solid does indeed show a low C–H stretch at 2750 cm^{-1} strongly supporting the postulated η^5-cyclohexadienyl structure.

Of more importance is a comparison of the ^{1}H NMR spectra[9] of the solid prepared above with the spectra of known η^5-cyclohexadienyl complexes (see Table I).[12-22] The position of the ring proton at 5.42 ppm corresponds to the proton on carbon 4, which is para to the CH_2 group, supporting the thesis that protonation must have occurred at the α-position of the complexed ring of naphthalene.

If instead of adding H_2O, D_2O is added to the dianion solution, the peak at 2.69 ppm has collapsed to a singlet from a doublet with a geminal coupling constant of 12.5 Hz. The low coupling constant between the methylene proton and the proton adjacent to it allows the assignment of the methylene proton to the exo position.[23] Hence, the mode of attack of the electrophile is endo. This is further supported by the fact that the low C–H stretch in the IR is still present for the D^+ addition reaction. It is highly likely, considering the steric bulk of the $Cr(CO)_3$ group, as well as probable charge distributions in the dianion, that the proton first attacks the chromium atom. Recently,[24] a chromium hydride, very similar to the one that would be formed, was isolated and characterized. The chromium hydride could then undergo a hydride transfer to the α-position to give the η^5-cyclohexadienyl complex.[25]

The ^{13}C NMR[9] of the anion is also supportive of the assigned structure; all but one peak behave as would be expected for structure V. Assignments were made utilizing ^{13}C–H coupling data and comparing the data with that of known η^5-cyclohexadienyl complexes.[26-30] The ^{13}C NMR data, coupled with the other spectroscopic results, is overwhelming evidence in favor of the postulated structure.

There are many novel aspects of this reaction that we hope to exploit further. This is the first η^5-cyclohexadienyl complex prepared by first reducing the parent arene complex followed by addition of an electrophile. Previous η^5-cyclohexadienyl complexes have been prepared from the reaction of the arene complex with nucleophiles such as H^- and R^-. Also novel is the mode of attack. Nucleophiles attack the ring exo to the metal center, while in the reaction of H^+ with the dianion, the mode of attack is endo. Also of interest is the fact that this is the first isolated η^5-cyclohexadienyl complex where the parent arene is not a benzene species but, instead, a polynuclear aromatic. Moreover, this work should provide a basis for the understanding of all the reductive electrochemistry of (arene)tricarbonylchromium complexes.

Acknowledgment. We thank the National Science Foundation for support of this research (Grant CHE78-06661).

---

(16) Connelly, N. G.; Kelly, R. L. *J. Chem. Soc., Dalton Trans.* **1974**, 2334–2337.

(17) Fisher, E. O.; Schmidt, M. W. *Chem. Ber.* **1966**, *99*, 2206–2212.

(18) Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. C* **1969**, 2024–2030.

(19) Semmelhack, M. F.; Hall, H. T.; Farina, R.; Yoshifugi, M.; Clark, G.; Bargar, T.; Hirostu, K.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 3535–3544.

(20) Fisher, E. O.; Schmidt, M. W. *Chem. Ber.* **1967**, *100*, 3782–3788.

(21) Walker, P. J. C.; Mawby, R. *Inorg. Chim. Acta* **1973**, *7*, 621–625.

(22) Jones, D.; Wilkinson, G. *J. Chem. Soc.* **1964**, 2479–2481.

(23) The coupling between the methylene endo proton and the proton on the adjacent carbon is in the range 5.0–6.0 Hz, while only one report of coupling between the exo proton of the methylene group and an adjacent proton is 2.0 Hz.

(24) Darensbourg, M. Y.; Deaton, J. C. *Inorg. Chem.* **1981**, *20*, 1644–1646.

(25) A similar mechanism has been shown for the addition of CH_3I to $(\eta^5\text{-}C_9H_7)(CO)_3Cr^-$ and $(\eta^5\text{-}C_{13}H_9)(CO)_3Cr^-$: Nesmeyanov, A. N.; Ustynyuk, N. A.; Makarova, L. G.; Andrae, S.; Ustynyuk, Y. A.; Novikova, L. N.; Luzikov, Y. N. *J. Organomet. Chem.* **1978**, *154*, 45–63.

(26) Brill, T. B.; Kotlar, A. J. *Inorg. Chem.* **1974**, *13*, 470–474.

(27) Whitesides, T. H.; Budnick, R. A. *Inorg. Chem.* **1976**, *15*, 874–879.

(28) Dobosh, P. A.; Gresham, D. G.; Kawalski, D. J.; Lillya, C. P.; Magyar, E. S. *Inorg. Chem.* **1978**, *17*, 1775–1781.

(29) Colletta, F.; Gambaro, A.; Rigatti, G.; Venzo, A. *Spectrosc. Lett.* **1977**, *10*, 971–977.

(30) Jaouen, G.; Top, S.; McGlinchey, M. J. *J. Organomet. Chem.* **1980**, *195*, C5–C8.

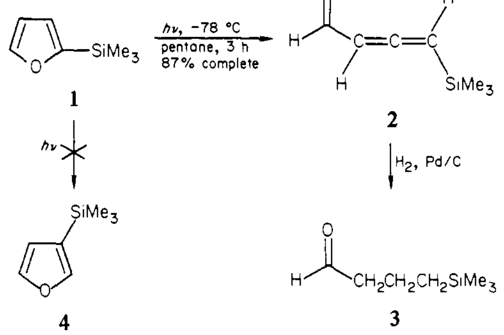
Extraordinary Photorearrangement of Silylfurans and Subsequent Thermal Rearrangements

Thomas J. Barton* and Gregory P. Hussmann

Department of Chemistry, Iowa State University
Ames, Iowa 50011

Received July 26, 1983

Although the photochemistry of furans has been extensively studied[1] since the initial report of Srinivasan,[2] no synthetic interest has developed due to the fact that complex product mixtures and low yields have inevitably resulted from these photolyses. We report here that silyl substitution allows remarkably clean photoisomerization of furans. Thus, irradiation[3] of a pentane solution of 2-(trimethylsilyl)furan (**1**)[4] for 3 h at –78 °C produced a clean mixture of unreacted **1** (87% completion) and a single product (68%) that was spectrally identified as 4-(trimethylsilyl)-2,3-butadienal (**2**).[5] This assignment was confirmed by catalytic hydrogenation (Pd/C) of **2** to afford 4-(trimethylsilyl)butanal (**3**).[6] Isolation of **2** by GC proved impossible due to decomposition to a large number of products, none of which was 3-(trimethylsilyl)furan (**4**), an expected[1] photoisomerization product of **1**.



Among the unprecedented features of the photolysis of **1** are the extreme cleanness, the high yield of an allene,[7] and the absence of a rearranged furan (i.e,, **4**).

In order to determine whether the silicon substitution was the controlling factor in changing the course of furan photochemistry, we chose next a close analogue of the previously studied 2,5-di-*tert*-butylfuran (**13**),[8] Irradiation of a pentane solution of 2,5-bis(trimethylsilyl)furan (**5**) at –78 °C for 2 h resulted in 65% disappearance of **5** and clean formation of two products: allenyl ketone **6** (84%)[9] and allenyl aldehyde **7** (10%).[9] Ketone **6** (an oil at room temperature) was isolated pure by repeated low-temperature crystallization from pentane, but aldehyde **7** was identified from its ^{1}H NMR spectrum alone, Quite surprisingly attempts to hydrogenate **6** led to quantitative conversion by palladium catalysis to 2,4-bis(trimethylsilyl)furan (**10**).[10] This

---

(1) Padwa, A. "Rearrangements in Ground and Excited States"; DeMayo, P., Ed.; Academic Press: New York, 1980; Vol. 3.

(2) Srinivasan, R. *J. Am. Chem. Soc.* **1967**, *89*, 1758.

(3) 450-W Hanovia through quartz, immersion well with internal water and external dry ice isopropyl alcohol cooling, 1% concentration.

(4) Lukevits, E. Ya.; Voronkov, M. G. *Khim. Geterotsikl. Soedin.* **1966**, *3*, 328; cf. *Chem. Heterocycl. Compd.* **1966**, *2*, 235.

(5) **2**: ^{1}H NMR (C_6C_6) δ 0.21 (s, 9 H), 5.13 (d, J = 7 Hz, 1 H), 5.45 (t, J = 7 Hz, 1 H), 9.52 ($HC{=}O$, d, J = 7 Hz); IR 1935 ($C{=}C{=}C$), 1692 cm^{-1} ($O{=}CC{=}C$),

(6) **3**: ^{1}H NMR (CCl_4) δ 0.15 (s, 9 H), 0.48 (m, 2 H), 1.72 (m, 2 H), 2.51 (m, 2 H), 9.72 (t, 1 H); IR $\nu_{C=O}$ 1730 cm^{-1}; calcd for $C_6H_{13}OSi$ ($M^+ - CH_3$) *m/e* 129.0736, measured *m/e* 129.0731.

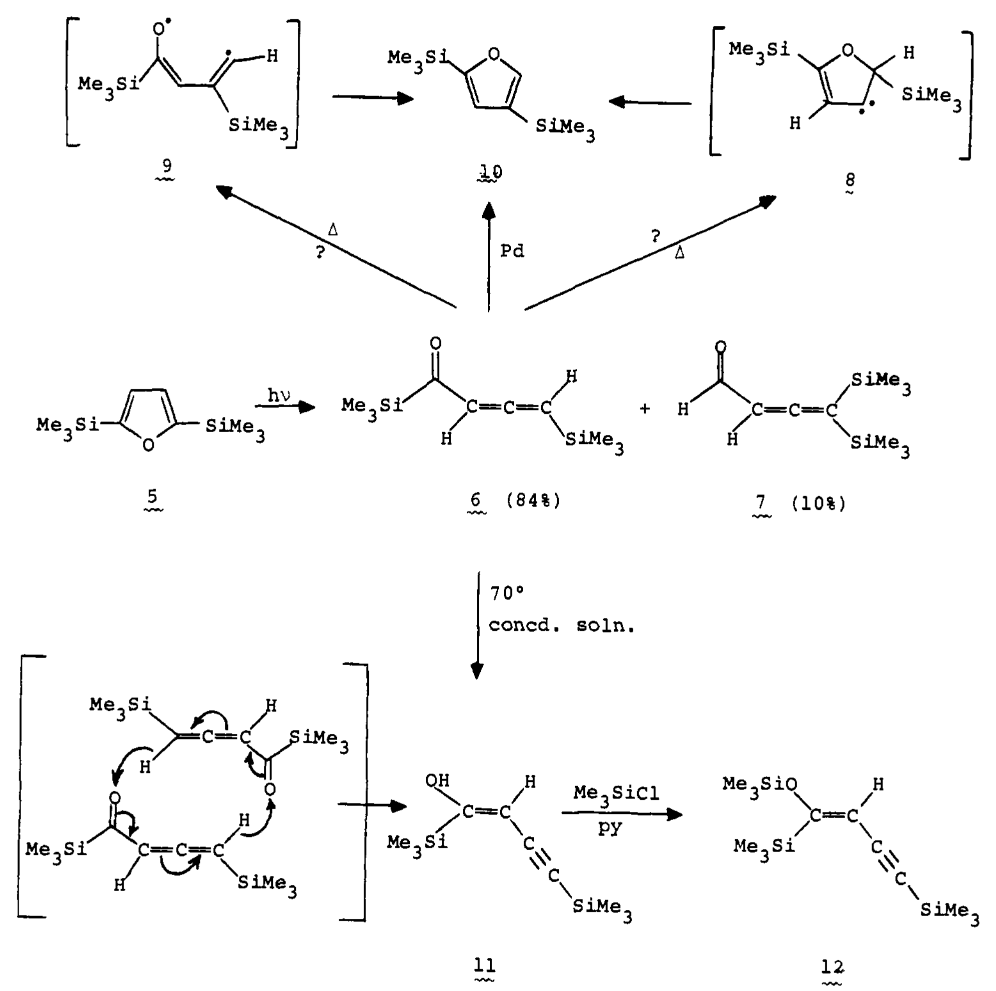
(7) The highest previously reported yield of an allene from furan photolysis is 9%.[8]

(8) van Tamelen, E. E.; Whitesides, T. H. *J. Am. Chem. Soc.* **1971**, *93*, 6129.

(9) **6**: ^{1}H NMR (CCl_4) δ 0.21 (s, 9 H), 0.22 (s, 9 H), 5.32 (d, J = 7 Hz, 1 H), 5.59 (d, J = 7 Hz, 1 H); CMR ($DCCl_3$) δ –1.5, –1.0, 87.6, 96.9, 216.8, 235.4; IR $\nu_{C=O}$ 1595, $\nu_{C=C=C}$ 1942 cm^{-1}; calcd for $C_{10}H_{20}OSi_2$ (M^+) *m/e* 212.1053, measured *m/e* 212.1059. **7**: ^{1}H NMR (CCl_4) δ 5.15 (d, J = 8 Hz, 1 H), 9.42; IR $\nu_{C=O}$ 1680, $\nu_{C=C=C}$ 1915 cm^{-1}.

0002-7863/83/1505-6316$01.50/0

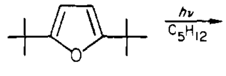
Scheme I



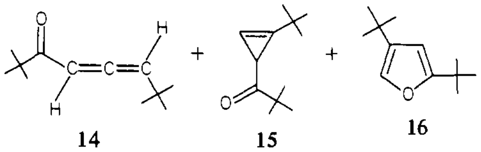
quantitative isomerization could also be achieved by attempted preparative GC of **6** or by heating a *dilute* benzene solution of **6** at 150 °C for 30 min. Equally surprising was the observation that heating very *concentrated* solutions of **6** (C_6H_6 or CCl_4) at 70 °C resulted in quantitative formation of a stable (albeit unisolable) enol **11**.[11] Quenching of this solution with trimethylchlorosilane afforded silyl enol ether **12**[12] in high yield.

The thermal isomerization of **6** to **10** can be imagined to occur through cyclization of **6** to carbene **8** followed by exclusive 1,2-silyl migration. However, we consider this cyclization geometrically unlikely and suggest that the reaction is initiated by a 1,2-silyl migration in **6** to afford diradical **9**, which closes to **10**.[13] The concentration dependence on the enolization of **6** to **11** suggests that it occurs via a bimolecular process, and a possible concerted 12-electron pathway is shown in Scheme I.[15]

The results for **5** are in striking contrast to those of the photolysis of the closely analogous 2,5-di-*tert*-butylfuran (**13**), which is reported[8] to produce a mixture of three major products, allenyl ketone **14**, acylcylopropene **15**, and 2,4-di-*tert*-butylfuran (**16**),



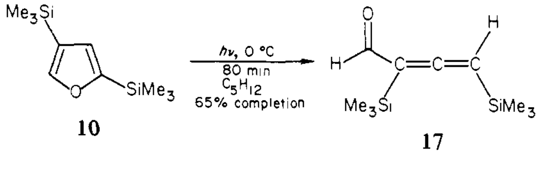
13



	14	15	16
ambient (ref 8)	9%	4%	9%
−78 °C	11%	9.5%	2.6%

in extremely modest yields. Other than silicon substitution, the only different parameter in our work and that of van Tamelen[8] is the reaction temperature. However, conducting the photolysis of **13** at −78 °C produced the same three products in yields very similar to those reported.

Furan **10** also undergoes facile photoisomerization (quantitative by NMR) to produce an allenyl aldehyde, **17**.[16]



10

17

---

[10] **10**: ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 9 H), 0.32 (s, 9 H), 6.60 (s, 1 H), 7.54 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ −1.4, 0.5, 118.2, 123.3, 151.3, 160.5; IR 2960, 1540, 1250 cm^{-1}; calcd for $C_{10}H_{20}OSi_2$ (M^+) *m/e* 212.1053, measured *m/e* 212.1046.

[11] **11**: ^{1}H NMR (C_6D_6) δ 0.18 (s, 9 H), 0.28 (s, 9 H), 5.05 (s, 1 H), 6.30 (s, OH); IR ν_{OH} 3440, $\nu_{C\equiv C}$ 2120 cm^{-1}.

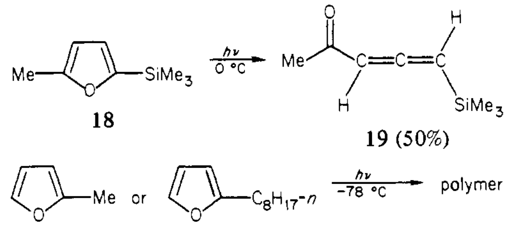
[12] ^{1}H NMR ($DCCl_3$) δ 0.18 (s, 9 H), 0.25 (s, 9 H), 0.39 (s, 9 H), 5.20 (s, 1 H); ^{13} NMR ($DCCl_3$) δ −2.3, 0.1, 1.5, 98.8, 102.0, 102.2, 173.0; IR $\nu_{C\equiv C}$ 2140, $\nu_{C=CO}$ 1565; calcd for $C_{13}H_{28}OSi_3$ (M^+) *m/e* 284.1448, measured *m/e* 284.1445.

[13] To our knowledge this is the first suggestion of a 1,2-silyl migration on an ethylenic framework. The thermal rearrangement of allenylsilanes has only been viewed as a 1,3-silyl shift.[14] This complex question, the related rearrangement of alkynylsilanes, and the effects of silyl substitution on the photochemical behavior of a variety of heterocyclic systems are all under active investigation in our laboratory.

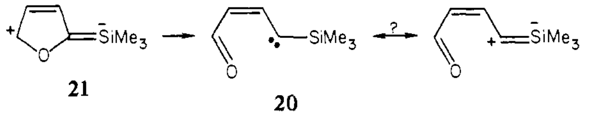
[14] Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, *95*, 8678.

[15] As would be expected for competitive unimolecular and bimolecular processes, heating of intermediate concentrations of **6** produced mixtures of **10** and **11**.

Further evidence of silicon control of furan photochemistry is found in the observation that irradiation of 5-methyl-2-(trimethylsilyl)furan (**18**) (*n*-pentane solution, 0 °C, 2 h, 45% completion) afforded a 50% yield of allenyl ketone **19** [^{1}H MR (C_6D_6) δ 0.21 (s, 9 H), 2.15 (s, 3 H), 5,15 (d, 1 H, J = 6 Hz), 5.45 (d, 1 H, J = 6 Hz); IR $\nu_{C=C=C}$ 1945, $\nu_{C=O}$ 1680 cm^{-1}; calcd for $C_8H_{14}OSi$ m/e 154.0814, measured m/e 154.0815], while under similar (except lower temperature) conditions 2-methylfuran and 2-*n*-octylfuran afford mainly polymers and no major volatile products.



A possible explanation for the facility and cleanness of the photochemistry of silylfurans as opposed to alkylfurans may be found in the ability of silicon to stabilize a polar excited state (and ground state) through inclusion of resonance structures such as **20** in the resonance hybrid, Alternatively, it might be argued that the role of silicon is to stabilize carbene **21**. We intend to directly generate carbene **21** and similar systems to probe this point.



Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Dow Corning Corp, for support of this work.

---

(16) **17**: ^{1}H NMR (pentane) δ 0.20 (s, 9 H), 0.31 (s, 9 H), 5.05 (s, 1 H), 9.80 (s, 1 H); IR (neat) 1920 and 1670 cm^{-1}; calcd for $C_{10}H_{20}OSi_2$ m/e 212.10528, measured m/e 212.10581.

Supported Palladium Catalysts for the Reduction of Sodium Bicarbonate to Sodium Formate in Aqueous Solution at Room Temperature and One Atmosphere of Hydrogen

Charles J. Stalder, Shuchi Chao, David P. Summers, and Mark S. Wrighton*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received June 15, 1983

We wish to report that the reduction of aqueous sodium bicarbonate, $NaCO_3H$, to aqueous sodium formate, $NaHCO_2$, can be effected at 298 K and 1 atm H_2 using various forms of supported Pd as a catalyst for the equilibrium represented by eq 1.

$$H_2 + NaCO_3H(aq) \xrightleftharpoons{\text{supported Pd}} NaHCO_2(aq) + H_2O \quad (1)$$

We were prompted to begin this investigation by a report that a Pd/carbon catalyst would give a significant amount of formate (13 mM) from aqueous 0.3 M bicarbonate.[1] There has been some confusion in the literature concerning the thermodynamics for reaction 1. In particular, Pourbaix diagrams[2] would suggest that reaction 1 would not proceed to a significant extent. The extent to which the reaction is unfavorable cannot be very great, however, because there is evidence that the enzyme formate dehydrogenase will effect the process represented by equation 1.[1,3] The enzyme catalysis[1,3] of reaction 1 establishes that the reaction should proceed to approximately 50% conversion of $NaCO_3H$ to $NaHCO_2$ at 1 atm H_2. There is much interest in the mild reduction of CO_2 and its aqueous equivalents, for a variety of fundamental and practical reasons, Heterogeneous Pd catalysts for the reaction represented by equation 1 have been studied previously, but the systems require elevated temperature and high pressure.[4] The enzyme catalysts do not work well at high ionic strength and are not durable.[1] There are a variety of reports claiming electrochemical reductions of CO_2, but none occur near the thermodynamic potential.[5] Photoelectrochemical efficiencies for the reduction of CO_2 in aqueous solution are low,[6] The results reported herein suggest that photoreduction of CO_2 in aqueous solution could be efficient, since the generation of H_2 at semiconductor photocathodes has been shown to be efficient under visible light illumination,[7]

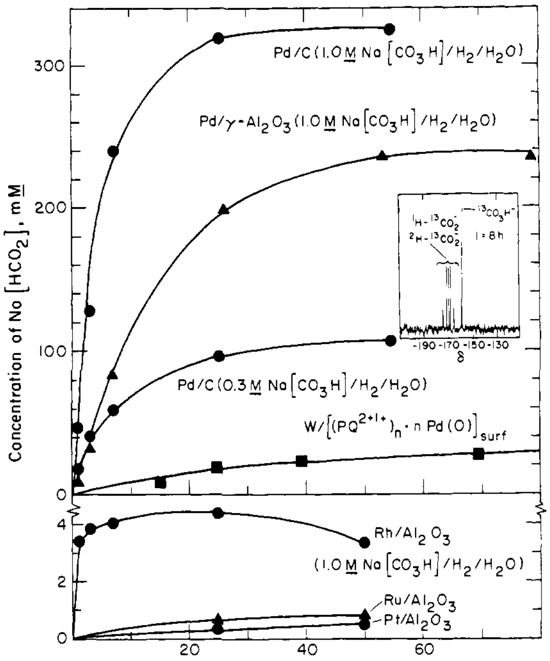


Figure 1. Concentration of $NaHCO_2$(aq) vs. reaction time for various catalysts for the reduction of $NaCO_3H$(aq) using an H_2 purge. The inset is a ^{13}C NMR for H_2 reduction of 99% ^{13}C 0.3 M $NaCO_3H$ in D_2O using 5% Pd/C at 8-h reaction time. Cf. also Figure 2b.

The reduction represented by equation 1 has been effected by using a variety of Pd-based catalysts (Table I and Figure 1). The typical procedure was to suspend 0.25 g of catalyst in 25 mL of an aqueous solution of $NaCO_3H$ purged slowly with H_2 gas or under static 1.7 atm H_2, The $NaHCO_2$ concentration was followed

---

(1) Klibanov, A. M.; Alberti, B. N.; Zale, S. E. *Biotechnol. Bioeng.* **1982**, *24*, 25.

(2) Pourbaix, M. In "Atlas of Electrochemical Equilibrium"; National Association of Corrosion Engineers, Ed.; 1974; p 450.

(3) (a) Woods, D. D. *Biochem. J.* **1936**, *30*, 515. (b) Ruschig, U.; Muller, U.; Willnow, P.; Hopner, T. *Eur. J. Biochem.* **1976**, *70*, 325.

(4) (a) Bredig, G.; Carter, S. R. *Chem. Ber.* **1914**, *47*, 541. (b) Farlow, M. W.; Adkins, H. *J. Am, Chem. Soc.* **1935**, *57*, 2222. (c) Ramaroson, E.; Kieffer, R.; Kiennemann, A. *J. Chem. Soc., Chem. Commun.* **1982**, 645.

(5) (a) Randin, J. P. In "Encyclopedia of Electrochemistry of the Elements"; Bard, A. J., Ed.; Marcel Dekker: New York, 1976; Vol. VII, pp 172. (b) Russell, P. G.; Kovac, N.; Srinivasan, S.; Steinberg, M. *J. Electrochem. Soc.* **1977**, *124*, 1329.

(6) (a) Lehn, J. M.; Zeissel, R. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 701. (b) Taniguchi, Y.; Yoneyama, H.; Tamura, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2034. (c) Halmann, M. *Nature (London)* **1978**, *275*, 115. (d) Inoue, T.; Fujushima, A.; Konishi, S.; Honda, K. *Ibid.* **1979**, *277*, 637.

(7) (a) Baglio, J. A.; Calabrese, G. S.; Harrison, D. J.; Kamieniecki, E.; Ricco, A. J.; Wrighton, M. S.; Zoski, G. D. *J. Am. Chem. Soc.* **1983**, *105*, 2246. (b) Aharon-Shalom, E.; Heller, A. *J. Electrochem. Soc.* **1982**, *129*, 2865.

0002-7863/83/1505-6318$01.50/0