Revisiting the Electronic Structure of Cobalt-Porphyrin Nitrene and Carbene Radicals with NEVPT2-CASSCF Calculations: Doublet versus Quartet Ground States

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ABSTRACT: Cobalt-porphyrin complexes are established catalysts for carbene and nitrene radical group transfer reactions. The key carbene, mono- and bis-nitrene radical complexes coordinated to [Co(TPP)] (TPP = tetraphenylporphyrin) have previously been investigated with a variety of experimental techniques and supporting (single-reference) DFT calculations that indicated doublet ($S = \frac{1}{2}$) ground states for all three species. In this contribution we revisit their electronic structures with multireference NEVPT2-CASSCF calculations to investigate possible multireference contributions to the ground state wavefunctions. The carbene (**[Co^{III}(TPP)(•CHCO$_2$Et)]**) and mono-nitrene (**[Co^{III}(TPP)(•NNs)]**) radical complexes were confirmed to have uncomplicated doublet ground states, although a higher carbene or nitrene radical character and a lower Co–*C*/*N* bond order was found in the NEVPT2-CASSCF calculations. Supported by EPR analysis and spin counting, paramagnetic molar susceptibility determination and NEVPT2-CASSCF calculations, we report that the cobalt-porphyrin bis-nitrene complex (**[Co^{III}(TPP)•(•NNs)$_2$]**) has a quartet ($S = 3/2$) spin ground state, with a thermally assessable multireference & multideterminant 'broken-symmetry' doublet spin excited state. A spin flip on the porphyrin-centered unpaired electron allows for interconversion between the quartet and broken-symmetry doublet spin states, with an approximate 10- and 200-fold higher Boltzmann population of the quartet at room temperature or 10 K, respectively.

INTRODUCTION

The application and mechanistic understanding of radical-type hypovalent group transfer reactions mediated by earth-abundant transition metal catalysts has seen tremendous advances in recent decades.[1] In this regard, cobalt(II)-porphyrin complexes evolved as excellent catalysts for the transfer of nitrene (•NR) and carbene (•CR'R") moieties to unsaturated bonds, C–H bonds and heteroatoms via radical-type mechanisms.[1,2] Carbene transfer[3] catalyzed by cobalt(II)-porphyrins thereby gives access to the (enantioselective) formation of a plethora of cyclic[4,5,6,7,8,9,10,11,12,13,14] and otherwise alkylated[15,16] products. Similarly, nitrene transfer[17] enables (enantioselective) synthesis of a variety of heterocyclic[18,19,20,21,22,23,24] and acyclic[25,26,27,28] nitrogen containing compounds.

Mechanistic studies in our lab have largely focused on the use of cobalt(II)-tetraphenylporphyrin (**[Co^{II}(TPP)]**) for the formation, and subsequent reactivity of the carbene and nitrene radical intermediates. While the product forming reactions proceed via stepwise radical-type mechanisms, formation of the carbene and nitrene radical intermediates on cobalt is the key step in these catalytic processes.[29,30] Specifically, axial approach of an (*in situ* generated) diazo compound, e.g. ethyl diazoacetate (EDA), onto **[Co^{II}(TPP)]** leads to destabilization of the Co-localized d_{z^2} singly occupied molecular orbital (SOMO), resulting in single-electron transfer from cobalt to the forming π^* bond with the carbene precursor (Scheme 1A and B). This leads to N$_2$ extrusion and single-electron population of the π-symmetric antibonding Co–*C* orbital. The thus formed **[Co^{III}(TPP)(•CHCO$_2$Et)]** complex is therefore best described as a 'carbene radical' coordinated to a cobalt(III) center. This complex was characterized by means of mass spectrometry and electron paramagnetic resonance (EPR) spectroscopy, of which the latter (in combination with density functional theory (DFT) calculations) indicated that the terminal 'carbene radical' complex has an electronic doublet ($S = \frac{1}{2}$) ground state and is in equilibrium with an off-cycle 'bridging' isomer wherein the carbene is bridged over cobalt and a pyrrolic nitrogen of the porphyrin.[29]
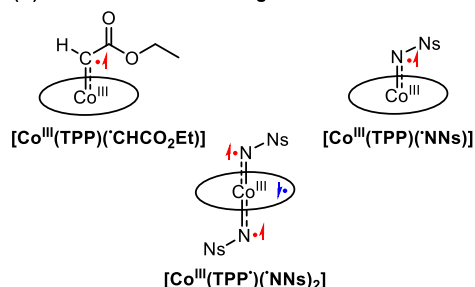
Related 'nitrene radicals' coordinated to a cobalt(III)-porphyrin also react with C=C and C–H bonds via stepwise radical-type mechanisms, and the exact structural and electronic nature of the 'nitrene radicals' was found to depend on the employed nitrene precursor.[31,32] Activation of an organic azide (e.g. nosylazide, NsN$_3$) leads to N$_2$ extrusion and cobalt(II)-to-nitrene single-electron transfer, leading to the formation of a mono-'nitrene radical' coordinated to a cobalt(III)-porphyrin; **[Co^{III}(TPP)(•NNs)]** (Scheme 1A and B). However, usage of the more oxidizing iminoiodinanes (e.g. PhI=NNs) leads to formation of bis-nitrene radical complexes, wherein a second 'nitrene radical' is formed involving porphyrin ligand-to-nitrene substrate single-electron transfer, leaving the oxidized porphyrin ligand in an overall mono-anionic ligand-centered radical state in the resulting **[Co^{III}(TPP)•(•NNs)$_2$]** complex (Scheme 1B). The mono- and bis-nitrene radical species were characterized by EPR, UV-vis, IR, vibrational circular dichroism (VCD) and X-ray absorption spectroscopy (XAS), in combination with high resolution mass spectrometry and DFT calculations.

Scheme 1. (A) Formation of carbene and mono-nitrene radicals on [Co^{II}(TPP)], **(B)** previous characterization of **[Co^{III}(TPP)($^{•}$CHCO$_2$Et)]**, **[Co^{III}(TPP)($^{•}$NNs)]** and **[Co^{III}(TPP$^{•}$)($^{•}$NNs)$_2$]** as having a doublet spin state, and **(C)** the work described in this contribution. Red (α, up) and blue (β, down) arrows indicate the spin of the unpaired electrons.
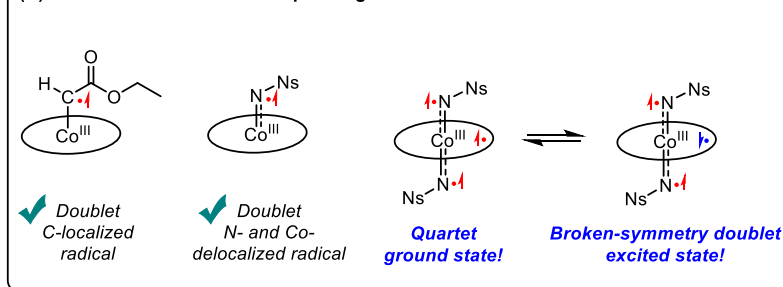
(A) Carbene or mono-nitrene radical formation on [Co^{II}(TPP)]
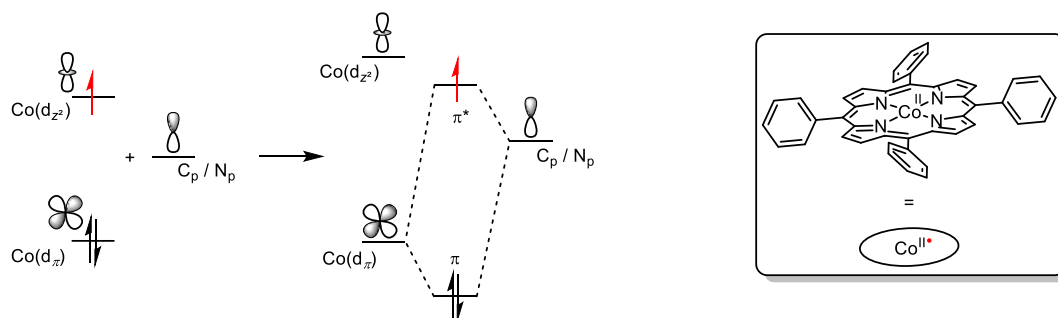
(B) Previous work: doublet ground states

[Co^{III}(TPP)($^{•}$CHCO$_2$Et)]   **[Co^{III}(TPP)($^{•}$NNs)]**

[Co^{III}(TPP$^{•}$)($^{•}$NNs)$_2$]

(C) This work: doublet *versus* quartet ground states

✔ *Doublet C-localized radical*   ✔ *Doublet N- and Co-delocalized radical*   *Quartet ground state!*   *Broken-symmetry doublet excited state!*

Importantly, EPR and DFT studies indicated that both the mono- and bis-nitrene radical complexes have a doublet ($S = ½$) spin state. However, DFT is not suitable for the description of complicated broken-symmetry/multireference wavefunctions,[33] which require post-Hartree-Fock multireference-type calculations such as NEVPT2 (*N*-electron valence state perturbation theory) corrected CASSCF (complete active space self-consistent field).[34,35] We have recently reported the importance of the latter in the correct description of the ground state wavefunction in open-shell cobalt complexes with redox-active ligands.[36] Therefore, given (*i*) our interest in cobalt(II)-porphyrin catalyzed carbene and nitrene radical transfer reactions, and (*ii*) the possible involvement of multireference contributions to the ground state wavefunctions in the key carbene and nitrene radical intermediates, we set out to revisit their electronic structures with NEVPT2-CASSCF calculations.

In this contribution we report that the carbene and mononitrene radical complexes of cobalt-TPP indeed have doublet ground states, which is largely consistent with the DFT calculated electronic structures. The bis-nitrene radical complexes, on the other hand, are now shown to have a quartet ground state with a thermally accessible low-lying multireference ('broken-symmetry') doublet excited state according to NEVPT2-CASSCF calculations, EPR analysis and spin counting experiments (Scheme 1C). As this complex has two accessible spin states that are close in energy, we foresee that the insights obtained in this contribution might lead to the application of bis-nitrene radical cobalt-porphyrins complexes in two-state reactivity.[37]

RESULTS AND DISCUSSION

We initiated calculations on the catalytically active terminal carbene radical **[Co^{II}(TPP)($^{•}$CHCO$_2$Et)]**, resulting from reaction between **[Co^{II}(TPP)]** and EDA.[29] Minima on the doublet ($S = ½$, $S^2 = 0.76$) and quartet ($S = 3/2$, $S^2 = 3.78$) potential energy surface (PES) were located with DFT calculations at the

literature benchmarked BP86/def2-TZVP level of theory,[29] employing an m4 energy grid and Grimme's version 3 ('zero' damping) dispersion corrections on full atomic models (no simplifications). The doublet state was found well below the quartet state ($\Delta G°_{298K} = -28.2$ kcal mol^{-1}), with a spin density distribution of 0.50 on the carbene-C (C) and 0.16 α-spin excess on Co, according to a ROKS (restricted open-shell Kohn Sham) calculation. The spin density distribution is nearly equal to the SOMO, which is the antibonding combination of the C_{p_y} (48.8%) and cobalt-d$_{yz}$ (15.9%) atomic orbitals, leading to an overall Co–C bond order of 1.21. **[Co^{III}(TPP)($^{•}$CHCO$_2$Et)]** therefore has a $(d_{xy})^2(d_{yz}+C_{p_y})^2(d_{xz})^2(C_{p_y}-d_{yz})^{1α}(d_{z^2}-C_\sigma)^0(d_{x^2-y^2})^0$ electronic structure according to DFT.

Next, NEVPT2-corrected CASSCF(11,10) calculations were performed, employing an active space of 11 electrons in 10 orbitals that describe the bonding and antibonding molecular orbitals between cobalt and the porphyrin (*L*) or carbene ligand. The doublet state was again found to be more stable than the quartet state ($\Delta G°_{298K} = -32.3$ kcal mol^{-1}), and is comprised of an 83% main contributor to the total wavefunction. However, 0.76 excess α-spin is located on C (0.98 on the CHCO$_2$ fragment), whereas the spin density on cobalt is negligible (0.02 β-spin). The contribution of cobalt to the SOMO is reduced to 5.5% from the d$_{yz}$ orbital, whereas the C_{p_y} orbital contributes 69.2% to this molecular orbital (MO), with an overall SOMO localization of 90.4% on the CHCO$_2$ carbene radical fragment and 5.7% on Co. A 6% contribution of a multireference state leads to some population of the Co(d$_{z^2}$)–C$_\sigma$ antibonding orbital from the corresponding bonding combination, somewhat weakening this bond (effective bond order: 0.98). Overall, the electronic structure of **[Co^{III}(TPP)($^{•}$CHCO$_2$Et)]** is described by NEVPT2-CASSCF(11,10) as $(d_{xy})^2(d_{xz})^2(d_{yz})^2(C_\sigma+d_{z^2})^2(C_{p_y})^{1α}(d_{z^2}-C_\sigma)^0(d_{x^2-y^2})^0$ (Figure 1A).
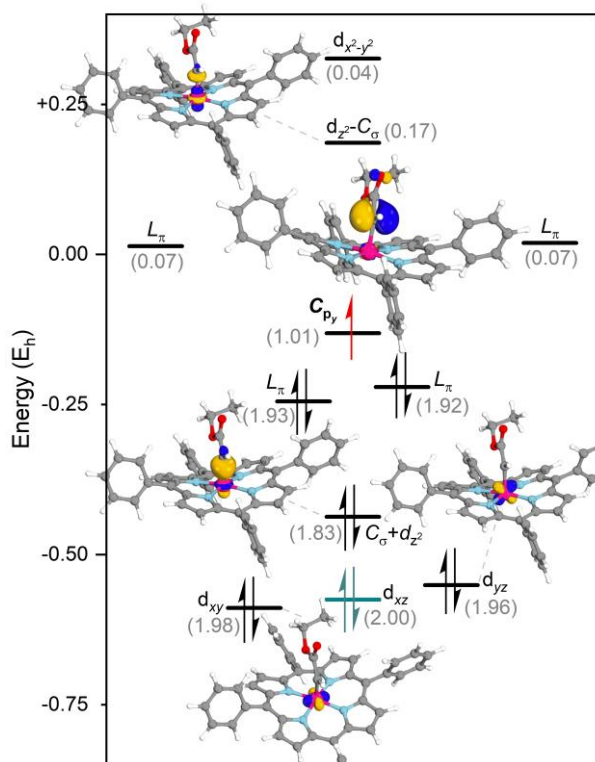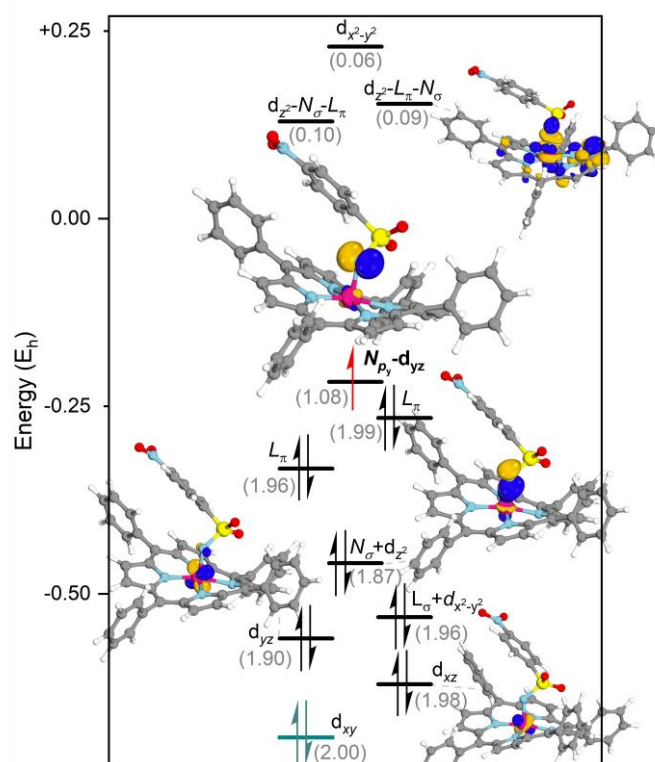
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Figure 1. Active spaces, graphical representation of a selection of active orbitals and occupancies in parenthesis from NEVPT2-CASSCF calculations on **[Co^{III}(TPP)($^{\bullet}$CHCO$_2$Et)]** (A) and **[Co^{III}(TPP)($^{\bullet}$NNs)]** (B) in the doublet state. Isosurface set at 80 (E$_h$ < −0.50) or 70 (E$_h$ > −0.50). The cyan orbital is uncorrelated and was consequently found in the inactive space.[38]

Whereas the unpaired electron is significantly delocalized over the cobalt–carbene bond according to DFT calculations, **[Co^{III}(TPP)($^{\bullet}$CHCO$_2$Et)]** is thus better described as a pure carbene radical wherein the unpaired α-spin electron is almost completely localized on the C_{p_y} orbital according to NEVPT2-CASSCF calculations. Although the SOMO has a small contribution from the d$_{yz}$ orbital, this does not lead to significant spin density on the cobalt(III) center. In addition, the Co–C bond order is even lower than previously assumed, consistent with the high reactivity of this intermediate.

A similar computational approach was used to investigate the electronic structure of the *N*-nosyl nitrene radical coordinated to a cobalt-TPP platform in **[Co^{III}(TPP)($^{\bullet}$NNs)]**. DFT calculations located the doublet ($S^2 = 0.76$) as the ground state and the quartet ($S^2 = 3.78$) was found at $\Delta G^{\circ}_{298K} = +10.9$ kcal mol^{-1}. According to a ROKS calculation the SOMO is comprised of an antibonding combination of the nitrene-N_{p_y} orbital (N_{p_y}, 42.8%) and Co-d$_{yz}$ orbital (33.8%), leading to a spin density distribution of 0.43 and 0.34 excess α-spin on *N* and Co, respectively, and a Co–N bond order of 1.39. The DFT calculated electronic structure of **[Co^{III}(TPP)($^{\bullet}$NNs)]** is therefore best described as $(d_{xy})^2(d_{yz}+N_{p_y})^2(d_{xz}+N_{p_x})^2(N_{p_y}-N_\sigma)^{1\alpha}(d_{z^2}-N_\sigma)^0(d_{x^2-y^2})^0$.

NEVPT2-CASSCF(13,10) calculations are largely consistent with these results, although the doublet–quartet energy difference is increased to $\Delta G^{\circ}_{298K} = −56.6$ kcal mol^{-1}. In the doublet ground state, the electronic wavefunction is dominated by an 86% main contributor and several states all having coefficients below 3%. The spin density distribution is again consistent with the formation of a nitrene radical, as 0.67 and 0.22 excess α-spin is found on *N* and Co, respectively. The SOMO is comprised of antibonding N_{p_y} (74.3%) and cobalt-d$_{yz}$ (8.4%) atomic orbitals, with a total localization of the SOMO on the NSO$_2$ fragment of 82.5% (Co: 11.9%). Again, the NEVPT2-CASSCF calculated bond order (1.20) is significantly smaller than predicted by DFT calculations, and the electronic configuration is overall best described as $(d_{xy})^2(d_{xz})^2(d_{yz})^2(N_\sigma+d_{z^2})^2(N_{p_y}-d_{yz})^{1\alpha}(d_{z^2}-N_\sigma-L_\pi)^0(d_{x^2-y^2})^0$ (Figure 1B).

The situation is more intricate for the bis-nitrene radical complex **[Co^{III}(TPP$^{\bullet}$)($^{\bullet}$NNs)$_2$]**. DFT analysis of the doublet state afforded an S^2 value of 1.67 (expectation value 0.75), revealing major spin contamination. The DFT solution is a broken-symmetry DFT approximation of the multireference & multideterminant doublet state that results from the presence of three unpaired electrons with one *antiferromagnetically* coupled to the other two. This state is captured by DFT as a mixture of the pure doublet and quartet spin states.[33] Being a single determinant and single-reference method, DFT is not suitable to describe this electronic structure properly, and therefore multireference methods such as NEVPT2-CASSCF[34,35] are needed for a correct description of the electronic structure of **[Co^{III}(TPP$^{\bullet}$)($^{\bullet}$NNs)$_2$]**.

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(A) [Co^{II}(TPP$^{•}$)($^{•}$NNs)$_2$]: doublet
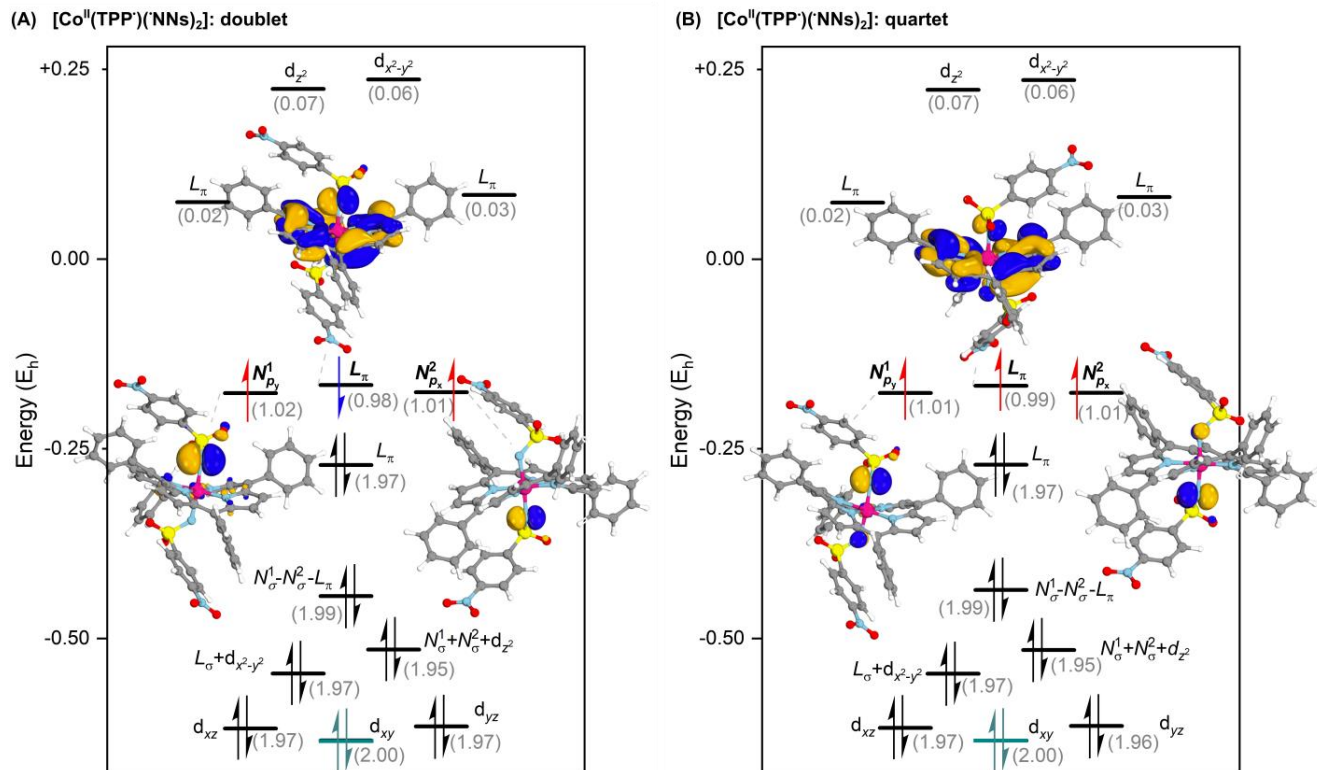
(B) [Co^{II}(TPP$^{•}$)($^{•}$NNs)$_2$]: quartet

Figure 2. Active spaces, graphical representation of the SOMOs and occupancies in parenthesis from NEVPT2-CASSCF(13,10) calculations on **[Co^{III}(TPP$^{•}$)($^{•}$NNs)$_2$]** in the doublet (A) quartet (B) spin state. Isosurface set at 70. The cyan orbital is uncorrelated and was consequently found in the inactive space.[38]

The NEVPT2-CASSCF(13,10) calculations revealed that the quartet state is slightly more stable than the broken-symmetry doublet state ($\Delta G°_{298K} = -1.4$ kcal mol^{-1}). This small energy difference, and the very similar geometrical parameters (see Figure S4 in the Supporting Information) of **[Co^{III}(TPP$^{•}$)($^{•}$NNs)$_2$]** in the doublet and quartet spin states suggest that the complex might have significant Boltzmann population of the broken-symmetry doublet excited state at adequate temperatures. Indeed, EPR spin counting at room temperature revealed that only ~8% of the total complex concentration resides in the doublet state.[31] The expectation value for the Boltzmann population of the doublet state is 8.6% for an energy difference of 1.4 kcal mol^{-1} at 298 K, which is consistent with the EPR spin counting experiment, suggesting that 91.4% of the complex resides in the (at room temperature EPR silent) quartet ground state. Determination of the paramagnetic molar susceptibility by Evans' method[39] afforded 1.51×10^{-3} emu mol^{-1}, which is too high for a pure doublet system (see SI) and therefore also indicates that higher spin states are present.

When the same EPR spin counting experiment was repeated at 10 K (see Figure S1 in the SI), we found that only ~0.3% of the total complex concentration resides in the doublet state. Moreover, the quartet ground state is detected at 10 K as broad resonances in the 0–6000 Gauss region that are clearly observed upon analysis of the first and double integral of the signal (Figure 3). The broad range of spectral features was well reproduced by the DFT calculated zero-field splitting parameters ($D = 0.33$ cm^{-1}, $D/E = 0.28$) and g values (2.005, 2.006, 2.0125) for **[Co^{III}(TPP$^{•}$)($^{•}$NNs)$_2$]** in the quartet state (see Figure S3 in the SI). Moreover, based on the double integrals, ~99.5% of the

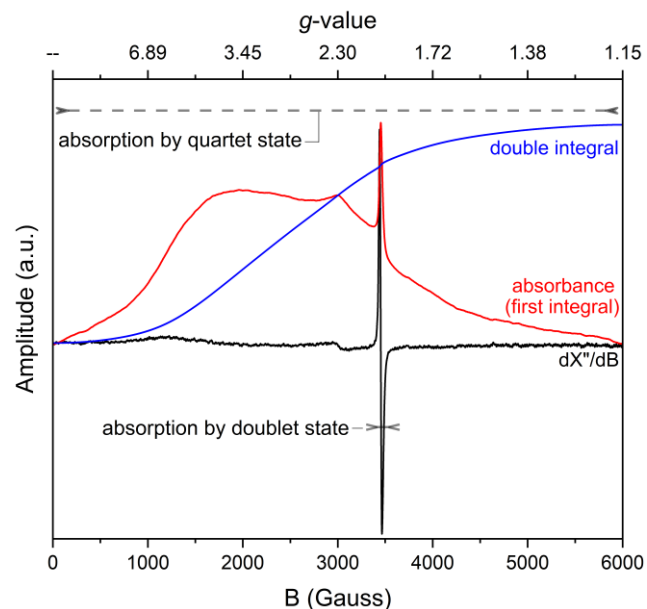total concentration resides in the quartet ground state and only ~0.5% in the doublet excited state (see SI).

Figure 3. X-band EPR spectrum (black), first integral (red) and double integral (blue) of a 2.425 μM solution of **[Co^{III}(TPP$^{•}$)($^{•}$NNs)$_2$]** in C$_6$D$_6$:TBAF at 10 K. The areas of absorbance for the quartet (top) and doublet (bottom) are indicated. Experimental parameters: microwave freq. 9.646369 GHz, power 20.00 mW, modulation amplitude 4.000 G.

Wavefunction analysis of the NEVPT2-CASSCF(13,10) calculations on **[Co^{III}(TPP$^{•}$)($^{•}$NNs)$_2$]** in the doublet and quartet states are consistent with the formation of two nitrene (N^1 and

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N^2) radicals bearing unpaired electrons of α-spin, and an unpaired electron on the porphyrin ligand having α- or β-spin for the quartet or multireference & multideterminant 'broken-symmetry' doublet state, respectively (Figure 2). Although these electronic structures are also approximated by DFT calculations, the multireference & multideterminant wavefunctions obtained from NEVPT2-CASSCF(13,10) calculations are required for the accurate description of the 'broken-symmetry' doublet spin state resulting from the presence of three unpaired electrons.

Specifically, the compositions of the three SOMOs in **[Co^{III}(TPP$^\bullet$)($^\bullet$NNs)$_2$]** in the 'broken-symmetry' doublet state are consistent with the formation of a bis-nitrene radical as the two most stable SOMOs of α-spin are respectively $N^1_{p_y}$ (63.5%) and $N^2_{p_x}$ (78.1%) localized (Figure 2A). The remaining SOMO of β-spin is mainly ligand centered (L_π, 73.8%), therefore consistent with the formation of a porphyrin-centered radical that is *antiferromagnetically* coupled to the two nitrene radicals. In the quartet ground state of **[Co^{III}(TPP$^\bullet$)($^\bullet$NNs)$_2$]**, the two most stable SOMOs are also mainly $N^1_{p_y}$ (62.2%) or $N^2_{p_x}$ (66.2%) localized, and the third α-spin electron is again mainly found on the ligand (L_π, 86.2%), but now *ferromagnetically* coupled to the two nitrene radicals (Figure 2B). The Co–N^1/N^2 bond orders are both 0.88, irrespective of the calculated spin state. Overall, the electronic structure of **[Co^{III}(TPP$^\bullet$)($^\bullet$NNs)$_2$]** is best described as $(d_{xy})^2(d_{xz})^2(d_{yz})^2(N^1_\sigma+N^2_\sigma+d_{z^2})^2(N^1_\sigma-N^2_\sigma-L_\pi)^2(N^1_{p_y})^{1\alpha}(N^2_{p_x})^{1\alpha}(L_\pi)^{1\alpha}(d_{z^2})^0(d_{x^2-y^2})^0$, with two nitrene radicals on a cobalt(III) center bound to a tetraphenylporphyrin-centered radical (oxidized porphyrin). In the less stable doublet state, a small but significant (9.8% contribution) multireference character is observed between the $N^1_{p_y}$ and L_π orbital, causing the latter to accommodate a β-spin instead of an α-spin electron.

CONCLUSIONS

We have revisited the electronic structures of the catalytically active intermediates in **[Co^{II}(TPP)]** catalyzed carbene and nitrene radical transfer; **[Co^{III}(TPP)($^\bullet$CHCO$_2$Et)]**, **[Co^{III}(TPP)($^\bullet$NNs)]** and **[Co^{III}(TPP$^\bullet$)($^\bullet$NNs)$_2$]**. In continuation of previous studies, we have employed full atomic models in this contribution and compared the wavefunctions as obtained from DFT with those of multireference NEVPT2-CASSCF calculations. We conclude that the doublet ground state electronic structures of **[Co^{III}(TPP)($^\bullet$CHCO$_2$Et)]** and **[Co^{III}(TPP)($^\bullet$NNs)]** are adequately described by DFT calculations in comparison to NEVPT2-CASSCF. However, our new insights suggest that **[Co^{III}(TPP)($^\bullet$CHCO$_2$Et)]** is better described as being a pure carbene radical coordinated to cobalt(III), with a low spin density on cobalt and a smaller contribution (5.7%) of cobalt to the SOMO than predicted by DFT. The contribution of cobalt to the unpaired electron density (0.22) and SOMO (11.9%) is somewhat larger in **[Co^{III}(TPP)($^\bullet$NNs)]**, overall resulting in a higher bond order for the mono-nitrene radical (1.20) in comparison to the carbene radical (0.98) coordinated to **[Co^{III}(TPP)]**.

EPR analysis and spin counting, paramagnetic molar susceptibility determination and NEVPT2-CASSCF calculations are all in agreement, and point to a spin quartet ($S = 3/2$) ground state of **[Co^{III}(TPP$^\bullet$)($^\bullet$NNs)$_2$]**, with the multireference & multideterminant 'broken-symmetry' doublet state being thermally accessible. The electronic structure of the bis-nitrene radicals coordinated to cobalt(III) and a tetraphenylporphyrin-centered radical allows for interconversion between the quartet and 'broken-symmetry' doublet states via a ligand-centered spin flip.

Concludingly, we would like to emphasize the importance of considering the quartet ground state and accessible doublet excited state in future (mechanistic) studies of bis-nitrene radical species on **[Co^{III}(TPP$^\bullet$)]**. This might lead to additional mechanistic insight, and possibly the application of thermal- or photo-excitation of the quartet to doublet state, potentially uncovering two-state reactivity in reactions involving these bis-nitrene species.

ASSOCIATED CONTENT

Supporting Information. Experimental details, EPR and paramagnetic molar susceptibility studies, geometries (xyz coordinates) and energies of stationary points (DFT) and description of the NEVPT2-CASSCF calculations.

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Notes

The authors declare no competing financial interest.

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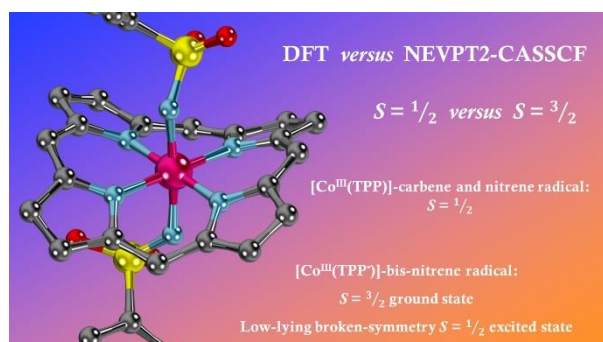
The ground state wavefunctions of cobalt-porphyrin carbene (**[Co^{III}(TPP)($^{•}$CHCO$_2$Et)]**), mono-nitrene (**[Co^{III}(TPP)($^{•}$NNs)]**) and bis-nitrene (**[Co^{III}(TPP$^{•}$)($^{•}$NNs)$_2$]**) radical complexes were revisited with NEVPT2-CASSCF calculations. The carbene and mono-nitrene radical complexes have doublet ground states, consistent with earlier DFT studies. However, **[Co^{III}(TPP$^{•}$)($^{•}$NNs)$_2$]** was found to have a quartet ground state with a thermally accessible multireference & multideterminant 'broken-symmetry' doublet excited state, according to EPR experiments and NEVPT2-CASSCF calculations.