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

Monalisa Goswami, Volodymyr Lyaskovskyy, Sérgio R. Domingos, Wybren Jan Buma, Sander Woutersen, Oliver Troepner, Ivana Ivanović-Buramazović, Hongjian Lu, Xin Cui, X. Peter Zhang, Edward J. Reijerse, Serena DeBeer, Matti M. van Schooneveld, Florian Felix Pfaff, Kallol Ray, and Bas de Bruin

1 Van’t Hoff Institute for Molecular Sciences (HIMS), Homogeneous and Supramolecular Catalysis and 2 HIMS, Photonics group, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands
3 Lehrstuhl für Bioanorganische Chemie, Department Chemie und Pharmazie, Universität Erlangen-Nürnberg. Egerlandstraße 1, D-91058 Erlangen, Germany
4 Department of Chemistry, University of South Florida, Tampa, Florida 33620-5250, United States
5 Max Planck Institut für Chemische Energiekonversion, Stiftstraße 34-36, 45470 Mülheim an der Ruhr, Germany
6 Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, 12489 Berlin, Germany

© 2015 American Chemical Society

Published: April 6, 2015

**ABSTRACT:** To fully characterize the CoIII–‘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 1P (P = meso-tetraphenylporphyrin (TPP)) and 1P2 (P = 3,5-Di(Bu)-ChenPhyrin) with organic azides 2Ns (NsNs), 2Ts (TsNs), and 2Troc (TrocN3) led to the formation of mono-nitrene species 3P1Ns, 3P2Ts, and 3P2Troc, respectively, which are best described as [CoIII(porph)(NR″•)] nitrene radicals (imidyl radicals) resulting from single electron transfer from the cobalt(II) porphyrin to the ‘nitrene’ moiety (Ns: R″ = SO2−-C6H4, NO2; Ts: R″ = SO2−-C6H4, NO2; Troc: R″ = C(O)OCH2CCl3). Remarkably, the reaction of 1P1 with N-nosyl iminoiodane (PhII=NNs) 4Ns led to the formation of a bis-nitrene species 5P1Ns. This species is best described as a triple-radical complex ([por•••]CoIII(NR″•)2) 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 3P2Ns 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 O3 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−, NsNH−, and OH−; NsNH− being the most plausible. Conversion of mono-nitrene species 3P1Ns into bis-nitrene species 5P1Ns upon reaction with 4Ns was demonstrated. Solutions containing 3P1Ns and 5P1Ns 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. Therefore, C–H insertion of carbenoid and nitrenoid species has emerged as a very promising protocol in the recent years. 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. 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). Given the ubiquity of nitrogen atoms in biologically active compounds, nitrene transfer reactions also have very important applications in making molecules of interest. However, the applicability of metal-nitrenoids has so far been
limited to alkene aziridination\textsuperscript{9,10} C–H amination\textsuperscript{11,12} and amidation.\textsuperscript{13}

Among several catalysts that have been reported for nitrene transfer reactions, the most successful ones are still based on non-abundant Rh\textsuperscript{4}–\textsuperscript{6,13–17} and Ru\textsuperscript{4,6,7,18–20} metals. Among the first row transition metals, there have been reports of Mn\textsuperscript{21,22}, Cu\textsuperscript{23–26} and Fe\textsuperscript{27} catalyzed systems. Besides being very efficient in carbene transfer reactions,\textsuperscript{28–31} cobalt(II) porphyrin catalysts have also attracted attention in nitrene transfer reactions. Until the early 2000s, it was quite common to use iminoiodanes\textsuperscript{32–36} or haloamine-T\textsuperscript{23,25,26} 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 azides\textsuperscript{37,38} 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 iminoiodanes 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 (1\textsuperscript{P1}–1\textsuperscript{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),\textsuperscript{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 azide\textsuperscript{41} (TcesN\textsubscript{3}, Tces = trichloroethoxysulfonyl = CCl\textsubscript{3}CH\textsubscript{2}O(SO\textsubscript{2})–) was found to be effective. Apart from the nitrene precursors itself, 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 1\textsuperscript{P4}, 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 1\textsuperscript{P4} facilitate nitrenoid formation\textsuperscript{42} and lead to an increased catalyst efficiency and lifetime. Enantioselective aziridination of alkenes was reported a few years ago using chiral cobalt(II)-porphyrin 1\textsuperscript{P3} with TcesN\textsubscript{3} and enantioselectivity of 99\% could be obtained.\textsuperscript{41}

The mechanistic aspects of two such catalytic nitrene transfer reactions with cobalt porphyrins have been elucidated by our groups previously (Scheme 1).\textsuperscript{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 (N\textsubscript{3}C(O)OMe, N\textsubscript{3}SO\textsubscript{2}Ph, N\textsubscript{3}C(O)Ph and N\textsubscript{3}P(O)(OMe)\textsubscript{2}) as nitrene sources was studied using density functional theory (DFT) and electron paramagnetic resonance (EPR) spectroscopy (Scheme 1a).\textsuperscript{43} The mechanism of cobalt(II) porphyrin-mediated aziridination of styrene with PhSO\textsubscript{2}N\textsubscript{3} was also studied (Scheme 1b).\textsuperscript{9}
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 the formation of a close-contact pair (D) of the thus-formed organic radical R• and the cobalt(II)–amido complex (por)CoII(N–HNR)•. 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 CoII(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)CoII(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 have thus far only been detected by means of X-band EPR spectroscopy.9,43 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 “bioinspired” 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 polyydentate redox non-innocent ligands, such as semiquinone-type radical ligands57–59 and their nitrogen analogs,60–62 reduced bipyridine and terpyridine ligands,63–66 α-iminopyridine ligands,67,68 and pyridine-2,6-dimine ligands.69–71 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,62 which play a key role in catalytic carbene transfer reactions.63,64 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 amylid ligand radicals are limited to only a few well-characterized examples,65 and related complexes bearing redox non-innocent nitrene ligands are even scarcer.9,45,65–67 Given the importance of these radicaloid nitrene species in metal-catalyzed nitrene transfer and C==H functionalization reactions,6,10,12,13,39–42,68 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 dianimagnetic bis-imido RuVII−porphyrin species (por)RuII(VI)(==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 1P4 and the bulkier (and chiral) H-bond donor appended porphyrin 1P2 (see Figure 1). Complex 1P3 serves as a model system for all reported cases where CoII porphyrins with H-bonding moieties were proven to give superior catalytic results and where H-bonding stabilizes the formed nitrene intermediates.41,8 In total, four different nitrene sources were employed. As mentioned before, these sources are known in

Scheme 2. Redox Non-Innocent Behaviour of Nitrene Ligands Coordinated to Open-Shell CoII(por) Species (A), a Simplified Bonding Scheme Explaining This Behavior (B), and Alternative Bonding Scheme Involving a Triplet Nitrene (C)
literature to be active in different nitrene transfer reactions like aziridination and amination. Three of these were organic azides $2_{N_{2}}$, $2_{\text{Troc}}$, and $2_{\text{Troc}}$ (see Figure 2): Nosyl azide ($2_{N_{2}}$; $N_{2}N_{2}N_{2}N_{2}N_{2}$; $N_{2}$ = Nosyl = $p$-$N_{2}O_{2}N_{2}N_{2}N_{2}N_{2}$), Tosyl azide ($2_{N_{2}}$; $N_{2}N_{2}N_{2}N_{2}$; $N_{2}$ = Tosyl = $p$-$N_{2}O_{2}N_{2}N_{2}N_{2}$), and Troc azide ($2_{\text{Troc}}$; $N_{2}N_{2}N_{2}N_{2}N_{2}$; $N_{2}$ =2,2,2-trichloroethyloxycarbonyl = $CCl_{3}CH_{2}O$-). The fourth nitrene transfer reagent investigated was the stronger oxidizing N-nosyl iminoiodane (PhI═NNs) $4_{N_{2}}$. 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-absorption spectroscopy (XAS) studies, the following method was employed: To a solution of the catalyst in benzene-

**Scheme 3. Different Combinations of Cobalt(II) Porphyrins and Organic Azides Used to Study the Formation of Mono-Nitrene Species**

![Scheme 3](image)

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) porphyrins 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 $1_{N_{2}}$ and $2_{N_{2}}$ 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 $p$-$SO_{2}Ar$ 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 $3_{N_{2}}$ 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 $3_{N_{2}}$ and its six-coordinate $NsNH^{+}$ and $OH^{-}$ adducts). Note that a variety of other six-coordinate analogs of $3_{N_{2}}$ 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 S5-5, 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 of these species were observed. The resulting solutions still of them heat overnight at 45°C.

However, upon heating the samples, the spin integrations gave only a rough qualitative comparison 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.

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 CoII porphyrin catalysts at r.t. For example, only 10% of the mono-nitrene species of the type 3P2, optimized with Turbomole at the b3-lyp, def2-TZVP level without dispersion corrections to match the solution data. Optimized geometry of six-coordinate NsNH amido adduct of 3P2 (full atom model, BP86, def2-TZVP) employing Grimme’s D3-dispersion corrections (disp3). Optimized geometry of six-coordinate OH hydroxido adduct of 3P1 (full atom model, BP86, def2-TZVP) employing Grimme’s D3-dispersion corrections (disp3).

Table 1. EPR Parameters of Nitrene Radical Complex 3P1
in Frozen Solution at 50 K and in Isotropic Solution at Room Temperature

<table>
<thead>
<tr>
<th></th>
<th>50 K</th>
<th>298 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g∥</td>
<td>g⊥</td>
</tr>
<tr>
<td>Exp</td>
<td>2.0087</td>
<td>2.0049</td>
</tr>
<tr>
<td>DFT *</td>
<td>2.0490</td>
<td>2.0154</td>
</tr>
<tr>
<td>5-coord</td>
<td>2.0087</td>
<td>2.0329</td>
</tr>
<tr>
<td>5-coordF</td>
<td>-18°</td>
<td>-97°</td>
</tr>
<tr>
<td>NsNH</td>
<td>-59</td>
<td>30</td>
</tr>
<tr>
<td>OH</td>
<td>-62</td>
<td>50</td>
</tr>
</tbody>
</table>

Geometry of 3P2, 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).

ªRoom Temperature in Frozen Solution at 50 K and in Isotropic Solution at 45°C.

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

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.8,41 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.

Spectroscopy of the Bis-Nitrene Species 5P1. In contrast to the use of organic azides that produced mono-nitrene species of the type 3 upon reaction with the cobalt(II) porphyrin complexes, reaction of an excess of N-nosyl iminiodiace 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 5) than that with nosyl azide 2Ns or tosyl azide 2Ts (Figure 3, top). The multiline spectrum revealed an isotropic g-value close to g⊥ (2.003) with well-resolved hyperfine interactions with the two equivalent Nnitrene atoms (ANitrene = 10.0 MHz) and the four equivalent Nporphyrin atoms (ANporphyrin = 3.5 MHz), again

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 π− ligand.

scheme 4. Reaction of Cobalt(II) Porphyrin 1P1 and Nitrene Transfer Reagent 4Ns To Give Bis-Nitrene Species 5P1.
further prepared the $^{15}$N-labeled iminoiodane $^{15}$N-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).

5P1 model of

![Image](60x128 to 300x202)

Figure 5. Top: Overlay of the isotropic X-band EPR spectra of unlabeled $^{5}$P$_{1}$N$_{s}$ (red) and labeled ($^{15}$N)$_{2}$$^{5}$P$_{1}$N$_{s}$ (blue). Bottom: Experimental and simulated isotropic EPR spectra of species ($^{15}$N)$_{2}$$^{5}$P$_{1}$N$_{s}$ in benzene-$d_6$. Freq. = 9.38126 GHz, mod. ampl. = 1 G, microwave power = 0.2 mW, $T$ = 298 K.

indicating formation of a “ligand radical” complex. The isotropic cobalt HFI in $^{5}$P$_{1}$N$_{s}$ ($A_{Co}^{iso}$ = 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 5 and Table 2).

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-$4$N$_{s}$ (PhI=$^{13}$NNs) and recorded the r.t. EPR spectrum of ($^{15}$N)$_{2}$$^{5}$P$_{1}$N$_{s}$ generated in a mixture of $^{1}$P$_{1}$ and $^{15}$N-$4$N$_{s}$. This led to clear differences in the hyperfine coupling pattern compared to the non-labeled analogue $^{5}$P$_{1}$N$_{s}$ (Figure 5, top).

EPR simulation using an expected 1.4 times larger $A^{N$-nitrene}$^{15}$N ($I = 1/2$) hyperfine coupling (14 MHz) compared to the unlabeled $^{15}$N $A^{N$-nitrene}$^{15}$N constant of 10 MHz ($I = 1$) in $^{5}$P$_{1}$N$_{s}$ and otherwise identical spectral parameters provided an excellent fit of the experimental spectrum (Figure 5, 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$_{1}$N$_{s}$, the intensity of the signal was not as strong as the mono-nitrene species, for example, $^{3}$P$_{1}$N$_{s}$. 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 iminoiodane substrate in benzene-$d_6$ could well be a reason for the low intensities obtained for species $^{5}$P$_{1}$N$_{s}$. It is also worth mentioning that the experimentally detected signal of species $^{5}$P$_{1}$N$_{s}$ stems from a (net) doublet spin state ($S = 1/2$), leading to the characteristic EPR data shown in Figure 5 and Table 2, but in DFT (b3-lyp) the doublet ($S = 1/2$) and quartet ($S = 3/2$; $\Delta G = +0.2$ kcal mol$^{-1}$) spin states of $^{5}$P$_{1}$N$_{s}$ are predicted to be of nearly equal energy.$^{25}$ 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 $S = 1/2$ state of bis-nitrene species only. Furthermore, a word about the higher reactivity (intrinsic instability) of these bis-nitrene species is worth mentioning. In contrast to the mono-nitrene species $^{3}$P$_{1}$N$_{s}$ which increased in time upon heating the solution to 45 °C, species $^{5}$P$_{1}$N$_{s}$ 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 $4$N$_{s}$, is quite dramatic. For example, on using the bulkier porphyrin complex $^{1}$P$_{2}$ in combination with the oxidizing N-nosyl iminoiodane $4$N$_{s}$ the bis-nitrene species was detected only in minor amounts. Instead, a major EPR signal corresponding to the mono-nitrene species was detected. Thus, it may be concluded that the bulky side groups on the porphyrin backbone of $^{1}$P$_{2}$ make it difficult for the second molecule of N-nosyl iminoiodane $4$N$_{s}$ to react.

In contrast to the decomposition observed for species $^{5}$P$_{1}$N$_{s}$ that was obtained from a mixture of $^{1}$P$_{1}$ and an excess of $4$N$_{s}$ mono-nitrene species $^{3}$P$_{2}$N$_{s}$ obtained from a mixture of $^{1}$P$_{2}$ and excess $4$N$_{s}$ 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 $^{5}$P$_{2}$N$_{s}$. However, a significant amount of mono-nitrene species $^{3}$P$_{2}$N$_{s}$ remained present in solution, even after heating for a period of 18 h (Figure 6). This was also

Table 2. Experimental (298 K)$^a$ and DFT$^b$ Calculated EPR Parameters of $^{5}$P$_{1}$N$_{s}$ and ($^{15}$N)$_{2}$$^{5}$P$_{1}$N$_{s}$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Equiv. Nuclei</th>
<th>Exp$^a$</th>
<th>DFT$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_{av}$</td>
<td></td>
<td>2.003</td>
<td>2.008</td>
</tr>
<tr>
<td>$A_{Co}^{iso}$</td>
<td>$A_{Co}^{iso}$</td>
<td>1 (I = 7/2)</td>
<td>-2.0</td>
</tr>
<tr>
<td>$A_{N-nitrene}^{15}$N$_{s}$</td>
<td>$A_{N-nitrene}^{15}$N$_{s}$</td>
<td>2 (I = 1)</td>
<td>10.0</td>
</tr>
<tr>
<td>$A_{N-nitrene}^{15}$N$_{s}$</td>
<td>$A_{N-nitrene}^{15}$N$_{s}$</td>
<td>2 (I = 1)</td>
<td>14.0</td>
</tr>
<tr>
<td>$A_{N-nitrene}^{15}$N$_{s}$</td>
<td>$A_{N-nitrene}^{15}$N$_{s}$</td>
<td>4 (I = 1)</td>
<td>3.5</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 $^{5}$P$_{1}$N$_{s}$ 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}$N$ hyperfine lines. $^e$Average of four $A^{N$-nitrene}$N$ hyperfine lines.
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 \( 1^{P1} \) is more stable than complex \( 1^{P2} \) when combined with \( N \)-nosyl iminoiodane \( 4_{\text{Ns}} \). 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 \( 1^{P2} \), as was previously observed in aziridination reactions and studied previously using DFT.\(^{8,41}\) At the same time, it also suggests that \( N \)-nosyl iminoiodane \( 4_{\text{Ns}} \) 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, \textit{vide infra}), only signals resulting from protonation, (one-electron) oxidation, and formation of \( \text{Na}^+ \) adducts can be expected in positive mode UHR-ESI-MS.

A reaction mixture of \( 1^{P1} \) with nosyl azide \( 2_{\text{Ns}} \) in \( C_6D_6/\text{MeCN} \) produced clear ESI-MS signals around \( m/z \ 872 \) characteristic for formation of the mono-nitrene species \( 3^{P1}_{\text{Ns}} \) (Scheme 3). The isotope distribution pattern and exact masses determined by ESI-MS match the theoretical values \((\Delta m/z < 0.004 \text{ Da})\) for the species in its protonated form \( [3^{P1}_{\text{Ns}} + \text{H}]^+ \) (Figure 7a). The relatively low intensity of the detected nitrene radical species derived from reaction of complex \( 1^{P1} \) with azide \( 2_{\text{Ns}} \) is likely a result of incomplete conversion to \( 3^{P1}_{\text{Ns}} \), 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 \( 3^{P1}_{\text{Ns}} \) is detected as a five-coordinate species in its protonated form with ESI-MS, this does not exclude \( 3^{P0}_{\text{Ns}} \) 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 \( 3^{P1}_{\text{Ns}} \) in negative mode ESI-MS measurements (cold-spray ionization). However, interestingly, in the positive mode ESI-MS measurements (cold-spray ionization), a \( \text{Na}^+ \) adduct of \( \text{NO}_2\text{PhSO}_2\text{NDH} \) was detected from a mixture of \( 1^{P1} \) and \( 2_{\text{Ns}} \). Note that formation of \( \text{NO}_2\text{PhSO}_2\text{ND}^+ \) 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 \( \text{NO}_2\text{PhSO}_2\text{NDH} \) amine ligand or the \( \text{NO}_2\text{PhSO}_2\text{ND}^- \) amide ligand (in both cases detected as the \( \text{Na}^+ \) 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 \( 1^{P1} \) and \( N \)-nosyl iminoiodane \( 4_{\text{Ns}} \) revealed signals pointing to the presence of bis-nitrene species \( 5^{P1}_{\text{Ns}} \) (Scheme 4). This species was observed as the protonated form of its hydrogen atom abstraction (HAA) reaction product \( ([5^{P1}_{\text{Ns}} + \text{H}^+ + \text{H}^+]) \), thus pointing to rapid HAA from the cosolvent MeCN (Figure 7b). Substantially weaker signals corresponding to the mono-nitrene species \( 3^{P1}_{\text{Ns}} \) were still detected \( ([3^{P1}_{\text{Ns}} + \text{H}^+]) \), which likely resulted from incomplete conversion of \( 1^{P1} \) to \( 3^{P1}_{\text{Ns}} \) and/or fragmentation of \( 3^{P1}_{\text{Ns}} \) to \( 3^{P0}_{\text{Ns}} \) 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 the simplified models \( 3^{P0}_{\text{Ns}} \) and \( 3^{P1}_{\text{Ns}} \) without \( \text{meso}-\text{phenyl} \) substituents on the porphyrin ring \( P^0 \) (Figure 8). According to these calculations, mono-nitrene species \( 3^{P1}_{\text{Ns}} \) formed from \( 1^{P1} \) and \( 2_{\text{Ns}} \) is best described as a CoIII species with one 1e reduced nitrene moiety and a normal, non-oxidized (por\(^{3+}\)) porphyrin ligand. Note again the experimental complex \( 3^{P1}_{\text{Ns}} \) needs not be five-coordinate. Coordination of an

Figure 6. EPR spectra of \( 1^{P1} \) with \( 4_{\text{Ns}} \). Sample obtained by heating the reaction mixture to 45 °C; spectra recorded at r.t. in benzene-\( d_6 \). Note the decrease in the intensity of the signal over time.

Figure 7. Observed (top) and simulated (bottom) ESI-MS spectrum with isotope distribution (a) \([3^{P1}_{\text{Ns}} + \text{H}^+] \) (870–876 au) and (b) \([5^{P1}_{\text{Ns}} + \text{H}^+ + \text{H}^+] \) (1070–1080 au).

Figure 8. Spin density plots (b3-lyp/def2-TZVP) of mono-nitrene species \( 3^{P0}_{\text{Ns}} \) (left) and bis-nitrene species \( 5^{P0}_{\text{Ns}} \) (right).
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 3CoIII_N6 considered computationally have almost identical spin density distributions as the one shown for five-coordinate mono-nitrene complex 3CoIII_N6 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 5CoIII_N6, on the other hand, is a triple-radical containing two 1e-reduced nitrene-moieties and a 1e-oxidized porphyrin ring (from por2− to the por3− radical monooxidation). As is clear from the positive and negative spin density distribution (Figure 8, right), two of the three unpaired electrons in 5CoIII_N6 are antiferromagnetically coupled, thus effectively leading to a (net) doublet state (S_total = 1/2). Both 3P1,Co and 5P0,Co were found to contain a low-spin d6 (S_Co = 0) CoIII 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 3P1,Co and a “porphyrin radical” ligand in 5P1,Co (Figures 9 and 10).

Figure 9. UV−vis spectra of a mixture of 1P1 and 2Ns, 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 1P1 with azide 2Troc to give mono-nitrene species 3P2,Troc formed after heating the solution overnight, and (right) reaction of complex 1P1 with iminoiodane 4Ns to give bis-nitrene species 5P1,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.76,77 The same is also true for binding donor ligands, such as pyridine or bipyridyl ligands, to the central metal ion of cobalt(II) porphyrins.78,79 Such shifts were indeed observed upon measuring UV−vis spectra of a mixture of 1P1 and 2Ns immediately upon mixing. In Figure 9, the UV−vis spectrum of a mixture of 1P1 and 2Ns 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 monoazide 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 3P1,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 3P1,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 3P1,Ns.

Illustrative spectra comparing 1P1 and species 3P2,Troc formed upon heating a solution of complex 1P1 in the presence of an excess of 2Troc are shown in Figure 10 (left).

Reaction of complex 1P1 with azide 2Troc 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 3P2,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 (por2−).80,81 This is what was observed upon formation of bis-nitrene species 5P1,Ns in the reaction of complex 1P1 with N-nosyl iminoiodane 4Ns (Figure 10, right). As mentioned before, when using iminoiodane 4Ns, formation of the bis-nitrene species is comparatively faster than formation of the mononitrenes when using azide 2Ns. Accordingly, in the case on measuring the UV−vis spectra of a mixture of 1P1 and 4Ns, 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 5P1,Ns. This is also in correspondence with the EPR measurements. Both the EPR and UV−vis signals characteristic for the nitrene radical species 5P1,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 3P2,Troc was found to be more stable than bis-nitrene species 5P1,Ns. UV−vis spectroscopy clearly indicated that solutions of 3P2,Troc obtained from complex 1P1
and \(4_{\text{Troc}}\) remained stable for even 2 days, while a significant amount of decomposition already occurred for \(5^\text{Ns}\) obtained from complex \(1P_1\) and \(4_{\text{Troc}}\) within 2 h. This points to a higher intrinsic reactivity of bis-nitrene species \(5^\text{Ns}\) compared to mono-nitrene species \(3^\text{Ns}\). Indeed, DFT calculations (using \(3'\) and \(5'\), which are simplified models of \(3^\text{Ns}\) and \(5^\text{Ns}\) without phenyl substituents on the porphyrin ring and having a N-SO\(_2\)Ph base nitrene instead of N-Ns) predict a ca. 1.3 kcal mol\(^{-1}\) lower activation energy for HAA from ethylbenzene for \(5'\) (\(\Delta G^\text{T} = +30.4\) kcal mol\(^{-1}\)) than for \(3'\) (\(\Delta G^\text{T} = +31.7\) kcal mol\(^{-1}\)).

**X-ray Absorption Spectroscopic (XAS) Studies.** To gain additional evidence for the coordination mode and the oxidation states of the two intermediates, i.e., the mono- and the bis-nitrene species, XAS measurements were performed. X-ray absorption near edge spectroscopic (XANES) studies were carried out at Co K-edge in order to directly probe the metal oxidation states in \(3^\text{Ns} \), \(3^\text{Troc} \), and \(5^\text{Ns} \) (Figure 11A).

![Figure 11. (A) XANES of \(1^\text{P_1}\) (red), \(3^\text{Ns} \) (green), and \(5^\text{Ns} \) (blue). Spectra are referenced to the first inflection point of a cobalt reference foil set to 7709.0 eV. (B) Fourier transform EXAFS spectra of \(5^\text{Ns} \) (dotted line) and the best fit (red line); the inset shows the EXAFS data on a wave vector scale weighted by \(k^3\) with respective representation. (C) Fourier transform EXAFS spectra of \(3^\text{Ns} \) (dotted line) and the best fit (red line); the inset shows the EXAFS data on a wave vector scale weighted by \(k^3\) with respective representation. For further details see Supporting Information.](image)

starting cobalt(II)-meso-tetraphenylporphyrin (TPP) complex \(1^\text{P_1}\) exhibited an edge inflection energy of ca. 7720.7 eV. A shoulder feature along the rising edge at 7715.4 eV corresponds 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 \(O_1\) 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 \(1s\) to 3d pre-edge transitions are in accord with the reported values for other cobalt(II) complexes. \(5^\text{Ns}\) XANES of \(5^\text{Ns} \) showed a +1.9 eV blue-shift of the edge inflection energy to 7722.56 eV, relative to complex \(1^\text{P_1}\), supporting metal-centered oxidation from cobalt(II) to cobalt(III). The \(1s\) to 3d pre-edge transition was also blue-shifted by ~1.0 to 7710.2 eV and the pre-edge increased in intensity (peak-area of 12.0 units). Most notably, \(5^\text{Ns}\) lacks the diagnostic 1s → 4p shakedown transition shoulder on the rising edge, providing strong evidence for a six-coordinate \(O_1\) cobalt site. Finally, the XANES data on \(3^\text{Ns} \) revealed the existence of edge and \(1s\) to 3d pre-edge transitions at nearly identical positions (7722.8 and 7710.2 eV, respectively) relative to \(5^\text{Ns}\), thereby indicating that both mono-nitrene complex \(3^\text{Ns} \) and bis-nitrene complex \(5^\text{Ns} \) are cobalt(III) species.

<table>
<thead>
<tr>
<th>complex</th>
<th>Co–N/C</th>
<th>Co–C/N</th>
<th>Co–C/N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(n)</td>
<td>(r)</td>
<td>(\sigma^2)</td>
</tr>
<tr>
<td>(3^\text{Ns} ) (EXAFS)</td>
<td>6</td>
<td>1.95</td>
<td>3.7</td>
</tr>
<tr>
<td>(3^\text{Ns} ) (Ns-NH(^+)) (DFT)</td>
<td>6</td>
<td>1.94</td>
<td></td>
</tr>
<tr>
<td>(5^\text{Ns} ) (EXAFS)</td>
<td>6</td>
<td>1.92</td>
<td>3.0</td>
</tr>
<tr>
<td>(5^\text{Ns} ) (DFT)</td>
<td>6</td>
<td>1.92</td>
<td></td>
</tr>
</tbody>
</table>

\(^\text{a}\)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 $3^\text{P}_1^\text{Ns}$ 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 $5^\text{P}_1^\text{Ns}$.

With these results in hand, we set out to consider plausible ligands that could occupy the sixth coordination site for the mono-nitrene species $3^\text{P}_1^\text{Ns}$. 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 $3^\text{P}_1^\text{Ns}$. The Ns-NH$_3$ amine and ammonia (NH$_3$) adducts of $3^\text{P}_1^\text{Ns}$ 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 $3^\text{P}_1^\text{Ns}$. The optimized geometries of NsNH$_3^-$, NH$_3^-$, and OH$^-$ adducts of $3^\text{P}_1^\text{Ns}$ 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 $5^\text{P}_1^\text{Ns}$ (Figure S8-2; 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$_3^-$ 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 $3^\text{P}_1^\text{Ns}$(NsNH$_3^-$) is in reasonable agreement with the EXAFS data (Table 3). This would mean, however, that $3^\text{P}_1^\text{Ns}$ is anionic (perhaps containing an NsNH$_3^+$ counterion). Formation of such a charged species in benzene is unexpected, and as such we cannot exclude the sixth ligand being the neutral NsNH$_3$ amine donor (despite a better agreement between the calculated and experimental XAS pre-edge intensities for the NsNH$_3^+$ 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 $3^\text{P}_1^\text{Ns}$ 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 $3^\text{P}_1^\text{Ns}$ to bis-nitrene species $5^\text{P}_1^\text{Ns}$ upon treatment with the strongly oxidizing N-nsyl iminoiodane $4^\text{Ns}$. On adding an excess of $4^\text{Ns}$ to a solution of previously formed mono-nitrene species $3^\text{P}_1^\text{Ns}$ clear EPR signals corresponding to bis-nitrene species $5^\text{P}_1^\text{Ns}$ appeared, once again displaying the strongly oxidizing nature of N-nsyl iminoiodane. Apparently, the ligand X can be replaced or converted to a nosyl nitrene radical moiety upon reaction of mono-nitrene $3^\text{P}_1^\text{Ns}$ with iminoiodane $4^\text{Ns}$.

**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 $5^\text{P}_1^\text{Ns}$. 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 $4^\text{Ns}$ is considered important to generate such species. The bis-nitrene species $5^\text{P}_1^\text{Ns}$ has a markedly different electronic structure from the mono-nitrene species $3^\text{P}_1^\text{Ns}$ ($3^\text{P}_2^\text{Troc}$ and $3^\text{P}_2^\text{Troc}$ and also differs markedly from the electronic structure of the previously reported diamagnetic bis-imido Ru$^{IV}$-porphyrin species (por)Ru$^{IV}$ (═N=N═)$_2$). 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 ($3^\text{P}_1^\text{Ns}$: $\sim 1.95$ Å; $5^\text{P}_1^\text{Ns}$: $\sim 1.92$ Å). The exact nature of the ligand X coordinated at the sixth available coordination site of the [Co$^{III}$[(por)(N$^+$R$^-$)]$_2$] nitrene radical species $3^\text{P}_1^\text{Ns}$ ($3^\text{P}_2^\text{Troc}$ and $3^\text{P}_2^\text{Troc}$ remains speculative. For $3^\text{P}_1^\text{Ns}$, 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$^-$ amido ligand) seem to be either the neutral NsNHD amine ligand or the anionic NsND$^-$ 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$^{39,40}$.

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

---

**Figure 12.** Left: The six-coordinate mono-nitrene species of the type $3^\text{P}_1^\text{Ns}$ obtained from $1^\text{P}_1$ and organic azide $2^\text{Ns}$. Right: The six-coordinate bis-nitrene species $5^\text{P}_1^\text{Ns}$ obtained from $1^\text{P}_1$ and N-nsyl-iminoiodane $4^\text{Ns}$.

---

*Journal of the American Chemical Society*
porphyrin ring. In addition, the bis-nitrene species \( 3P1_Ns \), though formed faster, lives shorter and is more reactive than the mono-nitrene species \( 3P1_N \). Degradation of bis-nitrene species \( 3P1_Ns \) occurs within hours after initial formation while decomposition of mono-nitrene species \( 3P1_N \) is much slower (solutions of \( 3P1_Ns \) 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 specially tailored cobalt(II) porphyrins like complex described here 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 \( 1P2 \) also has an implication on the type of intermediates formed, as was shown for the reactions of \( 1P1 \) and \( 1P2 \) with N-nosyl iminoiodane \( 4Ns \). 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 nitrene 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.

#### AUTHOR INFORMATION

**Corresponding Authors**
*b.debruin@uva.nl*
*XPzhang@usf.edu*

**Author Contributions**

\*These authors contributed equally.

**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

We thank Ed Zuidinga (HIMS, UvA) for additional CSI-MS measurements, Dr. Erik R. Farquhar for help with XAS data collection, and Dr. Moniek Tromp for helpful discussions. The work was financially supported by the European Research Council (grant agreement 202886; BdB), The Netherlands Organization for Scientific Research (NWO-CW VICI grant 016.122.613, BdB), CMST COST Action CM1305 (ECOST-BIO), COST action STSM (COST-STSM-CM1305−21241), the University of Amsterdam (UvA), the National Science Foundation (CHE-1152767; X.P.Z.), the National Institutes of Health (R01-GM098777; X.P.Z.), and the “Solar Technologies Go Hybrid” initiative by the State of Bavaria (L.I.B. and O.T.). K.R. acknowledges financial support from the Cluster of Excellence “Unifying Concepts in Catalysis” (EXC 314/1), Berlin. XAS data were obtained on NSLS beamline X3B (Brookhaven National Laboratory), with support from NIH grant P30-EB-009998 and the U.S. Department of Energy.

### REFERENCES

37. Driver, T. G. *Organometallics* 2010, 8, 3831−3846.


