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Photochemistry of 1,5-Cyclooctadiene Platinum Complexes for Photoassisted Chemical Vapor Deposition

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included C_4F_9I . The chain reactions were suppressed in the presence of the radical trap 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), which resulted in measured disappearance quantum yields of $\Phi = 0.037 \pm 0.003$ for (COD)PtMe₂ and $\Phi = 0.44 \pm 0.02$ for (COD)PtMeCl at 334 nm. Weak luminescence was observed for **1a** and **1b**, and it was determined that emissive decay is not competitive with Pt-CH₃ bond homolysis. DFT studies enabled assignment of both SBLCT and MLCT transitions in the



UV/vis spectra of 1a, while 1b only exhibits MLCT transitions. These effects can be attributed to the symmetry of the molecule and its electronic structure.

INTRODUCTION

Metallized organic thin films have many applications ranging from electronics¹⁻³ to energy harvesting^{4,5} to sensing.⁶⁻⁸ Chemical Vapor Deposition (CVD) is an attractive technique for the deposition of metals on organic thin films because it is chemically selective and the thickness of the films can be precisely controlled.⁹⁻¹¹ However, traditional thermal CVD processes usually require high temperatures (≥ 200 °C) which are not compatible with many organic substrates due to their sensitivity to heat.⁹⁻¹³ Photoassisted chemical vapor deposition (PACVD) is an alternative method in which CVD precursors are activated by photochemical reactions. PACVD is thus compatible with thermally sensitive substrates because low substrate temperatures can be used.

In developing model systems to study photoassisted CVD of metals, Ru complexes provided an excellent starting point due to the rich photochemistry that had already been reported for Ru compounds and the number of volatile Ru complexes that had been used for thermal CVD. In previous work, we investigated Ru compounds such as $(\eta^3-\text{allyl})\text{Ru}(\text{CO})_3\text{Br}$, CpRu(CO)₂Me, and (COT)Ru(CO)₃ as precursors for PACVD on functionalized alkanethiolate self-assembled monolayers (SAMs).¹⁴ A high quantum yield for ligand loss was postulated to be necessary to generate a sufficient concentration of coordinatively unsaturated species that could react with the functional groups on the SAM surfaces. In these studies, it has been demonstrated that dienes and simple alkyls such as methyl can be suitable ligands for PACVD precursors.

In considering possible precursors for PACVD of platinum, a literature search determined that few Pt complexes have been reported to have the necessary properties: volatility, thermal stability, and photosensitivity. However, it has been reported that (COD)PtMe₂ (**1a**, Figure 1) photochemically decomposes to metallic Pt in solution.¹⁵ Furthermore, **1a** has been reported to be sufficiently stable and volatile for conventional thermal CVD.^{16,17} Based on our earlier Ru studies, diene and methyl ligands were promising choices in a PACVD precursor.



Figure 1. Structures of precursors 1a and 1b.

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Figure 2. Molecular orbitals of 1a and 1b from gas phase DFT calculations.

Therefore, in the context of PACVD, a more extensive study of the photochemical decomposition of **1a** and of its chlorinated derivative (COD)PtMeCl **(1b)** was of interest.

Previous studies established that elemental platinum was one of the photochemical decomposition products of 1a in CH₃CN, but the other products were not identified.¹⁵ An additional result from the prior study was that photolysis of 1a in the presence of CH₃I leads to oxidative addition and formation of the tetramer $[Pt^{IV}(CH_3)_3I]_4$ with $\Phi = 0.005$ at 313 nm. 15 The lowest energy transition was assigned as a $\sigma_{\rm CH3}$ $\rightarrow \pi^*_{COD}$ LLCT transition, and it was suggested that internal redox would lead to a photoprocess similar that observed in methylcobalamine.¹⁸ Promotion of an electron out of the Pt-CH₃ bond would facilitate loss of the methyl group, a step required for photoassisted deposition of pure Pt. The photochemistry of 1a in CD2Cl2 was also consistent with radical chemistry, with the solvent serving as a chlorine source.¹⁹ The reaction mixtures in CD₂Cl₂ were complicated, but 1b and chlorinated hydrocarbons were identified as products. There is also a report that the fluoroalkylation of 1a with C_4F_9I was significantly enhanced by UV irradiation.²⁰ Although this is also consistent with the photochemistry of 1a generating radicals, the system is complicated by the photoreactivity of C_4F_9I . The common thread in all of these prior studies is implied radical chemistry. As a result, we postulated homolysis of a Pt–CH₃ bond to be the primary photoprocess of 1a, which would make it a promising candidate as a PACVD precursor. Because the quantum yields for decomposition of precursors are expected to affect the PACVD experiments, we have reexamined the photochemistry of 1a and 1b. We now report the quantum yields for photochemical decomposition of 1a and 1b and confirm the primary photoprocess as Pt–CH₃ homolysis through radical trapping experiments.

RESULTS AND DISCUSSION

Electronic Structure and Absorption Spectra of 1a and 1b. To provide a basis for understanding the photochemical reactions of 1a and 1b, density functional theory



Figure 3. Experimental UV-vis spectra: (a) 1a in heptane and acetonitrile from 270 to 400 nm; (b) 1b in heptane and acetonitrile from 250 to 400 nm; (c) Deconvoluted spectrum of 1a in heptane from 190 to 400 nm; (d) Deconvoluted spectrum of 1b in heptane from 190 to 400 nm.

(DFT) calculations were used to determine their optimized geometries, energies, and molecular orbitals. The molecular orbitals from these calculations are shown in Figure 2. For 1a, the highest occupied molecular orbital (HOMO) is predominantly the symmetric combination of Pt-CH₃ bonds while the lowest unoccupied orbital is associated primarily with the π^* orbital of COD. The natures of the HOMO and LUMO obtained in these calculations are consistent with the qualitative molecular orbital diagram that was previously adapted from the orbitals of cis-Pt(CH₃)₂(PH₃)₂ calculated using an X α method²¹ and with DFT calculations on a series of (COD)PtR₂ complexes.¹⁹ For 1b the three highest occupied molecular orbitals contain d_{Pt} orbitals and Cl lone pairs. However, the halide ligand is not photoactive and so will be neglected in the following discussion of the electronic structure of the complexes as it pertains to their photochemistry.

Figure 3 shows the absorption spectra of 1a and 1b, that exhibit several maxima in the region from 250 to 400 nm (Table 1). Solvatochromic shifts are evident in the absorption

 Table 1. Observed Electronic Absorption Maxima and

 Calculated Extinction Coefficients for 1a and 1b in Heptane

	λ_1 (nm)	ε	λ_2 (nm)	ε	λ_3 (nm)	ε	λ_4 (nm)	ε
1a 1b	247 267	3100 2700	289 290	1700 1400	327	920	360	180

spectra of **1b** while the solvatochromic shifts in the absorption bands are much smaller, or negligible for **1a** (Figure 3a and 3b). We attribute this to differences in the molecular symmetry of **1a** and **1b**. Solvatochromatism is associated with changes in transition dipole moment from the ground states to excited states.^{22,23} In **1a** the Pt–CH₃ bonds are symmetry equivalent, and so there is only a small change in transition dipole moment upon excitation leading to weak solvatochromic shifts. In contrast, in **1b** the $Pt-CH_3$ and Pt-Cl bonds are not equivalent, and the Pt-Cl bond has a large local dipole moment. There is therefore a large change in the transition dipole moment upon excitation, and larger solvatochromic effects are observed.

The excited state DFT calculations were employed to assign the main transitions. We note that assignments and calculations for 1a are in agreement with Klein et al.¹⁹ For 1a the longest wavelength transition (HOMO-LUMO) is the σ -bond-to-ligand charge transfer (SBLCT) $\sigma_{Pt-CH_3} \rightarrow \pi^*_{COD}$ (Figure 2a). At 327 nm there is a stronger band which has metal-to-ligand charge transfer (MLCT) character and arises from the HOMO-1 to LUMO transition, $d_{Pt} \rightarrow \pi^*_{COD}$. At even shorter wavelengths, 1a exhibits additional SBLCT and MLCT transitions. At 289 nm, there is a transition from the HOMO-3 orbital, which has d_{Pt} character, to the LUMO, with π^*_{COD} character. There is also a second MLCT transition at 247 nm which can be attributed to a transition from HOMO-4 to LUMO+1, which is characteristic of $d_{Pt} \rightarrow \pi^*_{COD}$.

For 1b, the calculated UV-vis spectrum is in agreement with experiment (Figure S1, Supporting Information). In contrast to the lowest energy SBLCT state for 1a, the lowest energy transitions for 1b arise from the HOMO to LUMO and LUMO+1 states, $d_{Pt} \rightarrow \pi^*_{COD}$ and $d_{Pt} \rightarrow \sigma^*_{Pt-CH_3} + \sigma^*_{Pt-Cb}$ which are MLCT in character (Figure 2b). Additional MLCT bands are also observed for 1b and involve transitions from the d_{Pt} orbitals to π^*_{COD} , σ^*_{Pt-Me} , and σ^*_{Pt-Cl} orbitals (HOMO-4 to LUMO+1, HOMO to LUMO+2, and HOMO-3 to LUMO +2). To the extent that the photochemistry of 1a and 1b is dominated by the nature of the lowest excited state, the SBLCT excited state of 1a is expected to exhibit different properties than the MLCT lowest excited state of 1b.

Quantum Yield for Photodecomposition of 1a. Based on prior studies,^{15,19} the primary photoprocess of **1a** was expected to be loss of a methyl radical to form the unstable Pt(I) intermediate **3a** (Figure 4). However, upon irradiating **1a** in hydrocarbon solvents, no products were observed,



Figure 4. Proposed photoreactivity of 1a in hydrocarbon solvents.

presumably due to the thermal recombination of **3a** and the methyl radical. This is consistent with the previously reported photochemistry, in which products were formed upon irradiation of **1a** in the presence of the alkyl halides CH_3I or CD_2Cl_2 , which served as radical traps.^{15,19} Therefore, in order to measure the quantum yield for homolysis, a trapping reagent is needed to prevent the back reaction of **3a** with the methyl radical. If the trapping reagent creates a thermally stable product for quantification, comparing the quantum yields for disappearance of starting material and appearance of product can provide additional mechanistic information.

Quantum Yield Determination for Disappearance of 1a in the Presence of C_4F_9 . The initial quantum yield experiments were informed by the report that fluoroalkylation of 1a with C_4F_9I was significantly enhanced by UV irradiation.²⁰ Therefore, in the first experiments, the reaction in Figure 5 was used to determine the quantum yield for



Figure 5. Fluoroalkylation of 1a under irradiation with UV light.

disappearance of 1a and the quantum yield for formation of 2a in the presence of $C_4 F_0 I$. As shown from the UV/vis spectra of **1a** and C_4F_9I in heptane (Figure S2, Supporting Information), an accurate photon count for absorption by 1a at 313 nm would be difficult to obtain because of the large absorbance of the trapping reagent and the known photoreactivity of C₄F₉I. The longer wavelength, 365 nm, was less suitable for a first experiment because the weak absorption of 1a could lead to long reaction times, especially if the quantum yields were low. Therefore, 334 nm was the best compromise option for a preliminary experiment and the quantum yield experiments were conducted using a 500 W Hg(Xe) arc lamp with a 334 \pm 10 nm bandpass filter. The consumption of 1a and the formation of 2a were monitored using ¹H-NMR spectroscopy (Figure S3, Supporting Information), by integration vs the residual protons in C_6D_6 as an internal standard.

Under these conditions, a quantum yield value of $\Phi = 5.52 \pm 0.40$ for the disappearance of 1a was experimentally obtained. Because according to the Stark–Einstein law, only one molecule is activated per photon absorbed in a photochemical reaction, quantum yields greater than 1 are attributed to chain reactions.^{24,25} Because both reactants are photosensitive and radicals have been implicated in their photochemistry, free radicals derived from 1a and/or C₄F₉I are

undoubtedly the chain initiators. This result is consistent with discussion of the possibility of radical intermediates in a previous report of the photoreaction of **1a** and $C_4F_9L^{20}$ However, radical chain reactions are unlikely to be relevant to the PACVD application that motivates this study because the photochemistry of PACVD occurs in the gas phase and the collisions between molecules are negligible compared to collisions in the liquid phase. In addition, the photosensitivity of C_4F_9I adds uncertainty as to the source of the chain carrying radicals. Our interest in the photochemistry of **1a** in the context of PACVD is in the efficiency of photochemical ligand loss. To obtain an accurate quantitative evaluation of photochemical decomposition efficiency of **1a**, it was necessary to inhibit radical chain reactions with a radical trap that is not photosensitive.

Quantum Yield Determination for Disappearance of 1a in the Presence of TEMPO. To inhibit radical chain decomposition pathways, 1a was photolyzed through a 334 nm $(\pm 10 \text{ nm})$ bandpass filter in the presence of the radical trap TEMPO, which is nearly UV transparent in that wavelength range (Figure 6). Several new ¹H-NMR signals appeared after



Figure 6. UV/vis spectra of 1a and TEMPO in heptane. The boxes indicate the transmission regions of Hg lines in the presence of bandpass filters with ± 10 nm cutoffs.

irradiation (Figure 7). The new peaks match the peaks of an authentic sample of Me-TEMPO, confirming that methyl radicals were successfully trapped by TEMPO during the photolysis reaction.

The quantum yield for photodecomposition of 1a never exceeded unity in the presence of TEMPO (Figure 8), indicating that chain reactions were not taking place under these conditions. Quantum yields at 334 nm increased linearly with TEMPO concentration until plateauing at 10 molar equiv of TEMPO, suggesting that all of the methyl radicals formed were being trapped efficiently at that point. The observed quantum yield for decomposition of 1a at 334 nm was 0.037 \pm 0.003 (Table 2). Within error, this value matches the quantum yield for formation of Me-TEMPO at 334 nm, 0.036 \pm 0.002 (Table 2). At 365 nm, 1a was not reactive under our experimental conditions. The low quantum yields observed during trapping by TEMPO implicate the photochemistry of C₄F₉I in the radical chain reactions observed in its presence. The observed quantum yields are also about an order of



Figure 7. ¹H NMR spectra of reaction mixtures from determination of the quantum yield for disappearance of 1a in the presence of TEMPO.



Figure 8. Quantum yields for disappearance of 1a at 334 nm as a function of molar ratio (TEMPO/1a).

Table 2. Quantum Yields for Disappearance of 1a-b and Product Formation^{*a*}

	$\Phi_{ ext{decomposition}}$	Major product	$\Phi_{ m formation}$		
1a	0.037 ± 0.003	Me-TEMPO	0.036 ± 0.002		
1b	0.44 ± 0.02	2b	0.18 ± 0.02		
^{<i>a</i>} Irradiation time: 180 s.					

magnitude greater than those previously reported for the formation of the tetramer $[Pt^{IV}(CH_3)_3I]_4$ in the presence of CH_3I .¹⁵

Quantum Yield for Photodecomposition of 1b. Photolysis of a solution of 1b resulted in formation of dichloro complex 2b as the major product. Disappearance of 1b and appearance of product 2b were monitored by ¹H NMR. Based on the photochemistry of 1a, we postulated that the primary photoprocess for 1b would also be homolysis of a Pt–C bond to form the unsaturated species 3b and a methyl radical (Figure 9). Intermediate 3b would abstract chlorine from 1b to



Figure 9. Proposed reaction pathway for photodecomposition of 1b.

form 2b, thus requiring two molecules of 1b to form one molecule of the product 2b. This is supported by the quantum yield for formation of 2b being approximately half of the quantum yield for disappearance of 1b (Table 2). This mechanism implies the formation of an equivalent of (COD)PtCH₃ (3a) in conjunction with the formation of 2b. Observation of black precipitate in the reaction mixtures is consistent with further decomposition of 3a to colloidal Pt. Formation of colloidal Pt has been reported to occur upon photolysis of 1a,¹⁵ which shares the common intermediate 3a (Figure 4).



Figure 10. ¹H-NMR spectra of the quantum yield reaction solutions of 1b.

The quantum yield for the disappearance of 1b is approximately an order of magnitude larger than for 1a. We attribute this to the SBLCT transition mixing with $\pi - \pi^*$ COD intraligand transition (HOMO-2 to LUMO) leading to a reduction in the efficiency of Me loss from 1a in a similar process to that reported by Kunkely and Vogler for methylcobalamin.¹⁸ DFT calculations on 1a suggest that the excitation energies are very similar for the $\pi - \pi^*$ COD intraligand transition and the SBLCT (360 nm) and MLCT (327 nm) transitions, enabling the mixing. In contrast for 1b, which has a much larger energy difference between the lowest energy MLCT state (HOMO to LUMO and LUMO+1) and the $\pi - \pi^*$ COD intraligand transition (HOMO-4 to LUMO), there is very little, or no, intermixing of the states. Thus, a larger quantum yield for photodecomposition by methyl loss is observed for 1b.

To check if there is thermal recombination between **3b** and methyl radical, TEMPO was used as a trapping reagent to trap the methyl radical (Figure 10). The presence of MeTEMPO in the reaction mixtures confirms that methyl radicals are being formed upon photolysis and trapped. However, as shown in Figure 11, there is no dramatic change in the quantum yield values upon addition of TEMPO. This suggests that the back reaction of **3b** with the methyl radical is not significant. This is a difference in behavior between **1a** and **1b**.

Luminescence Experiments. Photoluminescence was measured for 1a and 1b to determine if emission from the excited state was competitive with photochemical homolysis of the Pt-Me bond. When Ar-purged solutions of 1a and 1b were excited at their lowest energy absorption (Figures S4 and S5, Supporting Information), a weak, solvatochromic emission was observed such that the emission is red shifted in a polar solvent. This further supports the presence of a charge transfer excited state. Lifetimes of the emissive excited state were determined to be on the nanosecond time scale (Figures S6 and S7, Supporting Information). However, the luminescence



Figure 11. Quantum yields for disappearance of 1b and formation of 2b as a function of molar ratio (TEMPO/1b).

quantum yields ($\Phi = 0.004$ for 1a and $\Phi = 0.004$ for 1b) were too low for emission to compete well with the photochemical cleavage of the Pt–CH₃ bond in the excited state. Although the observed luminescence of 1a is weak, it displays a linear concentration dependence at two different wavelengths (Figure S8), consistent with luminescence from a single species.

CONCLUSIONS

The quantum yields for photochemical decomposition of $(COD)PtMe_2$ (1a) and (COD)PtMeCl (1b) were determined at 334 nm. Chain reactions initiated by photochemical formation of radicals occurred when 1a was irradiated in the presence of C_4F_9I , resulting in quantum yields higher than

unity. As a result, in the determinations of quantum yields for loss of 1a, TEMPO was used to scavenge the methyl radicals formed upon photolysis. For 1b, there was no dramatic change in the quantum yield values upon addition of TEMPO, suggesting that the back reaction of 3b with methyl radical was not significant. Weak luminescence was observed for 1a and 1b, and it was determined that emissive decay is not competitive with $Pt-CH_3$ bond homolysis. Based on DFT calculations the lowest energy transition of 1a is assigned as an SBLCT transition while the lowest energy transition of 1b is MLCT. Further, 1a exhibits both SBLCT and MLCT transitions at low energies but 1b undergoes only MLCT transitions.

This study suggests 1a and 1b are potential PACVD precursor candidates based on their photolytic loss of methyl groups. Looking at the quantum yield studies alone, 1b is a better candidate than 1a because it is more photoactive. However, quantum yield is not the only factor for precursor performance. For PACVD of metal deposits, clean precursor decomposition with loss of all the ligands is optimal. The colloidal Pt observed after generation of the unsaturated intermediate (COD)PtMe (3a) from both precursors is promising, but photolysis of 1b also generates a half equivalent of (COD)PtCl₂ (2b), which could lead to impurities during deposition. Thus, deposition studies with both 1a and 1b are of interest in sorting out what properties are more important in precursor design. Studies on PACVD from 1a and 1b are currently underway.

EXPERIMENTAL SECTION

General Procedures. Unless otherwise stated, all reactions were carried out under an inert atmosphere (N_2) using standard Schlenk techniques. Unless otherwise specified, reagents were purchased from Sigma-Aldrich, Fisher Scientific, or Oakwood Chemical and used without further purification. (COD)PtCl₂ was purchased from Strem Chemicals and used without further purification. An authentic sample of Me-TEMPO was synthesized according to previous literature.²⁶ Disposable poly(methyl methacrylate) cuvettes with a path length of 1.0 cm were purchased from Fisher Scientific. Diethyl ether was purified by distillation from sodium/benzophenone ketyl and stored over activated 4 Å molecular sieves. Dichloromethane was purified using an MBraun MS-SP solvent purification system and stored over activated 4 Å molecular sieves. Anhydrous methanol was purchased from Acros Organics and used without further purification.

¹H and ¹⁹F NMR spectra were obtained on a 300 MHz Mercury, 400 MHz Bruker, or 600 MHz Bruker instrument. Peaks were referenced to the residual protons of the deuterated solvents. UV–vis spectroscopy was performed on a Shimadzu UV-1650PC using quartz cuvettes with a path length of 1.0 cm. Photochemical quantum yield experiments were conducted in 3.0 mL quartz cuvettes with a path length of 1.0 cm. All irradiations for the photochemical quantum yield experiment were conducted using a 500 W Hg(Xe) arc lamp equipped with an electronic shutter (Newport Corporation), and wavelengths were isolated using bandpass filters (Newport Corporation and Edmund Optics).

(COD)PtI₂. The compound was synthesized using a modified literature procedure.²⁷ No precautions to exclude air were taken. A suspension of (COD)PtCl₂ (0.1013 g, 0.271 mmol) in 5 mL of acetone was prepared in a 10 mL round bottom flask which was equipped with a magnetic stir bar. The suspension was stirred for 10 min, and then NaI (0.0884 g, 0.590 mmol) was added. The solution turned yellow immediately. The mixture was stirred for 10 min. Acetone was removed by rotary evaporation. The residue was collected on a fritted funnel and washed at least 3 times with deionized water (30 mL). The solid was air-dried for 1 d in a desiccator. The final product was obtained as a yellow powder (yield:

0.1408 g, 93%). The compound was characterized by comparison to literature data.²⁸ ¹H NMR (300 MHz, CDCl₃): δ = 5.76 (t, ²*J*_{Pt-H} = 66 Hz, 4 H, CH), 2.54–2.39 (m, 4 H, CH₂), 2.04–1.82 (m, 4 H, CH₂) ppm.

(COD)PtMe₂ (1a). The compound was synthesized using a modified literature procedure.²⁷ A 25 mL Schlenk flask, which was equipped with a magnetic stir bar, was flame-dried and subsequently sealed with a rubber septum. (COD)PtI2 (0.3078 g, 0.5526 mmol) was added into the flask, and the flask was degassed again. The Schlenk flask was immersed into an ice-water bath, and then 15 mL of anhydrous diethyl ether were added into the flask. Slightly in excess of 2 equiv of methyl lithium (MeLi), which was titrated before use,² was added dropwise into the solution. The solution was stirred for 2 h and then hydrolyzed with an ice-cold saturated NH4Cl aqueous solution until no bubbles formed. The ether layer was separated from the aqueous layer using a 60 mL separatory funnel. The aqueous layer was extracted with 50 mL of ether at least 3 times. All of the organic layers were combined and dried with anhydrous MgSO₄. The solution was filtered using a Buchner funnel. Ether was removed using rotary evaporation. The crude product was purified by sublimation at 50 °C, 150 mTorr for 12 h. The final product was obtained as white crystals (yield: 0.1137 g, 61%). The compound was characterized by comparison to literature data.²⁸ ¹H NMR (300 MHz, $CDCl_3$): δ = 4.81 (t, ${}^{2}J_{Pt-H} = 38$ Hz, 4 H, CH), 2.41-2.21 (m, 8 H, CH₂), 0.74 (s, ${}^{2}J_{\text{Pt-H}} = 82 \text{ Hz}, 6 \text{ H}, \text{CH}_{3}) \text{ ppm.}$

(COD)PtMeCl (1b). The compound was synthesized using a modified literature procedure.²⁸ A 25 mL Schlenk flask which was equipped with a magnetic stir bar was flame-dried and sealed with a rubber septum. The flask was cooled under vacuum to room temperature and degassed. (COD)PtMe₂ (0.1008 g, 0.303 mmol) was added into the flask, and the flask was degassed again. Anhydrous DCM (3 mL) and anhydrous methanol (2 mL) were added into the Schlenk flask. Slightly in excess of 1 equiv of CH₃COCl (0.023 mL, 1.1 g/mL, 0.3220 mmol) was added into the flask dropwise. The mixture was stirred for 10 min and subsequently concentrated under vacuum. The suspension was recrystallized under -20 C° for 1 d. The solid was filtered and then washed twice with pentane (30 mL). The solid was air-dried overnight in a desiccator. The final product was obtained as white crystals (yield: 0.0812 g, 76%). The compound was characterized by comparison to literature data.³⁰ ¹H NMR (300 MHz, acetone-d₆): δ = 5.42 (t, ²J_{Pt-H} = 36 Hz, 2 H, CH), 4.54 (t, ²J_{Pt-H} = 75 Hz, 2 H, CH), 2.62–2.28 (m, 8 H, CH₂), 0.78 (s, ${}^{2}J_{Pt-H} = 73$ Hz, 3 H, CH_3) ppm.

Quantum Yields. Quantum yields were obtained using ferrioxalate actinometry and modified literature procedures.^{24,31} Potassium ferrioxalate was prepared as reported in the literature.³² All degassing and purging were done using Ar gas by standard Schlenk techniques. All manipulations, other than massing the compound, were carried out under red light. NMR samples were wrapped with aluminum foil to avoid irradiation by sunlight while taking samples to the spectrometer. The C₄F₉I solution (0.02 M in C₆D₆) and pure C₆D₆ were degassed by four freeze pump thaw cycles prior to use.

Actinometry. The number of photons absorbed was determined using ferrioxalate actinometry as previously reported.³¹ Briefly, an aliquot between 2.5–3.0 mL from the irradiated ferrioxalate solution was mixed with twice its volume of developer solution (0.05% phenanthroline (wt %), 0.75 M sodium acetate, and 0.2 M H_2SO_4). The resulting mixture was diluted with deionized water to a volume of either 10 mL or 25 mL. Developed ferrioxalate solutions were left to stand in the dark for at least 1 h before analyzing by UV–vis spectroscopy. A blank for UV/Vis can be prepared by using the aforementioned method but using a non-irradiated ferrioxalate solution.

Determination of Quantum Yields of 1a in the Presence of C_4F_9I . A small quantity (~3–4 mg, targeting ~0.002 M) of compound was placed into a 5 mL volumetric flask, which was equipped with a magnetic stir bar and subsequently sealed with a rubber septum and degassed. Then, 5 mL of 0.02 M C_4F_9I in C_6D_6 were added. The mixture was stirred until complete dissolution. A quartz cuvette which was equipped with a rubber septum was

degassed and then charged with 2.7 mL of sample solution that was ~0.002 M in compound and ~0.02 M in C_4F_9I . Potassium ferrioxalate $(3.5 \text{ mL of } 0.006 \text{ M in } 0.05 \text{ M H}_2\text{SO}_4)$ was added to a separate, nondegassed disposable poly(methyl methacrylate) cuvette. The cuvettes were photolyzed for a desired time interval using filtered light from a 500 W Hg(Xe) arc lamp, such that the cuvette containing the ferrioxalate solution was positioned directly behind the cuvette containing the compound. To determine the total number of photons emitted by the arc lamp, a control experiment was conducted by photolyzing 2.7 mL of 0.02 M C4F9I solution and 3.5 mL of ferrioxalate solution following the same procedure during the same time interval. Concentrations of starting material and photolysis product were determined by ¹H NMR and compared to the nonirradiated solution from the 5 mL volumetric flask. The number of photons absorbed was determined by ferrioxalate actinometry. During quantum yield determinations, the reactions were run to between 5% and 10% conversion.

Determination of Quantum Yields of 1a in the Presence of TEMPO. A small quantity of TEMPO (quantity varies based on equivalents of TEMPO) was massed into a 10 mL volumetric flask equipped with a magnetic stir bar, sealed with a rubber septum, and degassed. C₆D₆ was added to the volumetric flask, and it was stirred until complete dissolution. A small quantity of 1a (~4-6 mg, targeting ~0.002 M) was massed into a 10 mL Schlenk tube, equipped with a magnetic stir bar, sealed with a rubber septum, and degassed. Once the TEMPO had dissolved completely, 7.0 mL of the TEMPO in C₆D₆ solution were added to the Schlenk tube containing 1a and stirred until complete dissolution. Three quartz cuvettes that were equipped with a rubber septum were degassed. Two of the cuvettes were charged with 2.8 mL of sample solution that was ~0.002 M in compound and the appropriate quantity of TEMPO. The third cuvette was saved for a control experiment (vide infra). Potassium ferrioxalate (2.8 mL of 0.006 M in 0.05 M H₂SO₄) was added to separate, non-degassed disposable poly(methyl methacrylate) cuvettes. The samples were photolyzed for a desired time interval using filtered light from a 500 W Hg(Xe) arc lamp, such that the cuvette containing the ferrioxalate solution was positioned directly behind the cuvette containing the compound and TEMPO. To determine the total number of photons emitted by the arc lamp, a control experiment was conducted by photolyzing 2.8 mL of the TEMPO in C₆D₆ solution and 2.8 mL of ferrioxalate solution following the same procedure during the same time interval. Concentrations of starting material and photolysis product were determined by ¹H NMR and compared to the non-irradiated solution from the 5 mL volumetric flask. The number of photons absorbed was determined by ferrioxalate actinometry. During quantum yield determinations, the reactions were run to between 0.1% and 1.0% conversion.

Determination of Quantum Yields of 1b in the Presence of TEMPO. A small quantity of 1b (~3-4 mg, targeting ~0.002 M) and a small quantity of TEMPO (quantity varies based on equivalents of TEMPO) was massed into a 5 mL volumetric flask equipped with a magnetic stir bar, sealed with a rubber septum, and degassed. C₆D₆ was added to the volumetric flask, and it was stirred until complete dissolution. A quartz cuvette which was equipped with a rubber septum was degassed and then charged with 2.8 mL of sample solution that was ~0.002 M in compound and the appropriate amount of TEMPO. Potassium ferrioxalate (3.5 mL of 0.006 M in $0.05 \text{ M H}_2\text{SO}_4$) was added to a separate, non-degassed disposable poly(methyl methacrylate) cuvette. The cuvettes were photolyzed for a desired time interval using filtered light from a 500 W Hg(Xe) arc lamp, such that the cuvette containing the ferrioxalate solution was positioned directly behind the cuvette containing the compound. To determine the total number of photons emitted by the arc lamp, a control experiment was conducted by photolyzing 2.8 mL of TEMPO in C₆D₆ solution and 3.5 mL of ferrioxalate solution following the same procedure during the same time interval. Concentrations of starting material and photolysis product were determined by ¹H NMR and compared to the non-irradiated solution from the 5 mL volumetric flask. The number of photons absorbed was determined

by ferrioxalate actinometry. During quantum yield determinations, the reactions were run to between 5% and 10% conversion.

Luminescence Experiments. Room temperature photophysical measurements were performed using a $1 \times 1 \text{ cm}^2$ quartz cuvette with a long stem. All samples for photophysical measurements were tuned to an optical density no greater than 0.1 at the excitation wavelength and subsequently sparged with Ar for a minimum of 15 min. Absolute quantum yield measurements were measured using a Hamamatsu Quantaurus-QY Absolute PL quantum yield spectrometer. Fluorescence spectra were measured using a Horiba JY Fluoromax-4 fluorometer. Lifetime measurements were measured using the time correlated single photon (TCSPC) method on the aforementioned Fluoromax-4 spectrometer.

DFT Calculations. Calculations were carried out using Gaussian09.³³ The UV/vis spectra were obtained using the time-dependent DFT (TD-DFT).³⁴ The exchange-correlation potential used was B3LYP which is a hybrid potential that combines a portion of the exact exchange term calculated from Hartree–Fock theory and the correlation term from other sources.³⁵ For C, O, H, and Cl, the basis set employed was 6-311+G(2d,p) which incorporates diffuse functions.^{36–39} For Pt, the LANL2DZ basis set,^{40–42} which includes an effective core potential, was employed in the calculations. All structures reported in this paper are minima; frequency calculations have been made to confirm this in every case.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00616.

Calculated UV/vis spectrum of 1b, UV/vis of 1a and C_4F_9I in heptane, ¹H NMR spectrum of an irradiated (334 nm) sample of 1a and C_4F_9I in heptane, luminescence spectra of 1a and 1b, excited state decay profiles of 1a and 1b, ¹H NMR spectra for 1a and 1b (PDF)

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Notes

The authors declare no competing financial interest.

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