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Photooxidation Reactions of Cyclometalated Palladium(II) and Platinum(II) Complexes

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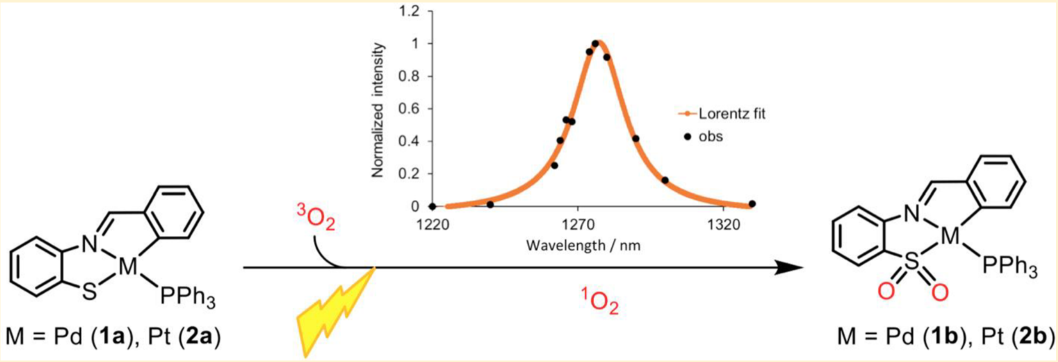
Supporting Information



ABSTRACT: New C,N,S-cyclometalated palladium(II) and platinum(II) complexes have been synthesized and their structural, electrochemical, and photochemical properties examined. The blue color of these complexes in solution changed to yellow under visible-light irradiation. By measurement of the absorption spectra for quantifying changes in color, isosbestic points for each complex clearly indicated the presence of only two species responsible for the change of color. X-ray analysis revealed that the visible-light-induced yellow species were S-oxygenated sulfinato complexes. Photosensitized generation of singlet oxygen ($^1O_2$) was confirmed by the direct detection of singlet oxygen luminescence at 1275 nm. The present cyclometalated palladium(II) and platinum(II) complexes are efficient photosensitizers of singlet oxygen, which rapidly reacts with coordinating sulfur atoms.

INTRODUCTION

Singlet molecular oxygen ($^1O_2$) is a reactive oxygen species, like peroxide, superoxide, etc. Because of the vital role of singlet oxygen in oxidation reactions with various chemical and biological molecules,[1] its physical and chemical properties have been well studied.[2] Singlet oxygen also has important applications in photodynamic cancer therapy and the photooxidation of toxic molecules.[3−6] Photosensitized generation by energy transfer from a photoexcited sensitizer to triplet oxygen ($^3O_2$) is the most common method for singlet molecular oxygen generation, and organic dyes, porphyrins, phthalocyanine derivatives, and fullerene derivatives have been used as photosensitizers.[7−10] Recently, transition-metal complexes have been shown to be attractive alternatives as singlet oxygen producers, separately well-studied organic photosensitizers.[11−18] In particular, the cyclometalated complexes have attracted much attention since the first report of singlet oxygen generation by a cyclometalated iridium(III) complex in 2002,[19,20] and octahedral iridium(III) complexes[21−26] and square-planar platinum(II) complexes[26−29] have been reported as cyclometalated complexes that can serve as photosensitizers for singlet oxygen.

In this study, new cyclometalated palladium(II) and platinum(II) complexes were prepared and characterized, and we found that these complexes, not limited to the platinum(II) complex, can readily be converted to the corresponding sulfinato species under visible-light irradiation. The production of singlet oxygen in the reactions was confirmed by monitoring the appearance of phosphorescence centered at 1275 nm under irradiation of the cyclometalated complex at 355 nm.[30] The results of the present study open a new avenue for the development of efficient photosensitizers of singlet oxygen.

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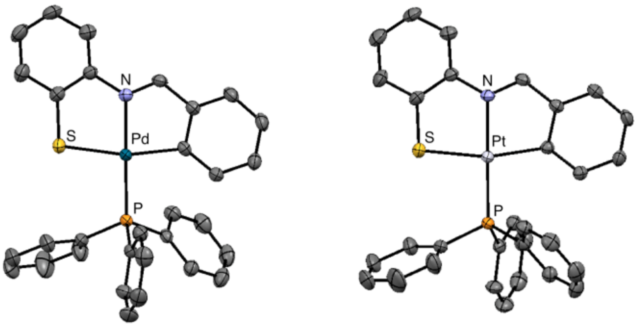
■ RESULTS AND DISCUSSION

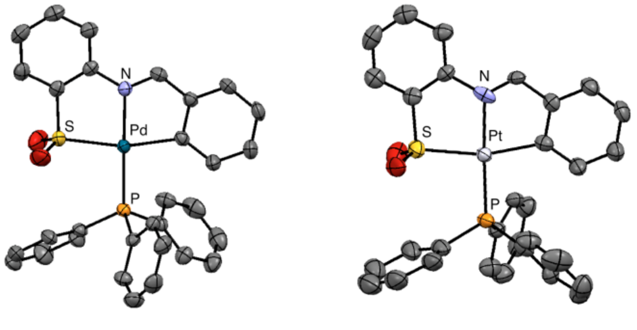
New cyclometalated palladium(II) and platinum(II) complexes with C,N,S-donor sets were isolated by column separation of the reaction mixtures obtained by the reactions of disulfide ligands containing Schiff base moieties with $[Pd(PPh_3)_4]$ or $[Pt(PPh_3)_4]$ and characterized by elemental analysis, ^{1}H NMR, IR, and UV−vis spectroscopy, single-crystal X-ray diffraction, and cyclic voltammetry.

The structures of these complexes (**1a** and **2a**) were determined by single-crystal X-ray diffraction (Table S1) and are depicted in Figure 1. The blue eluates in column chromatography contained the cyclometalated palladium(II) and platinum(II) complexes, and their CH_2Cl_2 solutions changed color to yellow under visible-light irradiation. The yellow solutions were also crystallized by slow evaporation (**1b** and **2b**), and the single-crystal X-ray diffraction data demonstrated them to be sulfinato species in which two oxygen atoms were bonded to the same sulfur-donor atoms in cyclometalated ligands (Figure 2). The palladium and platinum atoms in the cyclometalated complexes adopted a distorted square-planar coordination geometry with S−Pd(Pt)−C angles much smaller than 180° (Table S2).



1a **2a**

Figure 1. Molecular structures of **1a** and **2a** with ellipsoids drawn at the 50% probability levels. Hydrogen atoms and solvents were omitted for clarity.



1b **2b**

Figure 2. Molecular structures of **1b** and **2b** with ellipsoids drawn at the 50% probability levels. Hydrogen atoms and solvents were omitted for clarity.

The Pd(Pt)−N and Pd(Pt)−C distances were comparable to those found in other Schiff base palladium(II) [platinum(II)] complexes,[31−33] while the Pd(Pt)−S distances in the cyclometalated complexes, except for the corresponding sulfinato species, were significantly longer than those found in other palladium(II) [platinum(II)] thiolate complexes.[34,35] This can be explained by the strong trans influence exerted by the cyclometalated aryl carbon atom.[31−33] In contrast, the typical Pd(Pt)−S distances in the sulfinato species can be related to the lower trans influence, suggesting that the oxygenated sulfur atom is a stronger π acceptor than the coordinated thiolato sulfur atom[36] and more competitive with the cyclometalated aryl carbon atom for electron back-donation. The S═O distances of the sulfinato species were consistent with other sulfinato metal complexes (Table S2)[37] as well as the IR bands for SO_2 moieties (Figures S1 and S2).[38,39]

The absorption spectra of the cyclometalated palladium(II) and platinum(II) complexes showed the diagnostic peaks responsible for their blue color at around 600 nm (Figures S3 and S4). Although this spectral feature was similar to those of [Pt(dbbpy)(edt)] (dbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine and edt = 1,2-ethanedithiolate)[11] and [Pt(bpy)(bdt)] (bdt = 1,2-benzenedithiolate)[12] reported by Schanze and Gray and co-workers, respectively, which convert to sulfinato species when irradiated with visible light in the presence of oxygen, the long-wavelength bands of the present complexes with cyclometalated tridentate ligands arise from a highest occupied molecular orbital (HOMO)-to-lowest unoccupied molecular orbital (LUMO) transition (Figure S5), as supported by time-dependent density functional theory (DFT) calculations (Table S3 and Figure S6) and are assigned as an intraligand charge-transfer (ILCT) transition with a minor metal-to-ligand charge-transfer (MLCT) contribution instead of a platinum/sulfur → diimine charge transfer (MMLL′CT) observed for [Pt(diimine)(dithiolate)] complexes composed of two bidentate ligands.[12,40] The color changes from blue to yellow corresponded with the disappearance of absorption bands dominated primarily by ILCT transitions at ca. 600 nm and the appearance of ILCT bands mixed with MLCT transitions (HOMO−1 → LUMO) at ca. 400 nm with extinction coefficients between 2000 and 5000 M^{-1} cm^{-1}. Under aerobic conditions, the absorption bands of **1a** and **2a** changed with the photoirradiation time, and the presence of several isosbestic points was observed (Figure 3), confirming a color change between two clearly defined structures of the cyclometalated complexes and the corresponding sulfinato species (Figures S7 and S8).

To explore the photosensitized formation of singlet oxygen, we performed photooxidation of anthracene with **1a** and **2a** under visible-light irradiation. However, a dichloromethane solution of anthracene containing **1a** and **2a** showed no definite change in the UV−vis spectroscopy (Figure S9). We then tried to determine the rate constants for the quenching of singlet oxygen by **1a** and **2a** for comparison because anthracene has a known rate constant (8.5×10^5 M^{-1} s^{-1}) for the quenching of singlet oxygen in toluene.[41] The quenching rate constants were determined by a time-resolved phosphorescence quenching method. Decay traces of singlet oxygen phosphorescence at 1275 nm (Figure S10) were recorded at different **1a** or **2a** concentrations, and the quenching rate constants [$k_q = 1.10\ (\pm 0.05) \times 10^8$ M^{-1} s^{-1} for **1a** and $1.32\ (\pm 0.02) \times 10^7$ M^{-1} s^{-1} for **2a**] were evaluated from the slopes of the Stern−Volmer plots (Figure S11). These values are 2 or 3 orders of magnitude higher than that for anthracene, and this is the reason why **1a** and **2a** were not activatable photosensitizers for the photooxidation of anthracene. Thus, **1a** and **2a** undergo self-sensitized photooxidation

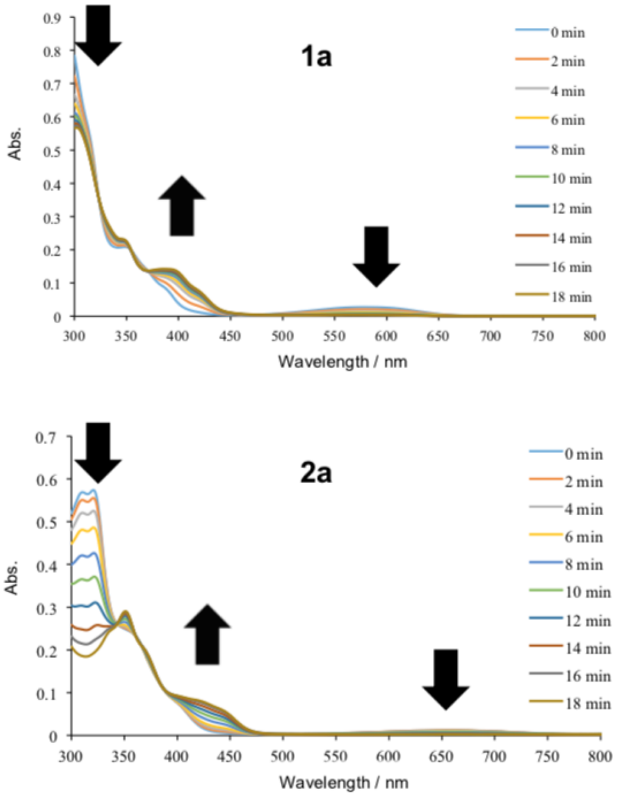


Figure 3. Time-dependent UV−vis absorption spectra of **1a** (3.02×10^{-5} M) and **2a** (3.16×10^{-5} M) in dichloromethane under photoirradiation ($\lambda > 400$ nm).

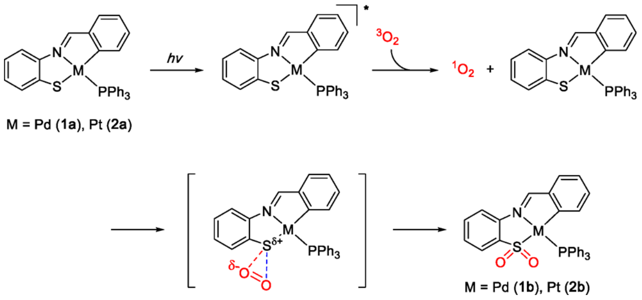
analogous to that of [Pt(diimine)(dithiolate)] complexes reported by Schanze and Gray,[11−13] leading to the formation of only sulfinato products.

In order to prove the production of singlet oxygen by energy transfer from the triplet excited states of **1a** and **2a** to the ground state of molecular oxygen, we studied the luminescence properties of these complexes (Figures S12 and S13). The very weak luminescence bands overlapped with the low-energy absorption bands (ca. 575 nm for **1a** and ca. 655 nm for **2a**) were observed in the 600−750 nm region for **1a** and at longer wavelengths beyond 650 nm for **2a** with lifetimes on the order of 10^{-8} and 10^{-6} s in degassed CH_2Cl_2 at 77 K, respectively. The difference of the lifetimes of **1a** and **2a** can be related to a stronger singlet oxygen phosphorescence signal (Figure S10) detected directly for **2a** with longer lifetime, enabling efficient triplet energy transfer to molecular oxygen.

The cyclic voltammograms of **1a** and **2a** showed quasi-reversible redox waves in the anodic regions (Figure S14), but sulfinato species **1b** and **2b** showed irreversible oxidation peaks in the more positive potential region. These results were related to the energies of HOMO obtained from DFT calculations for **1a**, **1b**, **2a**, and **2b** (Figure S5) and indicate that **1b** and **2b** formed by the oxidation of **1a** and **2a** are much more difficult to oxidize further. Although the energies of LUMO are not affected much by oxidation to the sulfinato species, because the orbitals are largely localized in cyclometalated ligands except for coordinated sulfur atoms, the oxidation products **1b** and **2b** showed irreversible reduction peaks at potentials slightly more positive than those for **1a** and **2a** in the cathodic regions (Figure S14 and Table S4). These features were also consistent with the results of DFT calculations (Figure S5).

In order to better understand the mechanism of sulfinato formation, the reactions of cyclometalated complexes with singlet oxygen generated by the thermolysis of naphthalene endoperoxides were carried out in the dark. The formation of sulfinato species could be followed by monitoring of the reduction of the absorption intensities of **1a** and **2a**. In fact, the intensities of the absorption peaks at ca. 600 nm decrease through the reactions with naphthalene endoperoxides at room temperature in the dark (Figure S15). This result indicates that the singlet oxygen generated via energy transfer from excited **1a** or **2a** to ground-state $^3O_2$ attacks the highly electron-rich sulfur atom of the ground-state cyclometalated complex, as shown by DFT calculations (Figure S5), resulting in conversion of the cyclometalated complexes to the corresponding sulfinato species. DFT was also used to investigate the nature of the intermediate in this sulfinato formation reaction, and it established the structures of the intermediates imposed by partial charge transfer between the electrophilic singlet oxygen and sulfur atoms of **1a** and **2a** (Figure S16).[11,12] A possible mechanism for photooxidation of the cyclometalated complex, which involves the formation of a reactive oxygen species ($^1O_2$) and yields a very stable sulfinato species, was thereby proposed, as shown in Scheme 1.

Scheme 1. Proposed Reaction Mechanism for the Photooxidation of 1a and 2a



■ CONCLUSIONS AND OUTLOOK

In summary, the cyclometalated palladium(II) and platinum(II) complexes, which were prepared by the reactions of disulfide ligands containing Schiff base moieties with $[Pd(PPh_3)_4]$ or $[Pt(PPh_3)_4]$, have potential as singlet oxygen photosensitizers and undergo photooxidation reaction to afford the corresponding sulfinato species. Further work will involve the preparation of some related cyclometalated complexes. We are working toward correlating the physicochemical properties of palladium(II) and platinum(II) complexes to their chemical reactivity.

■ EXPERIMENTAL SECTION

General Information. The reagents and solvents were purchased from commercial sources (Tokyo Chemical Industry, Wako Pure Chemical Industries, Sigma-Aldrich Japan, Kishida Chemical, Tanaka Kikinzoku Kogyo, or Strem Chemicals) and used without further purification. NMR spectra were recorded on a JEOL ECA-400 NMR spectrometer with tetramethylsilane as an internal standard. IR spectra were recorded on a Jasco FT/IR-4100 spectrometer using KBr pellets. UV−vis absorption spectra were recorded on a Jasco V-570 spectrometer. Cyclic voltammetry was carried out with a Bas CV-620A instrument using a three-electrode cell with a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode. Elemental analyses were obtained using a PerkinElmer 2400II CHN analyzer. Crystallographic data were collected by a Rigaku CCD Saturn 724 system using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Luminescence was measured by a homemade time-resolved spectroscopic apparatus composed of an excitation light source (Nd^{3+} YAG laser, Continuum Surelite, 532 nm), a monochromator (Nikon P250), and a photomultiplier tube (Hamamatsu Photonics R928). The sample solution was placed in a fused-silica dewar tube, and its temperature was kept at 77 K by liquid N_2.

Preparation of the Ligand and Complexes. *Ligand.* Benzaldehyde (302 mg, 2.83 mmol) was added to a solution of 2,2′-dithiodianiline (353 mg, 2.84 mmol) in 20 mL of ethanol under a nitrogen atmosphere in a Schlenk tube. The mixture was heated under reflux for 1 h. The resulting solution was allowed to cool to room temperature. The solution was concentrated to half, and the suspension was filtered. The resulting light-yellow powder (ligand) was washed with hexane and dried in vacuo. Yield: 213 mg, 17.7%. ^1H NMR (400 MHz, chloroform-*d*): δ 7.07 (dd, J = 7.3 and 1.4 Hz, 2H), 7.17 (tdd, J = 14.2, 6.8, and 1.5 Hz, 4H), 7.47−7.52 (m, 6H), 7.67 (dd, J = 7.8 and 1.4 Hz, 2H), 7.96−8.00 (m, 4H), 8.50 (s, 2H). Elem anal. Calcd for $C_{26}H_{20}N_2S_2$ (424.58): C, 73.55; H, 4.75; N, 6.60. Found: C, 73.39; H, 4.71; N, 6.61.

Complex 1a. Tetrakis(triphenylphosphine)palladium(0) (233 mg, 0.201 mmol) was added to a solution of the ligand (85.3 mg, 0.201 mmol) in 20 mL of toluene under a nitrogen atmosphere in a Schlenk tube. The mixture was heated under reflux for 2 h. The resulting dark-brown solution was cooled to room temperature and concentrated to oil. The brown oil was dissolved in a mixed solvent of dichloromethane and hexane (3:2). The solution was poured onto a silica gel column and eluted with the same mixed solvent. The purple band was collected and concentrated to dryness. Crystals of **1a** suitable for X-ray crystal structure analysis were grown by the slow evaporation of a dichloromethane solution. Yield: 32.4 mg, 27.8%. ^1H NMR (400 MHz, chloroform-*d*): δ 6.29 (dd, J = 7.3 and 4.2 Hz, 1H), 6.57 (t, J = 7.6 Hz, 1H), 6.74 (t, J = 7.1 Hz, 1H), 6.91−6.78 (m, 2H), 7.18−7.06 (m, 2H), 7.27 (d, J = 1.4 Hz, 1H), 7.50−7.32 (m, 9H), 7.74−7.64 (m, 6H), 8.37 (d, J = 8.7 Hz, 1H). IR (KBr, cm^{-1}): 1481, 1462, 1437, 1236, 1188, 1156, 1101. UV−vis [dichloromethane; λ_{max}, nm (ε, $M^{-1}cm^{-1}$)]: 355 (6480), 577 (924). Elem anal. Calcd for $C_{31}H_{24}NPPdS$ (579.99): C, 64.20; H, 4.17; N, 2.42. Found: C, 64.15; H, 4.10; N, 2.40.

Complex 2a. Tetrakis(triphenylphosphine)platinum(0) (250 mg, 0.201 mmol) was added to a solution of the ligand (85.4 mg, 0.201 mmol) in 20 mL of toluene under a nitrogen atmosphere in a Schlenk tube. The mixture was heated under reflux for 2 h. The resulting dark-brown solution was cooled to room temperature and concentrated to oil. The brown oil was dissolved in a mixed solvent of dichloromethane and hexane (3:2). The solution was poured onto a silica gel column and eluted with the same mixed solvent. The blue band was collected and concentrated to dryness. Crystals of **2a** suitable for X-ray crystal structure analysis were grown by the slow evaporation of a dichloromethane solution. Yield: 19.1 mg, 14.2%. ^1H NMR (400 MHz, chloroform-*d*): δ 6.32 (d, J = 7.8 Hz, 1H), 6.52 (td, J = 7.4 and 1.5 Hz, 1H), 6.67−6.58 (m, 1H), 6.87−6.72 (m, 2H), 7.09−6.95 (m, 2H), 7.14 (dd, J = 7.3 and 1.4 Hz, 1H), 7.47−7.34 (m, 9H), 7.80−7.58 (m, 6H), 8.23 (d, J = 9.6 Hz, 1H). IR (KBr, cm^{-1}): 1482, 1464, 1437, 1235, 1189, 1158, 1100. UV−vis [dichloromethane; λ_{max}, nm (ε, M^{-1} cm^{-1})]: 311 (18200), 321 (18400), 355 (7420), 656 (350). Elem anal. Calcd for $C_{31}H_{24}NPPtS$ (668.66): C, 55.68; H, 3.62; N, 2.09. Found: C, 55.76; H, 3.62; N, 2.05.

Complex 1b. Complex **1a** (50.0 mg, 86.2 μmol) in dichloromethane was irradiated with a xenon lamp (λ > 400 nm), and the color of the solution changed from blue to yellow. The yellow solution was concentrated to dryness, and the residue was dissolved in a mixed solvent of dichloromethane and methanol (19:1). The solution was poured onto a silica gel column and eluted with the same mixed solvent. The second yellow band (**1b**) was collected and concentrated to dryness. Yield: 49.7 mg, 94.3%. ^1H NMR (400 MHz, chloroform-*d*): δ 6.56 (dd, J = 7.3 and 4.2 Hz, 1H), 6.78 (td, J = 7.6 and 1.5 Hz, 1H), 7.06 (td, J = 7.5 and 1.1 Hz, 1H), 7.47−7.34 (m, 8H), 7.50 (tt, J = 5.6 and 1.8 Hz, 3H), 7.58 (dd, J = 7.7 and 1.4 Hz, 1H), 7.72 (td, J = 4.8 and 3.0 Hz, 1H), 7.84−7.74 (m, 6H), 7.90 (td, J = 5.0 and 2.4 Hz, 1H), 8.93 (d, J = 8.2 Hz, 1H). IR (KBr, cm^{-1}): 1481, 1438, 1239, 1178 ($\nu_{S=O}$), 1098, 1064, 1038 ($\nu_{S=O}$). UV−vis [dichloromethane; λ_{max}, nm (ε, M^{-1} cm^{-1})]: 305 (15100), 345 (6910), 395 (4510). Elem anal. Calcd for $C_{31}H_{24}NO_2PPdS\cdot 0.75CH_2Cl_2$ (675.69): C, 56.44; H, 3.80; N, 2.07. Found: C, 56.36; H, 3.83; N, 2.16.

Complex 2b. Complex **2a** (20.5 mg, 30.6 μmol) in dichloromethane was irradiated with a xenon lamp (λ > 400 nm), and the color of the solution changed from blue to yellow. The yellow solution was concentrated to dryness and dissolved in a mixed solvent of dichloromethane and methanol (19:1). The solution was poured onto a silica gel column and eluted with the same mixed solvent. The second yellow band (**2b**) was collected and concentrated to dryness. Yield: 14.6 mg, 67.8%. ^1H NMR (400 MHz, chloroform-*d*): δ 6.64 (d, J = 7.3 Hz, 1H), 6.85 (dd, J = 7.6 and 6.2 Hz, 1H), 7.09 (t, J = 7.1 Hz, 1H), 7.55−7.34 (m, 12H), 7.60 (d, J = 6.4 Hz, 1H), 7.85−7.71 (m, 6H), 7.85−7.90 (m, 1H), 9.21 (d, J = 9.6 Hz, 1H). IR (KBr, cm^{-1}): 1484, 1438, 1187 ($\nu_{S=O}$), 1099, 1069, 1038 ($\nu_{S=O}$). UV−vis [dichloromethane; λ_{max}, nm (ε, M^{-1} cm^{-1})]: 351 (9390), 445 (2180). Elem anal. Calcd for $C_{31}H_{24}NO_2PPtS\cdot 0.8CH_2Cl_2$ (768.60): C, 49.69; H, 3.36; N, 1.82. Found: C, 49.37; H, 3.36; N, 1.91.

Detection of Singlet Oxygen Generated by 1a and 2a. The singlet oxygen quenching rate constants by **1a** and **2a** were determined by means of time-resolved luminescence measurements in the near-IR (NIR) wavelength region. A Nd^{3+}:YAG laser (Continuum, Surelight, 355 nm, 1 Hz operation) was utilized as the light source. $O_2(^1\Delta_g)$ NIR phosphorescence from the sample solutions was dispersed with a monochromator (SolarTII, MS3504) and detected by a NIR-sensitive photomultiplier tube (Hamamatsu Photonics, H10330-45). Unwanted scattering light was excluded by an optical filter with a cutoff wavelength of 1100 nm. The output signals from the detecter were recorded by an oscilloscope (Tektronix, TDS 2022C). To determine the lifetime of $O_2(^1\Delta_g)$, the emission at 1275 nm was monitored. This emission was generated by photosensitization reactions of **1a** or **2a** with dissolved O_2. Stern−Volmer analysis in Figure S11 was done by plotting the lifetime of $O_2(^1\Delta_g)$ under a variety of different **1a** or **2a** concentrations. To obtain the dispersed spectrum of $O_2(^1\Delta_g)$ shown in Figure S10, the phosphorescence decays at various wavenumbers were measured and the time-integrated signal intensities at each decay were plotted against a wavelength of around 1275 nm. There were no differences in the $O_2(^1\Delta_g)$ phosphorescence spectra obtained by photosensitizers **1a** and **2a** in dichloromethane.

A mixture of **1a** (0.106 mg, 0.182 μmol) and anthracene (3.04 mg, 17.1 μmol) in 10 mL of dichloromethane was irradiated with a xenon lamp (λ > 400 nm), and the spectral changes were monitored by UV−vis spectroscopy. A mixture of **2a** (0.118 mg, 0.176 μmol) and anthracene (3.16 mg, 17.6 μmol) in 10 mL of dichloromethane was irradiated with a xenon lamp (λ > 400 nm), and the spectral changes were monitored by UV−vis spectroscopy.

Oxidation of 1a and 2a by Endoperoxide (4-Methyl-1,4-etheno-2,3-benzodioxin-1(4*H*)-propanoic Acid). Complex **1a** (0.878 mg, 1.51 μmol) was added to a solution of endoperoxide (3.79 mg, 15.0 μmol) in 20 mL of chloroform under a nitrogen atmosphere in a Schlenk tube. The mixture was warmed for 1 h at room temperature under dark conditions. The resulting light-purple solution was characterized by UV−vis spectroscopy. Complex **2a** (1.01 mg, 1.51 μmol) was added to a solution of endoperoxide (3.74 mg, 14.9 μmol) in 20 mL of chloroform under a nitrogen atmosphere in a Schlenk tube. The mixture was warmed for 1 h at room temperature under dark conditions. The resulting light-green solution was characterized by UV−vis spectroscopy.

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■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b01492.

Crystallographic data and experimental and calculated data (PDF)

Accession Codes

CCDC 1911429−1911432 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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