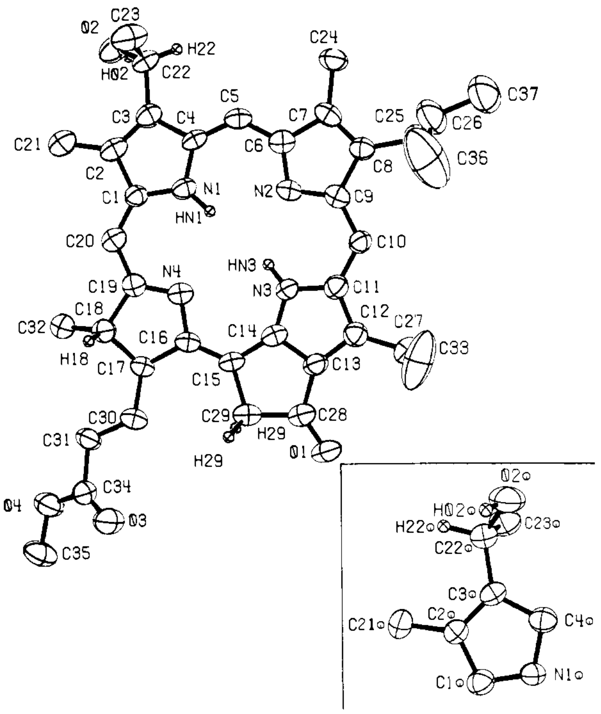


Figure 3. Molecular structure of one independent molecule of **1** and associated nomenclature. The insert shows ring I and the relative orientation of the 2-(1-hydroxyethyl) substituent for the second crystallographically independent molecule. Ellipsoids are drawn to enclose 50% probability except for those of the hydrogens, which are not to scale. Hydrogens on side chains other than the 2-(1-hydroxyethyl) have been eliminated for clarity.

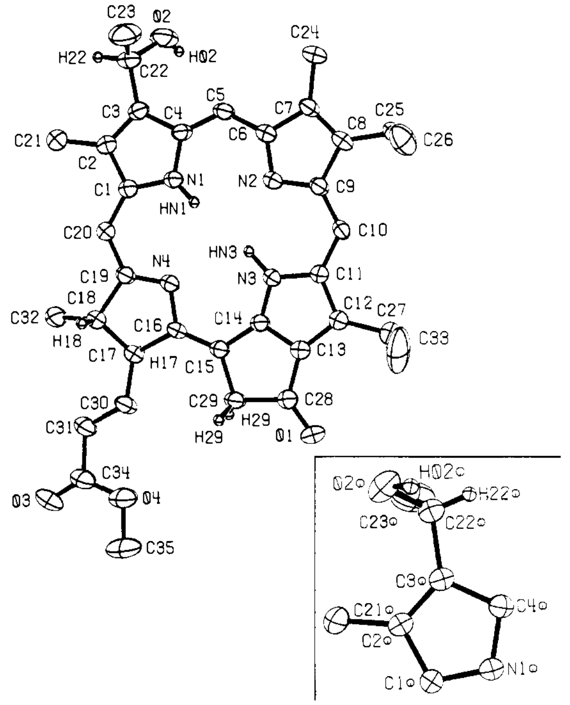


Figure 4. Molecular structure of one independent molecule of **5** and associated nomenclature. The insert shows ring I and the relative orientation of the 2-(1-hydroxyethyl) substituent for the second crystallographically independent molecule. Ellipsoids are drawn to enclose 50% probability except for those of the hydrogens, which are not to scale. Hydrogens on side chains other than the 2-(1-hydroxyethyl) have been eliminated for clarity.

graphic asymmetric unit in both structures consists of two independent molecules, the insert in each figure shows ring I and the geometry of the 2-(1-hydroxyethyl) group of the second molecule. Within a pair, the difference in orientation of the 2-(1-hydroxyethyl) substituents is conformational in nature. Their rotation enables the formation of dimers that are held together by two intermolecular hydrogen bonds between the hydroxyl group of ring I and the keto group of ring V (O2 and O1′, and O2′ and O1). However, neither 2-(1-hydroxyethyl) substituent in **1** is superimposable on the analogous group in **5**.[18] Thus, **1** and **5**, being *S* and *R*,[18] respectively, at position 2, are configurationally distinct, in agreement with the NMR and HPLC results.

Acknowledgment. This research was supported by grants from the National Science Foundation and Research Corporation (HPLC equipment) at the University of California and by the Division of Chemical Sciences, U.S. Department of Energy, Washington, D.C., under Contract No. DE-ACO2-76CH00016 at Brookhaven National Laboratory. We are grateful to Professor Norbert Pfennig (Konstanz) for providing us with the *Chlorobium vibrioforme* strain and the Chemistry Department at Brookhaven for use of the diffractometer.

Registry No. (2*S*)-**1**, 81873-38-3; (2*R*)-**1**, 59924-08-2; (2*S*)-**2**, 81873-39-4; (2*R*)-**2**, 59924-05-9; (2*R*)-**3**, 59924-07-1; (2*S*)-**3**, 81873-40-7; (2*R*)-**4**, 59954-19-7; (2*S*)-**4**, 81938-66-1; (2*R*)-**5**, 59924-06-0; (2*S*)-**5**, 81873-41-8; (2*R*)-**6**, 59954-18-6; (2*S*)-**6**, 61665-26-7.

Supplementary Material Available: Final positional and anisotropic thermal parameters for the non-hydrogen atoms of **1** and **5** (5 pages). Ordering information is given on any current masthead page.

---

(18) The enantiomorph was chosen such that the orientation of substituents in ring IV was consistent with the chemical studies and the previously defined absolute stereochemistry in that ring.[19] The absolute configuration of the chiral centers was not determined by the present crystallographic analyses.

(19) Brockmann, H., Jr. *Philos. Trans. R. Soc. London, Ser. B* **1976**, *273*, 277-285.

Spectroscopic Evidence for Directed Electronic Influences within Norbornyl Frameworks[1]

Leo A. Paquette* and Pana Charumilind

Evans Chemical Laboratories, The Ohio State University
Columbus, Ohio 43210

Received March 10, 1982

Revealing early studies by Jensen[2] and Traylor,[3] which gave indication of preferential electron supply to an *exo*-2-norbornyl substituent, have not been accorded proper importance because their key conclusions were couched in terms of a less than satisfactory[4] hyperconjugative model. Brown challenged "if there is a hunger for a directed electron contribution in the *exo*-norbornyl system, one can only hope that someone will demonstrate unambiguously the existence of such a directed electronic effect."[5] In the intervening years, several additional relevant experiments have been reported.[6-11] Also, norbornenes and 2-methylenenorbornanes

---

(1) Electronic Control of Stereoselectivity. 12. For part 11, see: Paquette, L. A.; Klinger, F. *J. Org. Chem.* **1982**, *47*, 272.

(2) Jensen, F. R.; Smart, B. E. *J. Am. Chem. Soc.* **1969**, *91*, 5686, 5688.

(3) Traylor, T. G.; Hanstein, W.; Berwin, H. J.; Clinton, N. A.; Brown, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 5715.

(4) Brown, H. C. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977; Chapter 14.

(5) Brown, H. C.; Guedin, B. G.; Takeuchi, K.; Peters, E. N. *J. Am. Chem. Soc.* **1975**, *97*, 610.

(6) Nugent, W. A.; Wu, M. M.-H.; Fehlner, T. P.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1976**, 456.

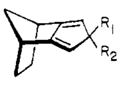
(7) (a) Huisgen, R.; Ooms, P. H. J.; Mingin, M.; Allinger, N. L. *J. Am. Chem. Soc.* **1980**, *102*, 3951. (b) Huisgen, R. *Pure Appl. Chem.* **1981**, *53*, 171.

(8) (a) Paquette, L. A.; Carr, R. V. C.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1980**, *102*, 1186. (b) Böhm, M. C.; Carr, R. V. C.; Gleiter, R.; Paquette, L. A. *Ibid.* **1980**, *102*, 7218. (c) Paquette, L. A.; Carr, R. V. C.; Arnold, E.; Clardy, J. *J. Org. Chem.* **1980**, *45*, 4907. (d) Paquette, L. A.; Bellamy, F.; Böhm, M. C.; Gleiter, R. *Ibid.* **1980**, *45*, 4913. (e) Paquette, L. A.; Carr, R. V. C.; Charumilind, P.; Blount, J. F. *Ibid.* **1980**, *45*, 4922.

0002-7863/82/1504-3749$01.25/0

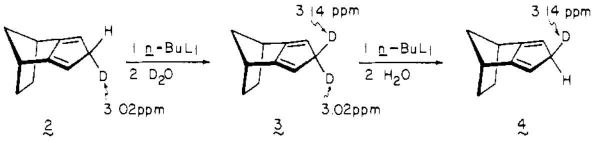
have been examined theoretically in an effort to assess their strong penchant for highly stereoselective addition.[12-14] Notwithstanding, conclusive proof of the phenomenon in question has not yet been brought forward in a form that would be universally accepted.

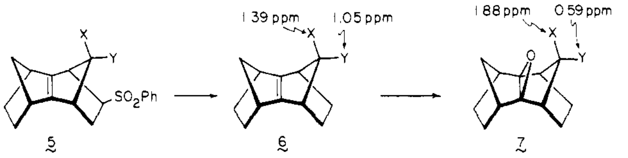
To resolve this longstanding question, we have made recourse to the simple innovation of removing the probes from the immediate vicinity of the norbornyl framework and arranging them symmetrically about a fused nodal plane as in **1**. Because of the location of the double bonds, a classical exo/endo distinction is not possible until three additional bonds have been traversed. Although reliance must consequently be placed upon long-range orbital interactions, our expectations ran high as a consequence of the unusual level of stereoelectronic control exhibited by these molecules in Diels–Alder reactions[15] and the strikingly large orbital interactions through four or more bonds that have been recently uncovered.[16] It is especially important to recognize that R_1 and R_2 in **1** differ only by virtue of the syn disposition of a methano or ethano bridge at the other, remote end of the structure.



1

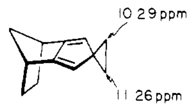
Quenching of the cyclopentadienide anion derived from **1** ($R_1 = R_2 = H$)[17] with D_2O in THF at −78 °C results in the regiospecific and π-facial stereoselective[18] formation of **2** as denoted by the appearance of a predominant singlet at 3.02 ppm in the proton-decoupled ^2H NMR spectrum of the product. Following repetition of this procedure to give **3**, a third exchange was carried out, and this d_1 anion was protonated so as to give **4**, which exhibits a major singlet at 3.14 ppm. Confirmation of these stereochemical assignments was achieved by means of independent cycloaddition of phenyl vinyl sulfone to **2** and **4**,[19] reductive desulfonylation of **5a** and **5b**, and peracid oxidation of the two d_1 *syn*-sesquinorbornenes.[19] The well-recognized anisotropy contributions of the oxirane oxygen[20] in **7a** and **7b** cause the inner D atom to be deshielded by 0.49 ppm and the outer to be shielded by 0.46 ppm.



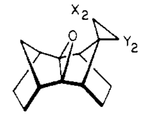


a, X = H, Y = D; b, X = D, Y = H

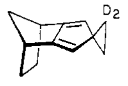
The carbon atoms within the three-membered ring of spirocyclopropane **8** similarly exhibit different chemical shifts.[21] The upfield position of the above-plane carbon atom in this hydrocarbon was ascertained by two complementary series of experiments. In the first, **8** was transformed via its phenyl vinyl sulfone adduct[22] into **9a**, where a clear-cut distinction between proximal and distal cyclopropane protons was realized by $Eu(fod)_3$ shift studies (ΔEu values:[23] $X_2 = 4.07$; $Y_2 = 1.75$). With these observations as our basis for stereochemical assignment, the d_2 derivatives **10** and **11** were prepared[18] and similarly transformed into **9b** and **9c**. With knowledge of the location of the isotopic labels in **10** and **11**, the specific ^{13}C shifts of interest in **8** became clearly apparent.



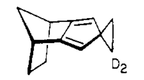
8



9a, X = Y = H
b, X = D, Y = H
c, X = H, Y = D

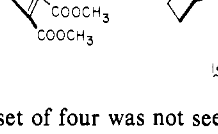


10

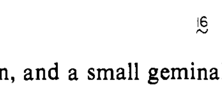


11

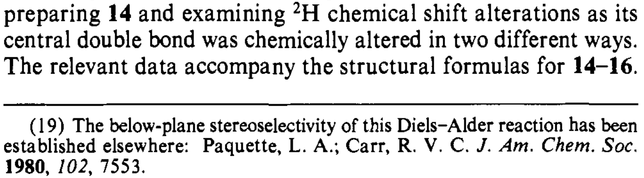
The four methylene carbons within the spirocyclic five-membered ring of **12** also emerge with distinctively different chemical shifts. Following the preparation of **13**,[18] the lowest field ^{13}C signal of the set of four was not seen, and a small geminal deuterium isotope effect was observed as expected.[24] In the case of **13**, knowledge of the locus of isotopic substitution was gained by preparing **14** and examining ^2H chemical shift alterations as its central double bond was chemically altered in two different ways. The relevant data accompany the structural formulas for **14–16**.



12



13



---

(9) Sugimoto, T.; Kobuke, Y.; Furukawa, J. *J. Org. Chem.* **1976**, *41*, 1457.

(10) (a) Avenati, M.; Hagenbuch, J.-P.; Mahaim, C.; Vogel, P. *Tetrahedron Lett.* **1980**, 3167. (b) Hagenbuch, J.-P.; Vogel, P.; Pinkerton, A. A.; Schwarzenbach, D. *Helv. Chim. Acta* **1981**, *64*, 1819.

(11) Watson, W. H.; Galloy, J.; Bartlett, P. D.; Roof, A. A. M. *J. Am. Chem. Soc.* **1981**, *103*, 2022.

(12) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4056.

(13) (a) Houk, K. N. In "Reactive Intermediates"; Jones, M. Moss, R. A., Eds.; Wiley-Interscience: New York, 1978; Vol. I, pp 326–327. (b) Rondan, N. G.; Paddon-Row, M. N.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 2436. (c) Caramella, P.; Rondan, N. G.; Paddon-Row, M. G.; Houk, K. N. *Ibid.* **1981**, *103*, 2438.

(14) Wipff, G.; Morokuma, K. *Tetrahedron Lett.* **1981**, 4445.

(15) (a) Paquette, L. A.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Bass, L. S.; Clardy, J., to be submitted for publication. (b) Paquette, L. A.; Hayes, P. C.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Blount, J. F., to be submitted for publication.

(16) (a) Martin, H.-D.; Schwesinger, R. *Chem. Ber.* **1974**, *107*, 3143. (b) Pasman, P.; Verhoeven, J. W.; deBoer, Th. J. *Tetrahadron Lett.* **1977**, 207. (c) Bartetzko, R.; Gleiter, R.; Muthard, J. L.; Paquette, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5589. (d) Paddon-Row, M. N.; Hartcher, R. *Ibid.* **1980**, *102*, 671. (e) Paddon-Row, M. N.; Patney, H. K.; Brown, R. S.; Houk, K. N. *Ibid.* **1981**, *103*, 5575.

(17) The tetrahedrally bound cyclopentadiene protons in this hydrocarbon are coincident with other signals and unfortunately cannot be reliably distinguished.

(18) The interesting stereoselective captures of electrophiles by this anion are to be detailed in a full paper: Paquette, L. A.; Charumilind, P.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R., to be submitted for publication.

(19) The below-plane stereoselectivity of this Diels–Alder reaction has been established elsewhere: Paquette, L. A.; Carr, R. V. C. *J. Am. Chem. Soc.* **1980**, *102*, 7553.

(20) (a) Tori, K.; Kitahonoki, K.; Takano, Y.; Tanida, H.; Tsuji, T. *Tetrahedron Lett.* **1964**, 559. (b) Tori, K.; Aono, K.; Kitahonoki, K.; Muneyuki, R.; Takano, Y.; Tanida, H.; Tsuji, T. *Ibid.* **1966**, 2921. (c) Paquette, L. A.; Fristad, W. E.; Schuman, C. A.; Beno, M. A.; Christoph, G. G. *J. Am. Chem. Soc.* **1979**, *101*, 4645.

(21) The cyclopropyl protons in **8** appear as a single sharp singlet at δ 1.36 (in $CDCl_3$ solution). As in **12**, the protons adjacent to the spiro center are splayed outward from the central core of electronic influence.

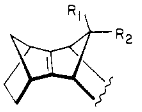
(22) Clean below-plane attack occurs under these conditions.[15a]

(23) Demarco, P. V.; Elzey, T. K.; Lewis, R. B.; Wenkert, E. *J. Am. Chem. Soc.* **1970**, *92*, 5734.

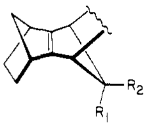
(24) Inamoto, Y.; Aigami, K.; Fujikura, Y.; Ohsugi, M.; Takaishi, N.; Tsuchihashi, K.; Ikeda, H. *Chem. Lett.* **1978**, 25 and pertinent references provided therein.

Without doubt, the carbon shielding effects operating in **12** are *reversed* relative to those in **8**!

The ^{13}C spectral data parallel exactly the differing stereoselectivities of dienophile capture exhibited by **8** and **12**. Thus, while **8** undergoes below-plane bonding to electron-deficient olefins with formation of adducts of type **17b**,[15a] **12** engages in Diels–Alder chemistry from its exo surface to give **18a**.[15,25] The *gem*-dimethyl derivative **1** ($R_1 = R_2 = CH_3$) behaves comparably to **12**, but no technique has yet been found to distinguish between these substituents (^{13}C shifts: 23.55 and 22.92 ppm).

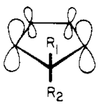


17a, $R_1 = R_2 = H$
b, $R_1,R_2 = (CH_2)_2$

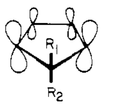


18a, $R_1,R_2 = (CH_2)_4$
b, $R_1 = R_2 = CH_3$

In isodicyclopentadiene, the influence of the norbornane σ-electron network is to cause disrotatory tilting within the subjacent π_s diene orbital toward the methano bridge (see **19**) with resultant minimization of closed-shell antibonding interaction on the endo surface during dienophile approach.[8] However, various theoretical calculations reveal this tilting to be critically dependent upon all σ orbital energies.[26] In fact, simple replacement of hydrogen atoms by alkyl groups at R_1 and R_2 (with $R_1 = R_2$) is adequate to reverse the mode of disrotation as in **20**. The exception is the spirocyclopropane **8**, where the high level of spiroconjugation[27] that develops as the result of strong π interaction with the symmetric Walsh orbitals of the three-membered ring[28] causes π_s once again to become tilted as in **19b**.[15] Consequently, in the ground state of those dienes whose π-electron character is of type **19**, R_2 should experience greater shielding than R_1. The reverse should be true in **20**, as observed experimentally. It follows that [4 + 2] cycloaddition occurs preferentially from the *less shielded* face of these dienes in order to profit from lower secondary antibonding influences along this pathway.



19a, $R_1 = R_2 = H$
b, $R_1,R_2 = (CH_2)_2$



20a, $R_1,R_2 = (CH_2)_4$
b, $R_1,R_2 = CH_3$

While ^{13}C shieldings are dominated chiefly by local paramagnetic electron currents,[29] local diamagnetic effects make the more important contribution to ^2H chemical shifts.[30] These differences may account for the spectral parameters of **2–4**.[31]

Registry No. 1 ($R, R_2 = H$), 6675-72-5; **2**, 81897-83-8; **3**, 81897-84-9; **4**, 81897-85-0; **5a**, 81969-70-2; **5b**, 81897-86-1; **6a**, 81897-87-2; **6b**, 81967-92-2; **7a**, 81897-88-3; **7b**, 81967-93-3; **8**, 81897-89-4; **9a**, 81897-90-7; **9b**, 81897-91-8; **9c**, 81967-94-4; **10**, 81897-92-9; **11**, 81967-95-5; **12**, 81897-93-0; **13**, 81897-94-1; **14**, 81897-95-2; **15**, 81897-96-3; **16**, 81897-97-4.

---

(25) Exceptions to this behavior are sometimes encountered with those dienophiles, e.g., dimethyl acetylenedicarboxylate and *N*-methyltriazolinedione, that possess a second π bond or nonbonded electron pairs orthogonal to that π bond which constitutes the seat of reaction. The consequences of these secondary electronic perturbations will be discussed elsewhere.

(26) Gleiter, R.; Böhm, M. C., private communication.

(27) Staley, S. W.; Howard, A. E.; Harmony, M. D.; Mathur, S. N.; Kattija-Ari, M.; Choe, J.-I.; Lind, G. *J. Am. Chem. Soc.* **1980**, *102*, 3639 and references cited therein.

(28) Gleiter, R.; Heilbronner, E.; de Meijere, A. *Helv. Chim. Acta* **1971**, *54*, 1029.

(29) Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden: London, 1980; Chapter 2.

(30) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: New York, 1969; Chapter 2-2.

(31) We are indebted to the National Cancer Institute (Grant CA-12115) for their generous financial support of this program.

Electrochemical Preparation of a Prussian Blue Analogue: Iron–Ruthenium Cyanide

Kingo Itaya,* Tatsuaki Ataka, and Shinobu Toshima

Research Institute of Electrical Communication
and Department of Applied Chemistry
Faculty of Engineering
Tohoku University, Sendai 980, Japan

Received December 23, 1981

Recent reports by Neff et al. have shown a method of preparation of Prussian blue (PB) on platinum and gold electrodes based on a chemical method.[1,2] We disclosed very recently an electrochemical method of synthesis for the preparation of thin films of PB[3] and have discussed the electron-transfer reactions and the possibilities for application in electrochromic displays.[3,4] The crucial point for the preparation of PB films in both the chemical and the electrochemical methods is that a ferric ferricyanide mixture obtained by mixing solutions of ferric ion, Fe^{3+}, and of ferricyanide ion, $Fe^{III}(CN)_6{}^{3-}$, is a clear solution where no precipitate is formed for several hours. Other mixing combinations lead immediately to heavy precipitates (gels) that have been called Prussian blue, Turnbull's blue, and Prussian white (Everitt's salt), depending on the valency values of the iron ions used.[5,6] Recently, Siperko and Kuwana obtained a copper hexacyanoferrate film on a glassy carbon electrode based on dissolution of copper layers on the substrate.[7]

We disclose here a method for the preparation of thin films of ferric ruthenocyanide, $Fe_4{}^{3+}[Ru^{II}(CN)_6]_3$, by means of an electrochemical reduction method and discuss the spectroelectrochemical results. Precipitation reactions for ruthenocyanide ion, $Ru^{II}(CN)_6{}^{4-}$, and ruthenicyanide ion, $Ru^{III}(CN)_6{}^{3-}$, are quite similar to those of ferric and ferrocyanide ions.[8,9] Both ferricyanide and ruthenicyanide yield red-brown solutions, but no precipitates, with ferric ion.[9] This result strongly encouraged us to extend the method employed in our previous paper[3,4] for the preparation of films of iron ruthenocyanide mixed-valency complexes.

The ruthenicyanide solutions used here were prepared by adding lead peroxide, PbO_2, to a solution of 1 mM $K_4Ru(CN)_6$, obtained from the Soekawa Chemical Co., in 0.01 M H_2SO_4. A fresh solution of reagent grade $Fe_2(SO_4)_3$ (1 mM) and $K_3Ru(CN)_6$ (1 mM) was prepared by mixing solutions of each. The electrodes, SnO_2, Pt, or glassy carbon, immersed in the above solution, were cathodically polarized under galvanostatic conditions by using a current density of about 20 $\mu A/cm^2$. A large platinum foil was used as a counterelectrode. The purple due to the formation of ruthenium purple (RP), $Fe_4{}^{3+}[Ru^{II}(CN)_6]_3$,[5,10] can be seen right from the beginning of the electrolysis. This behavior is basically the same as observed in the preparation of PB reported previously. However, the current efficiency for the deposition of RP was far below the value of 100% obtained in the case of PB.

Figure 1 shows cyclic voltammograms of an RP-modified Pt electrode in 0.5 M K_2SO_4 adjusted to pH 4.0 with sulfuric acid. The amount of RP (3 mC/cm^2) was estimated from a coulometric curve measured during the potential scan from 0.6 to −0.2 V vs. SCE (saturated calomel electrode). The peak potentials of the reductive and oxidative waves are 0.22 and 0.25 V vs. SCE, which are slightly dependent on the scan rate. Although the peak currents are directly proportional to the scan rate up to 50 mV/s, distortion of the wave is observed at higher scan rates. It is an

---

* Research Institute of Electrical Communication.

(1) Neff, V. D. *J. Electrochem. Soc.* **1978**, *125*, 886.

(2) Ellis, D.; Eckhoff, M.; Neff, V. D. *J. Phys. Chem.* **1981**, *85*, 1225.

(3) Itaya, K.; Shibayama, K.; Akahoshi, H.; Toshima, S. *J. Appl. Phys.* **1982**, *53*, 804.

(4) Itaya, K.; Ataka, T.; Toshima, S., submitted for publication.

(5) Ludi, A.; Güdel, H. U. *Struct. Bonding (Berlin)* **1973**, *14*, 1.

(6) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

(7) Siperko, L. M.; Kuwana, T., submitted for publication.

(8) Gmelin, "Handbuch der anorganischen Chemie"; 8th ed.; System Verlag Chemie G.m.b.H.: Berlin, 1932; No. 59, Part B, pp 643–652.

(9) DeFord, D. D.; Davidson, A. W. *J. Am. Chem. Soc.* **1951**, *73*, 1469.

(10) Robin, M. B. *Inorg. Chem.* **1962**, *1*, 337.

0002-7863/82/1504-3751$01.25/0