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Generation of an Unprecedented Excited State Oxidant in a Coordinately Unsaturated Platinum Complex

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Alteration of the ligand environment surrounding a metal center to afford an electronic structure with a specific photochemical activity is an area of widespread interest. The manipulation of metal diimine excited states[1,2] in the design of artificial photosynthetic receptors, molecular photonic devices, photocatalysis, and novel electron-transfer systems is actively pursued.[3−5] Coordinately saturated polypyridyl d^6 metal complexes [e.g., Ru(bpy)$_3$] have been extensively studied but are limited to outer-sphere electron-transfer reactions. Luminescent square-planar platinum diimine (*i.e.,* phenanthroline and bipyridine) complexes, however, are coordinately unsaturated, and potentially can be used for additional applications including bimolecular reactions. Work on platinum diimine chromophores over the last 20 years has primarily focused on halide and conjugated thiol ligands (e.g., toluene 1,2-dithiolate and 1,2-dicyanoethylene-1,2-dithiolate).[6−11] Current research goals in this area are directed toward (i) increasing the solubility properties of the Pt chromophores, (ii) improving the photochemical and thermal stability of these Pt chromophores, and, importantly, (iii) tuning the excited-state reduction and oxidation potentials for enhanced and more diverse reactivity. Herein, we report the synthesis and characterization of novel diimine dithiolate *o*-carborane platinum(II) complexes that are photochemically stable, soluble in solvents of varying polarities, and potent oxidizing agents in their excited state.

4,7-Diphenyl-1,10-phenanthroline[1,2-dithiolato-1,2-dicarba-*closo*-dodecaborane(12)]platinum(II) [**1**] and 4,7-diphenyl-1,10-phenanthroline-bis[1-thiolato-1,2-dicarba-*closo*-dodecaborane-(12)]platinum(II) [**2**] were synthesized as shown in Scheme 1. The complexes were purified by column chromatography to yield analytically pure crystalline solids.[12,13]

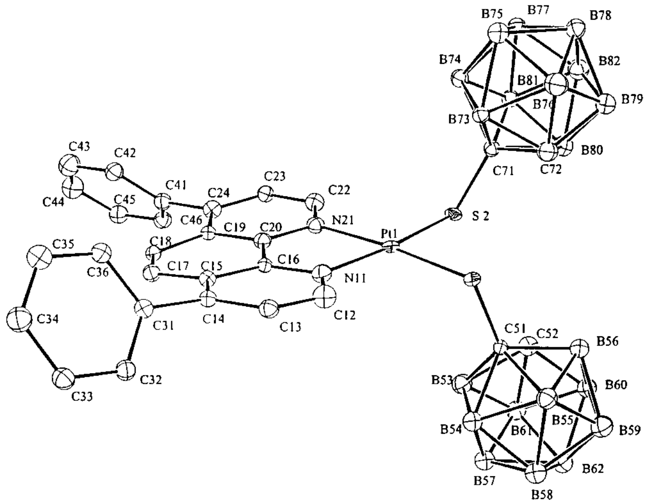
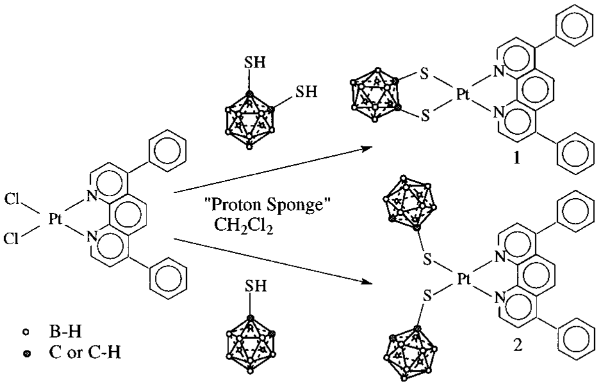


Figure 1. ORTEPII drawing of **2** with 50% probability ellipsoids showing the atomic numbering system. H atoms are not shown.

Scheme 1. Synthesis of Complexes **1** and **2**



The ORTEP drawing of **2** is shown in Figure 1.[14] The Pt−S carborane and Pt−N diimine bond lengths are 2.313(3), 2.2864(22), 2.082(8), and 2.078(7) Å, respectively, and are in agreement with other Pt diimine dithiolate structures.[15,16] The C−S bond lengths (1.773(9) and 1.806(10) Å) are consistent with a C−S single bond in a metal−thiolato−carborane complex.[17,18] Of particular note is the lack of molecular stacking observed in the crystal structure, since platinum(II) complexes are notorious for intermolecular stacking with short Pt−Pt or $\pi-\pi$ (3.24 and 3.51 Å, respectively) distances.[19,20] The three-dimensional space occupied by the *o*-carborane cage hinders close molecular interactions, and as a result these complexes are soluble in solvents of varying polarities.

A solution of **1** exhibits an intense absorption at 290 nm for the $\pi-\pi^*$ transition of diphenylphenanthroline, and a second absorption at longer wavelength that is strongly solvent dependent

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(12) The synthetic procedures for **1** and **2** are found in the Supporting Information section. Data for **1**: calcd, C, 45.07; H, 3.78; N, 3.62; found, C, 44.94; H, 3.93; N, 3.84. Data for **2**: calcd, C, 38.30; H, 4.36; N, 3.19; found, C, 38.51; H, 4.49; N, 3.08.

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(14) This is the first crystal structure of a bis(monothiolate) diimine platinum(II) complex as well as the first crystal structure of a thiolate−carborane−platinum complex. The complete crystallographic data for **2** are found in the Supporting Information.

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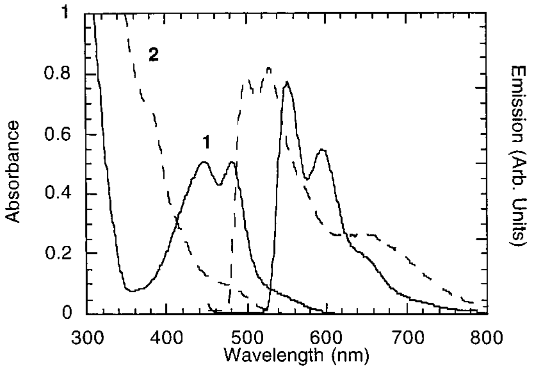

Figure 2. Electronic absorption and emission spectra of **1** (—) and **2** (— — —) in tetrahydro-2-methylfuran. Emission spectra recorded at 77 K (10^{-6} M chromophore concentration; excitation of **1** and **2** at 436 and 380 nm, respectively). No emission was observed for **2** at longer wavelength excitation.

[λ_{max} nm (solvent; M^{-1} cm^{-1}); 482 (C_6H_6; 6.1 × 10^3); 472 (C_6H_5Cl; 1.3 × 10^4); 460 (CH_3Cl; 1.1 × 10^4); 454 (CH_2Cl_2; 1.2 × 10^4); 446 ($(CH_3)_2CO$; 1.4 × 10^4); 437 (CH_3CN; 8.7 × 10^3)]. The absorption spectrum of **2**, however, is blue-shifted approximately 100 nm and partly obscured by the $\pi-\pi^*$ transition of the diphenylphenanthroline [λ_{max} nm (solvent); 380 (C_6H_6); 375 (CH_2Cl_2); 370 ($(CH_3)_2CO$); 360 (CH_3CN)]. Solutions of **1** and **2** in DMF, $CHCl_3$, CH_2Cl_2, and C_6H_6 are stable to irradiation into the long-wavelength absorption band compared to previous Pt(diimine)(dithiolate) complexes such as Pt(bpy)(tdt).[21,22] Cyclic voltammograms of **1** and **2** in CH_2Cl_2 (0.1 M $TBA^+PF_6^-$ vs Ag/AgCl) reveal a quasi-reversible reduction at −1.35 and −1.2 V, respectively, as well as a quasi-reversible oxidation at 1.4 V for complex **1** only. The oxidation of complex **2** is not observable within the solvent limit of 1.8 V.

The charge-transfer transition in Pt(diimine)(dithiolate) complexes was originally characterized as a ligand-to-ligand charge-transfer transition (LLCT) by Vogler and Kunkely,[22,23] and this assignment has been recently modified by Eisenberg to be a metal dithiolate to diimine charge-transfer transition.[24] A charge-transfer transition assignment from a mixed platinum thiolate HOMO to a π^* diimine LUMO for the *o*-carboranethiolate complexes is consistent with the following observations. The visible transition is only observable for the metal complex, and neither independent ligand absorbs in this region, substantiating the role of the metal in the transition. This transition is solvatochromic, suggesting that the HOMO has both metal (d) and dithiolate ligand character, and there is a dipole difference between the ground and excited state. The solvatochromism of the *o*-carborane dithiolate complex (ΔE 2100 cm^{-1}; C_6H_6 − CH_3NO_2) is smaller compared to previous aromatic dithiolate Pt diimine complexes, indicating that the dipole difference between the ground and excited state is of lesser magnitude. The LUMO is primarily of diimine character as evidenced by the quasi-reversible reduction for complexes **1** and **2** and its similarity to previous Pt(diimine)(dithiolate) complexes.

Photoluminescence from **1** and **2** is observed at 298 and 77 K, and the emission spectra at 77 K are shown in Figure 2. The emission is highly structured with well-resolved peaks at 542 and 593 nm for **1** and at 501 and 529 nm for **2**. For complex **1**, the vibrational spacing is about 1500 cm^{-1}. This spacing most closely corresponds to the C=C stretch of the diimine ligand. IR spectra of complex **1** and diphenylphenanthroline dichloride platinum(II) contain strong vibrations at 1425 and 1400 cm^{-1} corresponding to a C=C stretching mode. The 1,2-dithiol-1,2-dicarba-*closo*-dodecaborane(12) has stretching frequencies at 2600 and 1000 cm^{-1} for the B−H and C−S, respectively. This evidence supports an emissive state that originates from a metal (d) dithiolate to diimine charge-transfer excited state. At room temperature, emission from complex **1** is blue-shifted, of less intensity, and has a lifetime of 7 ns. As shown in Figure 3, a plot of the energy of emission vs the difference between the ground state oxidation and reduction potentials is well correlated for Pt(diimine)(1,2-dithiolate) complexes, and, importantly, complex **1** lies upon the line.[25]

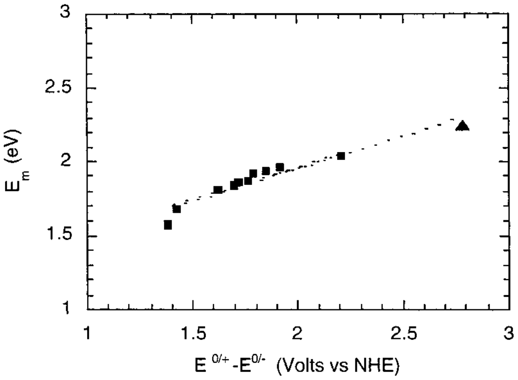

Figure 3. Plot of E_m (77 K) vs the difference between the ground-state oxidation and reduction potentials for the previous diimine dithiolate platinum(II) complexes[11] (squares) and complex **1** (triangle).

Two important conclusions can be drawn from these data, given that there is a strong correlation between the ground state redox potentials and the emission energy. First, the emissive state and the absorbing state are of the same origin. Second, the excited state energy of complex **1** is dramatically different from previous Pt(diimine)(1,2-dithiolate) complexes. The excited state reduction and oxidation potentials of complex **1** were estimated to be 1.09 and −0.63 V, respectively.[26] Comparison of these values to the previous ten Pt(diimine)(1,2-dithiolate) excited state potentials (reduction 0.56 ± 0.09 V; oxidation −1.41 ± 0.17 V)[11] reveals the excited state of complex **1** to be a stronger oxidant.

These novel platinum diimine thiolate *o*-carborane complexes possess several favorable properties for study, including an intense visible charge-transfer band, increased solubility, and an energetic excited state. On the basis of the evidence provided above, we are currently pursuing electron-transfer quenching experiments to determine the utility of these complexes, as well as exploring additional diimine and dithiolate molecular structures designed to afford more favorable properties such as longer excited state lifetimes in fluid solution.

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Supporting Information Available: Tables of X-ray experimental details and crystallography data for complex **2** are available (37 pages). Ordering information is given on any current masthead page.

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(25) The emissive state of **2** is still under investigation. The oxidation of **2** is not observed within the 1.8 V solvent window, but the complex should be to the right of complex **1** in Figure 3. The emission energy is calculated to be 2.48 V.

(26) The excited reduction and oxidation state potentials were estimated using $E = E(\mathrm{Pt}^{0/-}) + E_{00}$ and $E = E(\mathrm{Pt}^{+/0}) - E_{00}$, respectively. The absolute values estimated may be in error since we used ground state potentials that were not completely reversible. However, the relative excited state energy of complex **1** and the correlation to other Pt complexes are correct. E_{00} for **1** and **2** was determined to be 2.25 and 2.48 V, respectively.