

Photochemistry

Nitrene Photochemistry of Manganese N-Haloamides**

Gerard P. Van Trieste III, Kaleb A. Reid, Madeline H. Hicks, Anuvab Das, Matthew T. Figgins, Nattamai Bhuvanesh, Andrew Ozarowski, Joshua Telser, and David C. Powers*

Abstract: Manganese complexes supported by macrocyclic tetrapyrrole ligands represent an important platform for nitrene transfer catalysis and have been applied to both C–H amination and olefin aziridination catalysis. The reactivity of the transient high-valent Mn nitrenoids that mediate these processes renders characterization of these species challenging. Here we report the synthesis and nitrene transfer photochemistry of a family of Mn^{III} N-haloamide complexes. The *S* = 2 N-haloamide complexes are characterized by ¹H NMR, UV-vis, IR, high-frequency and -field EPR (HFEP) spectroscopies, and single-crystal X-ray diffraction. Photolysis of these complexes results in the formal transfer of a nitrene equivalent to both C–H bonds, such as the α-C–H bonds of tetrahydrofuran, and olefinic substrates, such as styrene, to afford aminated and aziridinated products, respectively. Low-temperature spectroscopy and analysis of kinetic isotope effects for C–H amination indicate halogen-dependent photoreactivity: Photolysis of N-chloroamides proceeds via initial cleavage of the Mn–N bond to generate Mn^{II} and amidyl radical intermediates; in contrast, photolysis of N-iodoamides proceeds via N–I cleavage to generate a Mn^{IV} nitrenoid (i.e., {MnNR}⁷ species). These results establish N-haloamide ligands as viable precursors in the photosynthesis of metal nitrenes and highlight the power of ligand design to provide access to reactive intermediates in group-transfer catalysis.

Introduction

Since Breslow's seminal discovery of Mn porphyrin-catalyzed amination of cyclohexane, Mn tetrapyrroles have emerged as an important platform for nitrene transfer catalysis.^[1] The combination of nitrene precursors, such as

How to cite: *Angew. Chem. Int. Ed.* **2021**, *60*, 26647–26655
International Edition: doi.org/10.1002/anie.202108304
German Edition: doi.org/10.1002/ange.202108304

iminoiodinanes^[1c,2] or N-haloamides,^[3] with Mn^{III} porphyrin catalysts enables nitrene transfer to C–H bonds and olefinic substrates to afford amines and aziridines, respectively (Figure 1). Enantioselective nitrene transfer catalysis has been

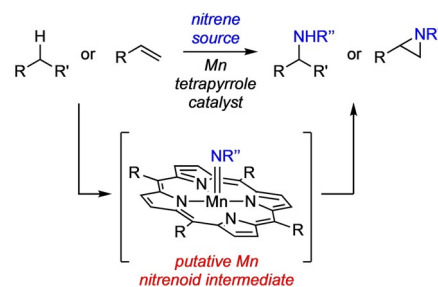


Figure 1. Mn tetrapyrrole-catalyzed nitrene transfer catalysis has been applied to both C–H amination and olefin aziridination reactions. Electrophilic Mn nitrenoids are proposed to mediate this family of nitrene transfer reactions.

realized using *D*₄-symmetric chiral Mn porphyrin catalysts.^[2c,4] More recently, White et al. have developed related Mn^{III} phthalocyanines as highly active catalysts for aliphatic C–H amination.^[5] In analogy to metalloporphyrin-supported metal oxo intermediates in C–H hydroxylation catalysis, the developed nitrene transfer catalysis is proposed to proceed via the intermediacy of reactive high-valent Mn nitrenoids.^[6]

The inherent reactivity of Mn nitrenoids relevant to catalysis renders these species challenging to observe.^[7] Stabilization of these intermediates via synthetic modification of the ancillary ligand set can attenuate the reactivity of the supported Mn nitrenoid and enable its isolation. Abu-Omar and co-workers leveraged triply anionic corrole ligands to stabilize and isolate Mn^V nitrenoid **1**, which was prepared by photolysis of a solution of mesityl azide and Mn^{III} tris-pentafluorophenylcorrole (Figure 2a).^[8] Complex **1** was found to be unreactive towards alkenes and alkanes but did participate in reaction with PPh₃ to afford the corresponding iminophosphine. Goldberg and co-workers reported the isolation of corrolazine-supported nitrenoid **2**, which was similarly found to be unreactive towards both olefins and C–H bonds (Figure 2b).^[9] Use of a tetraanionic tetraamido macrocyclic ligand (TAML) enabled the isolation of Mn^V imido complex **3** (Figure 2c).^[10] Further oxidation to the corresponding Mn^{VI} complex was necessary to engender nitrene transfer chemistry. In the context of porphyrin-supported nitrenoids, acylation of Mn^V nitrido complex **4** with trifluoroacetic anhydride affords Mn^V nitrenoid **5**, which was characterized by ¹H NMR and UV-vis spectroscopies and displays olefin aziridination activity (Figure 2d).^[6d,11]

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[**] A previous version of this manuscript has been deposited on a preprint server (https://doi.org/10.33774/chemrxiv-2021-plww9).

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
https://doi.org/10.1002/anie.202108304.

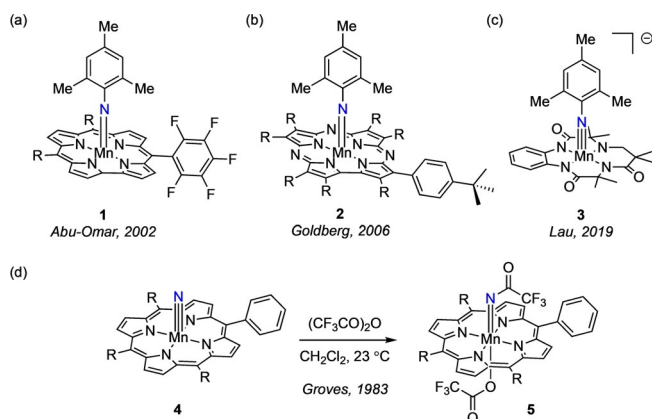


Figure 2. A small family of Mn^{V} nitrenoids has been characterized, including (a) corrole-supported **1**, (b) corrolazine-supported **2**, and (c) TAML-supported **3**. (d) Treatment of Mn^{V} nitride **4** with trifluoroacetic anhydride resulted in the observation of porphyrin-supported Mn^{V} nitrenoid **5**.

Synthetic photochemistry provides the opportunity to access reactive species under conditions that allow for characterization by time-resolved or cryogenic methods without necessitating stabilization via synthetic derivatization. In the context of Mn oxo chemistry, Newcomb and co-workers demonstrated that both Mn^{IV} and Mn^{V} oxo complexes could be accessed by photolysis of Mn oxyanion complexes (Figure 3a).^[12] Flash photolysis of Mn^{III} chlorate complex **6a** resulted in Cl–O bond homolysis to generate a Mn^{IV} oxo compound **7**; in contrast, flash photolysis of Mn^{III} perchlorate complex **6b** resulted in Cl–O bond heterolysis to generate

a Mn^{V} oxo complex **8**. Similar photochemically promoted O–X cleavage to generate Mn oxo complexes was described by Suslick and co-workers in the context of porphyrin-supported Mn nitrite and nitrate complexes,^[13] and Zhang and co-workers have described photogeneration of Mn oxo complexes from μ -oxo dimanganese precursors.^[14]

In contrast to metal oxo chemistry, photochemical strategies to generate the corresponding reactive metal nitrenoids are much less developed. While organic azide ligands can represent viable photoprecursors to metal nitrenes, the poor donicity of organic azides as ligands coupled with the thermal instability of these ligands towards N_2 loss results in a limited family of potential photoprecursors.^[15] Conceptually, haloamide ligands, which are X-type donors, could serve as nitrene precursors via N–X photoactivation. In analogy to oxyanion photochemistry pictured in Figure 3a, both N–X homolysis and heterolysis mechanisms are potentially available to haloamide complexes (Figure 3b). In 2018, we demonstrated that photolysis of a Rh_2 complex with an *N*-chloroamide ligand afforded the corresponding Rh_2 nitrenoid via N–Cl homolysis.^[16] Exploration of the generality of N–X photocleavage and the photoactivation modes available to a more diverse set of transition metal complexes is critical to generalizing *N*-haloamide photochemistry as an approach to the synthesis of catalytically relevant metal nitrenoids. At present, the synthetic chemistry of transition metal haloamide complexes is extremely limited, with only three structures reported,^[16,17] and while significant work has been carried out on the photolysis of organic *N*-haloamines,^[18] the corresponding photochemistry of inorganic *N*-haloamides is almost completely unknown.

Here we report the synthesis and characterization of a family of Mn porphyrins featuring *N*-haloamide ligands. These complexes are $S = 2$ species and are fully characterized in both solution phase and the solid state. This family of complexes includes the first examples of *N*-bromoamide and *N*-iodoamide complexes of transition metals. Photolysis of these complexes gives rise to the products of C–H amination and olefin aziridination. A combination of kinetic isotope effect analysis and low-temperature spectroscopy indicates that while the photolysis of Mn^{III} *N*-chloroamides proceeds via initial cleavage of the Mn–N bond to generate Mn^{II} and amidyl radical intermediates, photolysis of the corresponding *N*-iodoamide complexes proceeds via N–I cleavage to generate a Mn^{IV} nitrenoid that participates in both C–H amination and olefin aziridination. These observations represent the first example of a porphyrin-supported Mn^{IV} nitrenoid, highlight the impact of ligand design in the synthesis of novel photoprecursor ligands, and establish *N*-haloamides as a class of nitrene photoprecursor ligands.

Results and Discussion

In this section, we describe the synthesis and characterization of a family of porphyrin-supported Mn^{III} haloamide complexes (**13**) featuring variation of both the identity of the porphyrin meso-substituent and of the *N*-halogen. This suite of complexes provides the opportunity to investigate the

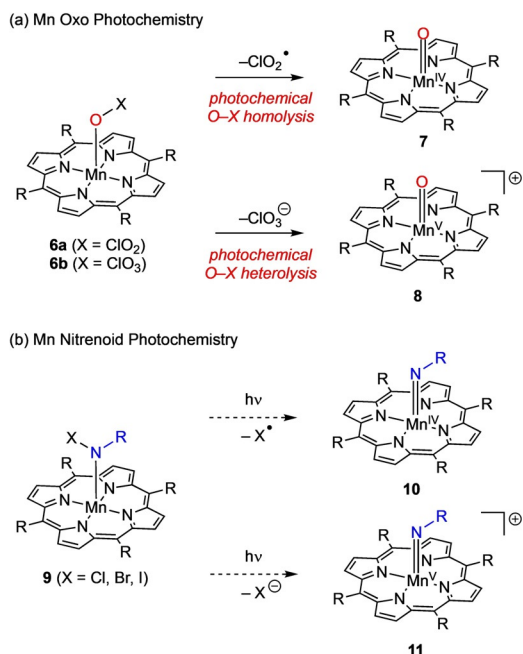


Figure 3. (a) Photolysis of Mn chlorate **6a** affords Mn^{IV} oxo **7** via Cl–O homolysis whereas photolysis of Mn perchlorate **6b** affords Mn^{V} oxo **7** via Cl–O heterolysis. (b) Corresponding Mn nitrenoid photochemistry would be enabled if control over hetero- and homolytic N–X cleavage processes could be achieved in haloamide complexes.

halogen-dependent photochemistry of Mn^{III} haloamides, which reveals the decisive impact of N–Cl (i.e., **13a**) versus N–I (i.e., **13e**) identity of differentiating Mn–N cleavage (i.e., photoreduction) and N–X cleavage (i.e., photooxidation) pathways.

Synthesis and Characterization

Sequential treatment of porphyrin-supported Mn^{III} chlorides **12** with AgBF₄ and M[NXTsX] (M = Na or K; i.e., haloamine-T) provided access to the corresponding Mn^{III} haloamide complex **13** (Figure 4; for characterization of the intermediate [MnL]BF₄ complexes, see the Supporting Information). The spectroscopic data for iodoamide **13e** is representative of the family of haloamides and is described in detail here; for characterization details of the other haloamide complexes, see the Supporting Information. The ¹H NMR spectrum of **13e** displays three paramagnetically shifted peaks corresponding to the methyl group (13.0 ppm), the aryl C–H bonds of the tosyl group and the meso substituents (8.3 ppm), and the pyrrole protons (−22 ppm; Figure S1). The UV-vis spectrum of **13e** displays absorbances at 383 nm ($\epsilon = 3.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), 479 nm ($\epsilon = 5.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), 585 nm ($\epsilon = 7.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), and 620 nm ($\epsilon = 8.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), which we assign as ligand-to-metal charge-transfer (LMCT), Soret, and Q-bands, respectively, based on comparison to other Mn^{III} porphyrins.^[12b] Based on the ratio of the molar absorptivities of the two Q-bands and the position of the Soret band, the ligand field strength of the *N*-iodoamide ligand is similar to that of chloride (i.e., Mn(TPP)Cl) and the ligand field strength of the haloamide ligands examined here is not sensitive to the identity of the *N*-halogen (Table S1).^[19] Consistent with previous reports of Mn^{III} porphyrin complexes,^[20] both ESI- and APCI-MS experiments provide signals that correspond to [Mn(TPP)]⁺. Raman spectra of complexes **13a** and **13e** are collected in Figure S25.

Consistent with the *S* = 2 ground state typical of Mn^{III} porphyrin complexes, compound **13e** displays a magnetic moment of 4.9 (Evans method, 23 °C) and does not display X-band EPR features at 4 K (2-Me-THF glass).^[19a,21a,25] Due to the lack of X-band EPR features for *S* = 2 compounds, we pursued high-frequency and -field EPR (HF-EPR) spectroscopic characterization of this suite of complexes (for spectra and resonance field versus microwave frequency plots of **13a**, **13d**, and **13e**, see Figures S4–S10). The spectra consist of very broad signals apparently due to the presence of slightly different Mn moieties (two in **13a**, **13d**, and **13e**). Representative HF-EPR spectra recorded at 319 GHz of the MnNXTs- (TPP), X = Cl, Br, I series are illustrated in Figure 5 and the derived spin Hamiltonian parameters (zero field splitting (ZFS): axial (*D*), rhombic (*E*) values, and *g* values) are collected in Table 1.^[26] The present study is the first, to our knowledge, to provide the ZFS parameters of a Mn^{III} tetrapyrrole with a nitrogen-donor axial ligand. The *D* values

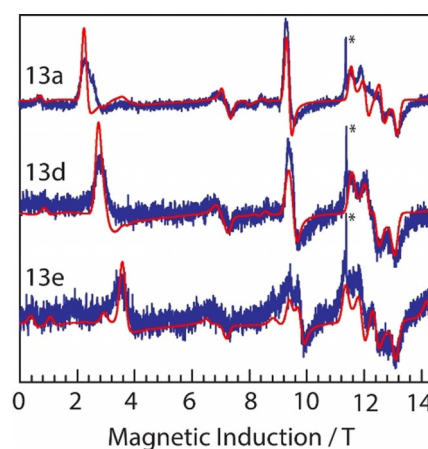


Figure 5. HF-EPR spectra of **13a**, **13d**, and **13e** collected at 319 GHz and 10 K. Blue: experimental; red: simulated with parameters given in Table 1. The asterisk indicates an impurity (organic or light-atom radical) signal at *g* = 2.003.

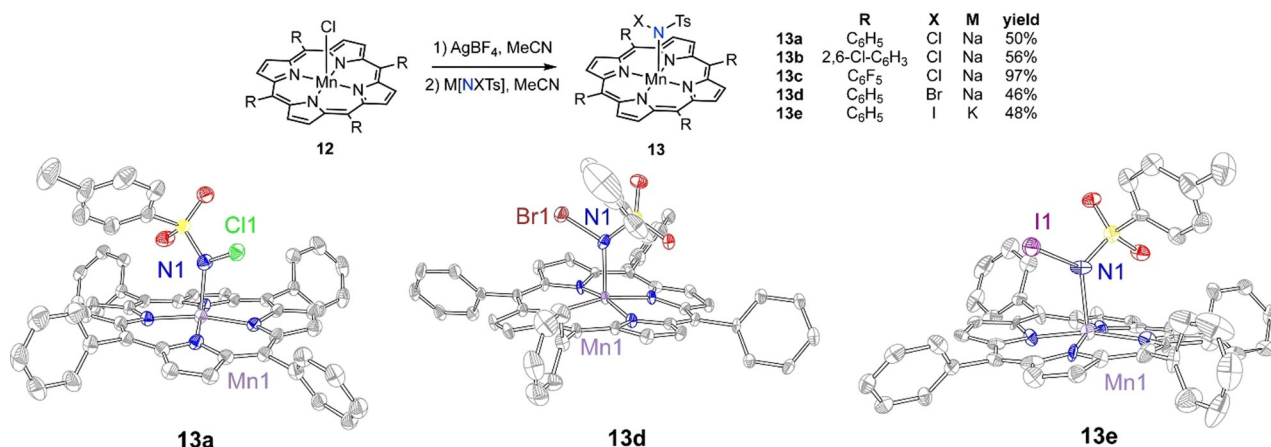


Figure 4. Top: General synthetic strategy for the Mn^{III} *N*-haloamide complexes **13**. Bottom: Displacement ellipsoid plots of the Mn *N*-haloamides **13**. H-atoms and solvent molecules have been omitted for clarity. Ellipsoids drawn at 50% probability. Selected bond lengths (Å): **13a**, N–Cl = 1.745(3); **13d**, N–Br = 1.884(6); **13e**, N–I = 2.056(7).

Table 1: Comparison of HFEPR data for compounds **13a**, **13d**, and **13e** with other axially coordinated Mn^{III} tetrapyrrole analogues. *E* is given in the same sign as *D* (TPFC = 5,10,15-tris(pentafluorophenyl)corrole trianion; TBP₈Cz = 2,3,7,8,12,13,17,18-octa(4-*tert*-butylphenyl)corrolazine).

	<i>D</i> [cm ⁻¹]	<i>E</i> [cm ⁻¹]	<i>E/D</i>	<i>g_x</i> , <i>g_y</i> , <i>g_z</i>
13a	−2.881	−0.095	0.033	1.994, 1.984, 1.979
13d	−2.707	−0.134	0.050	1.990, 1.995, 1.990
13e	−2.460	−0.243	0.099	2.004, 1.990, 1.991
Mn(TPP)Cl ^[21]	−2.290	≈ 0	0	1.98, 1.98, 2.00
Mn(TPP)Br·CDCl ₃ ^[22]	−1.091	−0.087	0.080	1.996, 1.985, 1.994
Mn(TPP)I·CDCl ₃ ^[22]	1.30	0.010	0.008	1.965, 1.971, 1.930
Mn(TPFC)(OPPh ₃) ^[23]	−2.69	−0.030	0.011	1.994, 1.994, 1.980
Mn(TBP ₈ Cz)(HOMe) ^[24]	−2.60	−0.015	0.006	2.00 (isotropic)

of the compounds measured here are similar to each other and to other Mn^{III} tetrapyrroles (i.e., $D = -2.5 \pm 0.5 \text{ cm}^{-1}$) bearing *O*- or *N*-bound axial ligands.^[21,25,27] Substitution of the amido halogen substituent has minimal impact on the *D* value, with *D* becoming slightly less negative from **13a** to **13d** to **13e**. This trend is significantly more dramatic in the corresponding MnX(TPP) series in which the halogen is bound directly to the Mn center.^[22] This observation is a consequence of the extensive spin–orbit coupling of heavier donors.^[28] The rhombicity does show a more significant dependence on the halogen identity, where **13a** is the least rhombic and **13e** is the most. We hypothesize that the high rhombicity value of MnNXTs(TPP) is due to the Ts–N–X apical unit breaking the fourfold symmetry observed in manganese tetrapyrroles, which generally feature rhombicity values close to zero, even in the case of corroles/corrolazines, which lack the true fourfold symmetry of the porphyrin macrocycle.^[21–25,27] Qualitatively, Mn–N π -bonding from N p_x (filled N lone pair) to Mn d_{xz} (half-filled), but not correspondingly from N p_y to Mn d_{yz} would distinguish the in-plane *x* and *y* directions (the principal ZFS direction is along *z*, normal to the porphyrin plane).^[21a]

X-ray quality crystals of each of the Mn^{III} haloamide complexes were obtained by cooling concentrated acetonitrile solutions to -35°C ; solid-state structures of **13** are collected in Figure 4 and relevant refinement data are collected in Tables S6–S10. The Mn^{III} center in **13e** is five-coordinate. The Mn ion lies 0.271 Å above the N₄ plane, and the *N*-iodoamide ligand occupies one of the axial coordination sites. The haloamide nitrogen is approximately trigonal planar, with Mn–N–I = 119.1(3)°, Mn–N–S = 128.8(4)°, and S–N–I = 112.1(4)°. The bond metrics of **13a–d** are consistent with those described for **13e** with two exceptions: 1) The N–X bond length varies predictably as a function of halogen identity (i.e., the N–Cl distance in **13a** is 1.745(3) Å, the N–Br distance in **13d** is 1.884(6) Å, and the N–I distance in **13e** is 2.056(7) Å) and 2) the Mn center in **13b** is six-coordinate with an MeCN ligand in the final coordination site, which results in elongation of Mn–N(1) in **13b** (2.252(4) Å) as compared to **13a** (2.070(3) Å) or **13c** (2.112(7) Å). Of note, complexes **13d** and **13e** are the first crystallographically characterized *N*-bromoamide and *N*-iodoamide complexes of a transition metal, respectively. For comparison of the metrical parameters of **13** with known chloroamides, see Table S13.

Photolysis of Mn^{III} Haloamides

Photolysis ($\lambda > 335 \text{ nm}$) of an optically dilute solution of **13e** (4:1 MeCN/THF solution) affords Mn^{II} complex **15**. UV-vis spectra collected periodically during the photolysis of a dilute solution of **13e** are characterized by well-anchored isosbestic points at 295, 408, 460, 514, 584, and 589 nm, which indicates the lack of steady-state intermediates (Figure 6). The final spectrum overlays with that of Mn^{II}TPP

(**15**), which was independently prepared by treatment of **12** with NaBH₄ (Figure S11). ESI-MS analysis of the photolysis reaction mixture indicates the presence of sulfonamide **14**, the product of formal nitrene transfer to the α -C–H bond of THF. Preparative-scale photolysis resulted in the isolation of sulfonamide **14** in 44% yield. The mass balance of the haloamide ligand is TsNH₂ (56% yield). Preparative scale photolyses of **13** result in isolation of Mn(TPP)X, which we hypothesize results from oxidation of **15** by HX equivalents generated during photolysis (via H-atom abstraction from solvent).

The wavelength dependence of the observed photochemistry of **13e** was evaluated using 335 nm, 400 nm, and 495 nm long-pass filters. Only the 335 nm filter resulted in the spectral evolution illustrated in Figure 6a; no photoconversion was observed with a 400 or 495 nm long pass filter during the time scale of the experiment. However, prolonged photolysis (5 days) of **13e** with a 400 nm long pass filter yielded aminated THF (**14**) (40%, Table S2). These data are con-

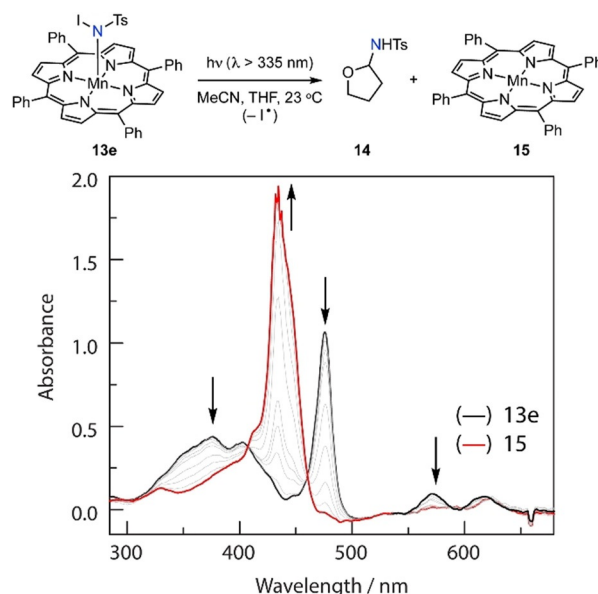


Figure 6. Photolysis ($\lambda > 335 \text{ nm}$) of **13e** affords sulfonamide **14** and Mn^{II} complex **15**. UV-vis spectra obtained periodically during the photolysis of **13e** display well-anchored isosbestic points at 295, 408, 460, 514, 584, and 589 nm, which indicate the lack of steady-state intermediates during the conversion of **13e** into **15**.

sistent with photochemistry arising from excitation of the LMCT band at 383 nm. Similar observations were reported by Suslick, namely that excitation of the analogous LMCT in Mn nitrate complexes was critical to accessing the corresponding Mn oxo complexes.^[13b]

Complex **13e** participates in nitrene transfer photochemistry with a variety of substrates that are commonly encountered in Mn-catalyzed nitrene transfer chemistry (Figure 7).

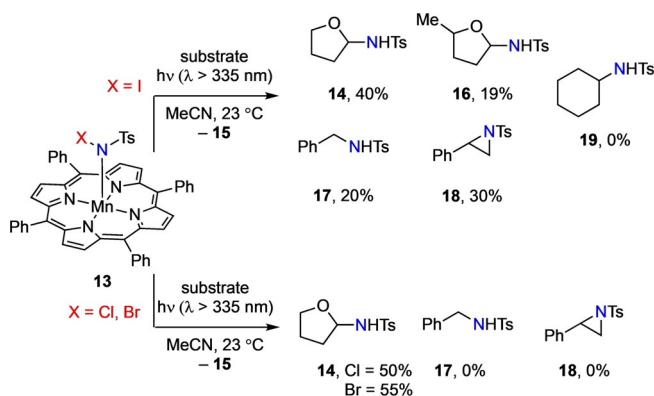


Figure 7. Nitrene transfer photochemistry of *N*-iodoamide complex **13e** with various C–H bonds and olefinic substrates. All yields are determined by ¹H NMR analysis with an internal standard of mesitylene. The formation of TsNH₂ accounts for the mass balance of nitrogen in these reactions.

Photolysis of a MeCN solution of **13e** ($\lambda > 335$ nm) in the presence of 2-Me-THF results in sulfonamide **16** (19% yield), the product of formal nitrene insertion into the less hindered α -C–H bond. To probe the C–H bond strength requirement for amination, we examined the photochemical amination of toluene (C–H bond dissociation energy (BDE) = 89.7 kcal mol^{−1}^[29]) and cyclohexane (C–H BDE = 99.5 kcal mol^{−1}^[30]): Toluene underwent benzylic amination to afford compound **17** in 20% yield; cyclohexane did not participate in detectable amination chemistry. Photolysis of **13e** in the presence of styrene results in aziridine **18** in 30% yield. In all cases, the mass balance is accounted for by TsNH₂ and transfer of the NTs fragment requires photochemical activation: Thermolysis of **13e** in the presence of these substrates results in the formation of **15** and TsNH₂.

Haloamide complexes **13a–13d** also participate in photochemical amination of THF. Photolysis ($\lambda > 335$ nm) of a 4:1 MeCN/THF solution of **13a** afforded sulfonamide **14** in a 50% yield. Similar reactivity was observed for **13b**, **13c**, and **13d** (55, 70, and 63% yield of **14**, respectively). In contrast to iodoamide **13e**, photolysis of **13a–13d** in the presence of either toluene or styrene does not result in the products of nitrene transfer.

Determination of Kinetic Isotope Effects (KIEs)

To gain insight into the mechanism of C–H amination, we measured the deuterium kinetic isotope effect ($k_{\text{H}}/k_{\text{D}}$) for THF amination. Experimentally, solutions of photoprecursors

13 were photolyzed in a 1:1 solution of THF/[D₈]THF and the $k_{\text{H}}/k_{\text{D}}$ was determined by integration of the ESI-MS signals for **14** and **14-d₇**. Photolysis of a solution of **13e** at 23 °C afforded a $k_{\text{H}}/k_{\text{D}}$ = 18(3). For comparison, photolysis of **13a** in a 1:1 THF/[D₈]THF solution afforded a $k_{\text{H}}/k_{\text{D}}$ = 6(1).

Cryogenic Photolysis

Low-Temperature Photolysis of N-Chloroamide 13a. To evaluate the primary photoproducts obtained from the described *N*-haloamide complexes, we pursued low-temperature photolyses of these compounds in frozen solvent matrices. Photolysis of a 2-Me-THF glass of **13a** at 77 K resulted in the evolution of two new peaks in the UV-vis spectrum at 427 and 439 nm (Figure 8a). These peaks are well matched to spectral features of Mn^{II} complex **15**, which could be generated by photoreduction of **13a** via Mn–N homolysis (for comparison of the UV-vis spectrum following photolysis at 77 K with the spectrum of independently synthesized compound **15**, see Figure S24). To further confirm that the photolysis of **13a** generates Mn^{II}(TPP), we measured the X-band EPR spectrum at 4 K and 9.35 GHz following irradiation of a 2-Me-THF glass of **13a** at 77 K (Figure 8b). Mn^{III} complex **13a** does not display an X-band EPR spectrum. Following photolysis, the measured spectrum exhibits features at g_{\perp} = 6 and g_{\parallel} = 2, which are consistent with those of independently prepared Mn^{II} complex **15** and are as expected for an axial $S = 5/2$ system with $D \gg h\nu$.^[31] The differences in peak shape shown in Figure 8b are due to differential axial ligation. Compound **15** is formed by photocleavage of the Mn–N bond and thus has no axial ligand, whereas independently synthesized **15** has an axial THF ligand.^[31b] The observed EPR features were insensitive to the photolysis matrix: Photolysis of a solvent-free thin film of **13a** resulted in the evolution of an EPR spectrum of **15** (Figure S14).

Low Temperature Photolysis of N-Iodoamide 13e. Photolysis of a 2-Me-THF glass of **13e** at 77 K results in the evolution of a new peak in the UV-vis spectrum at 441 nm, which is distinct from the spectrum observed from photolysis of **13a** (Figure 9a). The X-band EPR spectrum of this sample measured at 4 K and 9.35 GHz (Figure 9b) is significantly richer than that from the photolysis of **13a** (Figure 8b). Features across the entire field range are observed, corresponding to $g = 0.8, 1.2, 1.5, 2.0, 3.5$, and 5.0. Such an EPR spectrum is inconsistent with either $S = 3/2$ or $5/2$ with $|D| \gg h\nu$. Rather, it can be simulated as an $S = 5/2$ complex with relatively small zfs ($|D| = 0.18$ cm^{−1} (5.4 GHz) and $|E| = 0.0037$ cm^{−1}; $|E/D| = 0.020$).^[32,33] The spectral features of Mn^{II} complex **15** are not observed in the spectrum obtained following photolysis of **13e**, nor are features expected of a potential Mn^{IV} complex with simple X-type axial ligands or of free triplet tosyl nitrene.^[34]

Analysis of the temperature dependence of the EPR spectrum of **20** supports a high-spin configuration (i.e., $S = 5/2$). Warming the sample from 4 K to 77 K results in the disappearance of the rich spectral features; only a signal at $g = 2.0$ is observed, which we hypothesize is from an organic radical generated in the photolysis. Subsequent re-cooling of

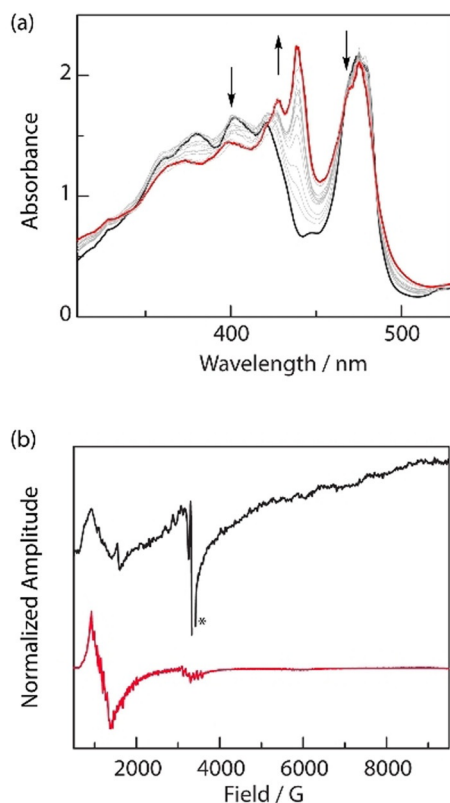
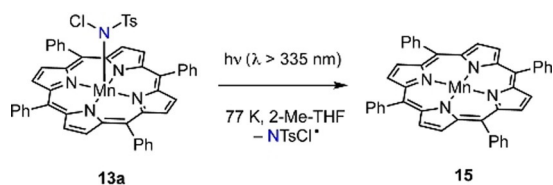


Figure 8. Low-temperature (77 K) photolysis of Mn(TPP)(NCITs) (**13a**) results in photoreduction to generate Mn^{II} complex **15**. (a) UV-vis spectra obtained periodically during the photolysis of **13a** at 77 K display well-anchored isosbestic points at 295, 408, 460, 514, 584, and 589 nm. The peaks that grow in at 427 and 439 nm are attributed to Mn^{II} complex **15** (a concentrated sample was utilized in this photolysis experiment, which resulted in detector saturation at 474 nm). (b) X-band EPR spectra following photolysis of **13a** (black) and of Mn^{II}(TPP) (**15**) (red). *The peak at $g=2.0$ has been truncated for clarity.

the sample to 4 K results in the reappearance of the spectral features illustrated in Figure 9b (Figure S15). These observations confirm that the loss of spectral features upon warming to 77 K is due to spin–spin relaxation and not sample degradation.

Warming a sample of **20** generated in a 1:1 THF/[D₈]THF mixture at 77 K to ambient temperature affords amination product **14** with $k_H/k_D = 18$, which indicates that low-temperature and room-temperature photolyses generate the same reactive intermediate.

Computational Analysis

Density functional theory (DFT) optimization of the geometry of compounds **13a**, **13d**, and **13e** has been pursued

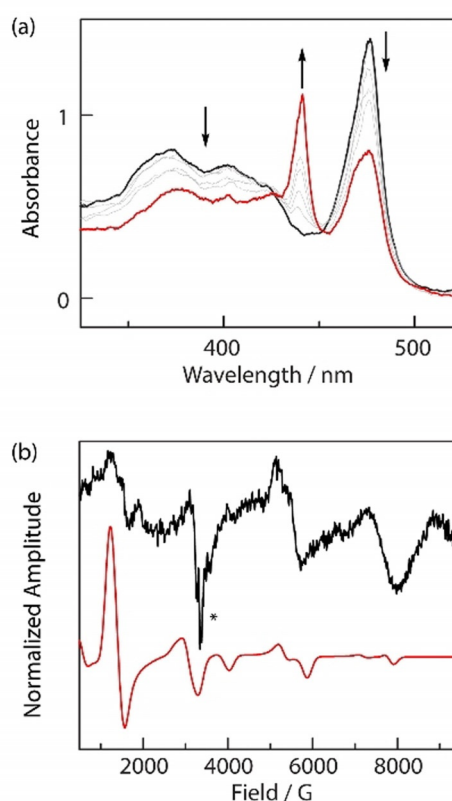
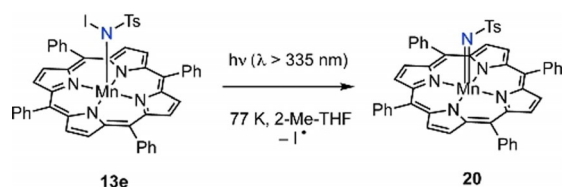


Figure 9. Low-temperature (77 K) photolysis of Mn(TPP)(NITs) (**13e**) results in N–I cleavage to generate Mn^{IV} nitrenoid complex **20**. (a) UV-vis spectra obtained periodically during the photolysis of **13e** at 77 K display well-anchored isosbestic points at 429, 449, 511 nm. (b) X-band EPR spectra following photolysis of a 2-Me-THF glass of **13e** at 77 K (black). This spectrum was simulated with $S=5/2$ spin Hamiltonian parameters $D=0.18 \text{ cm}^{-1}$ and $E=0.0037 \text{ cm}^{-1}$, $g=2.00$ (red). *The peak at $g=2.0$ has been truncated for clarity.

as singlet, triplet, and quintet electronic configurations (see the Supporting Information for computational details). The singlet and triplet configurations are higher in energy than the quintet by 35 kcal mol^{−1} and 17 kcal mol^{−1}, respectively (Table S23). For comparison of optimized structures with crystallographically determined structures, see Tables S20–S22. Optimization of **20** indicates that doublet, quartet, sextet, and octet states are similar in energy, with the quartet being the lowest in energy and the sextet and doublet states 2.6 kcal mol^{−1} and 3.9 kcal mol^{−1} higher, respectively (Table S24). The similarity of the various spin states of **20** suggests that accurate description of this species requires a multireference ground state.

Ground-state reaction thermodynamics were calculated for Mn–N and N–X cleavage from compounds **13a**, **13d**, and **13e** (Table S25). For **13a**, Mn–N cleavage is preferred to N–Cl cleavage while for **13e** these pathways are approximately

isoenergetic. These results are consistent with the expectation that N–X bond strength decreases for the heavier halogens,^[35] computed N–X BDEs for complexes **13** (Table S27), and the experimental observation of Mn–N cleavage for **13a** and N–I cleavage for **13e**.

Discussion

Development of photochemical strategies to generate metal nitrenoid species promises to provide opportunities to study reactive intermediates that display fleeting lifetimes. Organic azide ligands have been recognized as potential photoprecursors to metal nitrenes, but few kinetically stable transition metal adducts of these ligands have been characterized.^[15] We have been attracted to photoactivation of N–X bonds within haloamide ligands as a potentially generalizable strategy to photochemically generate nitrene fragments within the primary coordination sphere of transition metal ions. This strategy is motivated by the ubiquity of N–X photoactivation in the organic chemistry of haloamines^[18] and by analogy to the oxo photochemistry of metal oxanion complexes.^[12,13] Unlike the organic chemistry of *N*-haloamines, however, the synthetic chemistry and photoactivity of *N*-haloamide complexes is almost completely undeveloped.

Application of *N*-haloamide ligands in nitrene photochemistry requires predictable and selective N–X activation chemistry. In the context of Mn^{III} haloamide photochemistry, homolytic N–X bond cleavage would afford a Mn^{IV} nitrenoid while heterolytic N–X bond activation would result in Mn^V nitrenoids (Figure 10). In addition to these potential N–X activation modes, activation of the Mn–N bonds could give rise to Mn^{II} and amidyl radicals.^[13c,36] Analogous O–X homolysis and heterolysis as well as M–O homolysis pathways have been documented in the oxo photochemistry of metal oxanion complexes.^[12,13]

The Mn nitrenoid fragment in **20** is potentially redox non-innocent; thus the formal oxidation states of the Mn nitrenoids in the forgoing discussion are based on counting the nitrenoid fragment as a 2- ligand (i.e., imido nomenclature). In the context of a formally Mn^{IV} imido complex, *N*-centered non-innocence could result in a species more appropriately described as either a Mn^{III} adduct of an iminyl radical anion (RN^{•−}, *S* = 1/2) or as a Mn^{II} adduct of a singlet nitrene ligand (*S* = 0).^[37] Applying the Enemark–Feltham

nomenclature,^[38] the Mn^{IV} imide would be described as {MnNR}⁷.

We have prepared a family of Mn^{III} *N*-haloamides, Mn(TPP)(NXTs), as potential photoprecursors to reactive high-valent Mn nitrenoids relevant in Mn tetrapyrrole-catalyzed nitrene transfer (Figure 1). Solution-phase and solid-state characterization indicate the family of prepared complexes are *S* = 2 Mn^{III} species. UV-vis spectroscopic measurements indicate that the donor strength of the *N*-haloamides is similar to that of chloride and is not meaningfully impacted by the identity of the *N*-halogen atom. HFEPR indicates that the haloamide complexes are representative of Mn tetrapyrroles with light-atom axial donors, with enhanced rhombicity that may be due to anisotropic Mn–N π -bonding.

Photolysis of each of the prepared *N*-haloamide complexes in the presence of weak C–H bond donors, such as THF, results in formal nitrene transfer chemistry. Given previous demonstrations of C–H amination via amidyl radical intermediates,^[39] the observation of amination products is insufficient to differentiate between the potential photo-generation of a high-valent nitrenoid or *N*-centered radical intermediates. Halogen-dependent photochemistry is observed with other substrates that are commonly encountered in nitrene transfer chemistry. Whereas *N*-chloroamide **13a** does not participate in photochemical aziridination of styrenes, *N*-iodoamide **13e** does undergo photochemical aziridination. These observations suggest that reactive nitrogen fragments generated from **13a** and **13e** differ; if both haloamides underwent similar photoactivation, one would expect that the resultant reactive species would display homologous substrate functionalization activity.

Analysis of the kinetic isotope effects for C–H functionalization demonstrates the decisive role of the halogen substituent on the resultant photochemistry and provides a direct reporter on the nature of the C–H cleavage event. Amination of THF by photolysis of *N*-chloroamide **13a** proceeds with $k_H/k_D = 6(1)$, which is consistent with values for H-atom abstraction reactions at *N*-centered radicals.^[40] In contrast, amination of THF by photolysis of *N*-iodoamide **13e** proceeds with $k_H/k_D = 18(3)$. This large k_H/k_D value exceeds the classical limit for H-atom transfer reactions between light atoms and is consistent with the large KIEs that are often encountered for amination via metal nitrenoids.^[41]

Cryogenic photolysis provides both the opportunity to directly evaluate the course of the described photoreactions and evidence for the decisive impact of halogen identity on the resultant reactive nitrogen species. Both UV-vis and EPR spectroscopies indicate that the primary photoproduct obtained from chloroamide **13a** is Mn^{II} complex **15**. The Mn–N homolysis that would generate complex **13** would also afford an amidyl radical intermediate, which would give rise to the observed amination products. In contrast, photolysis of iodoamide **13e** affords Mn^{IV} nitrenoid **20**, the product expected of homolytic activation of the N–I bond of **13e**. Experimental data is consistent with the formation of an *S* = 5/2 species (i.e., an Mn^{III} iminyl radical complex). The Soret band of **20** (442 nm) is distinct from reported porphyrin-supported Mn^{IV} oxo compounds (420 nm), which are all *S* = 3/

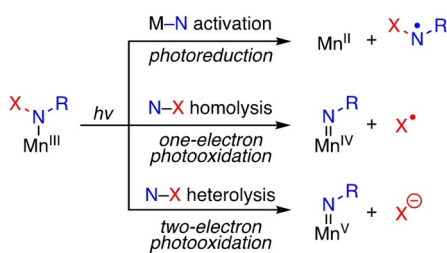


Figure 10. Summary of potential photoactivation pathways for Mn^{III} *N*-haloamide complexes.

2 (Table S5).^[12b,42] Additionally, the similarity of the UV-vis spectra of **15** and **20** suggests that **20** is a $S=5/2$ system (Figure S23). DFT analysis of the potential spin states of **20** suggests multireference contributions to the electronic ground state. The observed preference for Mn–N activation in **13a** and for N–I activation in **13e** is consistent with the relative N–Cl and N–I bond strengths and with computed ground-state thermodynamics for Mn–N and N–X cleavage reactions. These results highlight the ability to control the course of the photoreaction by careful design of the photocleavable ligands.

Conclusion

Synthesis and characterization of reactive intermediates capable of C–H functionalization reactions is central to the rational development of new selective and efficient catalysts. Synthetic photochemistry provides a platform to generate reactive intermediates under conditions in which they can be kinetically trapped, for example by providing a synthetic strategy to generate these species under cryogenic conditions. Application of synthetic photochemistry requires the availability of appropriate photoprecursor molecules and specifically access to photolabile ligands that exhibit predictable photoactivation modes. Here we have advanced *N*-haloamides as photolabile ligands in the synthesis of Mn nitrenoids. Isolation of homologous Mn^{III} complexes featuring *N*-chloro-, *N*-bromo-, and *N*-iodoamide ligands provided the opportunity to observe the decisive impact of the halogen substituent on the observed photochemistry. Whereas the Mn^{III} chloroamide complex undergoes photoreduction via direct homolytic Mn–N activation, the corresponding Mn^{III} iodoamide undergoes N–I activation to unveil a reactive Mn nitrenoid that participates in both C–H amination and olefin aziridination chemistry. A combination of low-temperature spectroscopy and analysis of C–H functionalization kinetic isotope effects indicates the critical photochemical difference between *N*-chloro- and *N*-iodoamide ligands. These observations mirror the competition between ligand-centered photoactivation chemistry and photoreduction reactions that are often encountered in the corresponding metal nitride and metal oxo photochemistries. The findings described here begin to delineate the design parameters needed to elicit ligand-centered bond activation to generate metal nitrenoids. We anticipate the development of general strategies in the synthetic photochemistry of metal nitrenoids will expand access to reactive nitrenoids relevant to catalysis, and we are actively working to expand the generality of the haloamide strategies described here.

Acknowledgements

The authors acknowledge the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Catalysis Program (DE-SC0018977), the Welch Foundation (A-1907), and an Alfred P. Sloan Fellowship to DCP for financial support. A portion of this work was performed at the

National High Magnetic Field Laboratory, which is supported by NSF Cooperative Agreement DMR-1644779 and the State of Florida. Crystal structures of **13a**, **13b**, and **13c** were collected at NSF's ChemMatCARS Sector 15, which is principally supported by the Divisions of Chemistry (CHE) and Materials Research (DMR), NSF, under Grant NSF/CHE-1834750. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. DOE Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract DE-AC02-06CH11357.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: C–H Amination · Group Transfer Catalysis · Metal Nitrenes · Photochemistry · Reactive Intermediates

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Manuscript received: June 22, 2021

Accepted manuscript online: October 18, 2021

Version of record online: November 16, 2021