

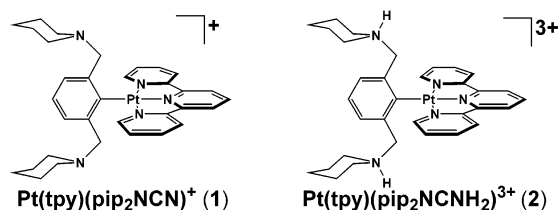
## An Outer-Sphere Two-Electron Platinum Reagent

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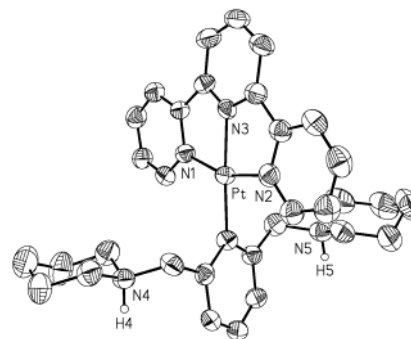
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Late transition metal compounds typically undergo two-electron changes in oxidation state by inner-sphere mechanisms (e.g., oxidative addition and reductive elimination reactions). This behavior suggests that we can design cooperative two-electron reagents, shuttles or reservoirs that reversibly transfer two electrons at the same potential in multi-redox catalytic reactions or molecular devices. In the case of platinum, an obvious practical problem is that the interconversion between square planar Pt(II) and octahedral Pt(IV) by outer-sphere electron transfer is slow and characterized by irreversible electrochemistry because of the accompanying large molecular reorganization.<sup>1,2</sup> However, high concentrations of coordinating anions can facilitate interconversion, and the cyclic voltammogram (CV) can exhibit an apparent two-electron wave, albeit with a large peak-to-peak separation ( $\Delta E_p = E_{pa} - E_{pc}$ ).<sup>2-4</sup> Our general approach is to design complexes with rigid meridional (*mer*) coordinating ligands and strong/hard donor groups that are capable of stabilizing both four-coordinate Pt(II) and six-coordinate Pt(IV) geometries. Although several previously investigated systems are capable of supporting both oxidation states, the electronic and steric properties of the ligands in these complexes result in CVs characterized by one-electron waves corresponding to generation of Pt(III).<sup>5</sup> Here we report the first example of a platinum complex, Pt(tpy)(pip<sub>2</sub>NCN)<sup>+</sup> (**1**), that meets our criteria and provides proof-of-concept by undergoing a nearly electrochemically reversible two-electron oxidation process.

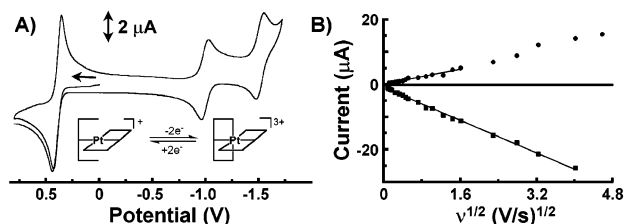


Complexes **1** and **2** were isolated as salts by standard methods.<sup>6</sup> The tridentate coordination geometry of the tpy ligand was confirmed by <sup>1</sup>H NMR experiments (CDCl<sub>3</sub> (**1**), CD<sub>3</sub>CN (**2**)). The resonance for the aromatic proton of the tpy  $\alpha$ -carbon appears as a doublet with well-resolved <sup>195</sup>Pt satellites ( $J_{Pt-H} = 56$  (**1**); 48 Hz (**2**)) due to three-bond coupling with the Pt center. The resonance for the pip<sub>2</sub>NCN<sup>-</sup> benzylic protons appears without <sup>195</sup>Pt satellites (s, 3.65 ppm (**1**); d, 4.63 ppm  $J_{H-H} = 4$  Hz (**2**)), as expected for monodentate coordination of the pip<sub>2</sub>NCN<sup>-</sup> ligand.<sup>6</sup> The structure of the protonated complex was confirmed by an X-ray crystallographic study of crystals of **2**(Cl<sup>-</sup>)<sub>3</sub>·4H<sub>2</sub>O, obtained from treatment of a solution of **1** with excess HCl(aq) (Figure 1).<sup>7</sup>

The CV of [Pt(tpy)(pip<sub>2</sub>NCN)][BF<sub>4</sub>]<sup>-</sup> (**1**(BF<sub>4</sub><sup>-</sup>)) in acetonitrile solution (0.1 M TBAPF<sub>6</sub>, 0.25 V/s) exhibits two reversible one-electron reduction waves at  $E^{\circ'} = -0.98$  V ( $E^{\circ'} = (E_{pa} + E_{pc})/2$ ;  $i_{pc}/i_{pa} = 0.80$ ) and  $E^{\circ'} = -1.50$  V ( $i_{pc}/i_{pa} = 0.52$ ), with a  $\Delta E_p$  of 65 and 61 mV versus Ag/AgCl, respectively (Figure 2A). As expected for a Nernstian one-electron process, the average value of  $\Delta E_p$  for the first reduction process ( $E^{\circ'} = -0.98$  V) is  $59 \pm 6$



**Figure 1.** ORTEP diagram of Pt(tpy)(pip<sub>2</sub>NCNH<sub>2</sub>)<sup>3+</sup> (**2**). For clarity, C atoms are not labeled, and all H atoms have been omitted with the exception of those bonded to N(amine) atoms.



**Figure 2.** (A) CV of [Pt(tpy)(pip<sub>2</sub>NCN)][BF<sub>4</sub>]<sup>-</sup> (**1**(BF<sub>4</sub><sup>-</sup>)) in acetonitrile (0.1 M TBAPF<sub>6</sub>, 0.25 V/s). (B) Dependence of  $i_{pa}$  for the 0.4 V oxidation (■) and  $i_{pc}$  for the -0.98 V reduction (●) on the square root of the scan rate ( $v^{1/2}$ ) for **1**(BF<sub>4</sub><sup>-</sup>). Lines represent linear fits of all oxidation data and reversible reduction data (0.02–2.5 V/s).

mV for 14 measurements with scan rates from 0.02 to 2.5 V/s. The complex also undergoes a nearly reversible two-electron oxidation process at  $E^{\circ'} = 0.40$  V ( $i_{pc}/i_{pa} = 1.08$ ,  $\Delta E_p = 74$  mV). Although the ratio (2.1) of the peak anodic current ( $i_{pa}$ ) of the oxidation process to the peak cathodic current ( $i_{pc}$ ) of the first reduction wave is somewhat less than 2.8 ( $=2^{3/2}$ ), which is predicted for a Nernstian two-electron process, it clearly exceeds the expected value (1.0) for a one-electron step.

Under identical conditions, neither free tpy, pip<sub>2</sub>NCNBr (2,6-(CH<sub>2</sub>N(CH<sub>2</sub>)<sub>5</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>Br),<sup>6</sup> nor Pt(pip<sub>2</sub>NCN)Cl is reduced at potentials more positive than -2.10 V, suggesting that the one-electron reduction processes for **1** are associated with the Pt(tpy) unit. In support of this assignment, Pt(tpy)(dmph)<sup>+</sup> (dmph<sup>-</sup> = 2,6-(CH<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>5</sub><sup>-</sup>) in acetonitrile solution undergoes two reversible one-electron reductions at similar potentials ( $E^{\circ'} = -0.96$  V,  $\Delta E_p = 60$  mV;  $E^{\circ'} = -1.49$  V,  $\Delta E_p = 64$  mV). The reversible two-electron oxidation wave observed for **1** is absent in CVs of related compounds. Neither Pt(tpy)(dmph)<sup>+</sup>, pip<sub>2</sub>NCNBr, nor pip<sub>2</sub>NCNBrH<sub>2</sub><sup>2+</sup> is oxidized at potentials <1.2 V, and Pt(pip<sub>2</sub>NCN)Cl undergoes irreversible oxidation near 0.8 V. Taken together, these data indicate that both the pip<sub>2</sub>NCN<sup>-</sup> and the terpyridyl ligands play important roles in the unusual redox chemistry of **1**. The availability of the amine lone electron pairs is critical to facilitating reversible two-electron oxidation and stabilizing the resulting Pt(IV) center (e.g.,

Figure 2A). For example, protonation of the piperdyl groups, as in **2**, results in irreversible oxidation near 0.4 V accompanied by electrode fouling.

CVs of **1** were recorded for the first reduction process (−1.2 to −1.7 V) and the oxidation process (0.2 to 0.6 V) over a range of scan rates from 0.005 to 25.6 V/s. For the reduction,  $\Delta E_p$  is essentially invariant ( $59 \pm 6$  mV) from 0.02 to 2.5 V/s, and the cathodic peak current exhibits an approximately linear dependence on the square root of the scan rate ( $\nu^{1/2}$ ), as predicted by the Randles–Ševčík equation for Nernstian diffusion control:<sup>8,9</sup>

$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C \nu^{1/2} \quad (1)$$

where  $n$  is the electron stoichiometry,  $A$  is the electrode area,  $D$  is the diffusion coefficient, and  $C$  is the concentration (Figure 2B). In contrast,  $\Delta E_p$  for the oxidation process increases steadily from 43 to 224 mV as the scan rate is increased from 0.01 to 20.5 V/s. Thus, over the range of scan rates for which the peak-to-peak separation of the first reduction process is essentially invariant,  $\Delta E_p$  for the oxidation process ranges from 43 to 150 mV. This behavior is consistent with some structural reorganization resulting in slow reaction kinetics. At the slowest scan rates,  $\Delta E_p$  (43 mV, 0.01 V/s) and  $E_{pa} - E_{pa/2}$  (30 mV, 0.01 V/s)<sup>4</sup> approach the two-electron Nernstian limits of 29.5 and 28.25 mV, respectively.<sup>10,11</sup> However, the process has slightly less than ideal behavior (e.g.,  $\Delta E_p = 43$  mV,  $i_{pc}/i_{pa} = 1.27$ , 0.01 V/s), suggesting that the oxidized product is not long-lived at room temperature. This instability is not surprising, as we know of no Pt(IV) tpy complexes in which the tpy ligand is tridentate.<sup>12</sup> At 273 K, the chemical reversibility approaches ideal behavior, but the process is less electrochemically reversible as indicated by an increase in  $\Delta E_p$  (e.g.,  $\Delta E_p = 91$  mV,  $i_{pc}/i_{pa} = 1.00$ , 0.01 V/s). While the lifetime of the oxidized product is improved at low temperature, the rate of electron transfer at the electrode is decreased, and the overall process is under increased kinetic control.

To verify the electron stoichiometry of the oxidation process for **1**,  $i_{pa}$  is plotted against  $\nu^{1/2}$  in Figure 2B. Although the process clearly exhibits non-Nernstian behavior as discussed earlier, the data are remarkably linear over the entire range of scan rates (0.005–20.5 V/s) as predicted by eq 1. The ratio (2.19) of the slope of the best fit line to that obtained for the first reduction process can be used to estimate a value for  $n_{ox}/n_{red}$  (=1.7) that is consistent with the notion that oxidation of **1** involves the transfer of two electrons per Pt center.

The accumulated data do not permit identification of the mechanism of two-electron transfer. Nevertheless, the observed kinetic control of the reaction and the structural rearrangement anticipated for the interconversion of Pt(II) and Pt(IV) suggest that the electron transfers are not concerted. The reaction can be viewed as the ligation accompanying the first electron transfer effectively driving the second charge-transfer step. Accordingly, the observation that  $\Delta E_p$  and  $E_{pa} - E_{pa/2}$  exceed the Nernstian two-electron values at slow scan rates is consistent with stepwise electron transfer in which the second electron-transfer step is slightly more favorable than the first (i.e.,  $E_2^{\circ} > E_1^{\circ}$ ).<sup>10</sup> It is noteworthy that the anodic shift of  $E_{pa}$  with increasing scan rate is smaller than the cathodic shift of  $E_{pc}$ . As a consequence,  $E^{\circ}$  shifts from 0.40 V at 0.005 V/s to 0.44 V at 20 V/s. This behavior is consistent with the formation of an organized structure, such as a five- or six-coordinate complex, prior to or during anodic electron transfer. The conversion of Pt(IV) to Pt(II) and axial bond cleavage during the reverse process are likely to require less preorganization, making  $E_{pc}$  less sensitive to scan rate.

The facile Pt(II)/Pt(IV) interconversion contrasts sharply with well-studied platinum couples.<sup>2,3,5</sup> This behavior may be in part related to the relative instability of a Pt(III) center bonded to somewhat constrained ligands that favor *mer*-coordination geometries. The special role of the  $\text{pip}_2\text{NCN}^-$  ligand in facilitating electron transfer is further suggested by comparison with  $\text{W}_2(\text{CO})_8(\mu\text{-SBz})_2^{2-}$  (HSBz = benzyl mercaptan).<sup>13</sup> Two-electron oxidation of the dimer at −0.87 V versus  $\text{Ag}/0.01 \text{ M AgNO}_3$  ( $\Delta E_p = 42$  mV, 0.2 V/s) is accompanied by only modest structural rearrangement ( $\sim 0.1 \text{ \AA}$  decrease in W–W distance,  $\sim 25^\circ$  change in W–S–W and S–W–S bond angles).<sup>13</sup> Although the variation of  $\Delta E_p$  with scan rate (104 mV, 20 V/s) is somewhat less pronounced than that observed for **1**, values of  $\Delta E_p$  and  $E_{pa} - E_{pa/2}$  (37 and 32 mV, respectively, 0.005 V/s) are similar to those observed at slow scan rates. It is conceivable that weakly favorable interactions between the  $\text{pip}_2\text{NCN}^-$  amine groups and the Pt(II) center in **1** preorganize the complex for electron transfer.

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**Supporting Information Available:** Experimental procedures and characterization for all compounds (PDF). Tables of crystallographic data, structure refinement details, atomic coordinates, interatomic distances and angles, anisotropic displacement parameters, and calculated hydrogen parameters for  $\mathbf{2}(\text{Cl}^-)_3$  (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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