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Meso-N-methylation of a porphyrinoid complex: Activating the H-atom transfer capability of an inert Re^{V}(O) corrolazine†

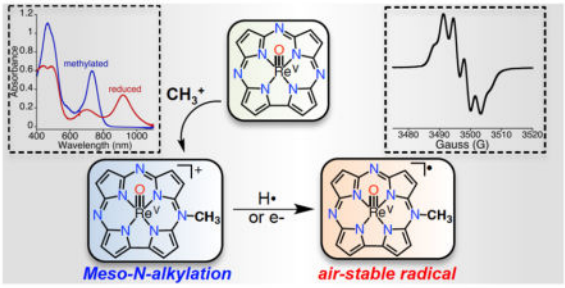
Evan E. Joslin§, **Jan Paulo T. Zaragoza**, **Maxime A. Siegler**, and **David P. Goldberg**

Department of Chemistry, The Johns Hopkins University, 3400 N. Charles Street, Baltimore, MD 21218, USA

Abstract

The selective alkylation of a single *meso*-N atom of a corrolazine macrocycle is reported. Alkylation has a dramatic impact on the physicochemical properties of Re^{V}(O)(TBP$_8$Cz). New electron-transfer and hydrogen-atom-transfer reactivity is also seen for this complex, including one-electron reduction, which gives an air-stable 19π-electron aromatic radical complex.

Graphical Abstract



Meso-N-methylation of a corrolazine macrocycle results in changes in both the physicochemical properties and in the reactivity of a Re^{V}(O) corrolazine complex.

The development of novel porphyrinoid compounds is essential for applications in a range of fields that rely on porphyrinoid structures, including bioinorganic models of heme proteins,[1] electrochemical energy storage systems,[2] new dye-sensitized solar cells (DSSCs),[3a,b] and molecules for photodynamic therapy (PDT).[3c] The synthesis of ring-contracted porphyrins, and in particular, ring-contracted tetraazaporphyrins, or corrolazines (Cz),[1a,b, 4] has been a focus of our research group. The corrolazine ligands are able to support a range of metal ions in various oxidation states, including high-valent metal-oxo and metal-imido species.[5] However, synthetic modification of the corrolazine ring has thus far been limited to the peripheral substituents on the β-carbon positions.[4]

†Electronic Supplementary Information (ESI) available: Experimental, crystallographic, and computational details. CCDC 1510757 for **2**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

Correspondence to: David P. Goldberg.

§Present Address: Sewanee: The University of the South, 735 University Avenue, Sewanee, TN, 37383, USA.

Porphyrins and corroles can be modified at the *meso*-carbon atoms, leading to a large array of porphyrinoid compounds with varying structural, electronic, and reactivity properties.[6] The *meso*-N atoms in Cz, and in the related porphyrazines and phthalocyanines, appear to preclude facile alkyl-functionalization at the *meso* position.[7] We envisioned that alkylation of the *meso*-N positions might be feasible given that protonation of these positions was occurring in the former complexes.[8] If a generalized alkylation procedure could be devised, it would open a pathway to *meso*-N substituted porphyrinoid compounds with a range of new steric and electronic properties.[9] Such a synthetic strategy would allow access to *meso* substitution in corrolazines and porphyrazines similar to what has been seen in porphyrin chemistry.

Herein we describe the synthesis of a cationic rhenium corrolazine $[Re^{V}(O)(\mathit{N}\text{-}MeTBP_8Cz)]^{+}[OTf]^{-}$ (**1**), which has been alkylated at one of the *meso*-N atoms of the Cz ring. To our knowledge, this synthesis is the first report of direct, selective alkylation at a *meso*-N position in a porphyrinoid compound.[9] The methylated *meso*-N site was confirmed by single crystal X-ray diffraction (XRD). The selective alkylation of the starting $Re^{V}(O)(TBP_8Cz)$ complex has a profound effect on the spectroscopic features, redox potentials and reactivity of this metallocorrolazine complex. The unalkylated $Re^{V}(O)$ complex is unreactive toward electron- and hydrogen-atom donors, whereas alkylated **1** undergoes one-electron reduction to give an air-stable 19π-electron radical complex. The stabilization of organic radicals with extended porphyrinoid π systems has been the focus of much effort,[9b, 10] and reduced **1** is a rare example of such a species. A PCET mechanism is indicated from kinetic and thermodynamic analyses of the reaction of **1** with H-atom donors.

The synthesis of **1** was accomplished by refluxing $Re^{V}(O)(TBP_8Cz)$ with excess MeOTf in toluene (Scheme 1). The solution slowly changes from dark-green to brown upon the formation of complex **1**. Purified complex **1** can be isolated as a dark brown solid in 38% yield. The *meso*-N methylation causes a red-shift and a decrease in the extinction coefficient of the Soret band (464 nm), and a red-shifting of the Q-band (732 nm) by 62 nm compared to $Re^{V}(O)(TBP_8Cz)$ (Fig. 1a). The changes in the absorbance spectrum are similar to the changes seen for *meso*-N protonation of $Re^{V}(O)(TBP_8Cz)$, as well as Mn corrolazines.[8] The ^{1}H NMR spectrum for **1** shows that the two-fold symmetry of the starting $Re^{V}(O)$ complex has been disrupted (Fig. 2). The NMR spectrum indicates that methylation occurs on one of the *meso*-N atoms that does not lie on the mirror plane bisecting the pyrrole-pyrrole linkage. The singlet at 5.05 ppm arises from the new *meso*-CH_3 group, which is shifted downfield by the aromatic ring current. Similar chemical shifts are seen for porphyrins methylated at the *meso*-carbon position.[11] Additional support of the assignment of **1** as the monoalkylated product is afforded by LDI-MS, where the parent ion was found at 1572.53 *m*/*z* (M^{+}) (calc'd 1572.81 *m*/*z*).

Crystallization of complex **1** was not successful, but addition of the proton donor $[H(OEt_2)_2]^{+}[B(C_6F_5)_4]^{-}$ (HBArF) to **1** in CH_2Cl_2 led to red shifts in both the Soret and Q-bands (Fig. 1b) indicative of *meso*-N protonation, and resulted in crystallization of the dicationic derivative $[Re^{V}(O)(\mathit{N}\text{-}MeTBP_8Cz)(H)]^{2+}[BArF]^{-}_{2}$ (**2**). The crystal structure is shown in Fig. 3, and confirms that methylation has occurred at a single *meso*-N atom. The proton on the opposing *meso*-N position was successfully located from difference Fourier

maps (Fig. S9, ESI†), and two $BArF^-$ counterions were found in the crystal lattice, confirming the charge balance. The structure exhibits a short Re–O bond of 1.6643(17) Å, and an out-of-plane ($N_{pyrrole}$) distance for Re of 0.744 Å, both of which are similar to the neutral $Re^V(O)$ complex. The phenyl groups adjacent to the N–CH_3 substituent are canted to accommodate the methyl group (C_α–C_β–C_{ipso}–C_{ortho}) (dihedral angle: 64.2°, 65.7°), as compared to the adjacent phenyl groups (dihedral angle: 44.0°, 29.2°). The angles around the N–CH_3 group (C(1)–N(7)–C(97) = 117.9(2)°; C(16)–N(7)–C(97) = 117.7(2)°; C(1)–N7–C16 = 124.3(2)°) are indicative of sp^2 hybridization, with the CH_3 group lying slightly above the mean plane of the 23-atom macrocyclic core (CH_3-plane = 0.43 Å). The ^1H NMR spectrum of **2** (Fig. S5, ESI†), generated in situ by addition of HBArF to **1** in CD_2Cl_2, displays a broad resonance at 12.8 ppm consistent with *meso*-N protonation. Unfortunately, the dicationic species **2** is extremely moisture-sensitive and converts back slowly to **1** even in anhydrous CH_2Cl_2, making further reactivity studies difficult.

The influence of remote *meso*-N-methylation on the Re–O bond was probed by ATR-IR spectroscopy. The IR spectra for **1** with natural abundance ^{16}O (**1-^{16}O**) and isotopically enriched ^{18}O (**1-^{18}O**) (>99%, incorporated from $H_2{}^{18}O$)[8c] in the terminal oxo position is shown in Fig. S3 (ESI†). Comparison of the spectrum for **1-^{16}O** with $Re^V(O)(TBP_8Cz)$ does not reveal any obvious new peaks. However, the IR spectrum for **1-^{18}O** reveals a new peak at 953 cm^{-1} in comparison with **1-^{16}O**, which is consistent with a Re–O stretch (Fig. S3, ESI†). A value of $\nu(Re–^{16}O)$ = 1011 cm^{-1} was calculated by using a simple diatomic oscillator model, which falls under an intense corrolazine vibrational mode centered at 1001 cm^{-1}, also seen in other corrolazine compounds.[12] The Re–O stretch in **1-^{18}O** is shifted to higher energy by 8 cm^{-1} as compared to $\nu(Re–^{18}O)$ = 945 cm^{-1} for unmethylated $Re^V(^{18}O)(TBP_8Cz)$.[8c] This shift is quite similar to the 11 cm^{-1} upshift observed for ν(Re–O) upon *meso*-N protonation of $Re^V(O)(TBP_8Cz)$.[8c] Thus both remote *meso*-N methylation and protonation appear to cause a slight strengthening of the Re–O bond in these complexes (an influence from a change in symmetry on ν(Re–O) cannot be ruled out). To support these assignments, frequency calculations were performed via density functional theory (DFT) computations. Geometry-optimized structures for truncated models of **1** and $Re^V(O)(TBP_8Cz)$ were obtained at the PBE0/LANL2TZ/6-31G** level of theory, (Fig. S15, ESI†). These structures led to calculated values of ν(Re–O) = 1054 cm^{-1} for the parent compound and 1063 cm^{-1} for **1**. Although these vibrational frequencies are larger than the experimental data,[13] the difference between the calculated ν(Re–O) values for **1** and the parent complex is $\Delta\nu$(Re–O)) = 9 cm^{-1}, in excellent agreement with experiment.

Further insights regarding the electronic differences between **1** and $Re^V(O)(TBP_8Cz)$ were obtained through cyclic voltammetric measurements (Fig. S4, ESI†). Complex **1** exhibits two reversible waves at −561 mV and −906 mV versus Fc^+/Fc in CH_2Cl_2. This electrochemical profile is different from $Re^V(O)(TBP_8Cz)$, which shows only one reversible wave at +565 mV, assigned to a Cz ring oxidation.[8c] The addition of the methyl group makes Cz ring oxidation inaccessible over the solvent window, and the redox couples at −561 mV and −906 mV for **1** can be assigned to consecutive Cz ring reductions. We have shown

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previously that monoprotonation of $Re^{V}(O)(TBP_8Cz)$ to form $[Re^{V}(O)(TBP_8Cz)(H)]^+$ led to a similar disappearance of the ring oxidation wave at +565 mV and the appearance of an *irreversible* Cz ring reduction wave at −645 mV. Attempted reaction of this complex with H-atom, O-atom and electron transfer substrates led either to no reaction or deprotonation. These results contrast those for **1**, where a *reversible* ring reduction is observed. The electrochemical data show that complex **1** is significantly more difficult to oxidize than $Re^{V}(O)(TBP_8Cz)$, but should be susceptible to reduction by an appropriate one-electron reducing agent.

Addition of the one-electron reducing agent $Cr(C_6H_6)_2$ to **1** in CH_2Cl_2 led to the changes in the UV-vis spectrum seen in Fig. 4a. Isosbestic conversion is observed, giving a new species with λ_{max} = 440, 489 nm, 920 nm. The decrease in the extinction coefficient of the Soret band and the appearance of a long-wavelength band at 920 nm is consistent with a radical delocalized on the corrolazine **π**-system. The 920 nm band is significantly more red-shifted than the analogous red-shifted peaks in corrolazine **π**-radical-cations.[8c,14] However, a similarly red-shifted band at 915 nm was recently reported for a P^{V} porphyrazine **π**-radical complex.[10b] The new 920 nm species can be quantitatively converted back to **1** by titration with the one-electron oxidant $Cp_2Fe^+PF_6^-$ (Fig. S11, ESI†). Taken together, the data indicate that cationic **1** undergoes a reversible, one-electron reduction to give a neutral **π**-radical complex, $[Re^{V}(O)(N\text{-}MeTBP_8Cz)]^{\bullet}$ (**3**) (Scheme 2). This complex could be isolated as a red-brown solid by removal of solvent *in vacuo*, which then slowly decays with a half-life of 23 h under aerobic conditions at 23 °C (Fig. S12, ESI†). Thus **3** is a rare example of an isolable, air-stable porphyrinoid **π**-radical complex, and can be described as a 19**π** electron aromatic system. Very few other 19**π** electron porphyrinoid species are known.[10]

The neutral complex $Re^{V}(O)(TBP_8Cz)$ is unreactive toward H-atom donors. However, given that **1** could be reduced by one electron-transfer agents, we examined this complex for its ability to react with H-atom donors. The reaction of **1** with TEMPOH ($BDE(O–H)_{DMSO}$ = 72 kcal/mol)[15] in CH_2Cl_2 at 23 °C led to conversion to **3** (Fig. S13, ESI†). For TEMPOH, $E_{1/2}$ = 0.71 V (vs Fc^+/Fc) makes outer-sphere ET to **1** prohibitively disfavored (ΔG_{ET} = +1.27 eV). A second H-atom donor, phenylhydrazine ($PhNHNH_2$ BDE $(N–H)_{DMSO}$ = 75 kcal/mol) also reacts with **1** to give the same UV-vis spectral changes as TEMPOH (Scheme 2). These reactions indicate that **1** is capable of abstracting H atoms from weak O–H and N–H bonds.

Reaction of **1** with excess $PhNHNH_2$ led to the fluid solution EPR spectrum for **3** shown in Figure 4b. A narrow, six-line signal centered near g ≈ 2 is seen. This spectrum can be assigned to an S = ½ radical delocalized over the Cz **π** system and split by ^{14}N hyperfine coupling. DFT calculations for the doublet state for **3** (PBE0/LANL2TZ/6-31G** level of theory) yield a spin density plot (Figure S16, ESI†) that shows the unpaired electron is delocalized in a Cz **π** orbital that includes the three *meso*-N atoms, consistent with the observed ^{14}N hyperfine coupling. In comparison, the **π**-cation radical complex $[Re^{V}(O)(TBP_8Cz]^{\bullet+}$ exhibits a sharp singlet at g = 2.00 with no ^{14}N hyperfine splitting,[8c] and the spin density calculated for this complex (Fig. S16, ESI†) is concentrated on the pyrrole carbon atoms.

Mechanistic insights regarding the HAT reactivity of **1** were obtained from kinetic measurements. Reaction of **1** with excess TEMPOH led to pseudo-first-order decay of **1** and production of **3** as seen by UV-vis, and varying the TEMPOH concentration led to a linear second-order plot with k_2 = 0.76(2) M^{-1} s^{-1}. A kinetic isotope effect = 1.4 was found with TEMPOD. Concerted HAT reactions involving metal-oxo complexes often exhibit larger KIEs,[16] although with some exceptions.[17] The relatively small KIE seen for **1** may suggest a proton-coupled electron-transfer (PCET) process.[18] It is reasonable to speculate that a weakly basic *meso*-N atom of the Cz ring is the initial proton acceptor, which then is likely rapidly deprotonated by the OTf^- counterion.[8b] However, the exact fate of the proton in the PCET reactions with **1** is not known at this time.

In summary, a facile method for alkylation of *meso*-N-substituted porphyrinoid compounds has been reported. The post-cyclization treatment of other porphyrazines and phthalocyanines with appropriate alkyl electrophiles should be straightforward, opening the door to a wide range of new porphyrinoid compounds. The attachment of the methyl group to the *meso*-N atom in **1** has a profound influence on spectral properties and redox potentials, and reduction of **1** leads to a rare, air-stable 19π-electron radical species. Complex **1** is also capable of abstracting hydrogen atoms from weak O–H and N–H bonds, suggesting that porphyrinoid π-radical complexes in synthetic systems or heme proteins may have as yet undiscovered potential for oxidative reactivity toward substrates. The strategy of *meso*-N alkylation may also allow for the future installation of pendant groups orthogonal to the tetrapyrrolic plane of the Cz ligand, which may help in activating or stabilizing metal-oxygen intermediates.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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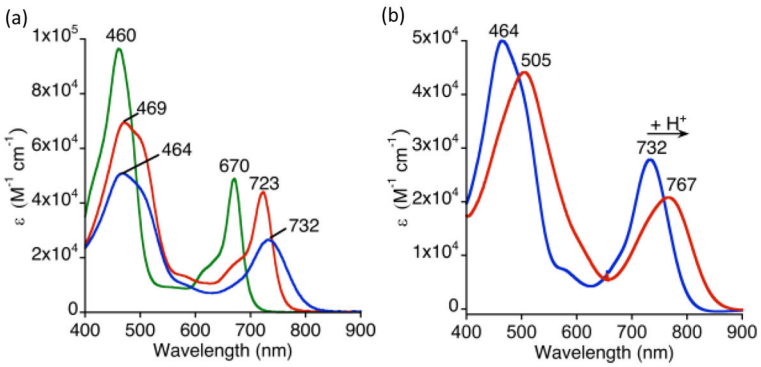


Fig. 1.

UV-vis spectra of (a) neutral $Re^{V}(O)(TBP_8Cz)$ (green), *meso*-N-protonated $[Re^{V}(O)(TBP_8Cz)(H)]^{+}$ (red), and *meso*-N-methylated **1** (blue) in CH_2Cl_2. (b) UV-vis spectral changes upon addition of excess HBArF to **1** (blue) in CH_2Cl_2 to form dicationic **2** (red).

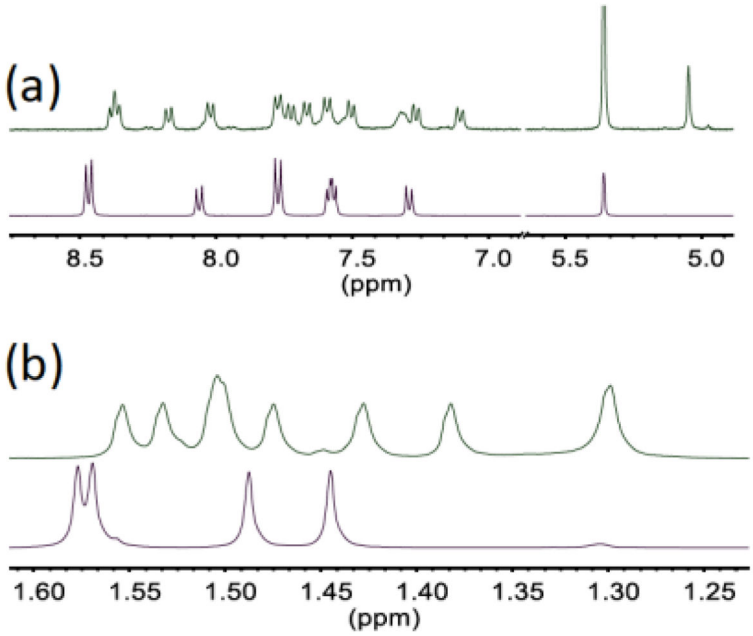


Fig. 2.

Comparison of ^{1}H NMR spectra showing the (a) aromatic and (b) t-Bu region of **1** (green) and $Re^{V}(O)(TBP_8Cz)$ (violet) in CD_2Cl_2 at 25 °C.

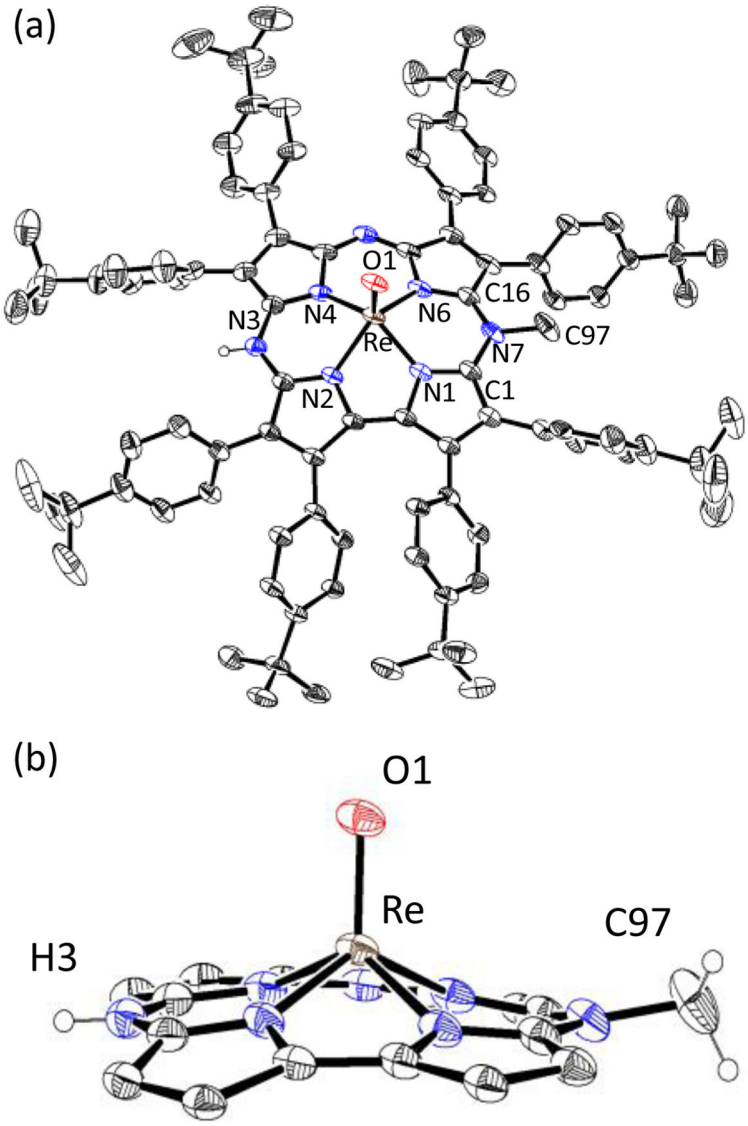


Fig. 3.

Displacement ellipsoid plots (40% probability level) at 110(2) K of (a) the dication of **2** and (b) side view with peripheral aryl groups omitted. All H-atoms except for the meso-H and disorder were removed for clarity.

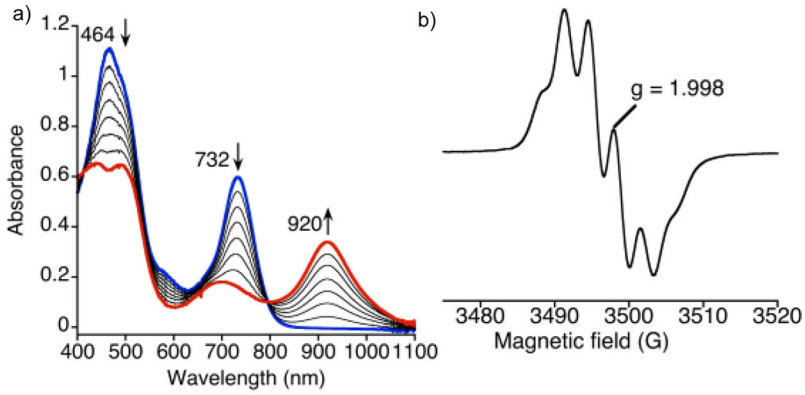
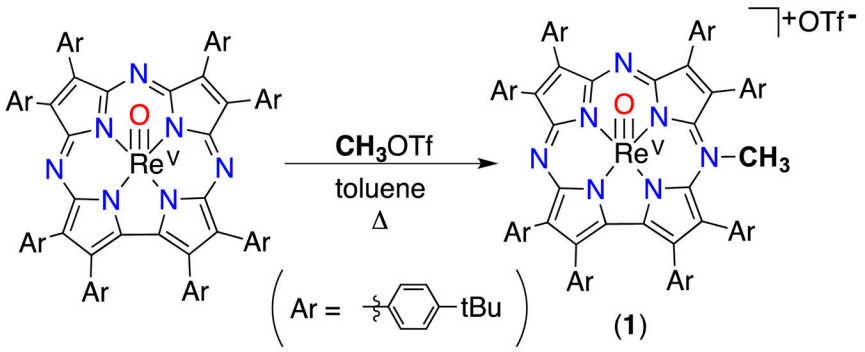
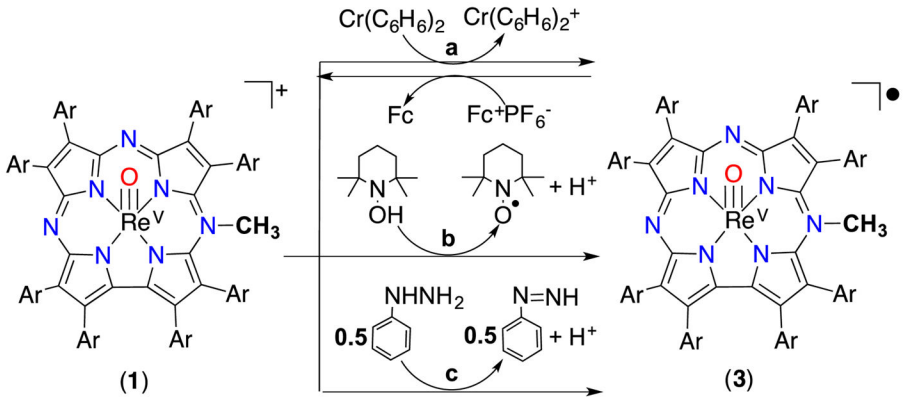


Fig. 4.

(a) UV-vis spectral titrations of **1** + $Cr(C_6H_6)_2$ (0 – 1 equiv) in CH_2Cl_2. (b) EPR spectrum of **1** (0.84 mM) and $PhNHNH_2$ (1.2 M) in CH_2Cl_2 at 295 K.



Scheme 1.
Synthesis of $[Re^{V}(O)(\mathit{N}\text{-MeTBP}_8Cz)]^{+}[OTf]^{-}$ (**1**).



Scheme 2.

Electron-transfer and hydrogen-atom-transfer reactions with *meso*-N-methylated **1** and the 19π-electron radical complex **3**.