porphyrin ring (por), and methyl esters (from MDA) instead of ethyl esters. The DFT data of these simplified models are in good qualitative agreement with the experimental data of species II and III, respectively (Table 1). DFT calculated EPR parameters of methyl diazoacetate (MDA) adducts of...
Co\textsuperscript{II}(por) do not agree at all with the experimental parameters of species I, but this is not surprising because it is known that classical DFT approaches do not perform well in predicting the EPR parameters of undistorted Co porphyrin systems\textsuperscript{28}. However, the EPR parameters of species I most likely belong to an axial adduct with a weak field ligand, because its EPR parameters qualitatively agree with those reported for Co(TPP)(H\textsubscript{2}O).\textsuperscript{23}

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{fig4.png}
\caption{Experimental and simulated X-band EPR spectra of the species formed upon addition of EDA to a toluene solution of Co(3,5-Di\textsuperscript{Bu}-ChenPhyrin). Experimental conditions: T = 40 K, frequency = 9.377430 GHz, modulation amplitude = 5 gauss, power = 2 mW.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{fig5.png}
\caption{Individual components I, II and III contributing to the EPR spectrum shown in Figure 4.}
\end{figure}
Table 1. Experimental\(^{(a)}\) and DFT calculated\(^{(b)}\) EPR parameters\(^{(c)}\)

<table>
<thead>
<tr>
<th></th>
<th>(g_x)</th>
<th>(g_y)</th>
<th>(g_z)</th>
<th>(A_{Co_x})</th>
<th>(A_{Co_y})</th>
<th>(A_{Co_z})</th>
<th>(A^H_x)</th>
<th>(A^H_y)</th>
<th>(A^H_z)</th>
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<tr>
<td>I(^{(a)})</td>
<td>2.558</td>
<td>2.520</td>
<td>2.004</td>
<td>255</td>
<td>208</td>
<td>270</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\text{Co}(\text{TPP})(\text{H}_2\text{O}))(^{(e)})</td>
<td>2.505</td>
<td>2.505</td>
<td>2.014</td>
<td>265</td>
<td>265</td>
<td>315</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>II(^{(a)})</td>
<td>2.228</td>
<td>2.120</td>
<td>2.005</td>
<td>110</td>
<td>115</td>
<td>300</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\text{Co}(\text{por})(\text{CHCOOMe})) 'bridging carbene'(^{(f)})</td>
<td>2.332</td>
<td>2.183</td>
<td>2.070</td>
<td>-39</td>
<td>234</td>
<td>491</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>III(^{(a)})</td>
<td>2.060</td>
<td>2.048</td>
<td>2.030</td>
<td>40</td>
<td>56</td>
<td>(n^d)</td>
<td>160</td>
<td>40</td>
<td>(n^d)</td>
</tr>
<tr>
<td>(\text{Co}(\text{por})(\text{CHCOOMe})) 'terminal carbene'(^{(f)})</td>
<td>2.010</td>
<td>2.002</td>
<td>1.975</td>
<td>-67</td>
<td>-19</td>
<td>6</td>
<td>-77</td>
<td>-50</td>
<td>-13</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Parameters from spectral simulations. \(^{(b)}\) Orca, b3-lyp/TZVP. \(^{(c)}\) Hyperfine couplings in MHz. \(^{(d)}\) \(n\) = not resolved \(^{(e)}\) taken from reference 23.

The same reaction mixtures used for the above EPR investigations were also analyzed with electrospray ionization mass spectrometry (ESI-MS). The ESI-MS spectrum of \(\text{Co}(\text{TPP})\) exposed to 4 eq of EDA in toluene reveals a major signal corresponding to \([\text{Co}(\text{TPP})(\text{CHCOOEt})]^{+}\) (m/z = 757.20), along with very low intensity signals corresponding to \([\text{Co}(\text{TPP})]^+\) (m/z = 671.10) and \([\text{Co}(\text{TPP})(\text{CHCOOEt})_2]^{+}\) (m/z = 843.30).

Similar results were obtained for \(\text{Co}^{\text{II}}(3,5-\text{Di'Bu-Phyrin})\). Major peaks of \([\text{Co}(3,5-\text{Di'Bu-Phyrin})(\text{CHCOOEt})]^{+}\) (m/z = 1425.7) were detected in both toluene and \(\text{CD}_2\text{Cl}_2\). Peaks corresponding to the alkyl species \([\text{Co}(3,5-\text{Di'Bu-Phyrin})(\text{CH}_2\text{COOEt})]^{+}\) (m/z = 1426.7) in toluene and \([\text{Co}(3,5-\text{Di'Bu-Phyrin})(\text{CHDCOOEt})]^{+}\) (m/z = 1427.7) in \(\text{CD}_2\text{Cl}_2\) were also observed. They are indicative for hydrogen atom abstraction from the solvent, in agreement with the radical deactivation pathway of the \(\text{Co}(\text{TPP})(\text{CHCOOEt})\) carbene species reported by Cenini and coworkers.\(^7\) The spectrum in \(\text{CD}_2\text{Cl}_2\) revealed also a strong signal corresponding to \([\text{Co}(3,5-\text{Di'Bu-Phyrin})(\text{CHCOOEt})_2]^{+}\) (m/z = 1511.7). This signal was also present in toluene, but in lower intensity.

The observed 2:1 carbene:Co adducts likely have a comparable structure to that reported for \([\text{Co}^{\text{III}}(\text{OEP})(\text{CHCOOEt})_2]\text{NO}_3\) (OEP = octaethylporphyrin) \((i.e.\ with\ two\ ‘carbene’\ moieties\ bridging\ between\ the\ cobalt\ and\ pyrrole\ nitrogen\ atoms,\ and\ located\ on\ opposite\ sides\ of\ the\ porphyrin\ ring;\ see\ Figure\ 11,\ species\ \(F^*\)).\(^{12d}\) However, cyclopropanation of a pyrrole double bond, insertion of the carbene into a C–H bond or a Büchner ring expansion cannot be ruled out.\(^{29}\)

6.3.2 Electronic structures of the ‘terminal carbene’ and ‘bridging carbene’ species

The singly occupied molecular orbitals (SOMO) and spin density plots of the ‘bridging carbene’ and ‘terminal carbene’ isomers of \(\text{Co}^{\text{II}}(\text{por})(\text{CHCOOMe})\) were calculated using DFT methods and are presented in Figure 6.

According to these calculations, the ‘bridging carbene’ complex is clearly a metal centered radical, with its unpaired electron residing mainly in the cobalt 3d\(_{z^2}\) orbital, in good agreement with the measured EPR parameters (Table 1).
The spin distribution in the ‘terminal carbene’ complex is strikingly different. The unpaired electron resides mainly on the ‘carbene’ carbon, i.e. the α-carbon of the methyl 2-ylidene-acetate moiety, and is slightly delocalized over the neighboring cobalt and oxygen atoms. This electronic structure agrees well with the EPR spectrum of II, which is indicative of an ‘organic radical’. Hence the ‘terminal carbenes’ are best described as carbon centered radicals (or ‘carbene radicals’) rather than true transition metal carbene moieties in the classic sense.

Species II and III represent an interesting example of equilibrium between two redox isomers. The ‘bridging carbene’ II is a d⁷ CoII complex, while the d⁶ CoIII terminal carbene complex III has the unpaired electron located on the ‘carbene ligand’. This is a situation somewhat similar to the recently reported dynamic interconversion between two [Rh(trop₂PPh)(PPh₃)] electromers³⁰ or valence tautomers³¹ of CoIII(catecholato)–CoII(semiquinato).³²

Occupation of spin density on the ‘carbene’ carbon is not completely unexpected. The LUMO of an electrophilic Fischer-type carbene is carbon-centered, and allows for one-electron reduction to a corresponding carbon-centered radical with external reducing agents.³³ Casey and coworkers showed that reduction of chromium pentacarbonyl...
alkoxyaryl complex by one electron led to a carbon centered radical anion, persistent at −50 °C, as evidenced by EPR spectroscopy. Since then, several other group 6 carbene radical anions have been reported to have nucleophilic carbon character and to undergo e.g. dimerization, coupling with electron-deficient alkenes and hydrogen atom abstraction reactions. So clearly Fischer-type carbene ligands are redox non-innocent and intramolecular electron transfer from the electropositive metal centre to the carbene moiety cannot be excluded as an alternative pathway for formation of ‘carbene radicals’. This is exactly what happens for the ‘terminal carbene’ species CoII(por)(CHCOOMe) (Figure 7A). A schematic representation of the relevant orbital interactions is shown in Figure 7.

The interaction with the singlet :CHCOOMe moiety pushes the energy of the cobalt d_{z^2} orbital above the energy of the antibonding MO constructed from the carbon p_y orbital and cobalt d_{yz} orbital, thus resulting in intramolecular electron transfer from cobalt to the carbene moiety (Figures 7A and 7B). Partial occupation of the Co–C π* antibonding orbital thus substantially reduces the metal-carbon bond order. Hence the ‘carbene’ species loses typical Fischer-type character, gains unusual radical reactivity, and becomes more nucleophilic. However, its open-shell radical character, putting discrete unpaired spin density on the ‘carbene’ carbon, is an important difference from any closed-shell Fischer and Schrock-type carbene descriptions.

Exactly the same electronic structure arises if the bonding is considered as a triplet carbene interacting with the CoII(por) species (Figure 7C). Formation of a Co–C σ-bonding pair from the unpaired electrons in the cobalt d_σ orbital and the triplet carbene sp^2 orbital leaves an unpaired electron in the p_y orbital, effectively generating the same carbene radical ligand. Formal oxidation state counting leads to a cobalt(III)-carbene anion radical in each case.

![Figure 7](image_url)

**Figure 7.** Redox non-innocent behavior of carbenes coordinated to open-shell CoII(por) species explained by a simplified MO bonding scheme.
The radical character of the ‘carbene’ carbon atom of Co(II)(CHCOOR) species is likely responsible for the formation of the alkyl species Co(III)(CH2COOEt) through hydrogen atom abstraction. A similar behavior was observed for Rh(II)(TMP) (TMP = tetramesitylporphinato) which reacts with diazo compounds to form Rh(III)(TMP)(alkyl) species. In the previous Chapter we reported comparable redox non-innocent behavior of carbenes bound to paramagnetic •Ir(II) species. The resulting Ir(III)(•CHR) ‘carbene radicals’ react with (Ir-coordinated) ethene to form new C–C bonds (or undergo similar hydrogen atom abstraction for more bulky ‘carbenes’).

6.3.3 Mechanistic DFT studies

Having established a clear picture of the (electronic) structure of the Co(II)(CHCOOR) ‘carbene radical’ species in the previous sections, we next addressed their potential as intermediates in the catalytic cyclopropanation reactions with computational DFT methods.

Computational methods

The BP86 functional is generally accurate in predicting the geometries of transition metal complexes, and has an excellent performance, especially for 3d metal compounds. Extensive DFT computational studies of cobalt porphyrins and related cobalamin derivatives have illustrated that the observed Co–C bond dissociation enthalpies (BDE) and internuclear distances are best reproduced by the non-hybrid BP86. Hence for reactions in which the making and breaking of cobalt-carbon bonds plays an important role, especially in cases where open-shell intermediates are involved, the use of the BP86 functional is preferred over B3LYP. The BP86 functional also gave accurate predictions of the thermodynamic energies and kinetic barriers associated with catalytic chain transfer and degenerative radical exchange processes of radical polymerization reactions controlled by Co(III) complexes. The Co–C bond should play an important role in predicting the energies and barriers for the Co(II)-catalyzed cyclopropanation reactions described in this paper. We therefore consistently used the non-hybrid BP86 functional in our studies.

Generally, Co(II) systems and their adducts Co(II)(L) have a low-spin d7 doublet (S = ½) ground state, and related DFT calculations reported by Yamada and coworkers have shown that the contribution of higher spin states to the cyclopropanation mechanism in reactions mediated by Co(salen) models can be neglected (even at the hybrid B3LYP level, which is known to favor higher spin states stabilities). Hence, all calculations were performed with complexes in their doublet (S = ½) spin states. The reported free energies in kcal mol⁻¹ are obtained from the calculated internal energies at the TZVP basis set on all atoms, adjusted for the zero-point energy, entropy, and approximately for the condensed phase reference volume (see Experimental Section). We used the non-functionalized cobalt porphyrin Co(por) as a smaller model of the experimental Co(TPP) complex. In addition we included some calculations using the Co(porAmide) model containing a 2-acetamidophenyl substituted porphyrinato ligand as a smaller model of the experimental Co(3,5-DiBu-ChenPhyrin) system, in order to account for possible effects of hydrogen bonding interactions between the carbonyl moiety of MDA and the ligand amide functionalities (Figure 8).
6.3.3.1 Formation of the ‘carbene’ complexes from Co\textsuperscript{II}(por) and MDA

We first focused on the formation of the terminal and bridging ‘carbene’ species Co(por)(•CHCOOR) from MDA and the Co\textsuperscript{II}(por). Experimentally, cobalt complexes with amide functionalized porphyrins exhibited higher activities in alkene cyclopropanation reactions as compared to Co(TPP). In view of these higher activities, we also investigated the same reactions with the amide-functionalized Co\textsuperscript{II}(porAmide) model, in order to study the possible effect of hydrogen bonding interactions between the amide functionality of the porphyrin and the carbonyl group of the diazoacetate on the rate of ‘carbene’ formation (Figure 9).\cite{4f}

Figure 9. Relevant hydrogen bonding interactions in formation and stabilization of the ‘carbene’ species.

The calculated free energies for the reaction of MDA with Co(por) and Co(porAmide) are plotted in Figure 10.

Figure 10. Free energy changes for the reaction of EDA with Co\textsuperscript{II}(por) (black) and with Co\textsuperscript{II}(porAmide) involving hydrogen bonding of the carbonyl group with the amide moiety (dashed blue). Selected bond distances (Å) are presented as well.
The DFT calculations predict the availability of three possible MDA adducts Co\textsuperscript{II}(por)(MDA) from the Co\textsuperscript{II}(por) species A and MDA. The carbonyl O-bound adduct B\textsuperscript{"}{ } has the lowest energy, +4.8 kcal mol\textsuperscript{−1} uphill relative to A. The nitrogen-bound adduct B\textsuperscript{'} is slightly higher in energy (+5.1 kcal mol\textsuperscript{−1}), and the carbon-bound adduct B has the highest energy (+8.9 kcal mol\textsuperscript{−1}). The carbon-bound adduct B,\textsuperscript{44} is however, the only productive adduct, allowing the elimination of dinitrogen (N\textsubscript{2}) to form the radical carbene species C via a relatively high barrier transition state TS\textsubscript{1} (+13.1 kcal mol\textsuperscript{−1} from B; +22.0 kcal mol\textsuperscript{−1} from A). This barrier is in good qualitative agreement with the relatively slow cyclopropanation kinetics of Co(TPP).\textsuperscript{4a,7,45}

Once formed, the ‘terminal carbene’ species C readily collapses to form the somewhat more stable ‘bridging carbene’ species C\textsuperscript{'}\textsuperscript{.\textsuperscript{4a,4f,45}} The energy difference between these species is, however, not large (1.5 kcal mol\textsuperscript{−1}), suggesting that these species should be in dynamic equilibrium with each other. The DFT calculations are in good agreement with the results from the EPR measurements. The calculated barriers for converting C into C\textsuperscript{'} (12.9 kcal mol\textsuperscript{−1}) and vice versa (14.4 kcal mol\textsuperscript{−1}) are low enough to establish a fast equilibrium at room temperature.

Hydrogen bonding between the amide N-H of Co(porAmide) and the carbonyl oxygen of MDA (Figure 9) lowers the energy of the carbon-bound adduct B, the transition state TS\textsubscript{1} and the carbene radical C by 1.7, 3.1 and 3.1 kcal mol\textsuperscript{−1}, respectively. The overall barrier for formation of species C from Co(porAmide) and MDA is lowered to 18.9 kcal mol\textsuperscript{−1}, in good qualitative agreement with the experimentally observed faster cyclopropanation reactions with amide functionalized cobalt porphyrins.\textsuperscript{4b-e,45}

Recently, a mechanistic study on Os(TTP)-mediated cyclopropanation indicated that the trans bis-‘terminal carbene’ osmium species is the active catalyst (TTP = 5,10,15,20-tetra-p-tolyldiporphyrinato).\textsuperscript{46} Hence, we also investigated the possibility of formation of analogous cobalt bis-carbene species (see Figure 11). In the absence of olefin, slow formation of a bis-carbene species from the ‘bridging carbene’ Co\textsuperscript{II}(por)(CHCOOMe) species C\textsuperscript{'} and MDA is both kinetically possible (\(\Delta G^\ddagger = 25.3\))
kcal mol\(^{-1}\)) and thermodynamically favorable (\(\Delta G^\circ = -4.3\) kcal mol\(^{-1}\)), according to the DFT calculations. These calculations are in agreement with the detection of the species in the ESI-MS spectra in low intensities (\textit{vide supra}). However, their formation under catalytic conditions in the presence of olefin is clearly kinetically disfavored from follow-up reactivity of \(\text{C}'\) with the olefinic substrate, which proceeds with much lower barriers (\textit{vide infra}). Consequently, bis-carbene species \(\text{Co}^{\text{II}}(\text{por})(\text{CHCOOR})_2\) should not play an (important) role under the catalytic conditions.

The \textit{trans} bis-carbene species \(\text{F} (-1.8\) kcal mol\(^{-1}\)) having one ‘terminal carbene’ and one ‘bridging carbene’ moiety can convert readily (\(\Delta G^\ddagger = 12.0\) kcal mol\(^{-1}\)) to the somewhat more stable \textit{trans} bis-‘bridging carbene’ species \(\text{F}' (-4.3\) kcal mol\(^{-1}\)), according to the DFT calculations. Other \textit{trans} bis-carbene isomers were found higher in energy, especially the \textit{trans} bis-‘terminal carbene’ isomer \(\text{F}'' (+27.3\) kcal mol\(^{-1}\) relative to \(\text{F}'\)). Hence, the involvement of \textit{trans} bis-‘terminal carbene’ species analogous to those proposed to be involved in Os(TPP)-mediated cyclopropanation can be safely excluded in the case of Co(por) systems.

6.3.3.2 Olefin cyclopropanation via ‘carbene radical’ addition to olefins

We tried to find transition states for direct reactions of olefins with the MDA adduct \(\text{B},\) \(\text{Co}^{\text{II}}(\text{por})(\text{MDA})\), in order to investigate the possibility of cyclopropanation proceeding via \(\text{C}–\text{C}\) coupling between the diazo adduct and olefin with simultaneous dinitrogen loss from the coordinated MDA moiety, as proposed by Cenini and coworkers.\(^7\) Despite several attempts in approaching the problem with different constraint geometry variations, however, we were unable to find such transition states. Similarly, we were unable to find transition states for the reaction of the ‘bridging carbene’ species \(\text{C}'\) with olefins. Therefore, we focused on the ‘terminal carbene’ species \(\text{C}\) as the remaining and most logical carbene transfer intermediate in the cyclopropanation mechanism. All free energies of the stationary points are referenced to the ‘bridging carbene’ species \(\text{C}'\), which should be the dormant state species in the catalytic cyclopropanation cycle according to the DFT calculations.

We investigated the reaction of the ‘terminal carbene’ radical species \(\text{C}\) with three different types of alkenes: styrene, methyl acrylate and propene. We chose propene as a model for aliphatic alkenes which generally do not form cyclopropanes effectively in \(\text{Co}^{\text{II}}(\text{por})\)-catalyzed cyclopropanation with diazo compounds. Styrene is a benchmark substrate for cyclopropanation catalyzed by various transition metals, whereas methyl acrylate is an example of an electron-deficient olefin that is successfully cyclopropanated by \(\text{Co}^{\text{II}}(\text{por})\) catalysts, but not by closed-shell Cu and Doyle-type Rh\(_2\) catalysts.

The computed carbene transfer mechanism from the ‘terminal carbene’ species \(\text{C}\) clearly proceeds via a stepwise radical process, which contrasts with the concerted carbene transfer processes generally observed for closed-shell late transition metal catalysts in olefin cyclopropanation. The reaction involves the (irreversible) addition of the carbon-centered ‘radical carbene’ species \(\text{C}\) to the olefin, thus generating the \(\text{Co}(\text{por})(\text{CHCOMe–CH}_2–\text{CHR}^•)\) species \(\text{D}\) having its unpaired electron spin density primarily localized at the \(\gamma\)-carbon of the ‘alkyl’ moiety (see Figures 12 and 13). Formation of the species \(\text{D}\) is associated with relatively large barriers (\(\text{TS}2\)). These barriers are somewhat lower, but very comparable to the barrier (\(\text{TS}1\)) for formation of \(\text{C}\), which is in excellent agreement with first order kinetics in both [EDA] and [styrene] observed experimentally in the Co(TPP)-catalyzed styrene cyclopropanation.\(^7,47\)
‘Carbene Radicals’ in Co$^{II}$ (por)-Catalyzed Olefin Cyclopropanation

**Figure 12.** Computed pathways for *trans*-cyclopropanation of propene ($\Delta G^o_{pr}$, green), styrene ($\Delta G^o_{st}$, blue) and methyl acrylate ($\Delta G^o_{ma}$, red) mediated by Co(por)(CHCOOMe). Free energies in kcal mol$^{-1}$ relative to the resting state ‘bridging carbene’ species C$. Selected bond distances (Å) are presented as well.

**Figure 13.** Computed pathways for *cis*-cyclopropanation of propene ($\Delta G^o_{pr}$, green), styrene ($\Delta G^o_{st}$, blue) and methyl acrylate ($\Delta G^o_{ma}$, red). Free energies in kcal mol$^{-1}$ relative to the resting state ‘bridging carbene’ species C$. Selected bond distances (Å) are presented as well.
Once formed, the ‘γ-alkyl radical’ type species D readily collapse to form the corresponding cyclopropanes, regenerating the starting CoII(por) species A to continue the catalytic cycle. This reaction can be described as a concerted radical type C–C bond formation with simultaneous homolysis of the Co–C bond. The overall computed carbene transfer steps are consistent with the expected bond length changes for the obtained two-step radical processes (see Figures 12 and 13).

The ring closure reactions from D are very low barrier processes (TS3 < 2.6 kcal mol\(^{-1}\) in all cases). The barriers are actually so low that apart from cyclopropanation no other follow-up reactivity can be expected. For this reason, despite their carbon radical character, the species C and D cannot, initiate free radical polymerization reactions.\(^{48}\)

These TS3 barriers are even lower than the barriers expected for C\(_{\beta}–C_{\gamma}\) bond rotation in these functionalized alkyls.\(^{49}\) As a result, the diastereoselectivity of cyclopropanation is predetermined in the C–C bond forming transition state TS2. In that sense, the computed two-step radical-type mechanism is not different from a concerted carbene transfer mechanism. We calculated pathways for formation of both the trans-cyclopropanes (Figure 12) and the cis-cyclopropanes (Figure 13) to gain some insight in the nature of diastereoselectivity of the CoII(por)-based catalytic systems. The geometries of the stationary points along the pathway for cis- and trans-cyclopropanation are very similar, and the differences are mainly energetic.

The two-step radical mechanism nicely explains the high activity of CoII(por) catalysts in the cyclopropanation of electron-deficient olefins like methyl acrylate, and their poor performance in cyclopropanation of electron-rich aliphatic alkenes. One-electron reduction of the redox non-innocent carbene ligand (by the CoII centre) should give the carbene carbon atom more nucleophilic character (Figure 7). Consequently, the relative energies of the transition states TS2 should depend on the electrophilicity of the olefin (that is quantified by the global electrophilicity parameter \(\omega\)).\(^{50}\) The \(\omega\) values are 0.60 eV for propene, 1.13 eV for styrene and 1.51 eV for methylacrylate,\(^{51}\) and correlate well with the calculated barriers. The relative stabilities of the species D are strongly dependent on the ability of the olefin R group (R = CH\(_3\), Ph, COOMe) to stabilize the γ-carbon radicals. Reported radical stabilization energies\(^{52}\) (RSE) are in the order: •CH(Me)CH\(_3\) \((-5.6\) kcal mol\(^{-1}\)) < •CH(COOMe)CH\(_3\) \((-9.6\) kcal mol\(^{-1}\)) < •CH(Ph)CH\(_3\) \((-14.3\) kcal mol\(^{-1}\)) and are in good qualitative agreement with the relative stabilities of the species D (stabilization with Me < COOMe < Ph). These RSE values should partly influence TS2 as well, hence explaining the relatively low TS2 barrier for styrene (that cannot be explained by the \(\omega\) value alone).

For steric reasons, the TS1\(_{cis}\) barriers for cis-cyclopropanation (Figure 13) are higher than the TS1\(_{trans}\) barriers for trans-cyclopropanation (Figure 12) in all cases. While the differences are very small for cyclopropanation reactions of propene and styrene, dipolar repulsion between the two carboxymethyl groups results in a quite substantial difference (2.4 kcal mol\(^{-1}\)) between the barriers for cis- and trans-cyclopropanation of methyl acrylate. This corresponds well with the high experimental trans:cis selectivity for cyclopropanation of methyl acrylate with EDA catalyzed by \(D_2\)-symmetric chiral porphyrin CoII complexes.\(^{4d}\)

The calculated trans:cis ratios for cyclopropanation of methyl acrylate, styrene and propene using the Co(por) catalyst are shown in Table 2. The calculated values are in excellent agreement with the available experimental data. The high trans:cis ratio obtained in cyclopropanation of methyl acrylate mediated by CoII(3,5-Di\'Bu-
ChenPhyrin) therefore seems to be general for Co\textsuperscript{II}(por) systems, and does not seem to be caused by its porphyrin steric bulk.

Table 2. DFT calculated barriers for olefin addition to radical carbene C, and calculated and experimental trans:cis ratios at room temperature.

<table>
<thead>
<tr>
<th>Olefin</th>
<th>$\Delta G_{\text{trans}}$</th>
<th>$\Delta G_{\text{cis}}$</th>
<th>trans:cis</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl acrylate</td>
<td>17.5</td>
<td>19.9</td>
<td>98:02</td>
<td>99:01\textsuperscript{[b]}</td>
</tr>
<tr>
<td>Styrene</td>
<td>18.2</td>
<td>18.5</td>
<td>68:32</td>
<td>75:25\textsuperscript{[b]}</td>
</tr>
<tr>
<td>Propene</td>
<td>21.3</td>
<td>21.5</td>
<td>55:45</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} Co\textsuperscript{II}(3,5-DitBu-ChenPhyrin), ref 4d; \textsuperscript{[b]} Co\textsuperscript{II}(TPP), ref 4a

### 6.3.3.3 Suppression of side product formation by ‘carbene dimerization’

One of the advantages of using Co\textsuperscript{II}(por) catalysts for cyclopropanation is their markedly suppressed ‘carbene’ dimerization activity under the practical catalytic conditions. Dimerization of diazo compounds to fumarates and maleates is the main side reaction in cyclopropanation mediated by most other catalysts (\textit{e.g.} closed-shell Cu and Doyle-type Rh\textsubscript{2} catalysts). To suppress this common side reaction, slow addition of the diazo compound to the reaction mixture and/or use of excess olefins are usually required. In the case of the Co\textsuperscript{II}(por)-based systems, these precautionary procedures are not necessary, as only trace amounts of carbene dimerization products are generally formed under the catalytic conditions.\textsuperscript{4,7} In the absence of olefin, Co\textsuperscript{II}(por) species do mediate slow carbene dimerization from the diazo substrates. This leads almost exclusively to the formation of maleates; apparently formation of the thermodynamically favored fumarates is kinetically suppressed. We investigated these phenomena computationally to get some insight in the reasons behind the low dimerization activity and high maleate selectivity of Co\textsuperscript{II}(por)-based catalytic systems.

![Formation of dimethyl maleate by dimerization of methyl diazoacetate. Selected bond distances (Å) are presented as well.](image)
The calculated pathway for dimerization of MDA reveals two similar and relatively high energy transition states $\text{TS4}$ (23.0 kcal mol$^{-1}$) and $\text{TS4}'$ (23.1 kcal mol$^{-1}$) for C–C bond formation between the ‘terminal carbene’ species C and MDA (Figure 14). These reactions are followed by loss of dinitrogen from the diazo compound with simultaneous formation of dimethyl maleate in both cases. Formation of the kinetic product dimethyl maleate instead of the thermodynamically more stable dimethyl fumarate is a result of the steric influence between the porphyrin ring and the attacking diazo acetate (Figure 14). We were unable to find a transition state for formation of dimethyl fumarate. Since the calculated barrier for dimer formation is higher than the barriers for radical addition of C to methyl acrylate or styrene (< 20 kcal mol$^{-1}$), carbene dimerization is expected to be suppressed, which is in good agreement with experimental observations under the catalytic conditions (i.e. in the presence of olefin).

6.4. Summary and Conclusions

On the basis of the results from the combined experimental (EPR and ESI-MS measurements) and computational (DFT calculations) studies, a catalytic cycle for Co$^{II}$(por)-mediated cyclopropanation of olefins is proposed to involve several unusual key intermediates as summarized in Figure 15.

![Figure 15. Catalytic cycle for Co(por) catalyzed cyclopropanation of olefins.](image-url)

The reaction proceeds via an unprecedented two-step radical addition-substitution pathway, in which the redox non-innocent behavior of the terminal carbene ligand in intermediate C plays a key role (Figure 15). The Co$^{II}$(por) catalyst A reacts with the diazo ester compound to form a transient adduct B, which loses dinitrogen in a rate-limiting step (TS1) to form the ‘terminal carbene’ intermediate C. The ‘terminal
‘Carbene Radicals’ in Co\textsuperscript{II}(por)-Catalyzed Olefin Cyclopropanation

carbene’ C exists in equilibrium with the somewhat more stable ‘bridging carbene’ C’. Both C and C’ species were detected experimentally in the reaction mixture of Co\textsuperscript{II}(3,5-Di’Bu-ChenPhyrin) with EDA by EPR spectroscopy. The electronic structure of C is noteworthy. The species is a carbon-centered radical and is best described as a one-electron reduced Fischer-type carbene. These results clearly underline the general importance of redox non-innocent ligands\textsuperscript{53} and represent a rare example of the involvement of a ligand radical in organometallic catalysis\textsuperscript{18,19}.

The ‘bridging carbene’ species C’ is not capable of carbene transfer to the olefin, and appears to be a dormant state in the catalytic cycle. The cobalt-centered radical C’ has to transform back to the carbon-centered radical C to allow carbene transfer to the olefin. This proceeds via radical addition of the ‘carbene radical’ C to the C=C double bond of the olefin to form a γ-alkyl radical intermediate D. The intermediates D then readily collapses in an almost barrierless ring closure reaction (TS3) to form the cyclopropane.

Addition of the ‘terminal carbene’ C to the olefin (TS2) proceeds with comparable barrier as its formation (TS1), thus explaining first order kinetics in both substrate and catalyst. Formation of C can be accelerated by stabilization of C and TS1 via hydrogen bonding. Calculated barriers for Co\textsuperscript{II}(por)-mediated carbene dimerization are higher than the highest barriers for the olefin cyclopropanation, thus explaining the suppression of carbene dimerization under catalytic conditions.

The proposed radical-type mechanism (Figure 15) agrees well with all available mechanistic and kinetic information, and readily explains the excellent performance of Co\textsuperscript{II}(por)-based systems in the cyclopropanation of electron-deficient olefins. The new insights obtained from these studies shed light on how to address further selectivity issues in catalytic cyclopropanation and will aid future development of new catalytic systems for remaining difficult substrates. Furthermore, these mechanistic insights may lead to the development of new type of radical ring closure processes by Co\textsuperscript{II}(por) catalysts (e.g. formation of five-membered rings from properly designed 1,4-dienes and carbene sources).

6.5. Experimental

EPR and ESI-MS

Sample preparation: Toluene was distilled under nitrogen from sodium wire; CD\textsubscript{2}Cl\textsubscript{2} was degassed using freeze-pump-thaw method and dried over 4 Å molecular sieves. Co(3,5-Di’Bu-ChenPhyrin)\textsuperscript{4b} and Co(TPP)\textsuperscript{54} were prepared according to published procedures. They were dissolved in toluene (c\textsubscript{Co(ChenPhyrin)} = 2.7·10\textsuperscript{-3} M; c\textsubscript{Co(TPP)} = 10\textsuperscript{-4} M) or CD\textsubscript{2}Cl\textsubscript{2} (c\textsubscript{Co(ChenPhyrin)} = 5.4·10\textsuperscript{-3} M) and each solution was transferred into a Teflon-valved EPR tube in a N\textsubscript{2}-filled glovebox and their CW X-band EPR spectra were recorded. Co(TPP) gave exactly the same spectrum as reported by Van Doorslaer and Schweiger.\textsuperscript{23} Next, 4 eq of EDA were added under N\textsubscript{2} atmosphere and the samples were shaken for 30-40 seconds and subsequently frozen in liquid nitrogen. Experimental X-band EPR spectra of these mixtures were recorded on a Bruker EMX spectrometer equipped with a He temperature control cryostat system (Oxford Instruments). The spectra were simulated by iteration of the anisotropic g values, (super)hyperfine coupling constants and line widths. We thank Prof. F. Neese for a copy of his EPR simulation program. After 24 hours, the samples were diluted with MeOH to the approx. concentration of 10\textsuperscript{-5} M and their ESI-MS spectra were recorded. ESI-MS measurements were performed on a Shimadzu LCMS-2010A liquid chromatograph mass spectrometer by direct injection of the diluted sample to the ESI probe.
Chapter 6

DFT

Geometry optimizations were carried out with the Turbomole program package\textsuperscript{55} coupled to the PQS Baker optimizer\textsuperscript{56} at the ri-DFT level using the BP86\textsuperscript{57} functional and the resolution-of-identity (ri) method.\textsuperscript{58} We used the SV(P) basis set\textsuperscript{59} for the geometry optimizations of all stationary points. All minima (no imaginary frequencies) and transition states (one imaginary frequency) were characterized by numerically calculating the Hessian matrix. ZPE and gas-phase thermal corrections (entropy and enthalpy, 298 K, 1 bar) from these analyses were calculated. Improved energies were obtained with single point calculations at DFT/BP86 level using the Turbomole def-TZVP basis set.\textsuperscript{60} Estimated condensed phase (1 L mol\textsuperscript{-1}) free energies, entropies and enthalpies were obtained from these data by neglecting the enthalpy RT term and subsequent correction for the condensed phase reference volume $S_{\text{CP}} = S_{\text{GP}} + \text{Rln}(1/24.5)$. Calculated EPR spectra were obtained with Orca\textsuperscript{61} at the DFT, b3-lyp,\textsuperscript{62} TZVP\textsuperscript{60} level, using the Turbomole optimized geometries.

6.6. Acknowledgements

We thank Xue Xu and Prof. Dr. X. Peter Zhang for provision of Co(3,5-DiBu-ChenPhyrin) and their contributions to the chapter.

6.7 Notes and References


6 According to these DFT calculations with small models of the actual catalysts and substrates, strictly planar models seem to cyclopropanate ethene via a concerted carbene transfer mechanism from discrete Co\textsuperscript{II}-carbene intermediates to the olefin, but more flexible analogs prefer a pathway via four-membered metallacyclic intermediate. In their earlier studies,\textsuperscript{6a} the same authors described the possibility of a radical pathway involving with 5-coordinate Co\textsuperscript{II}(salen)(L) for cyclopropanation with Co\textsuperscript{II}(salen) species in the presence of an axially coordinating neutral ligand L: (a) Ikeno, T.; Iwakura, I.; Yamada, T. \textit{Inorg. Chem.} 2002, 41, 517-520. (b) Iwakura, I.; Ikeno, T.; Yamada, T. \textit{Org. Lett.} 2004, 6, 949-952.


8 The order in [styrene] is somewhat more complex. A bell-shaped rate dependence on [styrene] was observed pointing to a first order dependence at low styrene concentrations. The decreased rates at higher styrene concentrations were ascribed to substrate inhibition kinetics by the authors, but catalysts poisoning by an impurity (e.g. the stabilizer in styrene) cannot be excluded, as the authors may have used non-purified styrene samples.

9 The same group recently reported first order kinetics in [catalyst] and [EDA], but zero order in [styrene] for related Co\textsuperscript{II}(salen) systems, suggesting that for these systems the energy barrier for the cyclopropanation step is considerably lower than that for formation of the active carbene-transfer intermediate: Caselli, A.; Buonomenna, M. G.; de Baldrironi, F.; Laera, L.; Fantauzzi, S.; Ragaini, F.; Gallo, E.; Golemmbe, G.; Cenini, S.; Drioli, E. \textit{J. Mol. Cat. A: Chem.} 2010, 317, 72-80.

Reactions of diazo esters with Co\textsuperscript{III}(por) complexes were extensively studied by the group of Johnson.\textsuperscript{12} Most notably the reactions exclusively led to formation of ‘bridging carbene’ species, where the carbene ended-up bridging between cobalt and one of the pyrrolato nitrogen atoms of the porphyrin ring.\textsuperscript{12} Also a bridging bis-carbene adduct was characterized crystallographically.\textsuperscript{16} Terminal carbene species could not be isolated. Recent investigations on reactions of diazoacetates with Co\textsuperscript{III}(salen) complexes suggest that also in this system a bridging carbene is preferred over a terminal carbene.\textsuperscript{13}


Related Rh\textsuperscript{II}(TMP) systems bind TEMPO reversibly ($K_{eq} \sim 10^8$), but undergo irreversible hydrogen atom and methyl group abstraction reactions from TEMPO at higher temperatures: Chan, K. S.; Li, X. Z.; Dzik, W. I.; de Bruin, B. \textit{Chem. Eur. J.} 2008, 130, 2051-2061.


As the EPR experiments were performed by freeze-quenching the EPR tube in liquid $N_2$, the detected distribution of the species II and III does not necessarily reflect their equilibrium distribution.


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