

The phosphorescence of in aqueous solution is quenched by 1,1'-bis(2-sulfoethyl)-4,4'-bipyridinium inner salt (BSEP). Transient absorption attributable to BSEP<sup>-</sup> ( $\lambda_{\max} \sim 610 \text{ nm}$ )<sup>19</sup> is observed in flash kinetic spectroscopic studies of aqueous solutions containing  $\text{Pt}_2(\text{P}_2\text{O}_5)_4\text{H}_8^{4-}$  and BSEP, thereby establishing an electron-transfer quenching mechanism:



Stern-Volmer analysis of the quenching yields  $k_q = 5.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  ( $[\text{Pt}_2(\text{P}_2\text{O}_5)_4\text{H}_8^{4-}] \sim 10^{-4} \text{ M}$ ;  $0.1 \text{ M NaClO}_4$ ;  $25^\circ \text{C}$ ). Both the quenching reaction and the bimolecular back-electron-transfer ( $k = 1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for  $\text{Pt}_2(\text{P}_2\text{O}_5)_4\text{H}_8^{3-}$  and BSEP<sup>-</sup>) are near the diffusion limit for such processes in aqueous solution at  $25^\circ \text{C}$ .

The  $^3\text{A}_{2u}(\text{d}\sigma^*\text{p}\sigma)$  state of  $\text{Pt}_2(\text{P}_2\text{O}_5)_4\text{H}_8^{4-}$  is an extremely powerful one-electron reductant in aqueous solution. Preliminary experiments have shown that species such as  $\text{Os}(\text{NH}_3)_5\text{Cl}^{2+}$  ( $E_{1/2} = -1.09 \text{ V vs. SCE}$ )<sup>20</sup> and nicotinamide ( $E_{1/2} = -1.44 \text{ V vs. Ag/AgCl}$ ;  $\text{CH}_3\text{OH}$ , pH 7.2)<sup>21</sup> are readily reduced by  $\text{Pt}_2$ -

(19) Maverick, A. W. Ph.D. Thesis California Institute of Technology, 1982.

(20) Gulen, J.; Page, J. A. *J. Electroanal. Chem.* **1976**, *67*, 215-230.

( $\text{P}_2\text{O}_5)_4\text{H}_8^{4-}$ . From these and related experiments it is apparent that  $\text{Pt}_2(\text{P}_2\text{O}_5)_4\text{H}_8^{4-}$  is a stronger reducing agent [ $E^\circ(3-/4-^*) < -1 \text{ V vs. NHE}$ ]<sup>22</sup> than  $\text{Ru}(\text{bpy})_3^{2+}$  ( $E^\circ = -0.88 \text{ V vs. NHE}$ )<sup>23</sup> in aqueous solution. We are now exploring several aspects of the photoredox chemistry of  $\text{Pt}_2(\text{P}_2\text{O}_5)_4\text{H}_8^{4-}$ , as the ease of generation of  $\text{Pt}_2(\text{P}_2\text{O}_5)_4\text{H}_8^{4-}$  suggests that it will be a useful reagent for a variety of substrate reductions.

**Acknowledgment.** We thank D. S. Kliger and R. A. Goldbeck for assistance with some of the laser flash spectroscopic experiments. We are indebted to A. W. Maverick, S. J. Milder, V. M. Miskowski, D. G. Nocera, and S. F. Rice for several helpful discussions. This research was supported by National Science Foundation Grant CHE78-10530.

(21) Meites, L.; Zuman, P.; Scott, W. J.; Campbell, B. H.; Kartos, A. M. "Electrochemical Data"; Wiley: New York, 1974; Part 1, AG85.

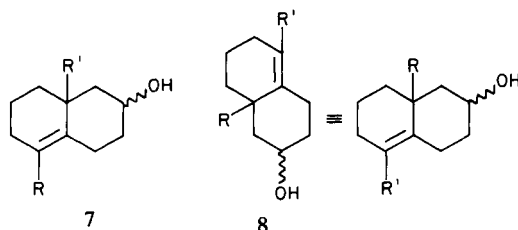
(22) It has not been possible to obtain a better estimate of  $E^\circ(4-/3-)$  from spectroscopic and electrochemical measurements, because the electrochemical oxidation of  $\text{Pt}_2(\text{P}_2\text{O}_5)_4\text{H}_8^{4-}$  in aqueous solution at  $25^\circ \text{C}$  is not reversible (cyclic voltammetric measurements; graphite electrode; scan speed,  $500 \text{ mV/s}$ ;  $\text{K}_4[\text{Pt}_2(\text{P}_2\text{O}_5)_4\text{H}_8]$ ,  $0.1 \text{ M NaClO}_4$ ).

(23) Navon, G.; Sutin, N. *Inorg. Chem.* **1974**, *13*, 2159-2164.

## Additions and Corrections

**On the Nonconcertedness of Allylic Cation Promoted  $\pi$ -Cyclization Reactions** [*J. Am. Chem. Soc.* **1981**, *103*, 1285]. MLADEN LADIKA, IVO BREGOVEC, and DIONIS E. SUNKO,\* Department of Chemistry, Faculty of National Sciences and Mathematics, University of Zagreb, 41000 Zagreb, Yugoslavia.

Page 1286: Structures 7 and 8 should be:



**Stereochemical Analysis of  $\gamma$ -Replacement and  $\gamma$ -Elimination Processes Catalyzed by a Pyridoxal Phosphate Dependent Enzyme** [*J. Am. Chem. Soc.* **1981**, *103*, 4921]. MICHAEL N. T. CHANG and CHRISTOPHER T. WALSH,\* Departments of Chemistry and Biology, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

Page 4925, Scheme VII: The last species is 4-S-2-ketobutyrate, not 4R as written.

Page 4925, 5th and 6th lines from the bottom, first column: The text should read "conversion of (Z)- and (E)-[4-<sup>2</sup>H]-vinyl-

glycines to (4S)- and (4R)-[<sup>1</sup>H,<sup>2</sup>H,<sup>3</sup>H]-2-ketobutyrate, respectively, can be interpreted." The S and R designations were inadvertently transposed.

Page 4923, Table II, line 3: The numbers 1027.5 and 1029.3 are incorrectly transposed. The (E)-[4-<sup>2</sup>H]-vinylglycine yields the 1029.3 sample of homoserine, the (Z)-vinylglycine yields the 1027.5 sample.

**Synthesis, Structure, and Stability of (i,o)-Bicyclo[6.2.2]dodeca-9,11-dienes. Generation of Unusually Expanded Carbon-Carbon Bond Angles** [*J. Am. Chem. Soc.* **1981**, *103*, 215]. PAUL G. GASSMAN\* and REBECCA C. HOYE, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455.

Page 217: In Table II for atom O2, the z value should be 0.4691 (1) instead of 0.4961 (1).

**$\alpha$ -Disulfoxide and Sulfinic Anhydride in the Peroxy Acid Oxidation of 2-Methyl-2-propyl 2-Methyl-2-propanethiosulfinate** [*J. Am. Chem. Soc.* **1981**, *103*, 6232-6235]. FILLMORE FREEMAN\* and CHRISTOS N. ANGELETAKIS, Department of Chemistry, University of California, Irvine, California 92717.

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