ORGANOMETALLICS

Halogen Photoelimination from Monomeric Nickel(III) Complexes Enabled by the Secondary Coordination Sphere

Seung Jun Hwang,[†] Bryce L. Anderson,[†] David C. Powers, Andrew G. Maher, Ryan G. Hadt, and Daniel G. Nocera*

Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138, United States

Supporting Information

ABSTRACT: Endothermic halogen elimination reactions, in which molecular halogen photoproducts are generated in the absence of chemical traps, are rare. Inspired by the proclivity of mononuclear Ni(III) complexes to participate in challenging bond-forming reactions in organometallic chemistry, we targeted Ni(III) trihalide complexes as platforms to explore halogen photoelimination. A suite of Ni(III) trihalide complexes supported by bidentate phosphine ligands has been synthesized and characterized. Multinuclear NMR, EPR, and



electronic absorption spectroscopies, as well as single-crystal X-ray diffraction, have been utilized to characterize this suite of complexes as distorted square pyramidal, S = 1/2 mononuclear Ni(III) complexes. All complexes participate in clean halogen photoelimination in solution and in the solid state. Evolved halogen has been characterized by mass spectrometry and quantified chemically. Energy storage via halogen elimination was established by solution-phase calorimetry measurements; in all cases, halogen elimination is substantially endothermic. Time-resolved photochemical experiments have revealed a relatively long-lived photointermediate, which we assign to be a Ni(II) complex in which the photoextruded chlorine radical interacts with a ligand-based aryl group. Computational studies suggest that the observed intermediate arises from a dissociative LMCT excited state. The participation of secondary coordination sphere interactions to suppress back-reactions is an attractive design element in the development of energy-storing halogen photoelimination involving first-row transition metal complexes.

INTRODUCTION

The small-molecule activation reactions that lie at the heart of energy storage and conversion, such as H₂ and H₂O oxidations and H⁺, O₂, and CO₂ reductions, are all multielectron/ multiproton transformations. Development of catalysts to effectively mediate these energy conversion transformations relies on the careful choreography of proton and electron delivery.^{1,2} Examples abound in both biological and synthetic catalysis of secondary coordination sphere effects that synchronize the electron and proton. Biological H₂ oxidation in Fe-only hydrogenase is accomplished via cooperation of secondcoordination-sphere bases, which enforce selective heterolytic cleavage of H₂.³⁻⁵ Similarly, installation of biomimetic proton relays in the secondary coordination sphere of transition metal complexes has emerged as a powerfully enabling design element for the development of selective catalysts based on earthabundant first-row transition elements.⁶ Introduction of a basic functionality, as either pendant carboxylates (i.e., hangman porphyrin 1)^{7–9} or tertiary amines (i.e., hydrogenase mimic 2),^{10,11} in the secondary coordination sphere of electrocatalysts allows controllable coupling of proton and electron delivery to substrates during electrocatalysis. This strategy has enabled the development of O_2 (Figure 1, 1) and H^+ (Figure 1, 1 and 2) reduction reactions. H-bonding from basic groups in the secondary coordination sphere has also been exploited in



Figure 1. Functionality in the secondary coordination sphere that has been useful for promoting multielectron catalysis and stabilization of energetic intermediates.

stoichiometric small-molecule reactions to generate isolable metal oxido complexes, such as 6 (Figure 1, 3).^{12,13}

Against this backdrop, HX-splitting photochemistry (X = Cl, Br) has been advanced as an approach to solar-to-fuels conversion in which proton reduction is coupled to halide oxidation to provide carbon-neutral, closed energy conversion cycles.^{14–16} Halogen photoelimination reactions are multielectron chemical transformations in which two electrons must be simultaneously managed in the formation of X–X bonds;

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this bond-forming transformation represents the energy-storing step in HX-splitting cycles. Whereas selective two-electron halogen elimination reactions have been realized for 4d and 5d metal complexes^{17–26} and some main-group compounds,^{27,28} a similar chemistry is underdeveloped for earth-abundant 3d metal complexes.^{29–31} The inherently shorter excited-state life-times of 3d metal complexes, as well as their attendant proclivity to participate in one-electron photoredox reactions, contribute to the challenges that must be overcome to achieve energy storage via halogen elimination from first-row complexes.^{32–34}

We have turned our attention to energy-storing HX photochemistry that is driven by first-row transition metal complexes under the rubric of two design principles. First, we have targeted mononuclear Ni(III) complexes based on the seminal work of Hillhouse that has demonstrated the selective twoelectron elimination of C-heteroatom bonds from high oxidation state Ni complexes (Figure 2).^{35–41} C-N and C-O



Figure 2. Oxidatively induced C–N and C–O reductive elimination reactions from Ni(II) amide and alkoxide complexes pioneered by Hillhouse. The reactions are proposed to proceed via single-electron oxidation to generate Ni(III) complexes followed by reductive elimination.

reductive elimination reactions are sluggish from Ni(II) complexes (i.e., 4 to 6), but become facile upon one-electron oxidation to Ni(III) (5) via single electron transfer to an external oxidant. Given the short excited-state lifetimes of first-row complexes, we reasoned that their generation by MLCT excitation would be insufficient to drive the targeted chemistry. Accordingly, we turned our attention to installing Ni(III) into the ground state of the putative photocatalyst. Second, owing to our success in oxygen- and hydrogen-based chemical transformation, we sought to utilize secondary coordination sphere effects to enforce selective halogen elimination from complexes with inherently short excited-state lifetimes to circumvent the exothermic back-reaction.



Figure 3. Photoextrusion from Ni(III) trichloride 7a proceeds via initial chlorine radical extrusion, which is stabilized by an arene-to-chlorine-atom charge transfer interaction (8a). Subsequent evolution of chlorine affords Ni(II) complex NiCl₂dppe (9a).

We report here a suite of Ni(III) trihalide complexes (Chart 1) supported by bidentate phosphine ligands, NiX₃(LL) (LL = bidentate phosphine), that engage in halogen elimination photoreactions both in solution and in the solid state. Timeresolved photochemical studies have identified halogen atom adducts of ligand-based aromatic groups to be intermediates in





the elimination reactions (Figure 3). The complexes also participate in high-yielding trap-free halogen elimination, which we have established to be substantially endothermic by solution-phase calorimetry. The excited states responsible for the observed halogen elimination reactions are ligand-to-metal in character, and the ability of these complexes to promote halogen elimination is attributed to the proclivity of the photoeliminating halogen atom to be guided from the primary coordination sphere via a secondary coordination sphere ligand effect arising from an aromatic—halogen interaction.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out in an N2-filled glovebox. Anhydrous solvents were obtained from drying columns and stored over activated molecular sieves.⁴² NiCl₂(dme) (dme = 1,2-dimethoxyethane), NiBr₂(dme), dppb (dppb = bis(diphenylphosphino)benzene), dppey (dppey = *cis*-bis(diphenylphosphino)ethylene), and NiCl₂(dppe) (dppe = 1,2-bis(diphenylphosphino)ethane) were obtained from Strem Chemicals. Bromine, dppe, and dcpe (dcpe = 1,2-bis(dicylohexylphosphino)ethane) were obtained from Sigma-Aldrich. PhICl₂,⁴³ dppe-OMe (dppe-OMe = 1,2-bis(di-4-methoxyphenyl)phosphine)ethane), and dppe-Cl (dppe-Cl = 1,2-bis(di-4chlorophenyl)phosphine)ethane) were prepared according to literature procedures.⁴⁴ Ni(III) complexes (7) and Ni(II) complexes (9) that are discussed herein are enumerated based on the halide (X) and supporting phosphine (LL) ligand: X = Cl, LL = dppe, 7a, 9a; X = Cl, LL = dppe-OMe, 7a-OMe, 9a-OMe; X = Cl, LL = dppe-Cl, 7a-Cl, 9a-Cl; X = Cl, LL = dppey, 7b, 9b; X = Cl, LL = dppb, 7c, 9c; X = Cl, LL = dcpe, 7d, 9d; X = Br, LL = dppe, 7e, 9e; X = Br, LL = dppe-Cl, 7e-Cl, 9e-Cl; X = Br, LL = dppe-OMe, 7e-OMe, 9e-OMe; X = Br, LL = dppev, 7f, 9f; X = Br, LL = dppb, 7g, 9g, Complexes 7a, 45 7b, 45 7c, 45 7f, 45 7g, 45 9a, 46 9a-OMe, 44 9b, 47 9c, 48 9d, 49 9e, 46 9e-OMe, 50 and 9f⁵¹ were prepared according to literature procedures. NMR spectra were recorded at the Harvard University Department of Chemistry and Chemical Biology NMR facility on a Varian Unity/Inova 600 spectrometer operating at 600 MHz for ¹H acquisitions and 162 MHz for ³¹P{¹H} acquisitions. NMR chemical shifts are reported in ppm with the residual solvent resonance as internal standard. ³¹P{¹H} NMR chemical shifts were referenced to an external 85% H₃PO₄ standard. Solution magnetic moments were determined using the Evans method in CH_3CN or CH_2Cl_2 and measured using ¹⁹F NMR (hexafluorobenzene added); diamagnetic corrections were estimated from Pascal constants.⁵² UV-vis spectra were recorded at 293 K in quartz cuvettes on a Spectral Instruments 400 series diode array blanked against the appropriate solvent. EPR spectra were recorded on a Bruker ELEXIS E-500 or E-580 spectrometer equipped with a Bruker ER4122 SHQE-W1 resonator and an Oxford

Instruments ESR 900 cryostat. EPR spectra were simulated using EasySpin 4.5.5 to obtain *g*-values and hyperfine constants. Isotopic abundance was accounted for by averaging the simulated spectra of all naturally occurring isotopes scaled by their natural abundance. The hyperfine coupling constants presented are that of the most abundant isotope.⁵³ The electrochemical experiment was recorded at ambient temperature in a glovebox with a CH Instrument 760D or 730C potentiostat. Cyclic voltammetry of a 1 mM CH₃CN solution of Ni complex 7a was measured with a scan rate of 100 mV/s in the dark (0.1 M $^{n}Bu_4PF_6$ as supporting electrolyte). A glassy carbon working electrode, BASi Ag/AgCl reference, and Pt wire counter electrode were used.

Preparation of Ni(II) Dihalide Complexes (NiX₃(LL)). Ni(II) complexes NiCl₂(dppe-Cl) (9a-Cl), NiBr₂(dppe-Cl) (9e-Cl), and NiBr₂-(dppb) (9g) were prepared by sequential treatment of NiX₂(dme) (X = Cl and Br) with an equimolar amount of the appropriate phosphine in THF, precipitation with pentane, and isolation by vacuum filtration.

Preparation of Ni(III) Trichloride Complexes (NiCl₃(LL)). The following preparation of complex 7a-OMe is representative of other members of this family. In a scintillation vial was added 60 mg (0.093 mmol) of NiCl₂(dppe-OMe) (9a-OMe) followed by 2 mL of CH₃CN. In a separate vial were added 15.3 mg (0.055 mmol, 0.6 equiv) of PhICl₂ and 2 mL of CH₃CN. PhICl₂ was added dropwise to the solution of 9a-OMe, during which time a color change from orange to green was observed. The solution was stirred with the exclusion of light for 5 min at 23 °C, at which time the solvent was removed in vacuo to yield a green solid. The residue was washed with pentane and dried in vacuo to afford 55 mg of the title complex as a green solid (86% yield). EPR (1:1 CH₃CN/PhCH₃) g-value: $g_1 =$ 2.258; $g_2 = 2.169$; $g_3 = 2.017$. $\mu_{\text{eff}} = 2.17 \ \mu\text{B}$. Complex 7a-Cl was prepared analogously: green solid; 81% yield. EPR (1:1 CH₃CN/ PhCH₃) g-value: $g_1 = 2.241$; $g_2 = 2.165$; $g_3 = 2.01$. $\mu_{\text{eff}} = 2.13 \ \mu\text{B}$. Complex NiCl₃(dcpe) (7d) was prepared analogously except CH₂Cl₂ was used as solvent and Et₂O was used to wash: green solid; 60% yield. EPR (1:1 CH₃CN/PhCH₃) g-value: $g_1 = 2.26$; $g_2 = 2.28$; $g_3 = 2.01$. $\mu_{\rm eff} = 2.10 \ \mu \text{B}.$

Preparation of Ni(III) Tribromide Complexes (NiBr₃(LL)). The following preparation of complex 7e-OMe is representative of other members of this family. A sample of NiBr₂(dppe-OMe) (9e-OMe) (60 mg, 0.081 mmol) was dissolved in 2 mL of CCl₄. A solution of 0.194 M Br₂ (206 μ L, 0.041 mmol, 0.5 equiv) in CH₂Cl₂ was added dropwise to give a black solution, which was stirred at 23 °C for 30 min in the dark. The volatiles were removed in vacuo to give the product as a dark brown powder. The residue was washed with pentane and dried in vacuo (80% yield). EPR (1:1 CH₂Cl₂/PhCH₃) *g*-value: *g*₁ = 2.208; *g*₂ = 2.208; *g*₃ = 2.025. μ_{eff} = 1.95 μ B. Complex 7e-Cl was prepared analogously: dark brown solid; 77% yield. EPR (1:1 CH₃CN/PhCH₃) *g*-value: *g*₁ = 2.201; *g*₂ = 2.191; *g*₃ = 2.025. μ_{eff} = 1.90 μ B.

Photochemistry. Steady-state photochemical reactions were performed using a 1000 W high-pressure Hg/Xe arc lamp (Oriel), and the beam was passed through a water-jacketed filter holder containing the appropriate long-pass filter, an iris, and a collimating lens. Samples were photolyzed in a constant-temperature circulating water bath. Photochemical quantum yields (Φ_p) were determined using 370 nm monochromatic light, which was generated with a 370 nm Hg line filter on a 1000 W Hg/Xe arc lamp. Potassium ferrioxalate solution (0.006 M) was used as a chemical actinometer.⁵⁴ The photo flux was determined from the average of actinometric measurements before and after irradiation of the reaction samples. Each $\Phi_{\rm p}$ determination was carried out in triplicate on solutions of the complex in CH₂Cl₂ or CH₃CN with benzene. Nanosecond resolved transient absorption (TA) spectroscopy experiments were performed using a system described previously,⁵⁵ but with an iHR320 spectrometer. The 355 nm laser pulses (8-10 ns at fwhm) used for excitation were generated using the third harmonic of a 10 Hz Nd:YAG pulsed laser. The whitelight continuum was provided by a Xe-arc lamp set to 2.0 ms pulses with 30 A current. A 250 or 1000 nm blaze grating (300 grooves/mm) was used for spectral acquisitions centered below 500 nm and above 500 nm, respectively. For full-spectrum TA acquisitions, the entrance slit was set to 0.16 mm (3.0 nm resolution) and the gate time for the CCD was 100 to 200 ns. For single-wavelength kinetics experiments, the entrance and exit slits were set to 3 nm resolution, and 1.0 kV bias was used for the photomultiplier tube (PMT). PMT outputs were collected and averaged with a 1 GHz oscilloscope (LeCroy 9384CM). The full spectra are averages of 50–200 four-spectrum sequences, and the single-wavelength kinetics traces are averages of 500–1000 acquisitions. CH₃CN solutions of complexes 7a–7d were prepared in 100 mL Schlenk flasks in an N₂-filled glovebox. During TA acquisitions the solutions were flowed without recirculation through a 3 mm diameter, 1 cm path length flow cell (Starna, type 585.2) using a peristaltic pump and positive N₂ pressure.

X-ray Crystallographic Details. Single crystals of 7c were obtained from a CH₂Cl₂ solution layered with toluene. Crystals of 7g were obtained from a CH₂Cl₂/PhCH₃ solution of the complex layered with a small amount of Br2 in CH2Cl2 solution. Diffraction data were collected either on a Bruker three-circle platform goniometer equipped with an Apex II CCD and an Oxford cryostream cooling device (100 K) with radiation from a graphite fine focus sealed tube Mo K α (0.710 73 Å) source or on a vertically mounted Bruker D8 three-circle platform goniometer equipped with an Apex II CCD and an Oxford Diffraction Helijet cooling device (15 K) with synchrotron radiation (0.413 28 Å) supplied to ChemMatCARS located at Advanced Photon Source (APS), Argonne National Laboratory (ANL). Crystals were mounted on a glass fiber pin using Paratone N oil. Data were collected as a series of φ and/or ω scans. Data were integrated using SAINT and scaled with multiscan absorption corrections using SADABS.⁵⁶ The structures were solved by intrinsic phasing using SHELXT (Apex2 program suite v2014.1) and refined against F^2 on all data by full matrix least-squares with SHELXL-97.57 All non-H atoms were refined anisotropically. H atoms were placed at idealized positions and refined using a riding model. Crystal data and refinement statistics are summarized in Table 1, and thermal ellipsoid plots are shown in Figure 4.

Table 1. Crystal Data and Structure Refinement for 7c and 7g

	1	NiCl ₃ (dppb) (7c)	NiBr ₃ (dppb) (7g)				
	formula	$C_{30}H_{24}Cl_3NiP_2$	C _{16.5} H ₁₅ Br _{1.5} Cl ₃ Ni _{0.5} P				
	CCDC no.	1040260	1040259				
	fw, g/mol	611.49	499.83				
	temp, K	100(2)	15(2)				
	cryst syst	monoclinic	monoclinic				
	space group	P2(1)	P2(1)/m				
	a, Å	9.7441(9)	8.7809(4)				
	<i>b,</i> Å	14.730(1)	21.401(1)				
	<i>c,</i> Å	10.2714(9)	10.6362(5)				
	α , deg	90	90				
	β , deg	113.297(2)	113.3720(7)				
	γ, deg	90	90				
	<i>V</i> , A ³	1354.1(2)	1834.8(2)				
	Ζ	2	4				
	R1 ^a	0.0525	0.0187				
	wR2 ^b	0.0861	0.0439				
	$\operatorname{GOF}^{c}(F^{2})$	0.983	1.039				
	R _{int}	0.0678	0.0210				
R	$1 = \sum F_0 - F $	$\left \sum F_{a}\right = b_{wR2} = 0$	$\sum (w(F_0^2 - F_c^2)^2)/$				
$\sum (w(F_o^2)^2)^{1/2}$. ^c GOF = $(\sum w(F_o^2 - F_c^2)^2/(n-p))^{1/2}$ where <i>n</i> is							
ne	ne number of data and <i>n</i> is the number of parameters refined						

X-ray crystal structures of 7c, 7g, 9c, and 9e are available from the Cambridge Crystal Structure Database (1040260, 1040259, 1401868, and 1401864, respectively).

Solution-Phase Calorimetry. Solution-phase calorimetry measurements were carried out using a Thermometric 2225 Precision Solution calorimeter. In the glovebox, a CH₂Cl₂ solution of Ni(II) dichloride was prepared. This solution was transferred to the glass cell of the calorimeter, which was equipped with an ampule-breaking rod.



Figure 4. Thermal ellipsoid plots of Ni(III) complexes 7c and 7g in which solvent molecules and H atoms have been removed for clarity. Ellipsoids are drawn at 50% probability.

A small glass ampule containing $PhICl_2$ was added, sealed, and loaded into the calorimeter. Following temperature equilibration (achieved standard deviation of 2 μ K after 2 h), the reaction was initiated by breaking the ampule and rotating the calorimeter to ensure complete mixing. Electrical calibrations were run before and after breaking the ampule. The enthalpy of chlorination of Ni(II) was determined by subtracting half the enthalpy of chlorination of PhI from the experimentally measured reaction enthalpy. Measured data were corrected for the enthalpy of solution of the solid PhICl₂, which was measured separately. Reported data are the average of three independent measurements.

Computational Details. All DFT calculations were performed using the Gaussian 09, revision D.01, software suite.⁵⁸ For all calculations, the $B3LYP^{59-61}$ hybrid exchange-correlation functional was used in combination with a split basis set (TZVP⁶² for Ni, P, and Br; TZV⁶³ for C and H). Starting geometries for gas-phase optimization were obtained from crystallographic coordinates; frequency calculations were carried out to ensure structures represented energetic minima. Time-dependent DFT (TD-DFT) single-point calculations were carried out on the gas-phase geometry optimized models using the same combination of functional and basis sets. Where used, solvation effects were included using the polarized continuum model (PCM). Ground- and excited-state potential energy surfaces (PESs) for metal-apical halide bond loss were constructed using constrained geometry optimizations coupled to subsequent TD-DFT calculations. Charge decomposition analyses (CDA) were carried out using the AOMix program (revision 6.82).⁶⁴ The degree of phosphine ligand donation was calculated using NiX₃ and phosphine ligands as fragments; the degree of phosphine ligand donation was calculated as the difference in total electron donation (sum of all occupied α and β molecular orbitals) from the phosphine ligand to NiX₃ and backdonation between NiX₃ and the phosphine ligand. Wave function contours were generated using the β -LUMO program.⁶⁵

RESULTS

Synthesis and Characterization of Mononuclear Ni(III) Complexes. Monomeric Ni(II) dihalide complexes were accessed by treatment of Ni(II) halide starting materials (NiX₂(dme) (X = Cl and Br)) with an equimolar amount of the appropriate bidentate phosphine ligand. Thermal ellipsoid plots of Ni(II) complexes 9c and 9e are illustrated in Figures S1 and S2, and crystallographic data are summarized in Table 1. Oxidation of Ni dichloride complexes 9a-9d with PhICl₂ afforded the corresponding monomeric Ni trichloride complexes NiCl₃(dppe) (7a), NiCl₃(dppe-OMe) (7a-OMe), NiCl₃(dppe-Cl) (7a-Cl), NiCl₃(dppey) (7b), NiCl₃(dppb) (7c), and NiCl₃(dcpe) (7d). Using a procedure adapted from Levason,⁴⁵ oxidation of Ni(II)Br₂(LL) complexes was accomplished by treatment with 0.5 equiv of Br₂ in CCl₄ to afford NiBr₃(dppe) (7e), NiBr₃(dppe-OMe) (7e-OMe), NiBr₃(dppe-Cl) (7e-Cl), NiBr₃(dppey) (7f), and NiBr₃(dppb) (7g). Cyclic voltammetry of Ni(III) compound 7a in CH₃CN showed a quasi-reversible wave at 0.40 V vs Fc⁺/Fc assigned to the Ni(II)/Ni(III) couple (Figure S3).

Ni(III) complexes display no ¹H NMR or ³¹P NMR spectra. Evans' method and variable-temperature EPR indicated the complexes are S = 1/2, as expected for mononuclear d⁷ complexes. The EPR spectrum of NiCl₃(dppey) (7b), shown in Figure 5, is exemplary of the series; the EPR spectra of remaining



Figure 5. EPR spectrum of NiCl₃(dppey) (7b) recorded at 8.0 K in 1:1 CH₃CN/toluene glass (-, black) and simulated (- red).

members of the series are shown in Figures S4–S14. The EPR spectra display pseudoaxial doublet signals with $g_{xy} g_y > 2$ and $g_z \approx 2.000$ and a four-line superhyperfine coupling pattern in the g_z direction (Table S3). The superhyperfine coupling is a direct probe of the coupling of the d_z^2 unpaired electron with the nuclear magnetic moment of the apical halide ligand (I = 3/2 for both Br and Cl) and is a measure of the degree of electron delocalization of the unpaired electron along the apical Ni(III)–X bond.⁶⁶ The superhyperfine coupling (A_z) varies depending on the phosphine ligand backbones and arene substituents on the bidentate phosphine ligands; superhyperfine coupling constants are tabulated in Table S3.

Single-crystal X-ray structures of representative Ni(III) complexes were obtained and indicate a distorted square pyramidal geometry about the Ni center (Figure 4), with shorter basal Ni(III)–X bonds and a longer apical Ni(III)–X bond (Table S4). For example, the apical Ni–Cl in complex 7c is 2.287(1) Å, whereas the basal Ni–Cl bonds are 2.224(2) and 2.219(2) Å, respectively.

The electronic absorption spectra of Ni complexes 7c and 9c are shown in Figure 6a; spectra of complexes 7 and 9 are shown in Figures S15–S21. The spectrum of Ni(II) complex 9c is representative of the Ni(II) complexes discussed herein and is dominated by an intense band at 285 nm ($\varepsilon = 2.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) that is flanked by a shoulder at 335 nm ($\varepsilon = 3.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and a much weaker band at 463 nm ($\varepsilon = 1.7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). Oxidation of complex 9c results in a bathochromic shift of the 335 nm absorption feature to 348 nm ($\varepsilon = 5.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) and a slight hypsochromic shift of the 463 nm absorption feature to 440 nm ($\varepsilon = 1.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). In addition, a pronounced absorption at 657 nm



Figure 6. (a) Extinction spectra of complex 7c (-, black) and complex 9c (-, red). (b) Photolysis of a 0.08 mM solution of complex 7c in CH₃CN (λ > 400 nm) at 25 °C.

 $(\varepsilon = 1.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1})$ for complex 7c is notably absent in Ni(II) complex 9c. The profiles of the bromide and chloride Ni(III) complexes are similar, but the former is red-shifted, indicating that the absorption spectra of the nickel halide complexes reported here are largely determined by X \rightarrow Ni(III) charge transfer.

Halogen Photoelimination Chemistry. Irradiation of CH_2Cl_2 solutions of $NiX_3(LL)$ (7) with visible light ($\lambda > 400$ nm) leads to clean conversion to the corresponding reduced $NiX_2(LL)$ (9) as determined by both UV–vis and ${}^{31}P\{{}^{1}H\}$ NMR. Well-anchored isosbestic points are observed in most cases studied (Figures 6b and S15–S21), and no P-containing side-products were observed by ${}^{31}P\{{}^{1}H\}$ NMR (Figures S22–S32). Halogen photoelimination quantum yields (Φ_p) from each of the Ni(III) complexes were measured actinometrically (against potassium ferrioxalate) and are summarized in Table 2.

Table 2. Quantum Yields of NiX₃(LL) Halogen Elimination Photochemistry^{*a*}

LL	NiCl ₃ (LL)	Φ_{p}	NiBr ₃ (LL)	Φ_{p}
dppe	7a	0.764	7e	0.169
dppe-OMe	7a-OMe	0.230	7e-OMe	0.352
dppe-Cl	7a-Cl	0.128	7e-Cl	0.056
dppey	7b	0.960	7 f	0.401
dppb	7c	0.077	7 g	0.047
dcpe	7 d	0.201		
	w/5% C ₆ H ₆ ^b	0.330		
	w/10% C ₆ H ₆ ^b	0.410		
	w/20% C ₆ H ₆ ^b	0.490		
	w/30% C ₆ H ₆ ^b	0.590		
	w/40% C ₆ H ₆ ^b	0.620		

^{*a*}In CH₂Cl₂, λ_{exc} = 370 nm bandpass filter. ^{*b*}In CH₃CN with percent addition of benzene.

The presence of an aromatic group in the second coordination sphere significantly enhances Φ_p . The photochemical quantum yield, Φ_p , for cyclohexyl phosphine complex NiCl₃(dcpe) is $\Phi_{\rm p}(7d) = 20.1\%$, whereas that for the dppe complex is $\Phi_{\rm p}(7\dot{\rm a}) = 76.4\%$ and near unity for the dppey complex 7b. We note that the presence of an aromatic solvent increases the Φ_p of 7d. The addition of benzene to CH₃CN solutions causes Φ_p to increase monotonically until 30% mixtures are attained, after which Φ_p levels off at ~60%. Addition of 30% CCl₄ showed no improvement in the photoefficiency ($\Phi_{\rm p}$ = 20.8%), suggesting that a change in solvent dielectric (ε (C₆H₆) = 2.27 and ε (CCl₄) = 2.24) is not the source of increased quantum yield for CH₃CN/benzene mixtures. A similar change in Φ_p was also observed for the addition of benzene to solutions of NiCl₃(dppb) (7c) (Φ_p = 8% in CH₃CN vs Φ_p = 35% with 30% benzene). Halogen photoelimination from substituted dppe-supported NiX₃(LL) complexes was also examined to probe the effects of the electronic properties of the phosphine without modifying the steric environment about the metal center. The quantum yields for para-OMe and para-Cl substituted dppe derivatives were determined to be 35.0% and 5.6% for 7a-OMe and 7a-Cl, respectively.

Time-Resolved Photochemistry. Figures S33-S42 show the transient absorption full spectra and single-wavelength kinetics of samples containing Ni(III)Cl₃(LL) complexes 7a-cfollowing laser excitation at 355 nm in CH₃CN. For each sample, the earliest achievable TA difference spectrum acquired (time delay = 40-70 ns) is a superposition of the bleach signal of the starting complex, the absorption of the final product, Ni(II)Cl₂(LL), and any transient species present promptly. The single-wavelength kinetics measurements show changes in absorbance with lifetimes ranging from 100 ns to 10 μ s, depending on the complex, indicating the decay of a transient species to the final Ni(II)Cl₂(LL) photoproduct, as confirmed by the full TA spectra taken at 50 μ s. In the case of high quantum yields for halogen elimination, the back-reaction in which the transient decays directly back to the original Ni(III)Cl₃(LL) complex is necessarily negligible. Therefore, to a good approximation subtraction of the 50 μ s TA spectrum from that of the early spectrum yields the absorption spectrum of the transient species. Accordingly, Figure 7a shows the resulting absorption spectrum (blue) for the transient generated from complex 7a. The spectrum of the transient displays an absorption maximum at 366 nm as well as a broad band with a maximum at 530 nm. These spectral features are similar to those of the chlorine atom charge transfer adduct of benzene (Figure 7a, black), generated by either laser flash photolysis or pulse radiolysis.⁶⁷⁻⁷⁰ This suggests that the observed transient intermediate is a Cl atom adduct formed with the ligand aryl group. A similar result is obtained for each $Ni(III)Cl_3(LL)$ complex 7a-c described herein, suggesting that each complex forms a similar transient intermediate.

Further support for the intermediacy of a Cl-atomlaromatic adduct formed along the pathway of the halogen elimination photochemistry of the NiX₃(LL) complexes was obtained by investigating substituted dppe-supported Ni(III) complexes. The λ_{max} of the transient intermediate is perturbed by the presence of substituents on the dppe ligand. As shown in Figure 7b–d, the λ_{max} of the transient spectrum red shifts with donor substitution on the aryl ring (7a, $\lambda_{max} = 530$ nm; 7a-Cl, $\lambda_{max} = 540$ nm; 7a-OMe, $\lambda_{max} = 610$ nm). This observed red shift in the energy of the Cl-atomlaromatic adduct with increasing donor properties of the substituent group is consistent with the spectral trend previously reported for Cl-atomlaromatic adducts as observed by pulse radiolysis experiments.⁶⁷



Figure 7. (a) Comparison between the absorption spectra of the transient species generated by laser flash photolysis of 7a (-, blue) and the chlorine atom charge transfer adduct of benzene (-, black), also generated by laser flash photolysis (data adapted from refs 76 and 70, respectively). The blue spectrum is generated by subtracting the TA difference spectrum of a 0.44 mM solution of 7a, NiCl₃(dppe), in CH₃CN acquired at a 50 μ s time delay from that acquired at a 40 ns time delay (λ_{exc} = 355 nm). The low-energy transient feature shifts to lower energy with the introduction of electron-donating substituents of the phenyl ring of dppe along the series (b) 7a, (c) 7a-Cl, and (d) 7a-OMe.

Given that Φ_p for halogen photoelimination increases with the addition of benzene (Table 2), we examined the TA spectrum of complex 7d in the presence of 30% benzene. The nanosecond-resolved TA spectrum of cyclohexyl phosphine Ni(III) complex 7d exhibits a weak feature with a maximum at 430 nm. The signal intensity of the observed transient intermediate at 430 nm increases substantially with the addition of benzene to the solution and it slightly red shifts; the time evolution of the transient decay remains essentially unchanged.

Solution-Phase Calorimetry. The chlorine photoelimination enthalpies were determined by solution calorimetry, which was accomplished by addition of $PhICl_2$ as a solid to solutions of $Ni(II)Cl_2(LL)$ complexes (9) (Figures S49–S51). The enthalpy for chlorination was obtained based on the equations:

$$P_{Ph_{2}}^{Ph_{2}} \stackrel{(I)}{\underset{CI}{\longrightarrow}} P_{I}^{II} \stackrel{(I)}{\underset{CI}{\longrightarrow}} P_{I}^{II} \stackrel{(I)}{\underset{CH_{2}CI_{2}}{\longrightarrow}} P_{I}^{II} \stackrel{(I)}{\underset{Ph_{2}}{\longrightarrow}} P_{I}^{II} \stackrel{(I)}{\underset{CI}{\longrightarrow}} P_{I}$$

$$PhICl_2 \xrightarrow[CH_2Cl_2]{} PhI + Cl_2 \qquad \Delta H_2$$
 (2)

$$\begin{array}{c} Ph_{2} \\ P_{P_{1}} \\ P_{P_{1}} \\ Ph_{2} \end{array} + 0.5 Cl_{2} \xrightarrow{Cl_{2}} \begin{array}{c} Ph_{2} \\ P_{P_{2}} \\ Ph_{2} \end{array} + 0.5 Cl_{2} \xrightarrow{Cl_{2}} \begin{array}{c} Ph_{2} \\ P_{P_{2}} \\ Ph_{2} \end{array} + 0.5 \Delta H_{3} = \Delta H_{1} - 0.5 \Delta H_{2} \end{array}$$
(3)

The heat of reaction was measured for eq 1. The known heat of reaction of chlorine release from solid PhICl₂ was corrected for the enthalpy of solution of the solid PhICl₂, which was measured separately. The enthalpies of Cl_2 addition to compounds of 9, listed in Table 3, were obtained from eq 3 and are

Table 3. Reaction	Enthalpy for	Chlorination	of Ni(II)
Complexes			

$NiCl_2(LL) + 0.5 Cl_2 \longrightarrow NiCl_3(LL)$		
LL	ΔH (kcal mol ⁻¹)	
dppe dppey dppb dcpe	-23.7 -20.8 -16.7 -7.0	

the average of three independent measurements. All complexes confront endothermic barriers to halogen elimination, with complex 7a possessing significant energy storage capacity for the Cl_2 photoelimination reaction.

Computational Results. DFT geometry optimization of 7f was performed as described in the Experimental Section. The DFT-based ground-state wave function is consistent with a Ni(III) center and an unpaired electron/hole residing in an antibonding Ni d_z^2 /halide p_z orbital, which results in a delocalized metal-to-apical-ligand bonding description as indicated by EPR spectroscopy (e.g., DFT-based spin densities of ~0.81 and ~0.23 for Ni(III) and the apical halide, respectively, for 7f). Additionally, the β -Mayer bond order for this complex is calculated to be ~0.44. To gain insight into the nature of the excited states of the Ni(III) compounds, TD-DFT calculations were performed using the optimized geometry of 7f. The calculated absorption spectrum largely reproduces the spectral features observed in the experimental data (Figure S54 and Table S19). On the basis of the TD-DFT results, the lower energy absorption feature (~575 nm) arises from an apical $Br(p(\pi)) \rightarrow Ni(d_{x^2-y^2})$ LMCT, while the higher energy absorption feature (~400-500 nm) largely consists of intense phenyl ring $\pi \to \operatorname{Ni}(d_{x^2-y^2})$ charge transfer (CT) transitions and weak basal Br(p(π)) $\rightarrow Ni(d_{r^2-\nu^2})$ LMCTs. These assignments are consistent with the photochemical results in that the lower energy CT feature decays upon irradiation, while the higher energy feature persists. Interestingly, an apical $Br(p(\sigma)) \rightarrow$ $Ni(d_{z^2})$ LMCT is predicted within the higher energy absorption envelope (~440 nm, state 7, SI Figure S54 and Table S19). In a molecular orbital picture, transitions to the unoccupied $Ni(d_{z}^{2})$ orbital (i.e., the β -LUMO) eliminate any formal Ni-apical halide bond order and would be expected to result in significant destabilization. We therefore explored the nature of the groundand excited-state PES for elongation of the Ni-apical halide bond for 7f. The CH₂Cl₂-corrected PESs for Ni-Br bond loss are given in Figure 8a, in which the TD-DFT calculated $\sigma \rightarrow \sigma^*$ excited-state energy is plotted as a function of ligand-metal bond distance. Note that this transition involves excitation of a $\beta p_z/d_{z^2}$ bonding electron to the $\beta p_z/d_{z^2}$ antibonding MO, β 156 and β 171 in Figures S52–S53. This LMCT state is clearly dissociative,⁷¹ as can be seen from the TD-DFT groundand excited-state surfaces, resulting in the formation of a oneelectron-reduced Ni(II) S = 0 metal center and a Br radical.

In addition to the PES, we have geometry optimized the resulting Cl-atomlaromatic charge transfer intermediate for both **8a** and **8e**. DFT frequency calculations indicate local energetic minima for both complexes, which is consistent with the TA spectroscopic results and previous reports of the energetics of halogenlarene complexes.⁷² The preferred halogen atomlarene interaction is roughly η_1 (C–X distances of ~2.6 and 2.9 Å for the Cl and Br radicals, respectively). Mulliken spin densities are consistent with significant charge transfer,



Figure 8. (a) CH₂Cl₂-corrected PESs (S = 1/2) of 7f as a function of Ni–Br(ap) bond cleavage. Ground-state energies are given as black squares, and the energies of the $\beta(p\sigma(Br(ap))) \rightarrow \beta(Ni(d(z^2)))$ LMCT excited state (7 in Table S19) are given as red squares. Note that the PES of this $\sigma \rightarrow \sigma^*$ excited state is repulsive and can, upon excitation, result in homolytic cleavage of the Ni(III)–Br bond to a Br radical and a low-spin, S = 0 Ni(II) metal center. (b) Computational results of the charge transfer transitions of NiX₃(dppe) complexes. Gas-phase TD-DFT-calculated absorption spectra for **8a** (black line) and **8e** (red line).

i.e., a closed-shell Ni(II) ion associated with a halide atom (e.g., spin densities of 0.00, 0.66, and 0.74 for Ni(II), Cl, and Br, respectively). The TD-DFT-calculated absorption spectra are given in Figure 8b. The absorption spectra are consistent with experimental observations (Figure S39); there are relatively intense charge transfer features predicted at ~500 and ~550 nm for the Cl and Br adducts, respectively (Figure 8b). The origin of these transitions arises from filled, bonding halide(p)larene-(p(π)) donor orbitals and the β -LUMO, which is an antibonding halide(p)larene(p(π)) molecular orbital (Figure S55 illustrates representative orbital contours).

The amount of total electron donation from the phosphine ligand to Ni(III) has been explored using CDA⁷³ as described in the Experimental Section. The values have been computed for all NiCl₃(LL) and NiBr₃(LL) complexes and are compared to the quantum yields in Figure S56. In general, a positive correlation between Φ_p and electron donation of the phosphine to Ni(III) is observed for NiCl₃(LL) and NiBr₃(LL) complexes.

Increased electron donation to Ni(III) should result in a lower Ni(III/II) reduction potential, which would oppose homolytic cleavage of the Ni(III)–X bond. This difference in donation should be reflected in the solution-phase calorimetry measurements. Indeed, the complexes with larger endothermic barriers to halogen elimination generally have higher quantum yields (e.g., 7a: 23.7 kcal/mol and $\Phi_p = 0.764$ versus 7d: 7.0 kcal/mol and $\Phi_p = 0.201$). Thus, experiment and theory together emphasize the dual contributions of the secondary coordination sphere and the excited-state relaxation/decay pathways in directing the outcome of the photochemistry.

DISCUSSION

The significant oxidizing power of Ni(III) suggested the possibility of developing a halogen elimination photochemistry based on Ni(III) complexes and thus the possibility of developing HX-splitting energy-storing cycles. To this end, we targeted NiX₃(LL) complexes (X = Cl, Br; LL = bidentate phosphine) (7), which are furnished from the oxidation of corresponding Ni(II) square planar NiX₂(LL) complexes (9) with halogen sources. All of the Ni(III) compounds are paramagnetic and possess a square pyramidal primary coordination sphere (Figure 4).

Steady-state photolysis of Ni(III) complexes 7 results in their clean conversion to Ni(II) complexes 9. The solution photochemistry is characterized by tightly anchored isosbestic points, and both UV-vis and ³¹P NMR indicate that the photoelimination proceeds cleanly (Figure 6). All of the complexes demonstrate an efficient halogen elimination photochemistry with quantum yields reaching 96%. In general, Cl₂ photoelimination proceeds at higher quantum efficiencies than Br₂ elimination from homologous complexes (Table 2). The origin of this difference in efficiencies between Cl and Br complexes is unclear and under current investigation. In solution, halogen is trapped by H atom abstraction from solvent, and consequently the photoevolved halogen equivalents are not observed.⁷⁴ The need to trap the eliminated halogen is circumvented when the photochemistry is carried out in the solid state. Solid-state photolysis of thin films of Ni(III) complexes 7 affords the Ni(II) complexes 9 and molecular halogen, which has been isolated, characterized, and quantified. Solution-phase calorimetry indicates that halogen addition to Ni(II) is substantially exothermic (Table 3), and thus photoelimination from NiX₃(LL) compounds represents an energy-storing transformation.

Preliminary transient spectroscopic experiments suggested that halogen photoelimination from NiCl₃(dppe)⁷⁶ was assisted by a secondary coordination sphere effect involving an areneto-chlorine-radical charge transfer intermediate. The generality of the proposed intermediate has now been established for the class of Ni(III)X₃(LL) complexes. TA spectra of the intermediate generated by NiCl₃(LL) photoexcitation display two distinct spectral features: an absorption in the UV region and a broad absorption in the visible region. The photointermediate observed in the TA spectrum of complexes with unsubstituted aryl phosphines exhibits a UV feature at ~350 nm and a band in the visible region at $\lambda_{\rm max}\approx 550$ nm. As shown in Figure 7a, the spectrum of the intermediates is consistent with that of halogenlaryl CT complexes, although it is red-shifted as compared to simple CT adducts owing to electron donation from the phosphine group. The CT absorption band further red shifts with the introduction of donor groups on the phenyl phosphine. The TA intermediate of 7a-Cl and 7a-OMe (Figure 7b and c) shifts to 540 and 600 nm, respectively, consistent with the observed shift of CT bands in arenelBr complexes resulting from aryl substitution with electron donors.

To probe the influence of aromatic residues on the halogen elimination photochemistry, the phenyl groups of the dppe were replaced with cyclohexyl groups. Complex 7d participates in solution-phase halogen elimination but with considerably attenuated quantum yield. A transient intermediate of 7d is observed, but it is weak and considerably blue-shifted from 7a. Halogen atom adducts of cyclohexane are known, and as observed here, the signal is weak and the charge transfer band is blue-shifted ($\lambda_{max} = 435$ nm) due to an increase in ionization

energy of cyclohexane as compared to an aromatic group.⁷⁸ In view of the predicted blue shift coupled with the clean conversion to starting material upon photolysis, we believe that the intermediate observed in the TA spectrum of 7d is also a Cl-radical complex, 8d. Upon the addition of increasing concentrations of benzene, the quantum yield approaches an asymptotic value of \sim 60%. We believe that the enhancement in quantum yield is due to specific radical $-\pi$ interactions, because addition of CCl_4 (similar dielectric to benzene) did not have a measurable influence on Φ_p . When the TA spectrum of complex 7d is measured in the presence of 30% benzene, the spectral feature exhibits a 15 nm bathochromic shift ($\lambda_{max} = 450 \text{ nm}$) and the rate of decay of the intermediate is essentially unchanged (Figures S45–S48). The enhancement in $\Phi_{\rm p}$ upon the addition of benzene without a change in the time evolution of the intermediate suggests that benzene is enhancing the initial dissociation of the chlorine radical from the nickel center, but does not react at a competitive rate with the generated intermediate. The observed decay rate of $\sim 10^5 \text{ s}^{-1}$ is considerably slower than the dissociation rates of $\sim 10^6 \text{ s}^{-1}$ observed for Clbenzene adducts.⁷⁰ Therefore, only a small and undetectable concentration of Cl-benzene complex would be formed during the experiment.

The computed excited state PES of 7f (Figure 8a) provides further support for rapid halide radical elimination. The excitedstate PESs are dissociative in both gas-phase and dielectriccorrected (CH₂Cl₂) calculations, suggesting a rapid dissociation of the halide radical from the photoreduced Ni center.^{79,80} The fate of the halide radical is then dictated by its subsequent backreaction or sequestration by solvent. Utilization of secondary coordination interactions with arene ligands appears to provide an effective pathway to guide the halogen atom out of the primary coordination sphere, thereby preventing the energetically favored back-reaction. For the resulting charge transfer intermediate, the nature of the dominant transitions observed in the TA spectra is predicted by TD-DFT calculations as arene to halide charge transfer, consistent with the spectral shift of the absorptions upon perturbation of the arene ring by the addition of methoxy groups.

Examination of the relationship of Φ_p with both reaction enthalpy and superhyperfine coupling reveals that Φ_p is not necessarily correlated with reaction thermodynamics or M-L covalency (Tables 3 and S3, respectively). However, complexes with larger endothermic barriers do tend to show higher quantum yields (Tables 2 and 3). Similarly, a positive correlation between ligand donor strength (as determined using CDA analyses) and Φ_{p} was observed. Generally, the increased Φ_{p} upon increased endothermicity of ligand loss and electron donation suggests that the important factors governing $\Phi_{\rm p}$ derive from the secondary coordination sphere as well as the relative rates of the various decay pathways of the dissociative electronic excited state. Nonradiative decay pathways have been shown to be sensitive to changes in ligand donor ability^{81,82} and appear to be suppressed in the $NiX_3(LL)$ complexes studied by electron-rich ligands. These contributions may be unraveled by ultrafast time-resolved spectroscopy.

CONCLUSION

Photochemical, transient spectroscopic, and computational results of the NiX₃(LL) complexes point to the formation of a relatively long-lived (3 μ s) transient species derived from a dissociative ligand-to-metal charge transfer (LMCT) excited state. The photodissociative Ni(III)-halogen intermediate is

stabilized by the interaction of the photoeliminating halogen atom with an aryl ring of the secondary coordination sphere. The efficiency of the photoelimination can be directly traced to the stability of the charger transfer halogenlaryl adduct. Interactions with aromatic groups of a coordinating ligand offer a means to suppress rapid back-reactions and increase the quantum yield for halogen elimination, which is the critical step in designing photocatalytic HX splitting cycles.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.5b00568.

³¹P{¹H} NMR analysis of photoreactions, EPR spectra, electrochemical data, steady-state photolysis data, TA spectra, thermograms, computational details including Cartesian coordinates, and complete ref 58 (PDF) Molecular geometries (XYZ)

X-ray crystallographic data (CIF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: dnocera@fas.harvard.edu.

Author Contributions

 $^{\mathsf{T}}S.$ J. Hwang and B. L. Anderson contributed equally to this work.

Notes

The authors declare no competing financial interest.

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