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Characterization of Porphyrin-Co(III)-‘Nitrene Radical’ Species Relevant in Catalytic Nitrene Transfer Reactions

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Supporting Information

ABSTRACT: To fully characterize the Co(III)–‘nitrene radical’ species that are proposed as intermediates in nitrene transfer reactions mediated by cobalt(II) porphyrins, different combinations of cobalt(II) complexes of porphyrins and nitrene reagents were combined, and the generated species were studied using EPR, UV–vis, IR, VCD, UHR-ESI-MS, and XANES/XAFS measurements. Reactions of cobalt(II) porphyrins 1P1 (P1 = meso-tetraphenylporphyrin (TPP)) and 1P2 (P2 = 3,5-Di’Bu-ChenPhyrin) with organic azides 2Ns (N3S = N3B = N3S), 2Ts (TsN3), and 2Troc (TrocN3) led to the formation of mono-nitrene species 3P1 Ns, 3P2 Ns, and 3P2 Troc, respectively, which are best described as [{Co(III)(por)(NR″•″•)}] nitrene radicals (imidyl radicals) resulting from single electron transfer from the cobalt(II) porphyrin to the ‘nitrene’ moiety (Ns: R = SO2C6H6; Troc: R = –C(O)OCH2CCl3). Remarkably, the reaction of 1P1 with N-nosyl iminoiodane (PhI=NNs) 4Ns led to the formation of a bis-nitrene species 5P1 Ns. This species is best described as a triple-radical complex [{(por••••)(CoII)(NR″•″•)}] containing three ligand-centered unpaired electrons: two nitrene radicals (NR″•″•) and one oxidized porphyrin radical (por••••). Thus, the formation of the second nitrene radical involves another intramolecular one-electron transfer to the ‘nitrene’ moiety, but now from the porphyrin ring instead of the metal center. Interestingly, this bis-nitrene species is observed only on reacting 4Ns with 1P1. Reaction of the more bulky 1P2 with 4Ns results again in formation of mainly mono-nitrene species 3P2 Ns according to EPR and ESI-MS spectroscopic studies. The mono- and bis-nitrene species were initially expected to be five- and six-coordinate species, respectively, but XANES data revealed that both mono- and bis-nitrene species are six-coordinate O₅ species. The nature of the sixth ligand bound to cobalt(III) in the mono-nitrene case remains elusive, but some plausible candidates are NH₃, NH₂, N₃NH, and OH; N₃NH being the most plausible. Conversion of mono-nitrene species 3P1 Ns into bis-nitrene species 5P1 Ns upon reaction with 4Ns was demonstrated. Solutions containing 3P1 Ns and 5P1 Ns proved to be still active in catalytic aziridination of styrene, consistent with their proposed key involvement in nitrene transfer reactions mediated by cobalt(II) porphyrins.

INTRODUCTION

Catalytic functionalization of C–H bonds is a desirable tool in organic and organometallic chemistry, as it is an atom-, time-, and cost-efficient alternative to traditional hydrocarbon functionalization.1–3 Therefore, C–H insertion of carbenoid and nitrenoid species has emerged as a very promising protocol in the recent years.4,5 The insertion of metal carbenoids into C–H bonds is now a well-established transformation, and many transition-metal catalysts that can catalyze such reactions have been disclosed in the past decade.6,7 In addition to catalytic cyclopropanation and C–H insertion, metal-catalyzed carbene transfer has also made it possible to perform insertions into X–H bonds (X = O, N, S, Si) and to convert alkenes to cyclopropanes (including some cycloaddition reactions).4 Given the ubiquity of nitrogen atoms in biologically active compounds,8 nitrene transfer reactions also have very important applications in making molecules of interest. However, the applicability of metal-nitrenoids has so far been

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limited to alkene aziridination, C–H amination and amidation. Among several catalysts that have been reported for nitrene transfer reactions, the most successful ones are still based on non-abundant Rh4−6,13−17 and Ru6,7,18−20 metals. Among the first row transition metals, there have been reports of Mn21,22 Cu23−26 and Fe27 catalyzed systems. Besides being very efficient in carbene transfer reactions,28−31 cobalt(II) porphyrin catalysts have also attracted attention in nitrene transfer reactions. Until the early 2000s, it was quite common to use iminioiodanes32−36 or haloamine-T23,25,26 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. With the efforts of various groups, organic azides37,38 were discovered to be potentially greener resources to transfer nitrenes, as the only byproduct formed during the generation of nitrenes from azides is dinitrogen. The other disadvantage of using iminioiodanes is their poor solubility and the fact that there is not much scope to change the pre-existing functionality on the nitrogen atom.

With the use of differently meso-substituted cobalt(II) porphyrins (P1−P4 in Figure 1) a variety of nitrene transfer reagents (Figure 2) have been employed. For example, with the use of reagents like diphenyl phosphoryl azide (DPPA),39,40 it is possible to further modify the substituent, as the nitrogen–phosphorus bond in the product aziridine is readily hydrolyzed. In the pursuit of finding more nitrene transfer reagents with easily removable groups on the nitrogen atom, trichloroethoxysulfonyl azide41 (TcesN3, Tces = trichloroethoxysulfonyl = CCl3CH2O(SO2)−) was found to be effective. Apart from the nitrene precursors themselves, specially tailored cobalt porphyrins, for example, with H-bonding functionalities, have further enhanced the applicability of these systems (see Figure 1; P1 = meso-tetraphenylporphyrin, P2 = 3,5-di’Bu-ChenPhyrin; P3 = 2,6-diMeO-ZhuPhyrin; P4 = 3,5-di’Bu-IbuPhyrin). With the use of 1P3, organic azides like tosyl azide can also be used as a viable nitrene source. H-bonding interactions between the nitrene moiety and the arms of the catalyst 1P4 facilitate nitrenoid formation and lead to an increased catalyst efficiency and lifetime. Enantioselective aziridination of alkenes was reported a few years ago using chiral cobalt(II)-porphyrin 1P3 with TcesN3 and enantioselectivity of 99% could be obtained.41

The mechanistic aspects of two such catalytic nitrene transfer reactions with cobalt porphyrins have been elucidated by our groups previously (Scheme 1).9,43 The mechanism of C–H bond amination of ethylbenzene, 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).43 The mechanism of cobalt(II) porphyrin-mediated aziridination of styrene with PhSO2N3 was also studied (Scheme 1b).9 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 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 π-interactions and explaining the unusual electronic structure of this intermediate is depicted in Scheme 2.

Experimental detection of these radicaloid species led us to investigate the subsequent stepwise C−H amination sequence computationally. According to these investigations, the amination reaction follows a stepwise radical pathway, in which the nitrene radical intermediate C readily abstracts a hydrogen atom from the benzylic position of the organic substrate. This leads to formation of a close-contact pair (D) of the thus-formed organic radical C• and the cobaltIII−amido complex (por)CoIII−NHR•. Subsequent back-attack of the organic radical onto the amido moiety in D, in a rebound-type mechanism, leads to release of the desired amine products with regeneration of the cobalt(II) catalyst, which proceeds with low activation barriers according to DFT.

Nitrene transfer to styrene also proceeds in a stepwise manner via radical addition of the nitrene radical C to the C═C double bond of styrene to form γ-alkyl radical intermediates D’ (Scheme 1b). The cobalt(III) ion in D’ has an intermediate (S = 1) spin-state with its unpaired electrons antiferromagnetically coupled to the unpaired electron of the γ-alkyl radical, thus explaining its overall doublet (S = 1/2) state. Species D’ easily collapses in an almost barrierless ring closure reaction to form the aziridine, thereby regenerating the cobalt(II) porphyrin catalyst. Additionally, the computed free energy profile well explained the superior performance of the reported CoIII(porAmide) system 1P4 with H-bond donor functionalities over the non-functionalized system 1P1 (see Figure 2).42

Thus, the DFT calculations and the X-band EPR data gathered thus far strongly indicate the formation of substrate-centered (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 CoIII(por) catalysts and employing organic azides as nitrene sources. These nitrene radicals have thus far only been detected by means of X-band EPR spectroscopy.43 Here we disclose their detection and characterization with a variety of spectroscopic and mass spectrometric techniques.

Ligand-centered radical complexes play a pivotal role in a number of bio- and “biospired” catalytic transformations, providing a powerful tool to control the reactivity and selectivity of the catalyst.41−46 Such species are well-studied and characterized for transition-metal complexes containing typical polydentate redox non-innocent ligands, such as semi quinone-type radical ligands87−89 and their nitrogen analogs,90−92 reduced bipyridine and terpyridine ligands,93−95 α-iminopyridine ligands,96−98 and pyridine-2,6-diimine ligands.99−101 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,102 which play a key role in catalytic carbene transfer reactions.65,66 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 amyl ligand radicals are limited to only a few well-characterized examples,65 and related complexes bearing redox non-innocent nitrene ligands are even scarcer.9,43,65−67 Given the importance of these radicaloid nitrene species in metal-catalyzed nitrene transfer and C−H functionalization reactions,68 we gathered more experimental evidence for the formation of the previously reported mono-nitrene radical complexes upon reaction of cobalt(II) porphyrins with nitrene transfer reagents.9,43 Furthermore, we here reveal the first example of a bis-nitrene species of 1P1 upon reacting the stronger oxidizing nitrene transfer agent N-nosyl iminoiodane 4Ns with 1P1. 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 RuIII-porphyrin species (por)RuIII((═ NR′)2)59−73. The work described herein further bears some similarity with the mono- and bis-nitrene species of non-heme iron complexes disclosed by Che and co-workers,66 but again the electronic structures reported herein are entirely different.

### RESULTS AND DISCUSSION

To study the key nitrene intermediates in nitrene transfer reactions mediated by cobalt(II) porphyrins, we chose to react a few of the commonly used nitrene sources with two different types of cobalt(II) porphyrins: the tetraphenyl-substituted porphyrin 1P1 and the bulkier (and chiral) H-bond donor appended porphyrin 1P2 (see Figure 1). Complex 1P2 serves as a model system for all reported cases where CoIII porphyrins with H-bonding moieties were proven to give superior catalytic results and where H-bonding stabilizes the formed nitrene intermediates.31,8 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 $2_{\text{Ns}}$, $2_{\text{Troc}}$ and $2_{\text{Tns}}$ (see Figure 2): Nosyl azide ($2_{\text{Ns}}$; $\text{Ns} = \text{Nosyl} = p$-$\text{NO}_2$-$\text{PhSO}_2$−), Tosyl azide ($2_{\text{Tso}}$; $\text{Tso} = \text{Tosyl} = p$-$\text{MePhSO}_2$−), and Troc azide ($2_{\text{Troc}}$; Troc =2,2,2-trichloroethoxycarbonyl = $\text{CCl}_3\text{CH}_2\text{O}$−)−). The fourth nitrene transfer reagent investigated was the stronger oxidizing N-nosyl iminodiode ($\text{Ph}=\text{NNN}$) $4_{\text{Ns}}$. To perform the EPR, ultra high-resolution electron spray ionization mass spectrometry (UHR-ESI), UV–vis, and X-ray absorption spectroscopy (XAS) studies, the following method was employed: 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.** 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 $2_{\text{Tso}}$ 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 cobalt(II) porphyrin is associated with appearance of signals corresponding to mono-nitrene species of the type 3 (for an example, see Figure S5-1; Supporting Information). The room-temperature (r.t.) EPR measurement of the same samples gave spectra characteristic for ligand radical species (Figure 3, top), and the simulated spectra fits best to a mono-nitrene species of the type 3.

The X-band EPR spectrum recorded from a reaction mixture of $1_{\text{P1}}$ and $2_{\text{Ns}}$ 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 3, bottom). 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 (e.g., optimization with and without dispersion corrections). It should further be noted at this point that complexes of type $3_{\text{P1}}_{\text{Ns}}$ need not be five-coordinate. Coordination of an additional ligand to the cobalt(III) center (see also Scheme S5-5; Supporting Information) 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 five-coordinate $3^{\text{P1}}_{\text{Ns}}$ and its six-coordinate $\text{NsNH}^+$ and $\text{OH}^+$ adducts). Note that a variety of other six-coordinate analogs of $3^{\text{P1}}_{\text{Ns}}$ investigated, containing either neutral or anionic ligands bound trans to the nitrene radical moiety, all have very similar calculated g-values and HFIs with cobalt and the nitrogen atom of the spin-bearing nitrene radical ligand (see Table S5-1, Supporting Information).

Additionally, a quite anisotropic cobalt hyperfine interaction (HFI) tensor was revealed by Q-band Davies ENDOR measurements. The Q-band Davies ENDOR experiment (Figure S5-2; Supporting Information) revealed broad features spanning 1–60 MHz. Apart from the characteristic proton signals centered 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
crystals recovered upon evaporation of the solvent) and were heated overnight at 45 °C. Higher intensities were observed immediately; and on letting the spin concentrations. However, upon heating the samples, the spin integrations gave only a rough qualitative comparison of the mono-nitrene species. It should be mentioned that the relaxation times of TEMPO and the comparison of the spin concentrations (double integration) with a sample of TEMPO of the same concentration. It should not be resolved. The geometry of 3NsN optimized with Turbomole (full atom model, BP86, def2-TZVP) employing Grimme’s D3-dispersion corrections (disp3); EPR parameters calculated with ORCA, (b3-lyp/def2-TZVP). X-band EPR spectroscopy in solution at room temperature in benzene- 80% referenced against a sample of TEMPO with the same concentration as the cobalt precursor. Similar rough spin counting reveals the presence of ~60% of EPR active 3P1 upon reaction of 1P1 with excess 2Ns after heating overnight at 45 °C.

EPR Spectroscopy of the Bis-Nitrene Species 5P1 Ns. In contrast to the use of organic azides that produced mono-nitrene species of the type 3, reaction of an excess of N-nosyl iminosulfonamide 4Ns with 1P1 at room temperature in benzene-d6 yielded an entirely different species (Scheme 4), as revealed by Figure 4. EPR spectra of 3P1 Troc (r.t.; benzene-d6) showing increasing intensities over time on heating at 45 °C.

Table 1. EPR Parameters of Nitrene Radical Complex 3P2 Ns in Frozen Solution at 50 K and in Isotropic Solution at Room Temperature

<table>
<thead>
<tr>
<th></th>
<th>50 K</th>
<th>296 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g1</td>
<td>g2</td>
</tr>
<tr>
<td>Exp</td>
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<td>2.0049</td>
</tr>
<tr>
<td>DFT a</td>
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<td>2.0154</td>
</tr>
<tr>
<td>5-coord</td>
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<td>2.0029</td>
</tr>
<tr>
<td>5-coordF</td>
<td>2.0311</td>
<td>2.0052</td>
</tr>
<tr>
<td>5-coordF</td>
<td>2.0387</td>
<td>2.0116</td>
</tr>
<tr>
<td>A10</td>
<td>A10 b</td>
<td>A11 b</td>
</tr>
<tr>
<td>Exp</td>
<td>-98</td>
<td>65</td>
</tr>
<tr>
<td>DFT a</td>
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<td>-89</td>
</tr>
<tr>
<td>5-coord</td>
<td>-59</td>
<td>30</td>
</tr>
<tr>
<td>5-coordF</td>
<td>-62</td>
<td>50</td>
</tr>
<tr>
<td>A8</td>
<td>A8 b</td>
<td>A8 b</td>
</tr>
<tr>
<td>Exp</td>
<td>n.r.</td>
<td>n.r.</td>
</tr>
<tr>
<td>DFT a</td>
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<td>-14</td>
</tr>
<tr>
<td>5-coord</td>
<td>-23</td>
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<tr>
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<td>-11</td>
<td>-9</td>
</tr>
<tr>
<td>5-coordF</td>
<td>-13</td>
<td>-10</td>
</tr>
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</table>

The multiline spectrum revealed an isotropic spectrum from Q-band Davies ENDOR measurements (see Supporting Information). The geometry of 3NsN optimized with Turbomole at the b3-lyp, def2-TZVP level without dispersion corrections to match the solution data. Optimized geometry of six-coordinate NsNH₂-amido adduct of 3NsN (full atom model, BP86, def2-TZVP) employing Grimme’s D3-dispersion corrections (disp3). Optimized geometry of six-coordinate OH-hydroxido adduct of 3NsN (full atom model, BP86, def2-TZVP) employing Grimme’s D3-dispersion corrections (disp3).

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 (see Supporting Information for discussion).

Interestingly, the mono-nitrene species 3 did not form instantaneously upon mixing the azides and the Co(PPh₃)₅porphyrin catalysts at r.t. For example, only 10% of the mono-nitrene species 3P2 Troc was formed upon mixing 1P2 and azide 2Troc at r.t. after 15 min. 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 well-resolved 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 1H NMR and GC-MS analysis of the crude reaction mixture). Among the series of complexes and nitrene precursors studied, the maximum intensities were obtained for the combination of 1P2 and 2Troc (see Figure 4). 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 2Troc. The concentration of this species was found to be ~80% referenced against a sample of TEMPO with the same concentration as the cobalt precursor. Similar rough spin counting reveals the presence of ~60% of EPR active 3P1 upon reaction of 1P1 with excess 2Ns after heating overnight at 45 °C.

X-band EPR spectroscopy in solution at r.t. A completely different isotropic spectrum was obtained with 4Ns Troc that was well-resolved as well compared to the use of organic azides that produced mono-nitrene species of the type 3. Reaction of an excess of N-nosyl iminosulfonamide 4Ns with 1P1 at room temperature in benzene-d6 yielded an entirely different species (Scheme 4), as revealed by

Figure 4. EPR spectra of 3P2 Troc (r.t.; benzene-d6) showing increasing intensities over time on heating at 45 °C.

Scheme 4. Reaction of Cobalt(II) Porphyrin 1P1 and Nitrene Transfer Reagent 4Ns To Give Bis-Nitrene Species 5P1 Ns.
DFT calculated EPR parameters (Figure 5 and Table 2). The spectrum could be satisfactorily simulated based on the small, even smaller than in the mono-nitrene case (25 MHz).

**Table 2.** Experimental (298 K) and DFT Calculated EPR Parameters of $^{15}$N$_{iso}$ and $^{15}$N$_{iso}$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Equiv. Nuclei</th>
<th>Exp $^a$</th>
<th>DFT $^b$</th>
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<tbody>
<tr>
<td>$g_{iso}$</td>
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<td>2.008</td>
<td></td>
</tr>
<tr>
<td>$A_{1}^{N}$/MHz</td>
<td>1 (7/2)</td>
<td>-2.0</td>
<td>-2.5</td>
</tr>
<tr>
<td>$A_{2}^{N}$/MHz</td>
<td>2 (1 = 1)</td>
<td>10.0</td>
<td>16.0 $^c$</td>
</tr>
<tr>
<td>$A_{3}^{N}$/MHz</td>
<td>2 (1 = 1)</td>
<td>14.0</td>
<td>22.4</td>
</tr>
<tr>
<td>$A_{4}^{N}$/MHz</td>
<td>4 (1 = 1)</td>
<td>3.5</td>
<td>-1.5 $^d$</td>
</tr>
</tbody>
</table>

$^a$Derived from spectral simulations shown in Figure 5. $^b$Geometry optimized with Turbomole (b3-lyp/def2-TZVP) using a simplified model of $^{15}$N$_{iso}$ 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 hyperfine. $^e$Average of four $A^{N}$-por hyperfine.
observed with ESI-MS measurements (Figure S4-20; Supporting Information). These results clearly show that the bis-nitrene species \( S \) is more reactive than the mono-nitrene species \( 3 \) and that complex \( 1P^1 \) is more stable than complex \( 1P^2 \) when combined with \( N \)-nosyl iminoiodane \( 4N^s \). 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 \( 1P^2 \), as was previously observed in azidination reactions and studied previously using DFT.\(^{8,41}\) At the same time, it also suggests that \( N \)-nosyl iminoiodane \( 4N^s \) is not a very benign nitrene transfer reagent for these reactions as it seems to undergoes subsequent side reactions with the catalyst (especially for the less bulky catalysts 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 \( 1P^1 \) with nosyl azide \( 2N^s \) in \( C_6D_6/MeCN \) produced clear ESI-MS signals around \( m/z 872 \) characteristic for formation of the mono-nitrene species \( 3P^1N^s \) (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 \( [3P^1N^s + H^+] \) (Figure 7a). The relatively low intensity of the detected nitrene radical species derived from reaction of complex \( 1P^1 \) with azide \( 2N^s \) is likely a result of incomplete conversion to \( 3P^1N^s \) as the measurements were performed within 30 min of sample preparation. At the same time, subsequent reactions with the cosolvent acetonitrile cannot be neglected. While \( 3P^1N^s \) is detected as a five-coordinate species in its protonated form with ESI-MS, this does not exclude \( 3P^0N^s \) from being six-coordinate (see Scheme S5-5; Supporting Information), as the sixth ligand might easily dissociate in the ionization chamber of the ESI-MS spectrometer. We were not able to detect \( 3P^0N^s \) 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_2PhSO_2N^−H^+D was detected from a mixture of \( 1P^1 \) and \( 2N^s \). Note that formation of NO_2PhSO_2N^−D^+ radicals, detected with EPR, has been reported earlier.\(^8\) On this basis, the most likely candidates for the sixth ligand coordinated to the mono-nitrene species are either the NO_2PhSO_2N^−D^+ amine ligand or the NO_2PhSO_2N^−H^+D amide 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 HAT).

ESI-MS spectra recorded from a mixture of \( 1P^1 \) and \( N \)-nosyl iminoiodane \( 4N^s \) revealed signals pointing to the presence of bis-nitrene species \( 5P^1N^s \) (Scheme 4). This species was observed as the protonated form of its hydrogen atom abstraction (HAA) reaction product ([\( 5P^1N^s + H^+ + H^+ \)]), thus pointing to rapid HAA from the cosolvent MeCN (Figure 7b). Substantially weaker signals corresponding to the mono-nitrene species \( 3P^1N^s \) were still detected ([\( 3P^1N^s + H^+ \)]), which likely resulted from incomplete conversion of \( 1P^1 \) to \( 3P^0N^s \) and/or fragmentation of \( 3P^1N^s \) to \( 3P^0N^s \) 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 the simplified models \( 3P^0N^s \) and \( 3P^0N^s \) without meso-phenyl substituents on the porphyrin ring (Panel 8). According to these calculations, mono-nitrene species \( 3P^1N^s \) formed from \( 1P^1 \) and \( 2N^s \) is best described as a Co\(^{III}\) species with one 1e reduced nitrene moiety and a normal, non-oxidized (por\(^{−}\)) porphyrin ligand. Note again the experimental complex \( 3P^1N^s \) needs not be five-coordinate. Coordination of an...
additional ligand to the cobalt(III) center cannot be excluded (Scheme S5-5; Supporting Information) and even seems likely (vide infra). However, note that all six-coordinate analogs of $3^\text{P0}_{\text{Ns}}$ considered computationally have almost identical spin density distributions as the one shown for five-coordinate mono-nitrene complex $3^\text{P1}_{\text{Ns}}$ in Figure 8. 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 (see also Table S5-1; Supporting Information).

The bis-nitrene species $5^\text{P0}_{\text{Ns}}$ on the other hand, is a triple-radical containing two 1e-reduced nitrene-moieties and a 1e-oxidized porphyrin ring (from por$^-$ to the por$^+$ radical monoaion). As is clear from the positive and negative spin density distribution (Figure 8, right), two of the three unpaired electrons in $5^\text{P0}_{\text{Ns}}$ are antiferromagnetically coupled, thus effectively leading to a (net) doublet state ($S_{\text{total}} = 1/2$). Both $3^\text{P1}_{\text{Ns}}$ and $5^\text{P0}_{\text{Ns}}$ were found to contain a low-spin $d^6$ ($S_{\text{Co}} = 0$) Co$^{III}$ center. Hence, formation of 5 involves one-electron oxidation of CoII to CoIII 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 $3^\text{P1}_{\text{Ns}}$ and a “porphyrin radical” ligand in $5^\text{P1}_{\text{Ns}}$ (Figures 9 and 10).

Figure 9. UV–vis spectra of a mixture of $1^\text{P1}$ and $2^\text{Ns}$ followed in time (after 40 min of sample preparation). Clear shifts in both the Q- and Soret-bands were observed corresponding to azide ligation to the cobalt(II) center.

Figure 10. UV–vis spectral changes upon reaction of (left) complex $1^\text{P2}$ with azide $2^\text{Troc}$ to give mono-nitrene species $3^\text{P2}_{\text{Troc}}$ formed after heating the solution overnight, and (right) reaction of complex $1^\text{P1}$ with iminoiodane $4^\text{Ns}$ to give bis-nitrene species $5^\text{P1}_{\text{Ns}}$ within 1 h.

Metal- (not porphyrin-) centered oxidation of CoII(por) to CoIII(por) is known to produce characteristic red-shifts of both the Soret- and Q-bands. Metal- (not porphyrin-) centered oxidation of CoII(por) to CoIII(por) is known to produce characteristic red-shifts of both the Soret- and Q-bands.80,81 This is what was observed upon formation of $1^\text{P1}$ and $2^\text{Ns}$ immediately upon mixing. In Figure 9, the UV–vis spectrum of a mixture of $1^\text{P1}$ and $2^\text{Ns}$ was followed in time (after 40 min 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 monoaazide adduct). Indeed, measuring EPR spectra of these same mixtures (again 40 min 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 $3^\text{P1}_{\text{Ns}}$.

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 $3^\text{P1}_{\text{Ns}}$) clearly revealed the presence of a new species in the UV–vis spectra (Figure S6-2, Supporting Information), concomitant with much higher EPR intensities corresponding to nitrene radical species $3^\text{P1}_{\text{Ns}}$. Illustrative spectra comparing $1^\text{P1}$ and species $3^\text{P2}_{\text{Troc}}$ formed upon heating a solution of complex $1^\text{P1}$ in the presence of an excess of $2^\text{Troc}$ are shown in Figure 10 (left).

Reaction of complex $1^\text{P2}$ 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 10, left). 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 $3^\text{P2}_{\text{Troc}}$. The additional band at ~753 nm is likely a charge-transfer band (e.g., a MLCT or LMCT band involving the nitrene radical and the cobalt(III) center).

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/nonoxidized) dianionic porphyrinato ligands (por$^-$). The is what was observed upon formation of bis-nitrene species $5^\text{P1}_{\text{Ns}}$ in the reaction of complex $1^\text{P1}$ with N- nospy iminoiodane $4^\text{Ns}$ (Figure 10, right). As mentioned before, when using iminoiodane $4^\text{Ns}$ formation of the bis-nitrene species is comparatively faster than formation of the mononitrenes when using azide $2^\text{Ns}$. Accordingly, in the case on measuring the UV–vis spectra of a mixture of $1^\text{P1}$ and $4^\text{Ns}$, the disappearance and shape changes of the Q- and Soret-bands was observed within an hour of making these samples (Figure 10, right). As shown in Figure 10, the species exhibited characteristic, strongly red-shifted bands at 863 and 977 nm. Similar spectral changes have been reported for CoIII complexes with a 1e-oxidized octaethylporphyrin ligand.82,83 Hence, we assign these spectral changes to formation of the bis-nitrene species $5^\text{P1}_{\text{Ns}}$. This is also in correspondence with the EPR measurements. Both the EPR and UV–vis signals characteristic for the nitrene radical species $5^\text{P1}_{\text{Ns}}$ were completely lost upon heating the mixture overnight at 45 °C.

In accordance with the EPR spectroscopic studies, once again the mono-nitrene species $3^\text{P2}_{\text{Troc}}$ was found to be more stable than bis-nitrene species $5^\text{P1}_{\text{Ns}}$. UV–vis spectroscopy clearly indicated that solutions of $3^\text{P2}_{\text{Troc}}$ obtained from complex $1^\text{P2}$
starting cobalt(II)-meso-tetraphenylporphyrin (TPP) complex \( \text{1P} \) exhibited an edge in the XAS of the \( \text{3P} \) and \( \text{5P} \) structures at 7715.4 eV corresponding to a 1s to 4p + LMCT shakedown transition, in accord with the observed four-coordinate square-planar structure of this complex. This transition is strongest in four-coordinate square-planar Co complexes, but is also observed in five-coordinate square-pyramidal geometries (it is not present in either \( T_2 \) or \( O_2 \) geometries). Finally, a broad 1s to 3d pre-edge peak was observed at 7708.9 eV, with preliminary peak fitting analysis indicating a peak area of approximately 8.1 units. The energies of the edge and 1s \( \rightarrow \) 3d pre-edge transitions are in accord with the reported values for other cobalt(II) complexes. XANES of \( \text{3P} \) showed a +1.9 eV blue-shift of the edge inflection energy to 7722.56 eV, relative to complex \( \text{1P} \), supporting metal-centered oxidation from cobalt(II) to cobalt(III). The 1s \( \rightarrow \) 3d pre-edge transition was also blueshifted by \( \pm 0.1 \) to 7710.2 eV and the pre-edge increased in intensity (peak-area of 12.0 units). Most notably, \( \text{5P} \) lacks the diagnostic 1s \( \rightarrow \) 4p shakedown transition shoulder on the rising edge, providing strong evidence for a six-coordinate \( O \) cobalt site. Finally, the XANES data on \( \text{3P} \) revealed the existence of edge and 1s \( \rightarrow \) 3d pre-edge transitions at nearly identical positions (7722.8 and 7710.2 eV, respectively) relative to \( \text{5P} \) and \( \text{3P} \), thereby indicating that both mono-nitrene complex \( \text{3P} \) and bis-nitrene complex \( \text{5P} \) are cobalt(III) species.

Importantly, similar to the observations for complex \( \text{3P} \), the absence of the 1s \( \rightarrow \) 4p shakedown transition in the XAS data of \( \text{3P} \) also points to the presence of a six-coordinate \( O \) cobalt(III) center for this complex. XANES data were also obtained for complex \( \text{3P} \) and compared with that for \( \text{3P} \) and \( \text{5P} \). Careful examination of the pre-edge of the XANES of different catalyst and oxidant combinations shows no distinct differences between the different generated intermediates (see Figure S3-1; Supporting Information). This indicates that six-coordinate \( O \) species were formed in all cases. Extended X-ray absorption fine structure (EXAFS) analysis revealed further structural details (Figures 11B–C and S3-2, S3-3 and Tables 3, S3-1, S3-2, and S3-3). For complex \( \text{5P} \), the first coordination sphere could be satisfactorily fitted by considering six N/O scatterers at a distance of 1.92 Å (Table 3). Although the additional outer-shell features could be satisfactorily accounted for by considering single scattering paths involving 8 carbons at 2.94 Å, 12 carbons at 3.35 Å, and 4 oxygen donors at 3.57 Å distance from cobalt, the fit could be significantly improved by introducing multiple-scattering pathways. The best fit for \( \text{5P} \) is represented by fit 12 in Table S3-1 and Figure 11B. It is important to note that efforts were also made to include the effect of the sulfur scatterers originating from the two –NNs units. However, all fits (fits 9–11 in Table S3-1) including any of 5-shell showed negative Debye–Waller factors in the fit parameters; and hence they were not considered in the fitting procedure.

Interestingly, consistent with the XANES data, our attempts to do a set of fits for a back transformation range limited to the first shell \( (r = 0.8 - 2.1 \text{ Å}) \) for \( \text{5P} \) also pointed to a six-

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### Table 3. A Comparison of the EXAFS Determined Metrical Parameters (for the first three shells) of \( \text{3P} \) and \( \text{5P} \) with That of the DFT Calculated Values for \( \text{3P} \) and \( \text{5P} \)

<table>
<thead>
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<td>( \text{3P} )</td>
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<td>( \text{3P} )</td>
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*Details of the EXAFS simulation and DFT structures can be found in the Supporting Information.*
coordinate geometry (fits 1–3; Table S3-2). This contrasts with previous assumptions considering mono-nitrene species $3^P_{1N}$ to be five-coordinate. The best fit to the data of the mono-nitrene species requires six N/O scatterers at $\sim$1.95 Å distance from the cobalt(III) center, which is slightly longer (although almost identical within the error of measurements) than the Co–N distance of 1.92 Å obtained from the EXAFS data of bis-nitrene species $5^P_{1N}$.

With these results in hand, we set out to consider plausible ligands that could occupy the sixth coordination site for the mono-nitrene species $3^P_{1N}$. Initially, we considered coordination of a neutral unreacted nosyl azide ligand under the conditions of the EXAFS measurements. However, DFT geometry optimizations and calculation of the Co K-edge features of the optimized structures with DFT methods revealed that such nosyl azide species have too long Co–N distances to explain the experimental XAS data (Figures S8-2; Supporting Information). The same holds for the aqua adduct of $3^P_{1N}$. The Ns-NH$_2$ amine and ammonia (NH$_3$) adducts of $3^P_{1N}$ have shorter Co–N bond distances, which substantially decreases the calculated intensity of the pre-edge transitions in the Co K-edge region. However, the best agreement between the calculated and experimental pre-edge intensities is obtained for anionic ligand adducts of mono-nitrene $3^P_{1N}$. The optimized geometries of NsNH$_2^-$, NH$_3^-$, and OH$^-$ adducts of $3^P_{1N}$ species have comparable Co–N and Co–X distances for the nitrene radical ligand and the sixth ligand X (Figure 12).

respectively. Hence, similar pre-edge intensities are also computed as obtained for bis-nitrene species $5^P_{1N}$ (Figure S8-3; Supporting Information). Considering the detection of the Na$^+$ adduct of NO$_2$PhSO$_2$NHD as mentioned earlier in the ESI-MS studies in combination with the above-mentioned calculated pre-edge intensities, the NsNH$^-$ amido ligand is perhaps the most probable candidate occupying the sixth coordination site of the mono-nitrene species. Notably, the DFT calculated geometrical parameters for $3^P_{1N}$(NsNH$^-$) is in reasonable agreement with the EXAFS data (Table 3). This would mean, however, that $3^P_{1N}$ is anionic (perhaps containing an NsNH$^+$ counterion). Formation of such a charged species in benzene is unexpected, and as such we cannot exclude the sixth ligand being the neutral NsNH$_2$ amine donor (despite a better agreement between the calculated and experimental XAS pre-edge intensities for the NsNH$_2^-$ amido ligand). At this point, we cannot fully exclude formation of dinuclear complexes with ligand X being for example a bridging amido ligand. However, we consider this possibility less likely in view of the fact that similar XAS data were gathered for $3^P_{1N}$-Troc, which is based on the bulky porphyrin P2. No peak corresponding to a Co scatterer was observed in the EXAFS spectrum, which would be expected for a homodinuclear Co···Co species. It is further worth mentioning that the sixth ligand X (Figure 12) does not prevent conversion of mono-nitrene species $3^P_{1N}$ to bis-nitrene species $5^P_{1N}$ upon treatment with the strongly oxidizing N-nosyl iminoiodane 4$_{Ns}^-$. On adding an excess of 4$_{Ns}$ to a solution of previously formed mono-nitrene species $3^P_{1N}$, clear EPR signals corresponding to bis-nitrene species $5^P_{1N}$ appeared, once again displaying the strongly oxidizing nature of N-nosyl iminoiodane. Apparently, the ligand X can be replaced or converted to a nosyl nitrene radical moiety upon reaction of mono-nitrene $3^P_{1N}$ with iminoiodane 4$_{Ns}$.

### CONCLUSIONS

In conclusion, 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-catalyzed 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 $5^P_{1N}$. This is the first report to demonstrate the formation of a bis-nitrene species of a cobalt porphyrin complex. The stronger oxidizing nature of the nitrene precursor 4$_{Ns}$ is considered important to generate such species. The bis-nitrene species $5^P_{1N}$ has a markedly different electronic structure from the mono-nitrene species $3^P_{1N}$, $3^P_{2Troc}$ and $3^P_{2Troc}$ and also differs markedly from the electronic structure of the previously reported diamagnetic bis-imido Ru$^{IV}$-porphyrin species (por)Ru$^{IV}$($\equiv$N$`$N$`$)$_2(=N$`$R$`$)$). Electronically, the mono- and the bis-nitrene species are markedly different; but XANES data for these species suggest that both are six-coordinate (O$_6$) complexes with similar averaged bond distances between cobalt(III) and the six N/O scatterers ($3^P_{1N}$: $\sim$1.95 Å; $5^P_{1N}$: $\sim$1.92 Å). The exact nature of the ligand X coordinated at the sixth available coordination site of the [Co$^{III}$($\equiv$N$`$N$`$)$_2$(por)]$^{III}$ species ($3^P_{1N}$, $3^P_{2Troc}$, and $3^P_{2Troc}$) remains speculative. For $3^P_{1N}$, the most probable candidates (based on a comparison between the experimental and DFT calculated Co K-edge XAS pre-edge intensities, complementary mass data, and the previously detected NsNHD$^+$ radical) seem to be either the neutral NsNHD amine ligand or the anionic NsNHD$^-$ amido ligand.

The revelation of the presence of a sixth ligand even in the mono-nitrene species implies that the use of additives in such catalytic nitrene transfer reactions should not have a positive effect on the catalytic reactions. This is indeed seen to be the case in the earlier reports from the Zhang group, where additives have only a detrimental effect on catalysis if any (except for ee enhancement in one case but in lower yields).

The two different types of catalytically relevant species detected are represented in Figure 12. Overall, these results signify the importance of the nature of nitrene sources in metal-catalyzed nitrene transfer processes. Depending on the nature of the nitrene precursor, the intermediates can be a result of a single oxidation of the catalyst at the metal center or a double oxidation where the second oxidation step occurs at the
porphyrin ring. In addition, the bis-nitrene species $5^\text{PI}_{N_2}$ though formed faster, lives shorter and is more reactive than the mono-nitrene species $3^\text{PI}_{N_2}$. Degradation of bis-nitrene species $5^\text{PI}_{N_2}$ occurs within hours after initial formation while decomposition of mono-nitrene species $3^\text{PI}_{N_2}$ is much slower (solutions of $3^\text{PI}_{N_2}$ in benzene-$d_6$ were stable for $>24$ h according to EPR and UV−vis). In addition, the studies described here clearly demonstrate the better performance of arms and the nitrene moiety. The steric in... help in preserving them for longer periods by the... implications in catalysis between these... decomposition of mono-nitrene species... intermediates formed, as was shown for the reactions of... $1^\text{PI}$ and $1^\text{PI}$ with N-nosyl iminoiodane $4_{N_2}$. Detailed studies of the differences in reactivity between the mono- and bis-nitrene and implications in catalysis between these 'cobalt(III)-nitrene radical' species are a topic of current investigation and should shed new light on the catalytic mechanisms of nitrone transfer processes catalyzed by cobalt(II) porphyrin complexes.

### ASSOCIATED CONTENT

#### Supporting Information

Experimental details, synthetic procedures, copies of NMR, MS, IR, VCD, EPR spectra, XANES/XAFS data, energies and geometries of stationary points (DFT), and supporting discussions. This material is available free of charge via the Internet at http://pubs.acs.org.

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