distance is 1.860 Å, the W=C—C angle is widened up to 164.6°, and the W=C—H angle is only 74.6°.[5] The less activated nature of the alkylidene C-H bond in **3** compared to **1** is also reflected in the larger C-H coupling constant (**3**, $^1J_{CH}$ = 125.8 Hz, vs. **1**, $^1J_{CH}$ = 82.3 Hz) and in the shift of the NMR signal for the alkylidene hydrogen atom from −1.2 ppm for **1** to the low-field value of 11.8 ppm found for **3**. Thus, donation of the second π-bond ($\pi\perp$) of the alkyne to the metal center exerts a marked influence on the geometry of the benzylidene ligand; it also determines the orientation of the alkylidene ligand such that the tungsten-alkylidene π-bond is orthogonal to the tungsten alkyne π-bonds; i.e., the plane of the benzylidene ligand is perpendicular to the P(1)-W-P(2) axis.

Due to interaction of the alkyne ligand with two perpendicular metal d_π orbitals, no high electronic barrier for alkyne rotation is expected.[11,13] In the structure of **3**, the preferred orientation of the alkyne is apparently along the P(1)-W-P(2) axis, but significant rotation from this orientation is observed, which is attributed to steric interaction between the acetylene phenyl groups and the trimethylphosphine ligands. In order to be able to probe the dynamic behavior of the alkyne ligand by NMR we prepared a sample of the complex $[(W{=}CHPh)(Cl)_2(PhC_2H)(PMe_3)_2]$ (**4**),[14] containing an unsymmetrically substituted alkyne. The calculated activation barrier for site exchange is $\Delta G^\ddagger$ = 50.61 ± 2.9 kJ mol^{-1} at 273 K.[15] This value is comparable to those obtained for formally related tungsten complexes containing four-electron-donor alkyne ligands.[11,17]

When the acetylene complex **3** is dissolved in phenylacetylene at 40 °C, slow polymerization of the alkyne is induced.[18] In the early phase (24 h) of the reaction compound **4** can be identified by NMR as the major organometallic component. Since the structural and dynamic studies reported here clearly show that the alkyne and alkylidene ligands in **3** and **4** do not interact with each other, we propose that dissociation of a trimethylphosphine ligand in **4** and coordination of a second phenylacetylene may lead to the active acetylene polymerization catalyst. In this situation the metal would not be able to provide d-electrons for independent π-bonding to the second alkyne ligand which then may interact with the alkylidene ligand according to Scheme I.[19]

Acknowledgment. This work was supported by the National Science Foundation (CHE-8411023). We thank Dr. Roman A. Gancarz for assistance in the use of the NMR line-shape program.

Supplementary Material Available: Tables of atomic coordinates, bond lengths, and bond angles for **2** (5 pages); table of observed and calculated structure factors for **2** (22 pages). Ordering information is given on any current masthead page.

(13) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am Chem. Soc.* **1979**, *101*, 585-591.

(14) **4** was prepared by the same method as **3**. However, pure samples of **4** are difficult to obtain. **4**: ^{1}H NMR (ppm, CD_2Cl_2, 298 K) 12.85 (t, 1, $^3J_{PH}$ = 6.9 Hz) (PhC_2H), 11.20 (t, 1, $^3J_{PH}$ = 4.5 Hz) ($CHPh$); ^{13}C NMR (ppm, CD_2Cl_2, 253 K) 289.6 ($^1J_{CH}$ = 125.7 Hz), 217.9 ($PhCCH$), 211.0 ($^1J_{CH}$ = 201.1 Hz), $PhCCH$); ^{31}P NMR (ppm, CD_2Cl_2, 193 K) −8.5, −5.1 ($^2J_{PP}$ = 141.0 Hz) (PMe_3), coalescence temperature 283 K.

(15) Free energies of activation were calculated from the Eyring equation by least-squares fit of rate constants obtained from line-shape analysis (^{31}P NMR) using the program DNMR3.[16]

(16) Kleier, D. A.; Binsch, G. *QCPE* **1970**, *11*, 165.

(17) (a) Ward, B. C.; Templeton, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 1532-1538. (b) Templeton, J. L.; Ward, B. C.; Chen, G.-G. J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1981**, *20*, 1248-1253. (c) Morrow, J. R.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1985**, *4*, 745-750.

(18) Polyphenylacetylene was isolated by precipitation from CH_2Cl_2 solution with CH_3OH and characterized by ^{1}H NMR.[2]

(19) Insertion of alkynes into metal-carbene bonds in high-valent[20] and in low-valent transition-metal carbene complexes[21] has been observed or implicated in a variety of systems. There are also a few examples for the formation of metallacyclobutenes via coupling of coordinated alkynes and carbene ligands.[22]

(20) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210-3222.

(21) (a) Dötz, K. H.; Kreiter, C. G. *J. Organomet. Chem.* **1975**, *99*, 309-314. (b) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282-7292. (c) Dötz, K. H. *Angew Chem.* **1984**, *96*, 573-594; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587-608 and references therein. (d) Semmelhack, M. F.; Tamura, R.; Schnatter, W.; Springer, J. *J. Am. Chem. Soc.* **1984**, *106*, 5363-5364. (e) Wulff, W. D.; Gilbertson, S. R., Springer, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 520-522 and references therein. (f) Parlier, A.; Rudler, H.; Platzer, N.; Fontanille, M.; Soum, A. *J. Organomet. Chem.* **1985**, *287*, C8-C12.

(22) (a) Tebbe, F. N.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 6151-6153. (b) McKinney, R. J.; Tulip, T. H.; Thorn, D. L.; Coolbaugh, T. S.; Tebbe, F. N. *J. Am. Chem. Soc.* **1981**, *103*, 5584-5586. (c) Calabrese, J. C.; Roe, D. C.; Thorn, D. L.; Tulip, T. H. *Organometallics* **1984**, *3*, 1223-1230.

Terminal Epoxidation of Farnesate Attached to Helical Peptides

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In the last stage of cholesterol biosynthesis, squalene is regio- and enantioselectively transformed to squalene 2,3-epoxide in the presence of an enzyme squalene monooxygenase.[1] A remarkably regioselective nonenzymatic oxidation of the terminal double bond of squalene was accomplished by van Tamelen and co-workers.[2] They showed that the regioselectivity was dependent on the solvent and the oxidizing agent. van Tamelen suggested that the solvent effect related to the conformation of the substrate in solution; in polar medium the terpene exists in a coiled conformation in which the internal double bond might be sterically shielded and hence less reactive than the terminal double bond. Accepting that squalene and related terpenes exist as coiled structures in polar solvents,[3] we envisioned an intriguing possibility to make this process asymmetric.[4] Upon coupling a terpene such as farnesic acid with a chiral helical molecule, the terpene moiety might be induced to coil only in one direction, for example in a screw form. Once such a preferential chiral helix formation is obtained in the terpene moiety, one face of the terminal double bond will preferentially be exposed to the oxidizing reagent. In this paper, we would like to describe experiments aimed at testing this concept.

Among several classes of compounds known to form helices,[5,6] we have chosen polypeptides, since they are easy to prepare on a large scale and their secondary structures (helices) are stable in many solvents.[7] The only potential drawback of polypeptides is their poor solubility in organic solvents. We first studied the chemical behavior of the substrate **1**, prepared from hexa-L-phenylalanine methyl ester;[8] however, to our great disappointment, neither NBS or MCPBA oxidation of **1** gave promising results. A possible explanation for this unsuccessful experiment was, we felt, that the low solubility of the hexapeptide **1** might result from aggregation of the β-sheet structure through intermolecular hy-

(1) For a review on this subject, see, for example: Harrison, D. M. *Nat. Prod. Rep.* **1985**, *2*, 525.

(2) For reviews on this subject, see: van Tamelen, E. E. *Acc. Chem. Res.* **1968**, *1*, 111. Also see: van Tamelen, E. E.; Storni, A.; Hessler, E. J.; Schwartz, M. A. *Bioorg. Chem.* **1982**, *11*, 133.

(3) The ^{13}C NMR spectrum of squalene in media of different polarity does not necessarily support this proposal (van Dommelen, M. E.; Wilson, A. R. N.; de Haan, J. W.; Buck, H. M. *Bull. R. Neth. Chem. Soc.* **1975**, *94*, 206), but we used it as a working hypothesis to design an experimental system.

(4) Asymmetric epoxidation of squalene was studied by Otsuka and his co-workers: Tani, K.; Hanafusa, M.; Otsuka, S. *Tetrahedron Lett.* **1979**, 3017.

(5) For example, see: Meurer, K. P.; Vogtle, F. *Top. Curr. Chem.* **1985**, *127*, 1.

(6) A possibility of utilizing optically active hexahelicene-2-carboxylic acid as a chiral inducer was studied by Dr. Yamasaki (1978-1979) and Dr. McWhorter, Jr., (1980) in our laboratories. However, asymmetric induction was not significant for this system.

(7) There are excellent books and reviews on the conformation of peptides. For example, see: *The Peptides*; Gross, E., Meienhofer, J., Eds.; Academic Press: New York, 1981; Vol. 4.

(8) Hexa-L-alanine methyl ester was also synthesized. However, as its solubility in organic solvents was extremely poor, we were unable to study its chemistry.

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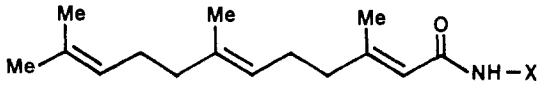
Table I

substr (mp, °C)	NBS epoxidation[a] asymmetric induction for terminal epoxidation[13,14]	NBS epoxidation[a] abs config of enantiomer in excess[15]	MCPBA epoxidation[b] asymmetric induction for terminal epoxidation[13,14]	MCPBA epoxidation[b] abs config of enantiomer in excess[15]
2 (102–105)	3%	*R*	2%	*S*
3 (152–155)	17%	*R*	9%	*S*
4 (197–198)	25%	*R*	12%	*S*
5 (186–188)	17%	*R*	6%	*S*

[a] NBS oxidation was performed in a 5:1 mixture of glyme and water at 0 °C with 0.9 equiv of NBS. Resultant bromohydrins were converted into the corresponding epoxides by treatment with K_2CO_3 in methanol at 0 °C. For experimental details, see the supplementary material. [b] MCPBA oxidation was performed in CH_2Cl_2 at 0 °C with 1.1 equiv of MCPBA. For experimental details, see the supplementary material.

drogen bonds.[7] Thus, it seemed most urgent to improve the solubility of the peptides so as to promote its helical folding. In this connection, recent papers by Narita and co-workers[9] drew our attention. They observed that incorporation of one or more α-aminoisobutyric acid (Aib) residues[10,11] in the polypeptide chain enhanced its solubility and promoted its helical folding. To test whether this method improved solubility, we synthesized peptides **2**–**5**[12] and found that they were indeed very soluble in organic



1 : X = –(Phe^L)$_6$–OMe

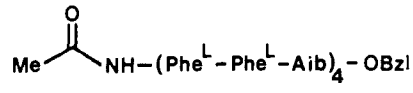
2 : X = –(Phe^L–Phe^L–Aib)$_1$–OBzl

3 : X = –(Phe^L–Phe^L–Aib)$_2$–OBzl

4 : X = –(Phe^L–Phe^L–Aib)$_3$–OBzl

5 : X = –(Phe^L–Phe^L–Aib)$_4$–OBzl

6 : X = –Me



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solvents such as benzene, methylene chloride, dimethoxyethane (glyme), DMF, and Me_2SO.

Epoxidation of **2**–**5** was carried out in the same systems as those studied by van Tamelen. The enantiomeric excess was estimated from NMR spectra[13] of the glycols obtained by hydrolysis[14] of epoxides. The absolute configuration of the enantiomer in excess was established as *R* form for the NBS oxidation and as *S* form for the MCPBA oxidation by chemical correlation with D-glyceraldehyde acetonide.[15]

The results summarized in Table I deserve several comments. First, as anticipated from van Tamelen's work, the regioselectivity of NBS oxidation in glyme–water is excellent; by oxidation with 0.9 equiv of NBS, approximately a 10:1 mixture[16] of the terminal monoepoxide and bis(epoxide), in addition to some recovered starting material, was obtained but no internal monoepoxide was detected. In the case of MCPBA oxidation, the ratio was approximately 2:1. Second, it is obvious that the noticeable asymmetric induction observed for the NBS oxidation of hexa-, nona-, and dodecapeptides **3**–**5** is not due to the effect of the chiral center at the first or second amino acid residue in the peptide backbone, cf. tripeptide **2**. IR spectra strongly suggest that peptides **3**–**5** exist as a 3_{10}- or α-helix form but **2** does not.[17,18] These observations are consistent with the hypothesis described above. Third, the possibility that the asymmetric induction might be due to an intermolecular interaction was excluded by the following control experiment. Farnesic acid methylamide (**6**) was subjected to NBS oxidation in the presence of dodecapeptide **7** in glyme–water. The asymmetric induction due to the intermolecular interaction was found to be virtually none.[19] Fourth, the major enantiomer formed in the NBS oxidation corresponds to the minor enantiomer formed in the MCPBA oxidation, which is expected from the hypothesis. Fifth, the attack of NBS or MCPBA on the terminal double bond took place from the direction that would be anticipated from a screw-form chirality induced on the terpenoid moiety from the right-handed 3_{10}- or α-helix peptide moiety. Sixth, the degree of asymmetric induction was higher for **4** than for **3**, which may be attributed to the fact that nonapeptide **4** forms a more stable helical structure than hexapeptide **3**.[11] However, the degree of asymmetric induction observed for

(9) (a) Narita, M.; Doi, M.; Sugasawa, H.; Ishikawa, K. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1473. (b) Narita, M.; Ishikawa, K.; Sugasawa, H.; Doi, M. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1731. (c) Narita, M.; Chen, J.-Y.; Sato, H.; Kim, Y. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2494.

(10) This interesting achiral amino acid is found in transmembrane channel polypeptides like alamethicin or suzukacillin; see: Nagaraj, R.; Balaram, P. *Acc. Chem. Res.* **1981**, *14*, 356. Jung, G.; Konig, W. A.; Leibfritz, D.; Ooka, T.; Janko, K.; Boheim, G. *Biochim. Biophys. Acta* **1976**, *433*, 164.

(11) Conformation of the peptides containing α,α-disubstituted α-amino acids has been extensively studied. For example, see: (a) Bavoso, A.; Benedetti, E.; Di Blasio, B.; Pavone, V.; Pedone, C.; Toniolo, C.; Bonora, G. M. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 1988 and references cited therein. (b) Vijayakumar, E. K. S.; Balaram, P. *Biopolymers* **1983**, *22*, 2133 and references cited therein.

(12) The experimental details for the synthesis of **2**–**5** are included in the supplemental material. (*E*,*E*)-Farnesic acid was purified by crystallization of its (*S*)-benzylthiouronium salt: Caliezi, A.; Schinz, H. *Helv. Chim. Acta* **1949**, *32*, 2556. The purity of **2**–**5** was assured by careful recrystallization, coupled with spectroscopic analysis.

(13) The signals due to diastereomeric amide NH groups are well separated. Photocopies of spectra are included in the supplemental material.

(14) Nakanishi, K.; Schooley, D. A.; Koreeda, M.; Dillon, J. *J. Chem. Soc., Chem. Commun.* **1971**, 1235. The ee values estimated from the NMR spectra of the epoxides agreed with those listed in Table I, although the NH signals in the epoxide NMR spectra were not separated as well as those in the diol spectra.

(15) The epoxide was converted into the S-Mosher ester of 5,6-dihydroxy-6-methylheptan-2-one and then compared with the authentic sample. The authentic S-Mosher ester of 5(*R*),6-dihydroxy-6-methylheptan-2-one was prepared from D-glyceraldehyde acetonide by Dr. James B. White in our laboratory. For details, see the supplementary material.

(16) By using 0.5 equiv of NBS, this ratio was improved to at least 25:1.

(17) The amide carbonyl bands observed in DME–D_2O for **2**, **3**, **4**, and **5** are 1664 (s) + 1640 (m), 1660 (s) + 1629 (w), 1658 (s) + 1630 (sh), and 1658 (s) cm^{-1}, respectively, and those in CH_2Cl_2 are 1667 (s) + 1636 (m), 1667 (s) + 1635 (w), 1663 (s) + 1635 (sh), and 1663 (s) cm^{-1}, respectively.[9] It is worthy of noting that the protons at the benzylic position of **3**–**5** appear as a well-separated AB pattern in their ^1H NMR spectra, while those of **2** as a sharp singlet.

(18) Linear peptides containing Aib appear to prefer to adopt a 3_{10}-helix conformation.[11] We have recently succeeded in the preparation of a single crystal of **5** suitable for an X-ray analysis.

(19) Taking into account the chemical yields of mono- and bisbromohydrins in the NBS oxidation of **3**–**5**, the observed asymmetric induction cannot be explained, at least as the major reason, in terms of a kinetic resolution at the transformation of monobromohydrin into bisbromohydrin. A control experiment on a system similar to **5** confirmed this: Vatele, J. M.; Kishi, Y., unpublished results.

dodecapeptide **5** does not seem to follow this trend, which may suggest that secondary interactions exist between the terpenoid and peptide moieties.

Although we still need to perform many experiments to develop a reliable mechanistic model to explain the observed phenomenon, our preliminary observations show an interesting potential in this area and investigation along this line is in progress in our laboratories.

Acknowledgment. We thank Dr. White for preparing the authentic sample for the determination of the absolute configuration and Drs. Yamasaki and McWhorter, Jr., for early exploratory studies. Financial support from the National Science Foundation (CHE 83-09457) is gratefully acknowledged. Postdoctoral fellowships to Dr. Budt (Deutsche Forschungsgemeinschaft) and to Dr. Vatele (French National Research Center) are gratefully acknowledged. NMR spectrometers used in this research were funded by NSF (CHE-84-10774) and NIH Shared Instrumentation Program (1 S10 RR01748).

Supplementary Material Available: Experimental details for the synthesis of **2-5**, ^{1}H NMR spectra of the key compounds, and ^{1}H NMR spectra for the determination of asymmetric induction (18 pages). Ordering information is given on any current masthead page.

"Quaternary Ammonium Amalgams" as Zintl Ion Salts and Their Use in the Synthesis of Novel Quaternary Ammonium Salts

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We propose that "quaternary ammonium amalgams" are Zintl ion salts of empirical formula $R_4N^+Hg_4^-$ and that these salts, upon treatment with NaA, can be used to synthesize less easily prepared quaternary ammonium salts, $R_4N^+A^-$. Production of "ammonium amalgams"[1] and quaternary ammonium amalgams[2-5] by reductions of salts at a mercury electrode have been reported many times, although a clear characterization of the nature of the "amalgam" produced and the presumed reduced ammonium species has not been obtained. An alternative description of these species can be given within the Zintl ion framework,[6] i.e., as ammonium salts of an anionic mercury species. To investigate this possibility, we undertook a study of the stoichiometry of the electroreduction reaction and the regeneration of the R_4N^+ from the product upon chemical oxidation. A mercury electrode consisting of a weighed amount of Hg in a glass cup contacted by a small (area, ca. 0.2 mm^2) Pt wire was used to electrolyze 30 mL of a 1.5 M $TBA^+PF_6^-$ (where TBA^+ is tetra-*n*-butylammonium)-acetonitrile (MeCN) solution at -20 °C, with the Hg maintained at -4.5 V vs. a silver wire quasi-reference electrode immersed in the same solution and held in a separate reference electrode chamber. The electrolysis was carried out until 50-100 C were passed. During electrolysis the Hg surface was covered with a black layer, and finely divided particles of product were dispersed into solution. The unreacted Hg was washed with pure solvent, dried with a tissue, and weighed. For three trials, the moles of Hg reacted per faraday was 4.1 ± 0.2. Thus, the reduction reaction can be written as

$$TBA^+ + 4Hg + e^- \rightarrow TBA^+Hg_4^- \quad (1)$$

Note, however, that in earlier papers, on the basis of analyses of the product isolated after electrolysis, quaternary ammonium/Hg ratios of 1:12-13[3] and 1:11.6-14.4[4] were proposed. One problem with isolation and analysis of product is its high reactivity with O_2 and moisture.

To study the regeneration of the quaternary ammonium ion from the product and the use of an electrolysis procedure to convert an easily obtainable salt, e.g., TBABr, to one with a different anion, e.g., $TBAPF_6$, bulk electrolysis at a large area (3 cm^2) Hg pool was undertaken. The cell was a three-compartment cell, with two fine-porosity sintered-glass disks separating the working and counter electrodes. The solution, 0.1 M TBABr-MeCN held at -20 °C, showed an interelectrode resistance initially of 2-3 kΩ. A potential of -10.0 V vs. Ag quasi-reference electrode was applied to the Hg pool; this value was chosen to be sufficiently negative that the actual potential drop at the Hg/solution interface would be maintained at the background reduction level as the solution resistance increased. After 2.5 h of electrolysis, the current, initially about 3.5 mA, decayed to 3.2 μA, and the interelectrode resistance increased to about 3 MΩ (as compared to 5-10 MΩ for pure MeCN in the cell). Thus, electrolysis had depleted the electrolyte via the reaction in eq 1 at the Hg pool and Br^- migration to the counter electrode chamber, where it was oxidized. The rest potential of the Hg pool after electrolysis was about 3.6-3.9 V more negative than the initial value. During electrolysis the Hg pool became covered with a black layer, and black, finely divided particles dispersed in the solution and eventually settled to the bottom of the cell. The addition of a sodium salt, NaA ($A = PF_6^-$, F^-), caused disappearance of the black material, via the proposed reaction

$$Na^+A^- + TBA^+Hg_4^- \rightarrow Na(Hg) + TBA^+A^- \quad (2)$$

where Na(Hg) represents sodium amalgam. A cyclic voltammogram of the MeCN solution after this procedure at a Pt electrode showed only a small wave for residual bromide ion (equivalent to ca. 4 mM), with the oxidation background occurring at potentials about 1 V more positive (PF_6^- and F^- oxidation vs. Br^- oxidation). This indicates better than 90% conversion of the Br^- salt to the A^- form. The product quaternary ammonium salt could be isolated by precipitation with ethyl ether, followed by filtration of the crystals. The NMR of the Bu_4N^+ in the product in deuteriochloroform was essentially the same as that for the starting material, $Bu_4N^+Br^-$, indicating regeneration of the cation upon oxidation of the reduction product. No products from solvent reduction[9] or tri-*n*-butylamine (characteristic of decomposition of TBA^+) was observed by NMR or IR spectroscopy, suggesting that side reactions that would compromise the coulometric measurement are not important. This electrochemical method should prove useful in preparing less easily obtainable quaternary ammonium salts from R_4NBr.

The electrochemical production of Zintl anions of mercury and other metals as salts of different cations appears promising. Indeed, reduction at an Hg pool in the presence of sulfonium and

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(2) See, for example: (a) McCoy, H. N.; Moore, W. C. *J. Am. Chem. Soc.* **1911**, *33*, 273. (b) Horner, L. In *Organic Electrochemistry*; Baizer, M. M., Lund, H., Eds.; Marcel Dekker: New York, 1983; p 397.
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(4) Braver, G.; Dusing, G. *Z. Anorg. Allg. Chem.* **1964**, *328*, 154.
(5) (a) Kariv-Miller, E.; Nanjundiah, C.; Eaton, J.; Swenson, K. E. *J. Electroanal. Chem.* **1984**, *167*, 141. (b) Kariv-Miller, E.; Andruzzi, R. *J. Electroanal. Chem.* **1985**, *187*, 175 and references therein.
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(7) Cottrell, W. R. T.; Morris, R. A. N. *J. Chem. Soc., Chem. Commun.* **1968**, 409.
(8) Kariv-Miller, E.; Lawin, P. B.; Vajtner, Z. *J. Electroanal. Chem.* **1985**, *195*, 435.
(9) Ouyang, J.; Bard, A. J., unpublished results on electroreduction of MeCN at Pt electrode show the formation of oligomers and polymers of MeCN with characteristic yellow color and absorbance and fluorescence spectra.

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