

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

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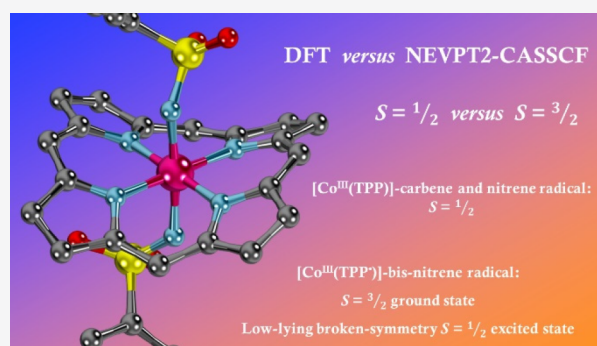
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**ABSTRACT:** Cobalt porphyrin complexes are established catalysts for carbene and nitrene radical group-transfer reactions. The key carbene and mono- and bisnitrene radical complexes coordinated to [Co(TPP)] (TPP = tetraphenylporphyrin) have previously been investigated with a variety of experimental techniques and supporting (single-reference) density functional theory (DFT) calculations that indicated doublet ( $S = 1/2$ ) ground states for all three species. In this contribution, we revisit their electronic structures with multireference N-electron valence state perturbation theory (NEVPT2)-complete-active-space self-consistent-field (CASSCF) calculations to investigate possible multireference contributions to the ground-state wave functions. The carbene ([Co<sup>III</sup>(TPP)(•CHCO<sub>2</sub>Et)] and mononitrene ([Co<sup>III</sup>(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 electron paramagnetic resonance analysis and spin counting, paramagnetic molar susceptibility determination, and NEVPT2-CASSCF calculations, we report that the cobalt porphyrin bisnitrene complex ([Co<sup>III</sup>(TPP)(•NNs)<sub>2</sub>] has a quartet ( $S = 3/2$ ) spin ground state, with a thermally accessible multireference and 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-fold higher Boltzmann population of the quartet at room temperature.



## 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.<sup>1</sup> 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.<sup>1,2</sup> Carbene transfer<sup>3</sup> catalyzed by cobalt(II) porphyrins thereby gives access to the (enantioselective) formation of a plethora of cyclic<sup>4–14</sup> and otherwise alkylated<sup>15,16</sup> products. Similarly, nitrene transfer<sup>17</sup> enables the (enantioselective) synthesis of a variety of heterocyclic<sup>18–24</sup> and acyclic<sup>25–28</sup> nitrogen-containing compounds.

Mechanistic studies in our laboratory have largely focused on the use of cobalt(II) tetraphenylporphyrin ([Co<sup>II</sup>(TPP)]), where TPP = tetraphenylporphyrin) 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.<sup>29,30</sup> Specifically, the axial approach of

an (in situ generated) diazo compound, e.g., ethyl diazoacetate (EDA), onto [Co<sup>II</sup>(TPP)] leads to destabilization of the cobalt-localized  $d_{z^2}$  singly occupied molecular orbital (SOMO), resulting in single-electron transfer from cobalt to the  $\pi^*$  bond forming with the carbene precursor (Scheme 1A,B). This leads to N<sub>2</sub> extrusion and single-electron population of the  $\pi$ -symmetric antibonding Co–C orbital. The thus-formed [Co<sup>III</sup>(TPP)(•CHCO<sub>2</sub>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 ( $S = 1/2$ ) ground state and is in equilibrium with an off-cycle

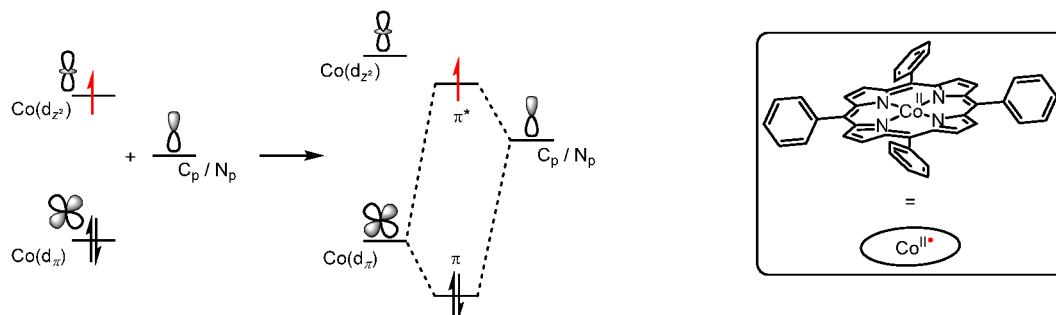
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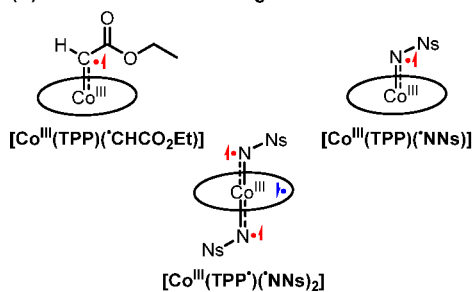


**Scheme 1. (A) Formation of Carbene and Mononitrene Radicals on  $[\text{Co}^{\text{II}}(\text{TPP})]$ , (B) Previous Characterization of  $[\text{Co}^{\text{III}}(\text{TPP})(\cdot\text{CHCO}_2\text{Et})]$ ,  $[\text{Co}^{\text{III}}(\text{TPP})(\cdot\text{NNs})]$  and  $[\text{Co}^{\text{III}}(\text{TPP}^*)(\cdot\text{NNs})_2]$  as Having a Doublet Spin State, and (C) the Work Described in This Contribution<sup>4</sup>**

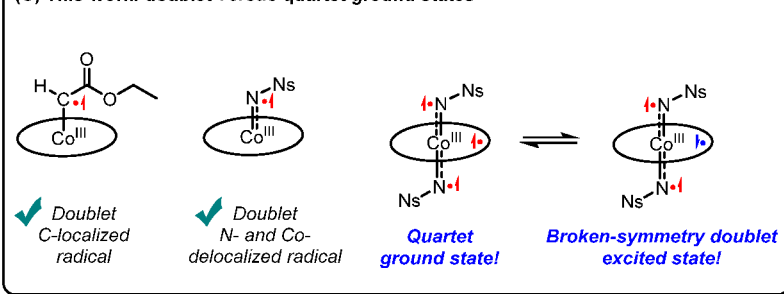
(A) Carbene or mono-nitrene radical formation on  $[\text{Co}^{\text{II}}(\text{TPP})]$



(B) Previous work: doublet ground states



(C) This work: doublet versus quartet ground states



<sup>4</sup>Red ( $\alpha$ , up) and blue ( $\beta$ , down) arrows indicate the spin of the unpaired electrons.

“bridging” isomer wherein the carbene is bridged over cobalt and a pyrrolic nitrogen of the porphyrin.<sup>29</sup>

Related “nitrene radicals” coordinated to 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 nitrene precursor employed.<sup>31,32</sup> Activation of an organic azide (e.g., nosylazide,  $\text{NsN}_3$ ) leads to  $\text{N}_2$  extrusion and cobalt(II)-to-nitrene single-electron transfer, resulting in formation of a mono“nitrene radical” coordinated to the cobalt(III) porphyrin  $[\text{Co}^{\text{III}}(\text{TPP})(\cdot\text{NNs})]$  (Scheme 1A,B). However, use of the more oxidizing iminoiodinanes (e.g.,  $\text{PhI}=\text{NNs}$ ) leads to the formation of bisnitrene 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 monoanionic ligand-centered radical state in the resulting  $[\text{Co}^{\text{III}}(\text{TPP}^*)(\cdot\text{NNs})_2]$  complex (Scheme 1B). The mono- and bisnitrene radical species were characterized by EPR, UV–vis, IR, vibrational circular dichroism, and X-ray absorption spectroscopy, in combination with high-resolution mass spectrometry and DFT calculations.

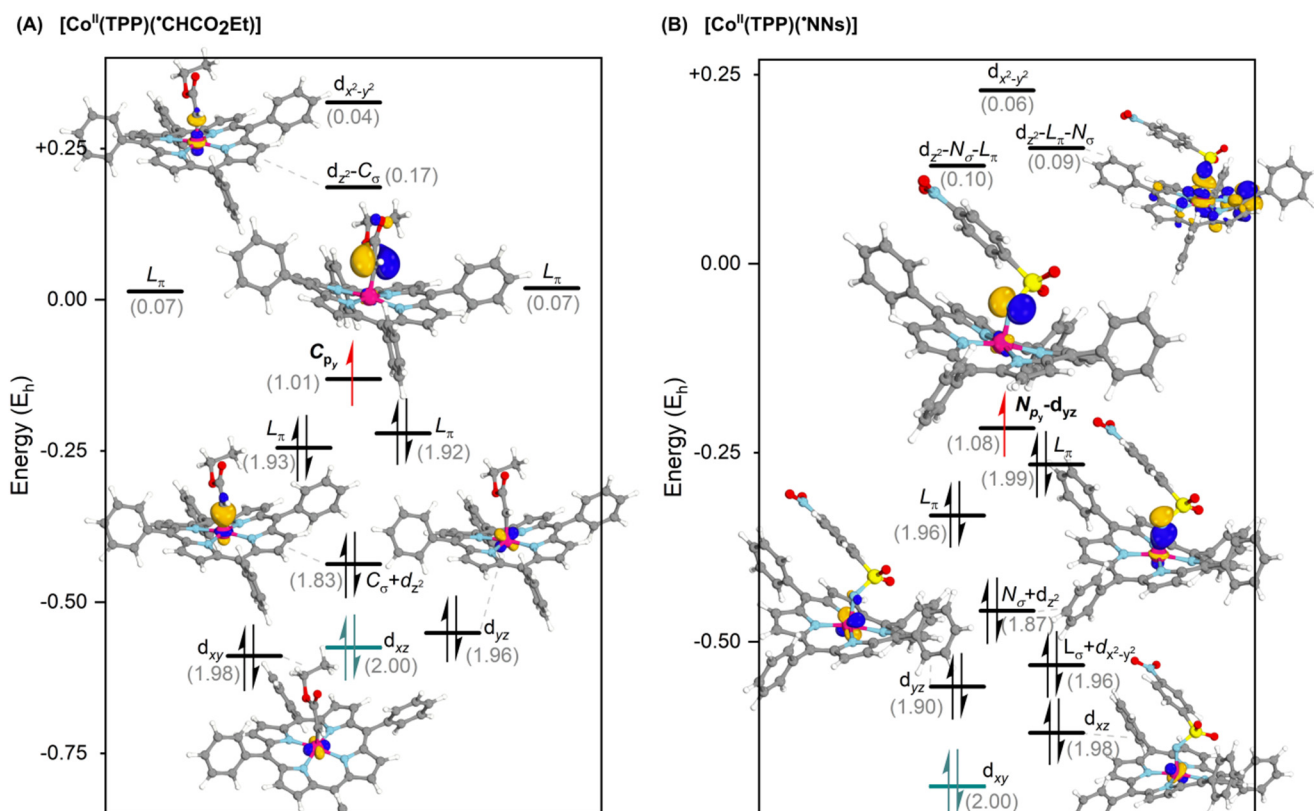
Importantly, EPR and DFT studies indicated that both the mono- and bisnitrene radical complexes have a doublet ( $S = 1/2$ ) spin state. However, DFT is not suitable for the description of complicated broken-symmetry/multireference wave functions,<sup>33</sup> which require post-Hartree–Fock multi-reference-type calculations such as N-electron valence state perturbation theory (NEVPT2)-corrected complete-active-space self-consistent field (CASSCF).<sup>34,35</sup> We have recently reported the importance of the latter in the correct description of the ground-state wave function in open-shell cobalt complexes with redox-active ligands.<sup>36</sup> 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 wave functions 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  $\text{Co}(\text{TPP})$  indeed have doublet ground states, which is largely consistent with the DFT-calculated electronic structures. The bisnitrene radical complexes, on the other hand, are now shown to have a quartet ground state with a thermally accessible low-lying multi-reference (“broken-symmetry”) doublet excited state according to NEVPT2-CASSCF calculations, EPR analysis, and spin-counting experiments (Scheme 1C). Because 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 bisnitrene radical cobalt porphyrin complexes in two-state reactivity.<sup>37</sup>

## RESULTS AND DISCUSSION

We initiated calculations on the catalytically active terminal carbene radical  $[\text{Co}^{\text{III}}(\text{TPP})(\cdot\text{CHCO}_2\text{Et})]$ , resulting from the reaction between  $[\text{Co}^{\text{II}}(\text{TPP})]$  and EDA.<sup>29</sup> Minima on the doublet ( $S = 1/2$ ;  $S^2 = 0.76$ ) and quartet ( $S = 3/2$ ;  $S^2 = 3.78$ ) potential energy surfaces were located with DFT calculations at the literature-benchmarked BP86/def2-TZVP level of theory,<sup>29</sup> 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 ( $\Delta G_{298\text{ K}}^\circ = -28.2 \text{ kcal mol}^{-1}$ ), with a spin density distribution of 0.50 on the carbene carbon (C) and 0.16  $\alpha$ -spin excess on cobalt, according to a restricted open-



**Figure 1.** Active spaces, graphical representation of a selection of active orbitals, and occupancies in parentheses from NEVPT2-CASSCF calculations on  $[\text{Co}^{\text{III}}(\text{TPP})(^*\text{CHCO}_2\text{Et})]$  (A) and  $[\text{Co}^{\text{III}}(\text{TPP})(^*\text{NNs})]$  (B) in the doublet state. The isosurface was 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.<sup>38</sup>

shell Kohn–Sham (ROKS) calculation. The spin density distribution is nearly equal to the SOMO, which is the antibonding combination of the  $C_{p_y}$  (48.8%) and Co  $d_{yz}$  (15.9%) atomic orbitals, leading to an overall Co–C bond order of 1.21.  $[\text{Co}^{\text{III}}(\text{TPP})(^*\text{CHCO}_2\text{Et})]$  therefore has a  $(d_{xy})^2(d_{yz}+C_{p_y})^2(d_{xz})^2(C_{p_y}-d_{yz})^{1\alpha}(d_z^2-C_\sigma)^0(d_{x^2-y^2})^0$  electronic structure according to DFT.

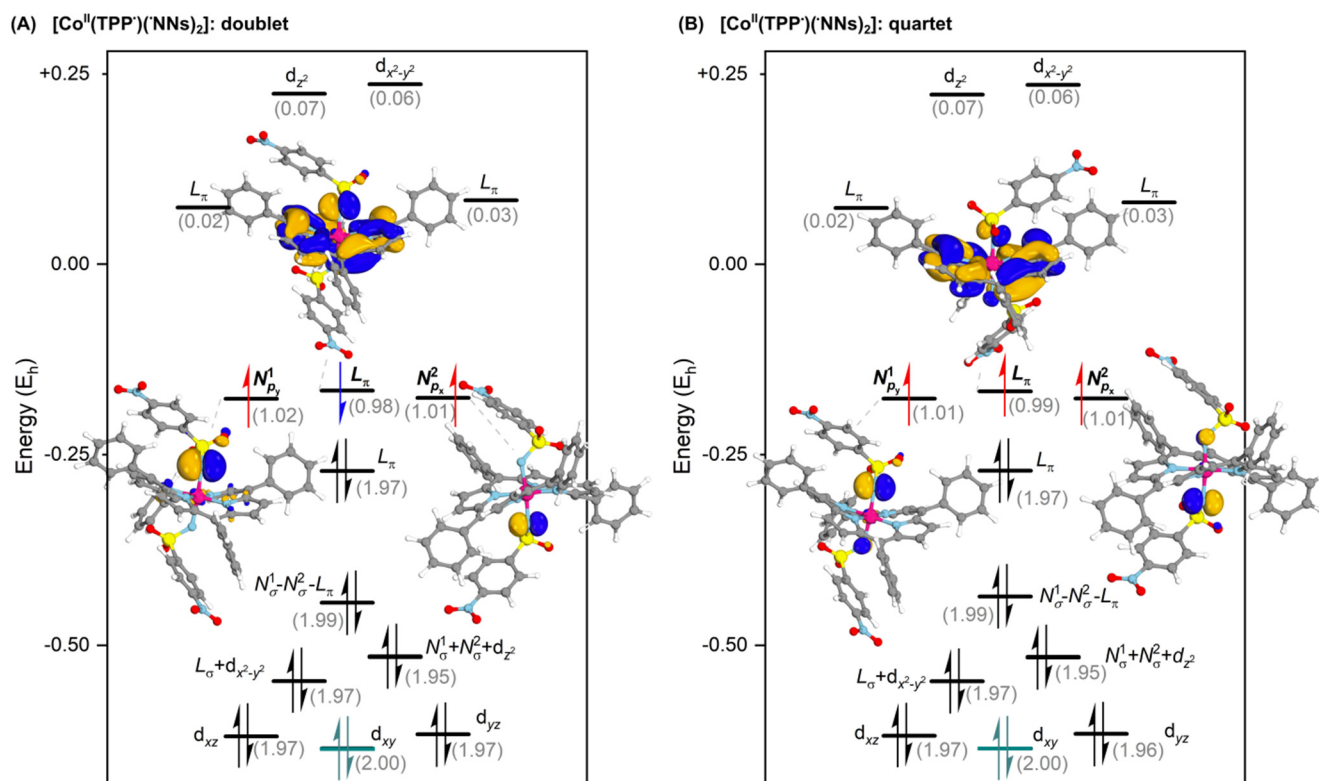
Next, NEVPT2-CASSCF(11,10) calculations were performed, employing an active space of 11 electrons in 10 orbitals that describe the bonding and antibonding molecular orbitals between cobalt and the porphyrin (L) or carbene ligand. The doublet state was again found to be more stable than the quartet state ( $\Delta G_{298\text{K}}^\circ = -32.3$  kcal mol<sup>-1</sup>) and is comprised of an 83% main contributor to the total wave function. However, 0.76 excess  $\alpha$ -spin is located on C (0.98 on the  $\text{CHCO}_2$  fragment), whereas the spin density on cobalt is negligible (0.02  $\beta$ -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  $\text{CHCO}_2$  carbene radical fragment and 5.7% on cobalt. 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  $[\text{Co}^{\text{III}}(\text{TPP})(^*\text{CHCO}_2\text{Et})]$  is described by NEVPT2-CASSCF(11,10) as  $(d_{xy})^2(d_{xz})^2(d_{yz})^2(C_\sigma+d_z^2)^2(C_{p_y})^{1\alpha}(d_z^2-C_\sigma)^0(d_{x^2-y^2})^0$  (Figure 1A).

Whereas the unpaired electron is significantly delocalized over the Co–C bond according to DFT calculations,

$[\text{Co}^{\text{III}}(\text{TPP})(^*\text{CHCO}_2\text{Et})]$  is thus better described as a pure carbene radical wherein the unpaired  $\alpha$ -spin electron is almost completely localized on the  $C_{p_y}$  orbital according to NEVPT2-CASSCF calculations. This is to be expected in post-Hartree–Fock calculations, which generally afford less delocalization (i.e., bond covalency) in comparison to computations at the DFT level.<sup>39</sup> Moreover, the SOMO has a small contribution from the  $d_{yz}$  orbital, but 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 Co(TPP) platform in  $[\text{Co}^{\text{III}}(\text{TPP})(^*\text{NNs})]$ . DFT calculations located the doublet ( $S^2 = 0.76$ ) as the ground state, and the quartet ( $S^2 = 3.78$ ) was found at  $\Delta G_{298\text{K}}^\circ = +10.9$  kcal mol<sup>-1</sup>. According to a ROKS calculation, the SOMO is comprised of an antibonding combination of the nitrene ( $N_{p_y}$ , 42.8%) and Co  $d_{yz}$  (33.8%) orbitals, leading to a spin density distribution of 0.43 and 0.34 excess  $\alpha$ -spin on N and Co, respectively, and a Co–N bond order of 1.39. The DFT-calculated electronic structure of  $[\text{Co}^{\text{III}}(\text{TPP})(^*\text{NNs})]$  is therefore best described as  $(d_{xy})^2(d_{yz}+N_{p_y})^2(d_{xz}+N_{p_x})^2(N_{p_y}-d_{yz})^{1\alpha}(d_z^2-N_\sigma)^0(d_{x^2-y^2})^0$ .

NEVPT2-CASSCF(13,10) calculations are largely consistent with these results, although the doublet–quartet energy difference is increased to  $\Delta G_{298\text{K}}^\circ = -56.6$  kcal mol<sup>-1</sup>. In the doublet ground state, the electronic wave function is dominated by an 86% main contributor and several microstates, all having coefficients below 3%. The spin density



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

distribution is again consistent with the formation of a nitrene radical because 0.67 and 0.22 excess  $\alpha$ -spin is found on N and Co, respectively. The SOMO is comprised of antibonding  $N_{\text{py}}$  (74.3%) and Co  $d_{\text{yz}}$  (8.4%) atomic orbitals, with a total localization of the SOMO on the  $\text{NSO}_2$  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  $(d_{\text{xy}})^2(d_{\text{xz}})^2(d_{\text{yz}})^2(N_{\sigma}+d_z)^2(N_{\text{py}}-d_{\text{yz}})^{1\alpha}(d_z-N_{\sigma}-L_{\pi})^0(d_{x^2-y^2})^0$  (Figure 1B).

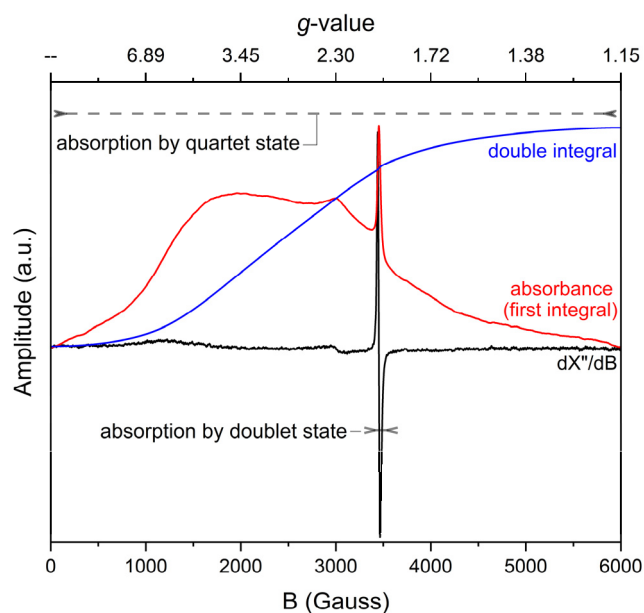
The situation is more intricate for the bisnitrene radical complex  $[\text{Co}^{\text{III}}(\text{TPP}^*)(\text{NNs})_2]$  (Figure 2). DFT analysis of the doublet state afforded an  $S^2$  value of 1.67 (expectation value 0.75), revealing major spin contamination. The DFT solution is a broken-symmetry DFT approximation of the multireference and 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.<sup>33</sup> Being a single-determinant and single-reference method, DFT is not suitable for describing this electronic structure properly, and therefore multireference methods such as NEVPT2-CASSCF<sup>34,35</sup> are needed for a correct description of the electronic structure of  $[\text{Co}^{\text{III}}(\text{TPP}^*)(\text{NNs})_2]$ .

The NEVPT2-CASSCF(13,10) calculations revealed that the quartet state is slightly more stable than the broken-symmetry doublet state ( $\Delta G_{298\text{ K}}^{\circ} = -1.4 \text{ kcal mol}^{-1}$ ). This small energy difference and the very similar geometrical parameters (Figure S4) of  $[\text{Co}^{\text{III}}(\text{TPP}^*)(\text{NNs})_2]$  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 and spin counting at room temperature revealed that only  $\sim 8 \pm 2.5\%$  of the total complex concentration resides in the doublet state.<sup>31,40</sup> The expectation value for the Boltzmann population of the doublet state is 8.6% for an energy difference of 1.4  $\text{kcal mol}^{-1}$  at 298 K, which is consistent with the EPR spin-counting experiment, suggesting that  $\sim 90\%$  of the complex resides in the (at room temperature EPR-silent) quartet ground state. Determination of the paramagnetic molar susceptibility by Evans' method<sup>41</sup> afforded  $1.51 \times 10^{-3} \text{ emu mol}^{-1}$ , which is too high for a pure doublet system (see the Supporting Information, SI) and therefore also indicates that higher spin states are present.

When the same EPR spin-counting experiment was repeated at 10 K (Figure S1), we found that  $<3\%$  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 G 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 ( $D = 0.33 \text{ cm}^{-1}$ ;  $E/D = 0.28$ ) and  $g$  values (2.005, 2.006, 2.0125) for  $[\text{Co}^{\text{III}}(\text{TPP}^*)(\text{NNs})_2]$  in the quartet state (Figure S3). Moreover, on the basis of the double integrals,  $>97\%$  of the total concentration resides in the quartet ground state and  $<3\%$  in the doublet excited state (see the SI).

Wave-function analyses of the NEVPT2-CASSCF(13,10) calculations on  $[\text{Co}^{\text{III}}(\text{TPP}^*)(\text{NNs})_2]$  in the doublet and quartet states are consistent with the presence of two nitrene ( $N^1$  and  $N^2$ ) radicals bearing unpaired electrons of  $\alpha$ -spin and an unpaired electron on the porphyrin ligand having  $\alpha$ - or  $\beta$ -spin for the quartet or multireference and multideterminant



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

“broken-symmetry” doublet state, respectively (Figure 2). Although these electronic structures are also approximated by DFT calculations, the multireference and multideterminant wave functions obtained from NEVPT2-CASSCF(13,10) calculations are required for an 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  $[\text{Co}^{\text{III}}(\text{TPP}^*)(\bullet\text{NNs})_2]$  in the “broken-symmetry” doublet state are consistent with the formation of a bisnitrene radical because the two most stable SOMOs of  $\alpha$ -spin are respectively  $N_{\text{p}_y}^1$  (63.5%) and  $N_{\text{p}_x}^2$  (78.1%) localized (Figure 2A). The remaining SOMO of  $\beta$ -spin is mainly ligand-centered ( $L_{\text{m}}$  73.8%) and 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  $[\text{Co}^{\text{III}}(\text{TPP}^*)(\bullet\text{NNs})_2]$ , the two most stable SOMOs are also mainly  $N_{\text{p}_y}^1$  (62.2%) or  $N_{\text{p}_x}^2$  (66.2%) localized, and the third  $\alpha$ -spin electron is again mainly found on the ligand ( $L_{\text{m}}$  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  $[\text{Co}^{\text{III}}(\text{TPP}^*)(\bullet\text{NNs})_2]$  is best described as  $(d_{xy})^2(d_{xz})^2(d_{yz})^2(N_{\sigma}^1 + N_{\sigma}^2 + d_z)^2(N_{\sigma}^1 - N_{\sigma}^2 - L_{\pi})^2(N_{\text{p}_y}^1)^{1\alpha}(N_{\text{p}_x}^2)^{1\alpha}(L_{\pi})^{1\alpha}(d_z)^0(d_{x^2-y^2})^0$ , 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  $N_{\text{p}_y}^1$  and  $L_{\pi}$  orbitals, causing the latter to accommodate a  $\beta$ -spin electron instead of an  $\alpha$ -spin electron.

## CONCLUSIONS

We have revisited the electronic structures of the catalytically active intermediates in  $[\text{Co}^{\text{III}}(\text{TPP})]$ -catalyzed carbene and nitrene radical transfer reactions:  $[\text{Co}^{\text{III}}(\text{TPP})(\bullet\text{CHCO}_2\text{Et})]$ ,  $[\text{Co}^{\text{III}}(\text{TPP})(\bullet\text{NNs})]$ , and  $[\text{Co}^{\text{III}}(\text{TPP}^*)(\bullet\text{NNs})_2]$ . In a continuation of previous studies, we have employed full atomic models in this contribution and compared the wave functions obtained from DFT with those of multireference NEVPT2-CASSCF calculations. We conclude that the doublet ground-state electronic structures of  $[\text{Co}^{\text{III}}(\text{TPP})(\bullet\text{CHCO}_2\text{Et})]$  and  $[\text{Co}^{\text{III}}(\text{TPP})(\bullet\text{NNs})]$  are adequately described by DFT calculations in comparison to NEVPT2-CASSCF. However, our new insights suggest that  $[\text{Co}^{\text{III}}(\text{TPP})(\bullet\text{CHCO}_2\text{Et})]$  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  $[\text{Co}^{\text{III}}(\text{TPP})(\bullet\text{NNs})]$ , overall resulting in a higher bond order for the mononitrene radical (1.20) in comparison to the carbene radical (0.98) coordinated to  $[\text{Co}^{\text{III}}(\text{TPP})]$ .

EPR analysis and spin counting, paramagnetic molar susceptibility determination, and NEVPT2-CASSCF calculations are all in agreement and point to a quartet ( $S = 3/2$ ) spin ground state of  $[\text{Co}^{\text{III}}(\text{TPP}^*)(\bullet\text{NNs})_2]$ , with the multireference and multideterminant “broken-symmetry” doublet state being thermally accessible. The electronic structure of the bisnitrene 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 emphasize the importance of considering the quartet ground state and accessible doublet excited state in future (mechanistic) studies of bisnitrene radical species on  $[\text{Co}^{\text{III}}(\text{TPP}^*)]$ . This might lead to additional mechanistic insight, and possibly the application of thermal excitation or photoexcitation of the quartet to doublet state, potentially uncovering two-state reactivity in reactions involving these bisnitrene species.

## EXPERIMENTAL SECTION

**General Considerations.** All reagents were of commercial grade and were used without further purification, unless noted otherwise. All reactions and measurements were performed under an inert atmosphere in a  $\text{N}_2$ -filled glovebox or by using standard Schlenk techniques (under argon), unless noted otherwise. Toluene was distilled from sodium, and  $\text{C}_6\text{D}_6$  was dried over molecular sieves prior to use. All solvents were deaerated by three freeze–pump–thaw cycles and backfilled with argon prior to use. PhINNs<sup>42</sup> and  $[\text{Co}^{\text{III}}(\text{TPP}^*)(\bullet\text{NNs})_2]$ <sup>32</sup> were prepared according to literature procedures. The magnetic moments in solution were determined via Evans’ method.<sup>41</sup> X-band EPR spectra were acquired on a Bruker EMX X-band spectrometer, equipped with an ER 4112HV-CF100 cryostat, and further analyzed and simulated using *EasySpin*.<sup>43</sup>

**Computational Studies.** DFT geometry optimizations were performed on full atomic models (no simplifications) using *TURBOMOLE 7.3*<sup>44</sup> at the BP86/def2-TZVP level of theory on an m4 grid, using Grimme’s version 3 (disp3, “zero damping”) dispersion corrections. Minima (no imaginary frequencies) were characterized by numerically calculating the Hessian matrix. Zero-field splitting parameter calculations were conducted with the *ORCA 4.1*<sup>45</sup> software package on geometries optimized in *TURBOMOLE* at the doublet spin surface. See the SI for additional information.

NEVPT2-CASSCF calculations were performed with the ORCA 4.1<sup>45</sup> software package on geometries optimized in TURBOMOLE at the doublet spin surface. The def2-TZVP basis set was used together with the RIJCOSX approximation in conjunction with the def2-TZVP/C fitting basis set to reduce computational cost. In all cases, the single root spin states (doublet and quartet) were calculated. For refined energy values, NEVPT2 calculations using the RI approximation were carried out on converged CASSCF wave functions. Canonical orbitals were generated for visualization using IboView.<sup>46</sup> See the SI for additional information.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00910>.

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

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### Notes

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