Open-shell nitrene- and carbene-complexes of cobalt
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Chapter 2

Characterisation of porphyrin-cobalt(III)-‘nitrene radical’ species relevant in catalytic nitrene-transfer reactions

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Introduction

Ligand-centred radical complexes play a pivotal role in a number of bio- and ‘bio-inspired’ catalytic transformations, providing a powerful tool to control the reactivity and selectivity of the catalyst. Such species are well-studied and characterized for transition metal complexes containing typical multidentate redox non-innocent ligands, such as semi-quinone-type radical ligands and their nitrogen analogs, reduced bipyridine and terpyridine ligands, α-iminopyridine ligands and pyridine-2,6-diimine ligands. More recently, considerable efforts have been made to understand the (electronic) structure and reactivity of monodentate redox non-innocent substrate-type ligands, such as carbenes, which play a key role in catalytic carbene transfer reactions. So far, only a few examples have been reported in which complexes bearing monodentate nitrogen-based radicaloid ligands were experimentally detected. Thus, well-studied complexes with redox active aminyl ligand radicals are limited to only a few well-characterized examples, and related complexes bearing redox non-innocent nitrene ligands are even scarcer.

‘Catalytic functionalization’ of C–H bonds is a holy grail in chemistry as it is an atom-, time-, and cost-efficient alternative to traditional hydrocarbon functionalization. In this context C–H insertion of carbenoid and nitrenoid species has emerged as a promising protocol. The insertion of metal carbenoids into C–H bonds is now a well-established transformation, and many transition metal catalysts that can catalyse such reactions have been disclosed in the past decade. In addition to catalytic cyclopropanation and C–H insertion, metal catalysed carbene transfer has also made it possible to perform insertions into X–H bonds (X = O, N, S, Si), and to convert alkynes to cyclopropenes (including some cycloaddition reactions). Given the ubiquity of nitrogen atoms in biologically active compounds, nitrene transfer reactions also have important applications in making molecules of interest. Cobalt(II) porphyrins have emerged as successful catalysts for nitrene transfer reactions. Its superiority lies not only in the performance but also in the fact that organic azides can be employed as nitrene sources. Till the early 2000s, it was quite common to use iminoiodanes or haloamine-T compounds as nitrene sources. These are, however, not the most benign nitrene sources as they lead to the formation of undesirable side products like phenyl iodide and other halogen containing compounds.

The mechanistic aspects of two nitrene transfer reactions catalysed by cobalt porphyrins have been elucidated by our group previously (Scheme 1). The mechanism of C–H bond amination of ethyl benzene, toluene, and 1,2,3,4-tetrahydronaphthalene (tetralin) using a series of different organic azides (N3C(O)OMe, N3SO2Ph, N3C(O)Ph and N3P(O)(OMe)2) as nitrene sources was studied using Density Functional Theory (DFT) and Electron Paramagnetic Resonance (EPR) spectroscopy (Scheme 1a). The mechanism of cobalt(II) porphyrin-mediated aziridination of styrene with PhSO2N3 was also studied (Scheme 1b). For both amination and aziridination reactions, the DFT calculations revealed a stepwise radical process involving coordination of the azide to the cobalt(II) centre, followed by release of dinitrogen to produce an unusual ‘nitrene radical’ intermediate C (Scheme 1). In addition, experimental EPR spectroscopic studies, combined with DFT calculated EPR properties being in good agreement with the experimental data, revealed the formation of a (por)CoIII–N•Y ‘nitrene radical’ adduct C from the catalyst in the presence of an excess of the azide in benzene. Formation of a nitrene moiety at cobalt(II) effectively leads to electron transfer from the metal to the nitrene, thus reflecting the redox non-innocence of the nitrene ligand. The spin density of this intermediate resides almost entirely on the nitrogen atom of the nitrene moiety. A simplified molecular orbital picture showing...
the frontier \(\pi\)-interactions and explaining the unusual electronic structure of this intermediate is depicted in Scheme 2.

**Scheme 1.**

a) DFT calculated mechanism of cobalt(II) porphyrin mediated benzylic C–H amination of ethylbenzene by \(N_3(C(O)OMe)\).

b) Cobalt(II) porphyrin mediated aziridination of styrene with \(PhSO_2N_3\). For both amination and aziridination reactions, the DFT calculations revealed a stepwise radical process involving coordination of the azide to the cobalt(II) center, followed by release of dinitrogen to produce an unusual ‘nitrene radical’ intermediate C.

**Scheme 2.** Redox non-innocent behaviour of nitrene ligands coordinated to open-shell \([Co^{II}(por)]\) species (A), a simplified bonding scheme explaining this behaviour (B), and alternative bonding scheme involving a triplet nitrene (C).

A thorough understanding of these key intermediates is essential to make advances in using these catalytic systems, to unleash their full potential in terms of activity and selectivity. Given the importance of these radicaloid nitrene species in metal-catalysed nitrene transfer and C–H functionalization reactions, we gathered more experimental evidences for the formation of the previously reported mono-nitrene radical complexes upon reaction of cobalt(II)-porphyrins with nitrene transfer reagents. Furthermore, we here reveal the first example of a bis-nitrene species of \(1^{\text{P1}}\) upon reacting the stronger oxidizing nitrene transfer agent \(N_3\text{-nosyl iminoiodane} 4_{\text{Ns}}\) with \(1^{\text{P1}}\) (see Figure 1 and Figure 2). This bis-nitrene species has a markedly different electronic structure than the
previously detected mono-nitrene species, and also differs from the electronic structure of the previously reported diamagnetic bis-imido RuVI-porphyrin species (por)RuVI[(=NR’’)]. The work described herein further bears some similarity with the mono- and bis-nitrene species of non-heme iron complexes disclosed by Che and coworkers, but again the electronic structures reported herein are entirely different.

Results and discussion
At the start of this project, the DFT calculations and existing X-band EPR data strongly indicated the formation of substrate-centred (por)CoIII-N•-R” ‘nitrene radicals’, which are proposed to be key intermediates in the mechanisms of the catalytic C–H amination and alkene aziridination reactions mediated by [CoII(por)] catalysts and employing organic azides as nitrene sources. These ‘nitrene radicals’ had thus far only been detected by means of X-band EPR spectroscopy. Here we disclose their detection and characterization with a variety of spectroscopic and mass spectrometric techniques.

Figure 1. Different [CoII(Por)] used to experimentally detect cobalt(III)-nitrene radicals in this study. P1 is the commercially available [CoII(TPP)] and P2 is a chiral D2-symmetric porphyrin with a chiral pocket.

Figure 2. Various nitrene transfer reagents commonly employed in nitrene-transfer reactions. The organic azides like Nosyl azide, Troc azide etc are more desirable than the iminoiodanes like or the Haloamine-T.
To study the key nitrene intermediates in nitrene transfer reactions mediated by $[\text{Co}^{\text{II}}(\text{Por})]$, we chose to react a few of the commonly used nitrene sources with two different types of $[\text{Co}^{\text{II}}(\text{Por})]$: The tetraphenyl-substituted porphyrin $1^{\text{P1}}$ and the bulkier (and chiral) H-bond donor appended porphyrin $1^{\text{P2}}$ (see Figure 1). Complex $1^{\text{P2}}$ serves as a model system for all reported cases where Co$^{\text{II}}$ porphyrins with H-bonding moieties were proven to give superior catalytic results and where H-bonds stabilise the formed nitrene intermediates. In total, four different nitrene sources were employed. As mentioned before, these sources are known in literature to be active in different nitrene transfer reactions like aziridination and amination. Three of these were organic azides $2_{\text{Ns}}$, $2_{\text{Ts}}$ and $2_{\text{troc}}$ (see Figure 2): Nosyl Azide ($2_{\text{Ns}}$; $\text{NsN}_3$; $\text{Ns} = \text{nosyl} = \text{p-NO}_2\text{-PhSO}_2$−), Tosyl Azide ($2_{\text{Ts}}$; $\text{TsN}_3$; $\text{Ts} = \text{tosyl} = \text{p-MePhSO}_2$−) and Troc Azide ($2_{\text{troc}}$; $\text{TrocN}_3$; troc = 2,2,2-Trichlorethoxycarbonyl = $\text{CCl}_3\text{CH}_2\text{O(CO)}$−). The fourth nitrene transfer reagent investigated was the stronger oxidizing $N$-Nosyl Iminiodiane (PhI=NN$\text{Ns}$) $4_{\text{N}}$. To perform the EPR, UHR-ESI, UV-Vis and XAS studies, the following method was used: To a solution of the catalyst in benzene-$d_6$ we added a 100-fold excess of the nitrene precursor. The catalyst concentrations of these solutions were typically 2.5 mM. The solvent used was benzene-$d_6$ in all cases and this was chosen to avoid any cases of C−H insertions as is known for these systems in toluene, cyclohexane and other related solvents. Unless mentioned otherwise, deuterated benzene was chosen as the solvent to further slow-down any C−H activation of the benzene ring itself.

**EPR spectroscopy of the mono-nitrene species $3^{\text{P1}}_{\text{Ns}}$**

Upon reaction of $1^{\text{P1}}$ with a 100-fold excess of $2_{\text{Ns}}$, and $1^{\text{P2}}$ with a 100-fold excess of either $2_{\text{Ts}}$ or $2_{\text{troc}}$ (Scheme 3), clear gradual changes in the X-band EPR spectra occurred that point to the formation of mono-nitrene radical species, revealing the redox non-innocence of the nitrene moiety. The disappearance of signals characteristic for the $[\text{Co}^{\text{II}}(\text{Por})]$ is associated with appearance of signals corresponding to mono-nitrene species of the type $3^{\text{P1}}_{\text{Ns}}$. An example of such a spectrum is shown in Figure 3 (left). The room temperature (r.t.) EPR measurement of the same samples gave spectra characteristic for ligand radical species and the simulated spectra fit best to a mono-nitrene species of the type $3^{\text{P1}}_{\text{Ns}}$.

**Scheme 3.** Scheme depicting different combinations of $[\text{Co}^{\text{II}}(\text{Por})]$ and organic azides used to study the formation of mono-nitrene species. To a solution of the catalyst in benzene-$d_6$ we added a 100-fold excess of the nitrene precursor. The catalyst concentrations of these solutions were typically 2.5 mM.
Figure 3. (Left) Disappearance of signals of $1^P_2$ with simultaneous appearance of new signals characteristic for $3P_2^{troc}$. (Right) Davies ENDOR spectrum of $3P_1^{N_s}$. Experimental conditions: 40 K, RF-pulse 20 µs, Inversion pulse 40 ns. Pink line represents spectral simulation according to the parameters extracted from the HFPR spectrum (depicted on the left). Due to relaxation effects, the broad wing around 30-35 MHz is suppressed in the experiment.

The X-band EPR spectrum recorded from a reaction mixture of $1P_1$ and $2N_s$ in frozen benzene-$d_6/o$-terphenyl solution at 50 K was quite isotropic, but the g-anisotropy is clearly resolved in high frequency (244 GHz) EPR measurements (Figure 4, right). The experimental g-anisotropy is very small, and smaller than calculated with DFT (Table 1). This may be caused by a small mismatch between the calculated and experimental geometries, as the calculated g-tensor is sensitive to the orientation of the $-SO_2$Ar fragment of the nitrene radical moiety with (e.g. optimization with and without dispersion corrections). It should further be noted at this point that complexes of type $3P_1^{N_s}$ need not be 5-coordinate. Coordination of an additional ligand to the cobalt(III) centre is perhaps even likely (vide infra), and this will also have some influence on the (calculated) g-tensor and hyperfine coupling parameters of the mono-nitrene complex, albeit very small (see Table 1 for a comparison of the experimental EPR parameters and the DFT calculated values of 5-coordinate $3P_1^{N_s}$ and its 6-coordinate NsNH$^-$ and OH$^-$ adducts).

Additionally, a quite anisotropic cobalt hyperfine interaction (HFI) tensor was revealed by Q-band Davies ENDOR measurements. The Q-band Davies ENDOR experiment (Figure 3, right) revealed broad features spanning 1-60 MHz. Apart from the characteristic proton signals centred around 52 MHz, strong lines are observed around 22 and 12 MHz. The position of these features is consistent with the $^{59}$Co hyperfine parameters estimated from the high field EPR spectrum (Figure 3), which are summarized in Table 1. Low frequency contributions (<8 MHz) are attributed to the porphyrin nitrogen atoms. The corresponding DFT calculated values match the experimental ones quite well (Table 1), albeit that the calculated anisotropy of the cobalt hyperfine tensor is a bit larger than in the experimental spectrum. Unfortunately, the anisotropic nitrene nitrogen hyperfine couplings were not resolved for technical reasons.
Interestingly, the mono-nitrene species 3 did not form instantaneously upon mixing the azides and the [Co(por)] catalysts at r.t. For example, only 10% of the mono-nitrene species $3^p_{troc}$ was formed upon mixing $1^p$ and azide $2_{troc}$ at r.t. after 15 minutes. These conversions were determined by comparison of the spin concentrations (double integration) with a sample of TEMPO of the same concentration. It should be mentioned that the relaxation times of TEMPO and the mono-nitrene species 3 are likely markedly different, and hence the spin integrations gave only a rough qualitative comparison of the spin concentrations. However, upon heating the samples, higher intensities were observed immediately; and on letting them heat overnight at 45 °C, the maximum intensities for all of these species were observed. The resulting solutions still contained the (excess) organic azide (as revealed by analysis of crystals recovered upon evaporation of the solvent) and were still catalytically active in aziridination of styrene (as confirmed by $^1$H NMR and GC-MS analysis of the crude reaction mixture).

Figure 4. Left: Experimental and simulated (Table 1) X-band EPR spectra of nitrene radical ligand complex $3^p_{Ns}$ in solution at r.t. Isotropic spectrum in solution recorded at r.t. ($\nu_{eq} = 9.38056$ GHz; Mod. Amp. = 1 G; MW power = 0.2 mW). Right: Experimental and simulated (Table 1) high field EPR spectra of nitrene radical ligand complex $3^p_{Ns}$ obtained by mixing $1^p$ and $2_{Ns}$ in frozen solution ($\nu_{eq} = 243.76176$ GHz, Mod. Amp. = 1 mT, power = 1 mW, 50 K).

Figure 5. EPR spectra of $3^p_{troc}$ (r.t.; benzene-$d_6$) showing increasing intensities over time on heating at 45 °C, only 10% of the mono-nitrene species $3^p_{troc}$ was formed upon mixing $1^p$ and azide $2_{troc}$ at r.t. after 15 minutes. These conversions were determined by comparison of the spin concentrations (double integration) with a sample of TEMPO of the same concentration.
Scheme

The maximum intensities were obtained for the combination of 3P1Ns optimized with Turbomole (full atom model) employing Grimme’s D3-dispersion corrections (disp3); EPR parameters calculated with ORCA, (b3-lyp/def2-TZVP); MHz; Data from Q-band Davies ENDOR measurements; Not resolved; Geometry of 3P1Ns (full atom model) optimized with Turbomole at the b3-lyp, def2-TZVP level without dispersion corrections to match the solution data. Optimized geometry of 6-coordinate NsNH- amido adduct of 3P1Ns (full atom model, BP86, def2-TZVP) employing Grimme’s D3-dispersion corrections (disp3). Optimized geometry of 6-coordinate OH- hydroxido adduct of 3P1Ns (full atom model, BP86, def2-TZVP) employing Grimme’s D3-dispersion corrections (disp3).

Among the series of complexes and nitrene precursors studied, the maximum intensities were obtained for the combination of 1P2 and 2trans (see Figure 5). This can be explained on the basis of better stabilization of the formed ‘nitrene radical’ intermediate by H-bonding between the amide arms of the porphyrin backbone in 1P2 and the nitrene transfer agent 2trans. The concentration of this species was found to be ~80% referenced against a sample of TEMPO with the same concentration as the cobalt precursor.

**EPR spectroscopy of the bis-nitrene species 5P1Ns**

In contrast to the use of organic azides that produced mono-nitrene species of the type 3P1Ns upon reaction with the cobalt(II) porphyrin complexes, reaction of an excess of N-nosyl iminoiodane 4Ns with 1P1 at room temperature in benzene-d6 yielded an entirely different species (Scheme 4), as revealed by X-band EPR spectroscopy in solution at r.t. A completely different isotropic spectrum was obtained with 4Ns (Figure 6, left) than that with nosyl azide 2trans or tosyl azide 2m (Figure 4, left). The multiline
spectrum revealed an isotropic g-value close to $g_e$ (2.003) with well-resolved hyperfine interactions with the two equivalent N-nitrene atoms ($A^\text{N-nitrene}_{\text{iso}} = 10.0$ MHz) and the four equivalent N-porphyrin atoms ($A^\text{N-porphyrin}_{\text{iso}} = 3.5$ MHz), again indicating formation of a ‘ligand radical’ complex. The isotropic cobalt HFI in $5^\text{P1}_\text{Ns}$ ($A^\text{Co}_{\text{iso}} = 2.0$ MHz) was very small, even smaller than in the mono-nitrene case (25 MHz). The spectrum could be satisfactorily simulated based on the DFT-calculated EPR parameters (Figure 6 and Table 2).

Scheme 4. Reaction of $[\text{Co}^{II}(\text{Por})]$ $1^\text{P1}$ and nitrene transfer reagent $4_\text{Ns}$ to give bis-nitrene species $5^\text{P1}_\text{Ns}$. Please note that the formation of a one-electron oxidized porphyrin ligand is indicated with a positive charge on the porphyrin ring, using the ‘π-cation radical’ convention commonly used in Cytochrome P450 chemistry, but this is in fact a mono-anionic por$^-$ ligand.

To prove that the largest detected nitrogen hyperfine couplings stem from the two equivalent nitrene moieties, we further prepared the $^{15}$N-labeled iminoiodane $^{15}$N-$4_\text{Ns}$ (PhI=$^{15}$NNs) and recorded the r.t. EPR spectrum of $(^{15}\text{N})_2$-$5^\text{P1}_\text{Ns}$ generated in a mixture of $1^\text{P1}$ and $^{15}$N-$4_\text{Ns}$. This led to clear differences in the hyperfine coupling pattern compared to the non-labelled analogue $5^\text{P1}_\text{Ns}$ (Figure 6, top).

Figure 6. (left) Overlay of the isotropic X-band EPR spectra of unlabeled $5^\text{P1}_\text{Ns}$ (red) and labeled $(^{15}\text{N})_2$-$5^\text{P1}_\text{Ns}$ (blue). (right) Experimental and simulated isotropic EPR spectra of species $(^{15}\text{N})_2$-$5^\text{P1}_\text{Ns}$ in benzene-$d_6$. Freq = 9.38126 GHz, mod. ampl. = 1 G, microwave power = 0.2 mW, $T = 298$ K.
Table 2. Experimental (298 K) a) and DFT b) calculated EPR parameters of $5^{P_1}_{Ns}$ and $(^{14}\mbox{N})_2-5^{P_1}_{Ns}$

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<th>Equiv. Nuclei</th>
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<th>DFT b)</th>
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<td>$g_{iso}$</td>
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<td>2.008</td>
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<td>$A_{Co-iso}$</td>
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<td>22.4</td>
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<td>$A_{N-por}$</td>
<td>4 (I = 1)</td>
<td>3.5</td>
<td>−1.5</td>
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a) Derived from spectral simulations shown in Figure 5; b) Geometry optimized with Turbomole (b3-lyp/def2-TZVP) using a simplified model of $5^{P_1}_{Ns}$ without porphyrin Ph substituents without dispersion corrections to match the r.t. solution EPR data; EPR parameters calculated with ORCA (b3-lyp/def2-TZVP); c) MHz; d) Average of two $A^{N-nitrene}$ hyperfines; e) Average of four $A^{N-por}$ hyperfines.

EPR simulation using an expected 1.4 times larger $A^{N-nitrene}_{iso-^{15}N}$ (I = ½) hyperfine coupling (14 MHz) compared to the unlabeled $^{14}N\cdot A^{N-nitrene}_{iso}$ constant of 10 MHz (I = 1) in $5^{P_1}_{Ns}$ and otherwise identical spectral parameters provided an excellent fit of the experimental spectrum (Figure 6, bottom; Table 2). Hence, the largest detected nitrogen hyperfine couplings indeed stem from the two equivalent nitrene moieties.

In case of the bis-nitrene species $5^{P_1}_{Ns}$ the intensity of the signal was not as strong as the mono-nitrene species, for example, $3^{P_1}_{Ns}$. On heating the sample shortly, the intensity increased only very slightly and was at least 10 times lower than that of the mono-nitrene species (spin counting amounts to ~8%, using a reference sample containing TEMPO at the same concentration as $1^{P_1}$). The poor solubility of the N-nosyl iminiodane substrate in benzene-$d_6$ could well be a reason for the low intensities obtained for species $5^{P_1}_{Ns}$. It is also worth mentioning that the experimentally detected signal of species $5^{P_1}_{Ns}$ stems from a (net) doublet spin state ($S = ½$), leading to the characteristic EPR data shown in Figure 6 and Table 2, but in DFT (b3-lyp) the doublet ($S = ½$) and quartet ($S = 3/2$; $\Delta G = +0.2$ kcal mol$^{-1}$) spin states of $5^{P_1}_{Ns}$ are predicted to be of nearly equal energy. As only the doublet state is detectable with EPR at r.t. in solution, the potential existence of a (slow) thermal equilibrium between the two spin states might also explain the relatively low EPR intensity of the signal, which stems from the $S = ½$ state of bis-nitrene species only. Furthermore, it is worth mentioning that the bis-nitrene species are intrinsically more reactive. In contrast to the mono-nitrene species $3^{P_1}_{Ns}$, which increased in time upon heating the solution to 45 °C, species $5^{P_1}_{Ns}$ decomposed at this temperature, causing the EPR signal of the bis-nitrene species to disappear completely overnight (i.e. in absence of other substrates). Catalyst decomposition may be less important in the presence of suitable substrates, as heating the solution in the presence of styrene did reveal the expected aziridination activity (as confirmed by $^1$H NMR and GC-MS analysis of the crude reaction mixture).
Steric and electronic influence of the catalyst on formation of the nitrene intermediates

The steric and electronic influence of the catalyst on the species obtained, even when using the more oxidizing $N$-nosyl iminoiodane $4_{Ns}$, is quite dramatic. For example, on using the bulkier porphyrin complex $1^{P2}$ in combination with the oxidizing $N$-nosyl iminoiodane $4_{Ns}$, the bis-nitrene species was detected only in minor amounts. Instead, a major EPR signal corresponding to the mono-nitrene species was detected (Figure 7). Thus, it may be concluded that the bulky side groups on the porphyrin backbone of $1^{P2}$ make it difficult for the second molecule of $N$-nosyl iminoiodane $4_{Ns}$ to react.

In contrast to the decomposition observed for species $5^{P1}_{Ns}$ that was obtained from a mixture of $1^{P1}$ and an excess of $4_{Ns}$, mono-nitrene species $3^{P2}_{Ns}$ obtained from a mixture of $1^{P2}$ and excess $4_{Ns}$ proved to be much more stable. On heating the latter sample to 45 °C, the signal intensity decreased, with the complete disappearance of the initially detected small amount of bis-nitrene species $5^{P2}_{Ns}$. In contrast, a significant amount of mono-nitrene species $5^{P2}_{Ns}$ remained present in solution, even after heating for a period of 18 h (Figure 7). These results clearly show that the bis-nitrene species $5$ are more reactive than the mono-nitrene species $3$, and that complex $1^{P2}$ is more stable than complex $1^{P1}$ when combined with $N$-nosyl iminoiodane $4_{Ns}$. The latter can perhaps be attributed to stabilizing H-bonding interactions between the nitrene radical moiety and the H-bond donating amido functionalities incorporated in the porphyrin backbone of $1^{P2}$. At the same time, it also suggests that $N$-nosyl iminoiodane $4_{Ns}$ is not a very benign nitrene transfer reagent for these reactions as it seems to undergo subsequent side reactions with the catalyst (especially for the less bulky ones and in the absence of another substrate).

UHR-ESI-MS spectrometry

To further corroborate the above observations in the EPR measurements, the reactions were also investigated with mass spectrometry. We investigated the formation of both the mono- and the bis-nitrene species. High resolution ESI-MS mass spectrometry proved to be a suitable method to detect the formation of both mono and bis-nitrene species. However, since these species are neutral (or perhaps anionic, *vide infra*), only signals resulting from protonation, (one-electron) oxidation and formation of Na*+ adducts can be expected in positive mode UHR-ESI-MS.
A reaction mixture of $^{1}$P1 with nosyl azide $^{2}$Ns in C$_{6}$D$_{6}$/MeCN produced clear ESI-MS signals around m/z 872 characteristic for formation of the mono-nitrene species $^{3}$P1$_{Ns}$ (Scheme 3). The isotope distribution pattern and exact masses determined by ESI-MS match the theoretical values ($\Delta$m/z < 0.004 Da) for the species in its protonated form [3$^{3}$P1$_{Ns}$+H$^{+}$]$^{-}$ (Figure 8). The relatively low intensity of the detected nitrene radical species derived from reaction of complex $^{1}$P1 with azide $^{2}$Ns is likely a result of incomplete conversion to $^{3}$P1$_{Ns}$, as the measurements were performed within 30 minutes of sample preparation.

At the same time, subsequent reactions with the co-solvent acetonitrile cannot be neglected. While $^{3}$P1$_{Ns}$ is detected as a 5-coordinate species in its protonated form with ESI-MS, this does not exclude $^{3}$P1$_{Ns}$ from being 6-coordinate as the 6$^{th}$ ligand might easily dissociate in the ionization chamber of the ESI-MS spectrometer. We were not able to detect $^{3}$P1$_{Ns}$ in negative mode ESI-MS measurements (cold-spray ionization). However, interestingly, in the positive mode ESI-MS measurements (cold-spray ionization), a Na$^{+}$ adduct of NO$_{2}$PhSO$_{2}$ND$^{•}$ was detected from a mixture of $^{1}$P1 and $^{2}$Ns. Note that formation of NO$_{2}$PhSO$_{2}$ND$^{•}$ radicals, detected with EPR, has been reported earlier. On this basis, the most likely candidates for the sixth ligand coordinated to the mono-nitrene species are either the NO$_{2}$PhSO$_{2}$NDH amine ligand or the NO$_{2}$PhSO$_{2}$ND$^{-}$ amido ligand (in both cases detected as the Na$^{+}$ adduct of the amine in the ESI-MS measurements, in the first case directly and in the second case after hydrogen atom transfer (HAT)).

ESI-MS spectra recorded from a mixture of $^{1}$P1 and N-nosyl iminoiodane $^{4}$Ns revealed signals pointing to the presence of bis-nitrene species $^{5}$P1$_{Ns}$ (Scheme 4). This species was observed as the protonated form of its hydrogen atom abstraction (HAA) reaction product ([5P1$_{Ns}$+H$^{+}$]+H$^{•}$), thus pointing to rapid HAA from the co-solvent MeCN. Substantially weaker signals corresponding to the mono-nitrene species $^{3}$P1$_{Ns}$ were still detected ([3P1$_{Ns}$ +H$^{+}$]), which likely resulted from incomplete conversion of $^{1}$P1 to $^{5}$P1$_{Ns}$ and/or fragmentation of $^{5}$P1$_{Ns}$ to $^{3}$P1$_{Ns}$ in the ionization chamber of the ESI-MS spectrometer.

Electronic structures and UV-Vis spectra of mono- and bis-nitrene species

To gain additional insight into the electronic structures of the generated nitrene species, we performed DFT geometry optimizations at the b3-lyp/def2-TZVP level using simplified models of $^{3}$P1$_{Ns}$ and $^{5}$P1$_{Ns}$ without meso-phenyl substituents on the porphyrin ring P$^{0}$ (Figure 9). According to these calculations, mono-nitrene species $^{3}$P1$_{Ns}$ formed from $^{1}$P1 and $^{2}$Ns is best described as a Co$^{III}$ species with one 1e reduced nitrene moiety and a normal, non-oxidized (por$^{2-}$) porphyrin ligand. Note again the experimental complex $^{3}$P1$_{Ns}$ need not be 5-coordinate. Coordination of an additional ligand to the
cobalt(III) center cannot be excluded and even seems likely (*vide infra*). However, note that all 6-coordinate analogs of $3^{6}_{P0}$ considered computationally have almost identical spin density distributions as the one shown for 5-coordinate mono-nitrene complex $3^{6}_{P0}$ in Figure 9. In these calculations full atom models were optimized at the BP86/def2-TZVP/disp3 level (Turbomole), followed by single point calculations at the b3-lyp/def2-TZVP level (ORCA), considering several different (neutral and anionic) ligands bound trans to the nitrene radical moiety.

![Figure 9. Spin density plots (b3-lyp/def2-TZVP) of mono-nitrene species $3^{6}_{P0}$ (top) and bis-nitrene species $5^{6}_{P0}$ (bottom).](image)

The mono-nitrene species $3^{6}_{P0}$ formed from $1^{6}_{P1}$ and $2^{6}_{Ns}$ is best described as a Co$^{III}$ species with one 1e reduced nitrene moiety and a normal, non-oxidized (por$^{2-}$) porphyrin ligand.

The bis-nitrene species $5^{6}_{P0}$, on the other hand, is a triple-radical containing two 1e-reduced nitrene-moieties and a 1e-oxidized porphyrin ring (from por$^{2-}$ to the por$^{**}$ radical monoanion). As is clear from the positive and negative spin density distribution, two of the three unpaired electrons in $5^{6}_{P0}$ are antiferromagnetically coupled, thus effectively leading to a (net) doublet state ($S_{\text{total}} = \frac{1}{2}$). Both $3^{6}_{P1}$ and $5^{6}_{P0}$ were found to contain a low-spin d$^6$ ($S_{Co} = 0$) Co$^{III}$ center.

The bis-nitrene species $5^{6}_{P0}$, on the other hand, is a triple-radical containing two 1e-reduced nitrenemoieties and a 1e-oxidized porphyrin ring (from por$^{2-}$ to the por$^{**}$ radical monoanion). As is clear from the positive and negative spin density distribution (Figure 8, right), two of the three unpaired electrons in $5^{6}_{P0}$ are antiferromagnetically coupled, thus effectively leading to a (net) doublet state ($S_{\text{total}} = \frac{1}{2}$). Both $3^{6}_{P1}$ and $5^{6}_{P0}$ were found to contain a low-spin d$^6$ ($S_{Co} = 0$) Co$^{III}$ center. Hence, formation of $5$ involves one-electron oxidation of Co$^{II}$ to Co$^{III}$ upon formation of the first nitrene-radical $3$ and a second intramolecular electron transfer from the porphyrin ring to the second nitrene moiety in the second step.

The DFT calculated electronic structures are qualitatively in agreement with UV-Vis measurements, revealing the presence of a non-oxidized porphyrin ring in $3^{6}_{P1}$ and a ‘porphyrin radical’ ligand in $5^{6}_{P0}$ (Figures 9 and 10). Metal- (not porphyrin-) centered oxidation of [Co$^{II}$por] is known to produce characteristic red-shifts of both the Soret- and Q-bands. Metal- (not porphyrin-) centered oxidation of [Co$^{II}$por] is known to produce characteristic red-shifts of both the Soret- and Q-bands. The same is also true for binding donor ligands, such as pyridine or bipyridyl ligands, to the central metal ion of [Co$^{II}$por]. Such shifts were indeed observed upon measuring UV-Vis spectra of a mixture of $1^{6}_{P1}$ and $2^{6}_{Ns}$ immediately upon mixing.
In Figure 10, the UV-Vis spectrum of a mixture of $1^\text{P1}$ and $2^\text{Ns}$ was followed in time (after 40 minutes of sample preparation). In these spectra, the observed shifts in the Q- and Soret-bands are due to formation of a simple azide adduct (mostly likely a mono-azide adduct). Indeed, measuring EPR spectra of these same mixtures (again 40 minutes after mixing the reagents) without any additional heating revealed extremely weak EPR signals in the region around $g = 2.0$, corresponding to formation of only a tiny amount of ‘nitrene-radical’ species $3^\text{P1,Ns}$.

**Figure 10.** UV-Vis spectra of a mixture of $1^\text{P1}$ and $2^\text{Ns}$ followed in time (after 40 minutes of sample preparation). Clear shifts in both the Q- and Soret-bands were observed corresponding to azide ligation to the cobalt(II) center. The observed shifts in the Q- and Soret-bands are due to formation of a simple azide adduct (mostly likely a mono-azide adduct).

Figure 11. UV-Vis spectral changes upon reaction of (top) complex $1^\text{P2}$ with azide $2^\text{troc}$ to give mono-nitrene species $3^\text{P2,troc}$ formed after heating the solution overnight. The shift in the Soret and the Q-band is indicative of oxidation of the metal from cobalt(II) to cobalt(III) and (or) ligation to the sixth coordination site, leaving the porphyrin ligand intact without oxidation upon formation of mono-nitrene radical species $3^\text{P2,troc}$.

Bottom spectra belong to reaction of complex $1^\text{P1}$ with iminoiodane $4^\text{Ns}$ to give bis-nitrene species $5^\text{P1,Ns}$ within 1 hour. The species exhibited characteristic, strongly red-shifted bands at 863 and 977 nm. Similar spectral changes have been reported for Co$^{\text{III}}$ complexes with a 1e-oxidized octaethylporphyrin ligand.
On measuring the UV-Vis spectra of these same solutions after heating them overnight at 45 °C (i.e. solutions that gave strong EPR signals characteristic for $3^\text{P}_1\text{Ns}$) clearly revealed the presence of a new species in the UV-Vis spectra (Figure 11, top), concomitant with much higher EPR intensities corresponding to ‘nitrile radical’ species $3^\text{P}_1\text{Ns}$. Illustrative spectra comparing $1^\text{P}_2$ and species $3^\text{P}_2\text{troc}$ formed upon heating a solution of complex $1^\text{P}_2$ in the presence of an excess of $2\text{troc}$ are shown in Figure 11.

Reaction of complex $1^\text{P}_2$ with azide $2\text{troc}$ resulted in red-shifts of the Soret band at 438 nm and shifting of the Q-band to 648 nm. In addition, a new peak at ~753 nm was also observed (Figure 11, top). The shift in the Soret and the Q-band is indicative of oxidation of the metal from cobalt(II) to cobalt(III) and (or) ligation to the sixth coordination site, leaving the porphyrin ligand intact without oxidation upon formation of mono-nitrile radical species $3^\text{P}_2\text{troc}$. The additional band at ~753 nm is likely a charge-transfer band (e.g. a MLCT or LMCT band involving the nitrile radical and the cobalt(III) centre).

Formation of porphyrin-based ligand radicals is known to cause drastic changes in the UV-Vis spectrum with appearance of red-shifted bands, disappearance of the Q-band and obvious shape-changes of the Soret band compared to unmodified (i.e. non-reduced/non-oxidized) dianionic porphyrinato ligands (por$^2^-$).$^{22}$ This is what was observed upon formation of bis-nitrene species $5^\text{P}_1\text{Ns}$ in the reaction of complex $1^\text{P}_1$ with $N$-nosyl iminoiodane $4\text{Ns}$ (Figure 11, bottom). As mentioned before, when using iminoiodane $4\text{Ns}$, formation of the bis-nitrene species is comparatively faster than formation of the mono-nitrenes when using azide $2\text{Ns}$. Accordingly, in the case on measuring the UV-Vis spectra of a mixture of $1^\text{P}_1$ and $4\text{Ns}$, the disappearance of the Q- and Soret-bands was observed within an hour of making these samples (Figure 11, bottom). As shown in Figure 11, the species exhibited characteristic, strongly red-shifted bands at 863 and 977 nm. Similar spectral changes have been reported for Co$^\text{III}$ complexes with a 1e-oxidized octaethylporphyrin ligand.$^{23}$ Hence, we assign these spectral changes to formation of the bis-nitrene species $5^\text{P}_1\text{Ns}$. This is also in correspondence with the EPR measurements. Both the EPR and UV-Vis signals characteristic for the nitrile radical species $5^\text{P}_1\text{Ns}$ were completely lost upon heating the mixture overnight at 45° C.

In accordance with the EPR spectroscopic studies, once again the mono-nitrene species $3^\text{P}_2\text{troc}$ was found to be more stable than bis-nitrene species $5^\text{P}_1\text{Ns}$. UV-Vis spectroscopy clearly indicated that solutions of $3^\text{P}_2\text{troc}$ obtained from complex $1^\text{P}_2$ and $4\text{troc}$ remained stable for even two days while a significant amount of decomposition already occurred for $5^\text{P}_1\text{Ns}$ obtained from complex $1^\text{P}_1$ and $4\text{Ns}$ within two hours. This points to a higher intrinsic reactivity of bis-nitrene species $5^\text{P}_1\text{Ns}$ compared to mono-nitrene species $3^\text{P}_1\text{Ns}$. Indeed, DFT calculations (using $3'$ and $5'$, which are simplified models of $3^\text{P}_1\text{Ns}$ and $5^\text{P}_1\text{Ns}$ without phenyl substituents on the porphyrin ring and having a N-SO$_3$Ph base nitrile instead of N-Ns) predict a ca. 1.3 kcal mol$^{-1}$ lower activation energy for HAA from ethyl benzene for $5'$ ($\Delta G^\dagger = +30.4$ kcal mol$^{-1}$) than for $3'$ ($\Delta G^\dagger = +31.7$ kcal mol$^{-1}$).

Note that the exact geometry of the mono-nitrene species, however, remains uncertain. It could either be 5-coordinate or 6-coordinate and none of the spectroscopic techniques undertaken so far are informative in this regard. So we take up X-Ray Absorption Spectroscopy (XAS) on these nitrile radical intermediates and some other cobalt porphyrin complexes that serve as reference compounds. This will be the topic of discussion for the next chapter.
Summary and conclusions
In this work, we have demonstrated that activation of both organic azides and iminoiodanes by cobalt(II) porphyrin complexes leads to formation of ‘cobalt(III)-nitrene radical’ complexes. Both species bear substantial spin density at the ‘nitrene-moiety’ and are key intermediates in cobalt-catalysed nitrene transfer reactions. Notably, for the less bulky porphyrin complexes, the obtained species are markedly different. While organic azides generate predominantly mono-nitrene species, hypervalent iodine reagents such as iminoiodanes produce bis-nitrene species such as \(5^\text{P1}_\text{Ns}\). The stronger oxidising nature of the nitrene precursor \(4\text{Ns}\) is considered important to generate such species. The bis-nitrene species \(5^\text{P1}_\text{Ns}\) has a markedly different electronic structure from the mono-nitrene species \(3^\text{P1}_\text{Ns}\), \(3^\text{P2}_\text{Ts}\), and \(3^\text{P2}_\text{troc}\), and also differs markedly from the electronic structure of the previously reported diamagnetic bis-imido Ru\(^{IV}\)-porphyrin species (por)Ru\(^{IV}\)(=NR’’). Depending on the nature of the nitrene precursor, the intermediates can be a result of a single oxidation of the catalyst at the metal centre or a double oxidation where the second oxidation step occurs at the porphyrin ring. In addition, the bis-nitrene species \(5^\text{P1}_\text{Ns}\), though formed faster, lives shorter and is more reactive than the mono-nitrene species \(3^\text{P1}_\text{Ns}\). Degradation of bis-nitrene species \(5^\text{P1}_\text{Ns}\) occurs within hours after initial formation while decomposition of mono-nitrene species \(3^\text{P1}_\text{Ns}\) is much slower. In addition, the studies described here clearly demonstrate the better performance of specially tailored \([\text{Co}^{\text{II}}(\text{Por})]\) like complex \(1^\text{P2}\), which not only give to higher conversions to the nitrene-radical species, but also help in preserving them for longer periods by the stabilizing effects of H-bonding between the catalyst amide arms and the nitrene moiety. The steric influence of the bulk in complex \(1^\text{P2}\) also has an implication on the type of intermediates formed, as was shown for the reactions of \(1^\text{P1}\) and \(1^\text{P2}\) with N-nosyl iminoiodane \(4\text{Ns}\). We will find out more about the spectroscopic oxidation state of the metal and the exact coordination mode of the mono-nitrene species in the next chapter.

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References and notes


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