

Structures and Reactions of Diplatinum Complexes

Thesis by
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Doctor of Philosophy

The logo for the California Institute of Technology (Caltech), featuring the word "Caltech" in a bold, orange, sans-serif font.

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ABSTRACT

A d^8 - d^8 complex $[\text{Pt}_2(\mu\text{-P}_2\text{O}_5(\text{BF}_2)_4)]^{4-}$ (abbreviated $\text{Pt}(\text{pop-BF}_2)^{4-}$) undergoes two $1e^-$ reductions at $E_{1/2} = -1.68$ and $E_p = -2.46$ V (vs Fc^+/Fc) producing reduced $\text{Pt}(\text{pop-BF}_2)^{5-}$ and superreduced $\text{Pt}(\text{pop-BF}_2)^{6-}$ species, respectively. The EPR spectrum of $\text{Pt}(\text{pop-BF}_2)^{5-}$ and UV-vis spectra of both the reduced and the superreduced complexes, together with TD-DFT calculations, reveal successive filling of the $6p\sigma$ orbital accompanied by gradual strengthening of Pt-Pt bonding interactions and, because of $6p\sigma$ delocalization, of Pt-P bonds in the course of the two reductions. Both reduction steps proceed without changing either d^8 Pt electronic configuration, making the superreduced $\text{Pt}(\text{pop-BF}_2)^{6-}$ a very rare $6p^2$ σ -bonded binuclear complex. However, the Pt-Pt σ bonding interaction is limited by the relatively long bridging-ligand-imposed Pt-Pt distance accompanied by repulsive electronic congestion. $\text{Pt}(\text{pop-BF}_2)^{4-}$ is predicted to be a very strong photooxidant (potentials of +1.57 and +0.86 V are estimated for the singlet and triplet $d\sigma^*p\sigma$ excited states, respectively).

Further study of the electronic excited states of $\text{Pt}(\text{pop-BF}_2)^{4-}$ in the presence of luminescence quenchers revealed Stern-Volmer type dynamic quenching of the triplet state by trialkyl and triaryl amines. Quenching of the singlet as well as the triplet was observed in the presence of Co^{II} trisbipyridine complexes, but sample decomposition and the observed presence of simultaneous static and dynamic quenching behaviors hampered quantitative analysis.

PUBLISHED CONTENT AND CONTRIBUTIONS

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T.V.D. participated in the conception of the project; conducted absorption, electron paramagnetic resonance, electrochemical, and spectroelectrochemical experiments; prepared and analyzed data; and participated in the writing of the manuscript.

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