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Ligand Redox Noninnocence in [Co\textsuperscript{III}(TAML)]\textsuperscript{0/−} Complexes Affects Nitrene Formation

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ABSTRACT: The redox noninnocence of the TAML scaffold in cobalt-TAML (tetra-amido macrocyclic ligand) complexes has been under debate since 2006. In this work, we demonstrate with a variety of spectroscopic measurements that the TAMl backbone in the anionic complex [Co\textsuperscript{III}(TAML\textsuperscript{red})]\textsuperscript{−} is truly redox noninnocent and that one-electron oxidation affords [Co\textsuperscript{III}(TAML\textsuperscript{aq})]. Multireference (CASSCF) calculations show that the electronic structure of [Co\textsuperscript{III}(TAML\textsuperscript{aq})] is best described as an intermediate spin (S = 1) cobalt(III) center that is antiferromagnetically coupled to a ligand-centered radical, affording an overall doublet (S = 1/2) ground-state. Reaction of the cobalt(III)-TAML complexes with PhINNs as a nitrene precursor leads to TAML-centered oxidation and produces nitrene radical complexes without oxidation of the metal ion. The ligand redox state (TAML\textsuperscript{red} or TAML\textsuperscript{sq}) determines whether mono- or bis-nitrene radical complexes are formed. Reaction of [Co\textsuperscript{III}(TAML\textsuperscript{aq})] with PhINNs results in the formation of [Co\textsuperscript{III}(TAML\textsuperscript{aq})(N\textsuperscript{−}N\textsuperscript{−}Ns)] and [Co\textsuperscript{III}(TAML\textsuperscript{aq})(N\textsuperscript{−}N\textsuperscript{−}Ns)\textsubscript{2}]−, respectively. Herein, ligand-to-substrate single-electron transfer results in one-electron-reduced Fischer-type nitrene radicals (N\textsuperscript{−}N\textsuperscript{−}Ns) that are intermediates in catalytic nitrene transfer to styrene. These nitrene radical species were characterized by EPR, XANES, and UV−vis spectroscopy, high-resolution mass spectrometry, magnetic moment measurements, and supporting CASSCF calculations.

INTRODUCTION

The use of base metals and redox noninnocent (or redox-active) ligands in radical-carbene, oxo, and nitrene transfer reactions has evolved as a powerful tool for the direct functionalization of (unactivated) C−H bonds and olefins.1 The functionalized products of these reactions are motifs in pharmaceuticals and agrochemicals and are therefore highly valued.2 N-group transfer reactivity is an efficient way to afford the direct synthesis of secondary amines and aziridines, of which the synthesis otherwise typically requires harsh reaction conditions or multiple steps.3 Generation of the essential catalytic metal-nitrene intermediates has been achieved with second- and third-row transition metals (Ru\textsuperscript{4}, Rh\textsuperscript{5}, Pd\textsuperscript{6}, Ag\textsuperscript{7}, and Au\textsuperscript{8}) as well as more abundant base metals (Mn\textsuperscript{9}, Fe\textsuperscript{10}, Co\textsuperscript{11}, Ni\textsuperscript{12}, and Cu\textsuperscript{13}).

Our group, in collaboration with the Zhang group, has studied the formation and reactivity of nitrene adducts of cobalt(II)-porphyrin complexes, which are competent catalysts for a range of (enantioselective) amination and aziridination reactions.4a−14 The mononitrene species generated on cobalt upon reaction with an organic azide is most accurately described as a one-electron-reduced Fischer-type nitrene radical.4b This interesting electronic structure is the result of metal-to-substrate single-electron transfer (SET), wherein cobalt is oxidized from Co\textsuperscript{II} to Co\textsuperscript{III} and the nitrene is reduced by one electron to produce a nitrene radical (N\textsuperscript{−}N\textsuperscript{−}) complex with single-electron population of the π symmetric Co−N antibonding orbital. Interestingly, the reaction of cobalt(II)-porphyrins with iminoiodinanes (PhINNs, Ns = nosyl) led to the formation of bis-nitrene radical species with two one-electron-reduced Fischer-type nitrene radicals (N\textsuperscript{−}N\textsuperscript{−}Ns) that are intermediates in catalytic nitrene transfer to styrene. These nitrene radical species were characterized by EPR, XANES, and UV−vis spectroscopy, high-resolution mass spectrometry, magnetic moment measurements, and supporting CASSCF calculations.

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macroyclic ligand (TAML) platform designed by Collins’ group. The general structure of a TAML that met the aforementioned requirements is depicted in Scheme 1. More-over, the potential redox noninnocence of TAML and related o-phenylenedicarboxamido complexes has been proposed in the literature, and for clarity, we will follow the nomenclature as presented in Scheme 1 for the fully reduced tetra-anion (red), mono-oxidized trianionic ligand-centered radical (sq), and fully oxidized dianion (q).16,17

Iron complexes of these TAML activators have found widespread use in oxidation chemistry, and TAML complexes with Cr, Mn, Fe, Co, Ni and Cu have been reported with many variations of the TAML scaffold.16,18 Interestingly, ligand-centered oxidation of an [FeV(TAMLred)(NTs)]− complex was shown to afford [FeV(TAMLsq)(NTs)], which is a more active nitrene transfer species toward activated C−H bonds (bond dissociation energy between 75 and 80 kcal mol−1) and thioanisole than the reduced analogue.19 A similar trend was observed for a manganese-imido complex, wherein [MnV(TAMLred)(NMes)]− (Mes = mesityl) proved to be unreactive and metal-centered oxidized complex [MnVI(TAMLred)(NMes)] could be used for hydrogen atom transfer reactions and nitrene transfer to thioanisole.20

Apparently, the redox activity of the TAML ligand varies from complex to complex, depending on the metal and other ligands, and both metal- and ligand-centered redox processes can be used to influence the nitrene-transfer reactivity. Specific [CoIII(TAMLred)]− complexes21 have been used for electrochemical water oxidation22,23 and oxygen reduction,24 cycloaddition of CO2 to epoxides,25 electrochemical sensing of H2O2,26 oxo transfer to C−H bonds,27 and electron-transfer reactions.28 However, to the best of our knowledge, no nitrene transfer reactions or stoichiometric reactions leading to the formation of Co(TAML)-based imido- or nitrene-complexes have been reported to date. Moreover, contrary to chemistry with iron, the existence of TAML-centered redox processes in cobalt complexes is still under debate (Figure 1).

Collins et al.21 reported the synthesis and characterization of an anionic [CoIII(TAMLred)]− complex with a diamidophenyl backbone in 1991. The anionic parent complex was characterized as a triplet with an S = 1 Co center and a fully reduced o-phenylenedicarboxamido ligand. The oxidation of this complex afforded a neutral S = 1/2 system for which crystallographic bond metrics indicated single-electron oxidation of the ligand and electron paramagnetic resonance (EPR) data hinted at a cobalt-centered radical (Figure 1). This data was interpreted in 1998 as corresponding to an S = 1 cobalt(III) center antiferromagnetically coupled to a ligand-centered radical ([CoIII(TAMLsq)]).28 Ghosh et al.29 reported an elaborate density functional theory (DFT) study on the ligand noninnocence of multiple variations of the TAML backbone and suggested that the electronic structure of [CoIII(TAMLred)] is better described as [CoIV(TAMLred)] (Figure 1). Their assignment was based on the Mulliken spin density, which was solely localized on cobalt. Collins and co-workers18 critically reinterpreted these spin densities as being evidence of an S = 1 CoIII center. It should be noted that multireference post-Hartree−Fock methods were not accessible at the time, and possible broken-symmetry solutions were apparently not explored. As such, optional antiferromagnetic coupling between an S = 1 Co center and a ligand-centered

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**Scheme 1. General Structure of the TAML Scaffold and the Potential Redox Noninnocence of the Backbone**

<table>
<thead>
<tr>
<th>X1</th>
<th>X2</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl, H, NO2, OMe</td>
<td>Cl, H</td>
<td>Et, Me, F</td>
</tr>
</tbody>
</table>

**Figure 1.** Interpretation of the ligand (non)innocence in cobalt-TAML complexes in chronological order. HFI = hyperfine interaction.
radical could have remained hidden in the applied DFT calculations.

Innocent behavior of the TAML scaffold was claimed in an electrochemical study reported in 2014 as well as in the characterization of Lewis acid-stabilized oxo-complexes, based on UV-vis, EPR, XANES (X-ray absorption near edge spectroscopy), and EXAFS (extended X-ray absorption fine structure) studies, in combination with DFT-calculated Mulliken spin densities. On the contrary, TAML-centered redox activity in $\text{[Co}^\text{III}(\text{TAML})\text{(OH)}]$ was claimed in 2018 on the basis of UV-vis, EPR, and XPS (X-ray photoelectron spectroscopy) studies.

Given (i) the contrasting descriptions of ligand and cobalt oxidation states in $\text{[Co}^\text{III}(\text{TAML})\text{]}$ complexes, (ii) our interest in generating cobalt-nitrene radical intermediates via ligand-to-substrate SET, and (iii) the previous characterization of $\text{[Fe(TAML)(imido)}$, $\text{[Mn(TAML)(imido)}$, and $\text{[Co(TAML)(oxo)}$ complexes, we set out to answer the following research questions:

Is the ligand in $\text{[Co(TAML)}$ complexes redox noninnocent, and can the different assignments in the literature be reconciled? (See Figure 2A.)

Can the $\text{[Co(TAML)}$ platform be used to generate (catalytically competent) cobalt-nitrene (radical) species, and what is the influence of the (ligand) oxidation state on the (electronic) structure of the targeted nitrene (radical) species? (See Figure 2B.)

In case the TAML ligand platform is indeed redox-active, can we use this feature for ligand-to-substrate SET to produce nitrene radical species at square planar cobalt(III) species? (See Figure 2B.)

The main findings of the investigations presented in this article are summarized in Figure 2C.

### RESULTS AND DISCUSSION

Ligand-Centered Oxidation of $\text{[Co}^\text{III}(\text{TAML})\text{]}$.

The parent $\text{[Co}^\text{III}(\text{TAML})\text{]}$ complex was obtained according to an adapted literature procedure.12 After a five-step synthesis procedure to obtain the ligand (TAMLH$_4$), coordination of CoII to the fully deprotonated ligand (generated using n-BuLi) and aerobic oxidation afforded $\text{Li[Co}^\text{III}(\text{TAML})\text{]}$ or PPh$_4[\text{Co}^\text{III}(\text{TAML})]$ after salt metathesis with PPh$_4$Cl (Scheme 2). Crystals suitable for single crystal X-ray diffraction (XRD) analysis of TAMLH$_4$ and PPh$_4[\text{Co}^\text{III}(\text{TAML})]$ were grown by the vapor diffusion of pentane into concentrated THF solutions of the ligand or complex, respectively. The solid state structure of PPh$_4[\text{Co}^\text{III}(\text{TAML})]$ displays a square planar geometry about cobalt and a noncoordinating THF molecule in the crystal lattice. As expected and in accordance with the literature, an analysis of the crystallographic bond metrics (Supporting Information) of the diamidophenyl ring in...
TAMLH₄ and PPh₄[CoⅢ(TAMLred)] supports the preservation of aromaticity upon coordination to cobalt, with the ligand being fully reduced ([TAMLred]) and the metal adopting the CoⅢ oxidation state. The effective magnetic moment of PPh₄[CoⅢ(TAMLred)], as determined via the Evans’ method, indicated a triplet (S = 1) ground state (μ_eff = 2.94μ_B). This is in accordance with the literature and is expected for an intermediate-spin CoⅢ center with two parallel metal-centered unpaired electrons. The DFT-optimized structure of [CoⅢ(TAMLred)] with (Thi)BF₄, and (D) UV−vis spectroelectrochemical (UV−vis−SEC) oxidation of PPh₄[CoⅢ(TAMLred)] in DCM (Details in the SI), (C) Oxidation of [CoⅢ(TAMLred)]²⁻ to [CoⅢ(TAMLsq)] with (Thi)BF₄ and (D) UV−vis Titration of PPh₄[CoⅢ(TAMLred)] in DCM (0.15 mM) with Increasing Amounts of (Thi)BF₄.

The effective magnetic moment of [CoⅢ(TAMLsq)] ([μ_eff = 1.88μ_B]) was found to be consistent with an overall net doublet (S = 1/2) ground state. Room-temperature X-band EPR studies in CH₂Cl₂ or toluene reveal a signal characteristic of a net S = 1/2 system with an unresolved electron density on cobalt (g_iso = 2.22) (Figure 3A). EPR measurements at 10 K in toluene glass showed a rhombic signal with g_z = 2.03, g_x = 2.16, g_y = 2.54, A^Co_x = 5.0 MHz, A^Co_y = 50.0 MHz, A^Co_z = 20.0 MHz, linear A strain =−0.18 (z direction), and quadratic A strain =−18 (x direction) and −2 (y direction). (C) Experimental (black) and simulated (blue) X-band EPR spectra of [CoⅢ(TAMLsq)(MeCN)] at r.t. in MeCN and the DFT (BP86/def2-TZVP/disp3)-optimized structure. Microwave freq. 9.3886 GHz, mod. amp. 3 G, and power 2.000 mW. Simulation parameters: g_iso = 2.00 (20.2 MHz), and A^iso = 36.0 (34.2) MHz.

Full and reversible redox events at E ≈ −1.18, +0.53, and +1.13 V vs Fe⁺/²⁺, which are attributed to metal-centered reduction (CoⅢ/Ⅱ) and two ligand-centered oxidations (TAMLred/aq and TAMLsq/aq) respectively (vide infra). UV−vis spectroelectrochemical (UV−vis−SEC) monitoring of the oxidation event at +0.53 V vs Fe⁺/²⁺ shows the disappearance of PPh₄[CoⅢ(TAMLred)] (λ_max = 510 nm) and the concomitant appearance of the characteristic absorption band of [CoⅢ(TAMLsq)] (λ_max = 623 nm) with an isosbestic point at 545 nm (Scheme 3B). For clarity we already assigned the electronic structure of [CoⅢ(TAMLsq)] in the following descriptions. In the following sections we will further elaborate on the measurements and calculations leading to this assignment.

Chemical oxidation of TAML complexes with ceric ammonium nitrate ([NH₄]₄[Ce(NO₃)₆]) typically requires excess oxidant and large volumes of solvent to extract the product. For purple-colored PPh₄[CoⅢ(TAMLred)] and Li[CoⅢ(TAMLsq)], oxidation with a stoichiometric amount of thianthrenium tetrafluoroborate ([Thi]BF₄) (E'ₜₜ = 0.86 V vs Fe⁺/²⁺) cleanly afforded the blue-colored [CoⅢ(TAMLsq)] complex (Scheme 3C). A UV−vis titration gave data identical to that obtained from UV−vis−SEC monitoring of the oxidation event at +0.53 V vs Fe⁺/²⁺ (Scheme 3D).

The effective magnetic moment of [CoⅢ(TAMLsq)] ([μ_eff = 2.94μ_B]) was found to be consistent with an overall net doublet (S = 1/2) ground state. Room-temperature X-band EPR studies in CH₂Cl₂ or toluene reveal a signal characteristic of a net S = 1/2 system with an unresolved electron density on cobalt (g_iso = 2.22) (Figure 3A). EPR measurements at 10 K in toluene glass showed a rhombic signal with g_z = 2.03, g_x = 2.16, g_y = 2.54, A^Co_x = 5.0 MHz, A^Co_y = 50.0 MHz, A^Co_z = 20.0 MHz, linear A strain =−0.18 (z direction), and quadratic A strain =−18 (x direction) and −2 (y direction). (C) Experimental (black) and simulated (blue) X-band EPR spectra of [CoⅢ(TAMLsq)(MeCN)] at r.t. in MeCN and the DFT (BP86/def2-TZVP/disp3)-optimized structure. Microwave freq. 9.3886 GHz, mod. amp. 3 G, and power 2.000 mW. Simulation parameters: g_iso = 2.00 (20.2 MHz), and A^iso = 36.0 (34.2) MHz.

Figure 3. (A) X-band EPR spectrum of [CoⅢ(TAMLsq)] in benzene at r.t. (black line: microwave freq. 9.390167 GHz, mod. amp. 4 G, and power 2.518 mW) and CH₂Cl₂ (blue line: microwave freq. 9.3966 GHz, mod. amp. 5 G, and power 2.000 mW) with g_iso = 2.22. (B) Experimental (black) and simulated (blue) X-band EPR spectrum of [CoⅢ(TAMLsq)] in toluene at 10 K. Microwave freq. 9.365984 GHz, mod. amp. 4 G, and power 2.000 mW. Simulation parameters: g_z = 2.03, g_x = 2.16, g_y = 2.54, A^Co_x = 5.0 MHz, A^Co_y = 50.0 MHz, A^Co_z = 20.0 MHz, linear A strain =−0.18 (z direction), and quadratic A strain =−18 (x direction) and −2 (y direction). (C) Experimental (black) and simulated (blue) X-band EPR spectra of [CoⅢ(TAMLsq)(MeCN)] at r.t. in MeCN and the DFT (BP86/def2-TZVP/disp3)-optimized structure. Microwave freq. 9.3886 GHz, mod. amp. 3 G, and power 0.7962 mW. Simulation parameters: g_iso = 2.00 (20.2 MHz), and A^iso = 36.0 (34.2) MHz.
to the erroneous description of multireference systems with DFT methods (vide infra). Interestingly, the isotropic X-band EPR spectrum measured in MeCN (Figure 3C) revealed an eight-line pattern at $g_{\text{iso}} = 2.00$ attributed to hyperfine coupling with cobalt ($A_{\text{Co,iso}} = 36.0$ MHz) in $\left[\text{Co}^{\text{III}}(\text{TAML}^{\text{aq}})\right]$(MeCN)], which is in excellent agreement with the DFT-calculated parameters (B3LYP/def2-TZVP: $g_{\text{iso}} = 2.00$, $A_{\text{Co,iso}} = 34.2$ MHz). Notably, this species has a single-reference doublet electronic structure with the unpaired electron residing in a cobalt-ligand $\pi^*$ orbital (strongly delocalized over cobalt and the ligand; see the SI).

The cobalt oxidation state of the four-coordinate complexes was further investigated using Co K-edge X-ray absorption near edge spectroscopy analysis. The Co K-edge XANES spectra of $\text{PPh}_4[\text{Co}^{\text{III}}(\text{TAML}^{\text{red}})]$ and $\left[\text{Co}^{\text{III}}(\text{TAML}^{\text{aq}})\right]$ in toluene are compared in Figure 4. The edge position was 7721 eV for both complexes. Both spectra are identical, which is in line with the same oxidation state (+III) and similar coordination geometry of cobalt in the two complexes. The +III oxidation state of cobalt was already found in $\text{PPh}_4[\text{Co}^{\text{III}}(\text{TAML}^{\text{red}})]$ (according to XRD-derived bond metric analysis, vide supra), and the observed edge position is equal to a related $\left[\text{Co}^{\text{III}}(\text{TAML})\right]^{-}$ complex.27 The shoulder at approximately 7715 eV in the Co K-edge XANES spectra is typical for square planar Co complexes, including square planar Co-porphyrin complexes and a related cobalt-TAML complex.14b,27 The main edge feature arises primarily from $1s \rightarrow 4p$ electron transitions, whereas the feature at 7715 eV is commonly assigned to $1s \rightarrow 4p_z$ and ligand-to-metal charge transfer (LMCT) shake-down transitions.37

In agreement with previous studies,27,29 DFT calculations with various GGA and hybrid functionals (BP86, B3LYP, PBE, and OPBE; see the SI for details) gave unsatisfactory results for the Co(TAML)-type complexes under investigation. An illustrative example of the problem encountered with DFT is found in the challenging description of the net-doublet ground state of the $\left[\text{Co}^{\text{III}}(\text{TAML}^{\text{aq}})\right]$ complex. Distinguishing between a genuine Co IV complex and a multireference electronic structure solution involving antiferromagnetic coupling between an $S = 1$ Co$^{\text{III}}$ center and a TAML ligand-centered radical (as indicated by the B3LYP broken-symmetry DFT solution) is very difficult, if not impossible, when relying only on single-reference computational methods (such as DFT).38 We therefore decided to turn to multireference N-electron valence state perturbation theory (NEVPT2)-corrected complete active space self consistent field (CASSCF) calculations for a proper description of the electronic structures of the Co(TAML)-type complexes described in this article.39

CASSCF calculations were initiated on the anionic $\left[\text{Co}^{\text{III}}(\text{TAML}^{\text{red}})\right]^{-}$ complex by the inclusion of all cobalt d orbitals and those ligand $\pi$ orbitals (L$_\pi$) that could have an interaction with cobalt. In the final CASSCF(14,13) calculation, all initial orbitals were preserved in the active space, except for the d$_{xy}$ orbital, which is uncorrelated (occupancy of 2.00).40 A selection of the most relevant active orbitals with their occupancies (in parentheses) is given in Figure 5A. Löwdin population analysis of the electronic configuration of the d shell gave $\langle d_{xy}\rangle^{2.00}$, $\langle d_{z^2}\rangle^{1.99}$, $\langle d_{xz}\rangle^{1.02}$, $\langle d_{yz}\rangle^{1.02}$, consistent with the assigned +III oxidation state of cobalt. Notably, the L$_\pi$ orbital at $-0.268$ eV has a weak bonding interaction with the d$_{xy}$ orbital and is fully filled (occupancy 1.91), consistent with the fully reduced oxidation state of the ligand.

CASSCF(13,12) calculations on the neutral $\left[\text{Co}^{\text{III}}(\text{TAML}^{\text{aq}})\right]$ complex included a similar active space as for the parent anionic complex and revealed substantial...
multireference character. The uncorrelated \(d_{z^2}\) and \(d_{x^2-y^2}\) orbitals (occupancy 2.00) were not preserved in the active space.\(^{29}\) The reduced charge on the complex causes increased stabilization of the cobalt d orbitals compared to the parent anionic complex, which increases overlap between the \(d_{z^2}\) and \(d_{x^2-y^2}\) orbitals (Figure 5B). Because of this stabilization, the bonding and antibonding combinations of the \(d_{z^2}\) and \(d_{x^2-y^2}\) orbitals are composed of substantial contributions from both \(d_{z^2}\) and \(d_{x^2-y^2}\). As a result of three orbitals being close in energy, significant population of the \(L_{\pi} - L_{\pi}^{a}\) antibonding combination (occupancy 0.64) from the \(d_{z^2} + L_{\pi} + L_{\pi}^{a}\) bonding combination (occupancy 1.38) occurs, while the \(d_{z^2}\) orbital is singly occupied (1.07). The net-doublet ground state of the neutral \([\text{Co}^\text{III}(\text{TAML}^\text{III})]\) complex is thus best described as an \(S = 1\) Co\(^{\text{III}}\) center that is antiferromagnetically coupled to an \(S = 1/2\) TAML-centered radical, leading to a net-doublet system with a \((d_{z^2})^{2 \text{00}}(d_{x^2-y^2})^{2 \text{00}}(d_{z^2} + L_{\pi})^{1 \text{38}}(d_{z^2} - L_{\pi}^{a})^{1 \text{07}}(L_{\pi} - L_{\pi}^{a})^{0.64}\) electronic structure, in agreement with the early interpretation of Collins.\(^{28}\) Excitation energies derived from the CASSCF(13, 12) calculations revealed that the absorption band observed at \(\lambda_{\text{max}} = 623\) nm (Scheme 3B,D) is indeed characteristic of the ligand-centered radical. The corresponding calculated excitation (at 625 nm) is composed of ligand-centered \(L_{\pi} \rightarrow L_{\pi} - d_{z^2}\) and metal-to-ligand \((d_{x^2-y^2} + L_{\pi} \rightarrow L_{\pi} - d_{z^2}\) and \(d_{z^2} \rightarrow L_{\pi} - d_{z^2}\)) charge-transfer processes, with the ligand-centered radical orbital being the acceptor in all cases.

The combined data from magnetic moment measurements, EPR, UV–vis, and XANES spectroscopy, and NEVPT2-CASSCF calculations reveal that the oxidation of \([\text{Co}^\text{III}(\text{TAML}^\text{III})]^\text{−}\) is ligand-centered, giving rise to the formation of \([\text{Co}^\text{III}(\text{TAML}^\text{III})]^\text{−}\), wherein cobalt retains its +III oxidation state and its square planar coordination geometry.

**Synthesis of \([\text{Co}^\text{III}(\text{TAML}^\text{III})(\text{NNs})_2]^\text{−}\) and \([\text{Co}^\text{III}(\text{TAML}^\text{III})(\text{NNs})]^\text{2−}\) via Ligand-to-Substrate SET.** With a proper understanding of their electronic structure, confirming that both complexes are square planar cobalt(III) species featuring a redox-active ligand but are in two different ligand oxidation states, we next set out to investigate nitrene formation at the anionic \([\text{Co}^\text{III}(\text{TAML}^\text{III})]^\text{−}\) and neutral \([\text{Co}^\text{III}(\text{TAML}^\text{III})]\) complexes. We were particularly interested in exploring the influence of the ligand oxidation state on the structure and overall composition of the targeted nitrene adducts.

The addition of 1 equiv of the nitrene precursor PhINNs to PPh\(_4\)[Co^\text{III}(\text{TAML}^\text{III})]^\text{red}] in CH\(_2\)Cl\(_2\) at rt led to a mixture of starting material, mononitrene adduct \([\text{Co}(\text{TAML})(\text{NNs})]^\text{2−}\), and trace amounts of bis-nitrene adduct \([\text{Co}(\text{TAML})(\text{NNs})_2]^\text{−}\), as revealed by negative-mode electrospray ionization high-resolution mass spectrometry (ESI-HRMS\(^{−}\)) analysis. Upon addition of 10 equiv of PhINNs to PPh\(_4\)[Co^\text{III}(\text{TAML}^\text{III})]^\text{red}] in CH\(_2\)Cl\(_2\) or toluene at rt, quantitative formation of bis-nitrene species \([\text{Co}(\text{TAML})(\text{NNs})_2]^\text{−}\) was achieved on the basis of ESI-HRMS\(^{−}\) and UV–vis analysis (Scheme 4 and Figure 6A,B).\(^{41}\) Although bis-nitrene formation was readily achieved for the anionic complex upon addition of excess PhINNs, the addition of 10 equiv of PhINNs to neutral complex \([\text{Co}^\text{III}(\text{TAML}^\text{III})]^\text{2−}\) in CH\(_2\)Cl\(_2\) or toluene at rt led to the quantitative formation of only mononitrene species \([\text{Co}(\text{TAML})(\text{NNs})]^\text{2−}\), as shown by ESI-HRMS\(^{−}\) and UV–vis analysis (Scheme 4 and Figure 6C,D). Also, the addition of alternative nitrene source PhINTs (10 equiv) to \([\text{Co}^\text{III}(\text{TAML}^\text{III})]^\text{2−}\) in CH\(_2\)Cl\(_2\) or toluene at room temperature led to the formation of mononitrene complex \([\text{Co}(\text{TAML})(\text{NTs})]^\text{2−}\), according to ESI-HRMS\(^{−}\) data. The effective magnetic moments of \([\text{Co}(\text{TAML})(\text{NNs})]^\text{2−}\) (2.75\(\mu_B\)) and \([\text{Co}(\text{TAML})(\text{NNs})]^\text{−}\) (1.53\(\mu_B\)) are consistent with the formation of (net) triplet (\(S = 1\)) and doublet (\(S = 1/2\)) systems, respectively. For clarity, we already included the assigned oxidation states of the ligand and cobalt for anionic bis-nitrene \([\text{Co}^\text{III}(\text{TAML}^\text{III})(\text{NNs})_2]^\text{−}\) and neutral mononitrene \([\text{Co}^\text{III}(\text{TAML}^\text{III})(\text{NNs})]^\text{2−}\) in Scheme 4 and Figure 6 and the following text. In the next sections, we will further elaborate on the measurements and calculations leading to these assignments.

As can be expected for an integer spin system, anionic bis-nitrene complex \([\text{Co}^\text{III}(\text{TAML}^\text{III})(\text{NNs})_2]^\text{−}\) is X-band EPR silent at both rt and at 10 K. Neutral mononitrene complex \([\text{Co}^\text{III}(\text{TAML}^\text{III})(\text{NNs})]^\text{2−}\) displays an isotropic EPR signal (Figure 7A) at \(g_{\text{iso}} = 2.091\) at rt, showing well-resolved \(^{57}\)Co \((A_{\text{iso}} = 89.5\) MHz) and poorly resolved (but necessary for accurate simulation) \(^{14}\)N \((A_{\text{iso}} = 18.9\) MHz) HFSs. The anisotropic low-temperature (20 K) EPR spectrum of \([\text{Co}^\text{III}(\text{TAML}^\text{III})(\text{NNs})]^\text{2−}\) recorded in toluene glass displays a slightly rhombic signal with small \(g\) anisotropy and multiple hyperfine coupling interactions, consistent with a net-doublet ground state (Figure 7B).\(^{42}\) The r.t. EPR spectrum of \([\text{Co}^\text{III}(\text{TAML}^\text{III})(\text{NTs})]^\text{2−}\) proved to be similar to that of \([\text{Co}^\text{III}(\text{TAML}^\text{III})(\text{NNs})]^\text{2−}\) (SI).

The Co K-edge XANES spectra for PPh\(_4\)[Co^\text{III}(\text{TAML}^\text{III})(\text{NNs})_2]^\text{−}\) and \([\text{Co}^\text{III}(\text{TAML}^\text{III})(\text{NNs})]^\text{2−}\) are shown in Figure 8. As was observed for the parent complexes PPh\(_4\)[Co^\text{III}(\text{TAML}^\text{III})]^\text{red}] and \([\text{Co}^\text{III}(\text{TAML}^\text{III})]^\text{2−}\), the edge position for both cobalt-nitrene complexes is detected at 7721 eV, suggesting that the cobalt centers in all four complexes have the same overall +III oxidation state. Interestingly, the intense shoulder absorption at 7715 eV observed in the spectra of PPh\(_4\)[Co^\text{III}(\text{TAML}^\text{III})(\text{NNs})_2]^\text{−}\) and \([\text{Co}^\text{III}(\text{TAML}^\text{III})(\text{NNs})]^\text{2−}\) (corresponding to \(1s \rightarrow 4p_n + \text{LMCT}\) shakedown transitions characteristic of square planar cobalt complexes) is no longer visible in the nitrene adducts, thus...
suggesting that both complexes undergo changes in coordination number and/or geometry. This was also observed in related CoIII(porphyrin)-mono- and bis-nitrene complexes that displayed an octahedral coordination environment, with an axial coligand (NsNH2, NsNH−, H2O, or solvent) present in case of the mononitrene species.14b Moreover, an additional low-intensity pre-edge feature at 7711 eV is observed clearly for [CoIII(TAMLq)(NNs)] (inset in Figure 8). The pre-edge feature in the XANES spectrum of PPh4[CoIII(TAMLq)-(NNs)2] is not well-resolved because of moderate data quality caused by low solubility of the complex. These pre-edge features arise from 1s→3d transitions, and in centrosymmetric (i.e., square planar and octahedral) complexes, these transitions are weak because of quadrupole transitions.14b However, symmetry breaking enables 3d−4p hybridization of metal atomic orbitals, causing the pre-edge to gain intensity as a result of dipole-allowed transitions. It thus seems that [CoIII(TAMLq)(NNs)] bears an unidentified sixth coordinating coligand (octahedral coordination geometry) but is not fully centrosymmetric.

Consistent with the above-mentioned experimental results, DFT calculations (BP86, def2-TZVP, disp3, and m4 grid) indicate that the formation of neutral mononitrene complex [CoIII(TAML5)(NNs)] (S = 1/2; ΔG°298 K = −20.3 kcal mol−1) from [CoIII(TAML5n)] (S = 1/2; reference point) is energetically
more favorable than the formation of the neutral bis-nitrene adduct [Co(TAML)(NNS)] (S = 1/2; $\Delta G^{\circ}_{298 K} = -14.5$ kcal mol$^{-1}$). However, the corresponding formation energies of the anionic mono- and bis-nitrene complexes [Co$^{III}$(TAML$^-$)(NNS)]$^{-}$ (S = 1; $\Delta G^{\circ}_{298 K} = -27.9$ kcal mol$^{-1}$) and [Co$^{III}$(TAML$^-$)(NNS)$_2$]$^{-}$ (S = 1; $\Delta G^{\circ}_{298 K} = -29.9$ kcal mol$^{-1}$) from [Co$^{III}$(TAML$^{red}$)]$^{-}$ (S = 1; reference point) are nearly equal (SI).

NEVPT2-corrected CASSCF calculations were performed to accurately describe the electronic structure of the nitrene species. All cobalt d orbitals, ligands L, and nitrene-localized p orbitals were included in the active spaces. CASSCF(14,13) calculations on [Co$^{III}$(TAML$^-$)(NNS)]$^{-}$ showed that the d$_z$ orbital is not preserved in the active space (occupancy 2.00) and that the d$_y$ orbital forms bonding (nitrene-N1 and -N2 localized, occupancy 1.94) and antibonding (mostly d$_z$, localized, occupancy 0.07) combinations with the nitrene N$_p$ orbitals. The d$_x$ and d$_z$ orbitals are both filled (occupancies 1.97 and 1.95, respectively), and L$_{2z}$-d$_{xz}$ (occupancy 0.10) is virtually empty. Given that the L$_{2z}$ orbital was doubly filled in [Co$^{III}$(TAML$^{red}$)]$^{-}$ (vide supra), this implies that the formation of [Co$^{III}$(TAML$^-$)(NNS)]$^{-}$ from [Co$^{III}$(TAML$^{red}$)]$^{-}$ is associated with the two-electron oxidation of the ligand. Interestingly, both nitrene nitrogen atoms bear a single unpaired electron in their N$_p$ orbitals (both occupancies 1.00).

The electronic structure is thus best described as (d$_{xy}$)$^{2.00}$(d$_z$)$^{1.97}$(d$_{xz}$)$^{1.95}$(N$_p^2$ + N$_p^2$ + N$_p^2$)$^{1.94}$(N$_p^2$)$^{1.93}$, consistent with a Co$^{III}$ center, a fully oxidized TAML backbone (TAML$^-$), and two one-electron-reduced Fischer-type nitrene radical substrates (N$^+$N$^-$). Moreover, the cobalt(III) center has undergone a spin transition from intermediate spin in [Co$^{III}$(TAML$^{red}$)]$^{-}$ to low spin in [Co$^{III}$(TAML$^-$)(N$^+$N$^-$)]$^{-}$ upon formation of the bis-nitrene radical species. As a result, the net total spin state does not change in the process and remains a triplet spin state (S = 1). The most relevant active orbitals and their occupation numbers are shown in Figure 9A. In addition, excitation energies derived from the CASSCF(14,13) calculation revealed that no intense absorption bands are expected in the 400-850 nm region (SI), consistent with the experimental spectrum depicted in Figure 6A.

The complex bears some resemblance to the previously reported cobalt-porphyrin bis-nitrene ([Co$^{III}$TP$^{+}\cdot\cdot\cdot$- (N$^+$N$^-$)$^2$])$^{14}$ and ruthenium-porphyrin bis-imido ([Ru$^{VI}$(TPP)(NTs)$_2$])$^{44}$ complexes (TPP = tetraphenylporphin). The ruthenium bis-imido complex is formed exclusively via metal-centered oxidation processes. However, whereas in the cobalt-porphyrin complex double nitrene-radical formation is the result of combined metal-to-substrate and (porphyrin) ligand-to-substrate SET processes, the formation of [Co$^{III}$(TAML$^-$)(N$^+$N$^-$)]$^{-}$ is an entirely (double) ligand-to-substrate single-electron-transfer process.

In a very similar fashion, CASSCF(13,12) calculations on [Co$^{III}$(TAML$^-$)(NNS)] reveal $\pi$ (d$_{xy}$ + N$_p$) and $\sigma$ (d$_{yz}$ + N$_p$) bonding interactions between cobalt and the nitrene, with occupations of 1.93 and 1.86 electrons, respectively. The d$_{xy}$ orbital is filled (occupancy 1.91), and the formerly half-filled L$_{2z}$-d$_{xz}$ orbital is now unoccupied (occupancy 0.12), indicating single-electron oxidation of the ligand (i.e., from TAML$^-$ to TAML$^2$). The single unpaired electron of the complex is mainly localized on the nitrene moiety (N$_p$ - d$_{xz}$ occupancy 1.06), again consistent with [Co$^{III}$(TAML$^-$)(N$^+$N$^-$)] being a Fischer-type nitrene radical complex with net $\pi$-bond order between cobalt and the nitrene of $\sim$0.5.$^{33}$ As for the anionic bis-nitrene complex, the neutral mononitrene complex is generated via ligand-to-substrate SET. Once again, the cobalt(III) ion does not change its oxidation state in the process, but it does undergo a spin flip from intermediate spin in [Co$^{III}$(TAML$^-$)] to low spin in [Co$^{III}$(TAML$^-$)(N$^+$N$^-$)]. The most relevant active orbitals and their occupations are shown in Figure 9B. Notably, neither [Co$^{III}$(TAML$^-$)(N$^+$N$^-$)$_2$] nor [Co$^{III}$(TAML$^-$)(N$^+$N$^-$)]$^{-}$ has significant multireference character.
Interestingly, ligand-to-substrate SET combined with a metal-based spin flip effectively leads to a shift in the spin density from the metal to the nitrene nitrogen(s) in both the neutral mononitrene and the anionic bis-nitrene complexes, without the oxidation of cobalt and without changing the net total spin state of the complex. The redox events clearly occur on the TAML backbone (electron donor) and the nitrene (electron acceptor), wherein the former undergoes one-electron or two-electron oxidation to accommodate one or two nitrene radicals on the CoIII center.

Intrigued by the influence of the ligand oxidation state on the structure of the nitrene species, the mono- and bis-nitrene species were probed for catalytic nitrene transfer reactivity in the benchmark aziridination of styrene (Scheme 5).1,2,19 A remarkable difference in the yield of aziridine product 1 was observed when using PPh4[CoIII(TAMLred)] (64%) or [CoIII(TAMLred)] (35%) as the catalyst in nitrene transfer reactions from PhINNs to styrene, suggesting that the anionic bis-nitrene and neutral mononitrene exhibit markedly different activity and/or stability properties. A thorough investigation of the applicability and mechanisms of PPh4[CoIII(TAMLred)] and [CoIII(TAMLred)] as aziridination catalysts is the subject of current investigations, which will be reported in due time. At this point it is worth mentioning that for cobalt-TAML complexes the reduced (anionic) [CoIII(TAMLred)] species are apparently more effective nitrene-transfer catalysts than the corresponding oxidized (neutral) [CoIII(TAMLred)] species, while for iron- and manganese-TAML complexes the reverse was observed.19,20

### CONCLUSIONS

In this work we have conclusively shown that the ligand in Co(TAML) complexes is reductively. The oxidation of [CoIII(TAMLred)] using (Thi)BF4 cleanly affords [CoIII(TAMLred)] via ligand-centered oxidation, with the electronic structure being best described as an intermediate spin (S = 1) cobalt(III) center that is antiferromagnetically coupled to a ligand-centered radical (S = 1/2).

Interestingly, cobalt-nitrene adducts of PPh4[CoIII(TAMLred)] and CoIII(TAMLred) can be cleanly generated from PhINNs via ligand-to-substrate single-electron transfer to afford PPh4[CoIII(TAML)(NNs)] and [CoIII(TAML)(NNs)], respectively. CAFCSC calculations revealed that both nitrene complexes are best described as one-electron-reduced Fischer-type nitrene radicals. The formation of a bis-nitrene adduct of PPh4[CoIII(TAMLred)] is attributed to the availability of two electrons within the reduced TAML framework for double ligand-to-substrate SET, whereas only one electron can be used for ligand-to-substrate SET on [CoIII(TAMLred)], which therefore affords the mononitrene adduct. Intriguingly, in both cases the combination of ligand-to-substrate SET and a spin flip from intermediate spin (S = 1) to low spin (S = 0) at the cobalt(III) center effectively results in a shift of the spin density from the metal to the nitrene moieties, without the oxidation of cobalt and without changing the net total spin state of the complex.

Preliminary catalytic styrene aziridination reactions using PPh4[CoIII(TAMLred)] or [CoIII(TAMLred)] as the catalyst reveal remarkable differences in activity/stability between the two systems. More elaborate studies on the underlying mechanisms, synthesis applicability, and differences between the two complexes in nitrene transfer catalysis will be reported in the near future.

**ASSOCIATED CONTENT**

3 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.9b11715.

- X-ray structure of TAMLH4 (CIF)
- X-ray structure of PPh4[CoIII(TAMLred)] (CIF)

Experimental details; synthesis procedures; relevant NMR, EPR, HRMS, XRD, UV–vis, electrochemical, and XANES data; geometries (xyz coordinates) of stationary points (DFT); and a description of the CAFCSC calculations (PDF)

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### REFERENCES


(33) Notably, a previous study (ref 23) on the electrochemical behavior of Na[Co\textsuperscript{III}(TAML\textsuperscript{red})] in MeCN displayed only one reversible oxidation event, whereas the second oxidation was found to be irreversible.

(34) Mak, S.-T.; Wong, W.-T.; Yam, V. W.-W.; Lai, T.-F.; Che, C.-M. Cobalt(III) alkyl complexes of 1,2-bis-(2-pyridinecarboxamido)-benzene (H\textsubscript{2}bpb) and 4,5-dichloro-1,2-bis-(2-pyridinecarboxamido)-benzene (H\textsubscript{2}bpc) and X-ray crystal structures of [Co(bpc)-(\text{CH\textsubscript{2}CH\textsubscript{2}CMe = CH\textsubscript{2}})(\text{H\textsubscript{2}O})] and [Co(bpb)Et(\text{H\textsubscript{2}O})]. *J. Chem. Soc., Dalton Trans.* 1991, 1915–1922.

(35) CASSCF calculations demonstrated that the absorption band at 623 nm is dominated by ligand-centered π → π* and metal-to-ligand charge-transfer excitations. See the CASSCF section on [Co\textsuperscript{III}(TAML\textsuperscript{sq})] for more details.


(40) We attempted to rotate the uncorrelated orbital(s) back into the active space. However, this was unsuccessful. Moreover, the inclusion of orbitals with occupancy 2.00 in the active space should be avoided.

(41) CASSCF calculations demonstrated that no intense characteristic absorption bands are expected in the 400–850 nm region. See the CASSCF section on [Co\textsuperscript{III}(TAML\textsuperscript{sq})(NNs)\textsubscript{2}] for more details.

(42) An accurate simulation of the experimental spectrum proved to be challenging and was unsuccessful.


(45) See the SI for a description of CASSCF-calculated UV−vis excitation energies and EPR g values.