Scheme I

Net Reaction
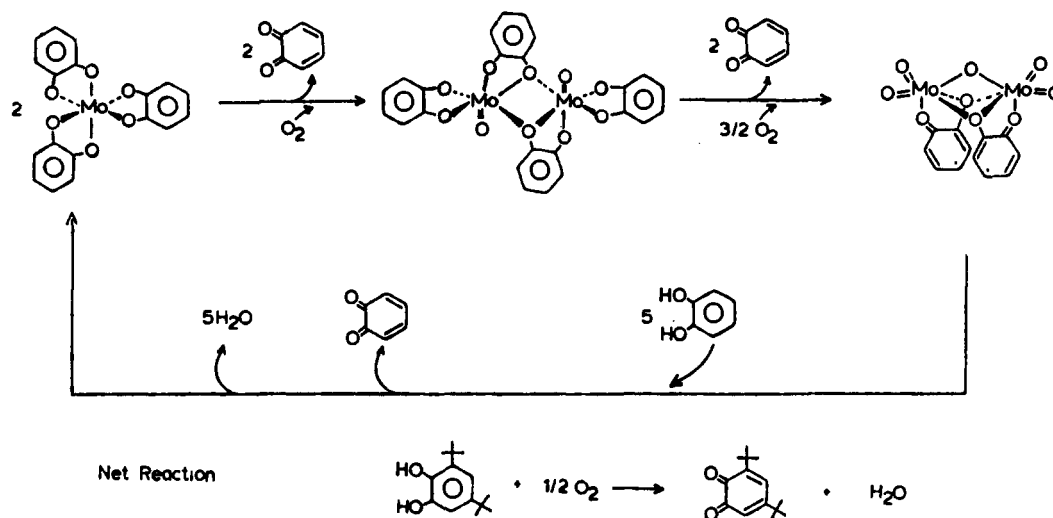

above, a scheme can be constructed, which relates the observed products by reactions with oxygen (Scheme I). Tertrachloro-1,2-benzoquinone, with a positive reduction potential, forms complexes with both V and Mo which are free of oxo ligands and are relatively inert to further oxidation by O_2. The reaction between $Mo(CO)_6$ and 3,5-di-*tert*-butyl-1,2-benzoquinone carried out in toluene with careful exclusion of oxygen gave $Mo(DBCat)_3$. This product showed two sharp *tert*-butyl resonances in the proton NMR spectrum at 1.27 and 1.11 ppm, indicating symmetrical equivalence of the three ligands, and a parent ion peak at m/e = 758 in the mass spectrum, indicating a monomeric structure similar to that of $Os(DBCat)_3$.[6] The infrared spectrum of the complex is quite similar to that of $Mo_2O_2(DBCat)_4$ with the Mo=O stretching band at 966 cm^{-1} missing. Upon exposure to trace quantities of oxygen the oxomolybdenum dimer is formed with free benzoquinone:
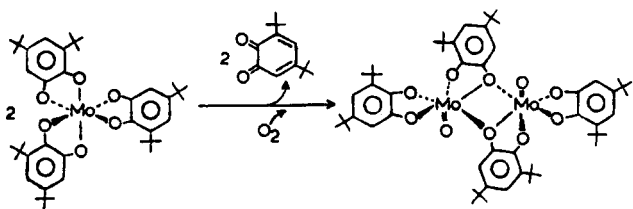

This reaction can be observed by appearance of the four *tert*-butyl resonances of the dimer at 1.717, 1.097, 1.056, and 1.020 ppm and signals for the benzoquinone at 1.128 and 0.769 ppm. This process is the first step in the reaction sequence described in Scheme I and is quite similar to the chemistry of the related vanadium complex.

The second reaction in the scheme, addition of oxygen to $Mo_2O_2(DBCat)_4$, has not been observed. The expected product of this step by analogy with the 9,10-phenanthrenequinone reaction would be $Mo_2O_5(DBSQ)_2$. Oxidation of $Mo_2O_5(DBCat)_2{}^{2-}$ led to dissociation of the quinone ligands,[7] suggesting that the strong interaction between π orbitals of the semiquinones in Mo_2O_5-$(PhenSQ)_2$ is an important stabilizing effect for the complex. Further air oxidation of $V_2O_2(DBCat)_2(DBSQ)_2$ led to V_2O_5.

To study the third step in the reaction scheme, Mo_2O_5-$(PhenSQ)_2$ was treated with 9,10-phenanthrenediol. The products formed were $Mo(PhenCat)_2(PhenSQ)$ and presumably water, although this was not observed directly. In a second reaction $Mo_2O_5(PhenSQ)_2$ was treated with 3,5-di-*tert*-butylcatechol in the hope of forming a mixed-quinone-ligand complex. The reaction produced $Mo(DBCat)_3$ exclusively, which was stable in the

presence of water but immediately formed $Mo_2O_2(DBCat)_4$ upon exposure to oxygen:
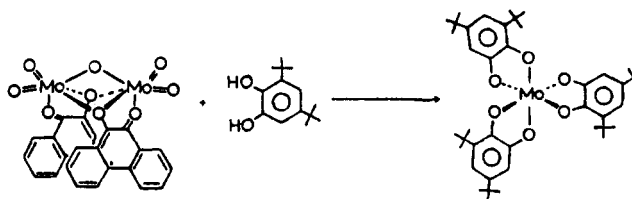
These reactions show that $Mo(DBCat)_3$ can be formed either by treating Mo(0) with benzoquinone or by using a Mo(VI) complex and the catecholate form of the ligand. They also illustrate steps in the series of reactions shown in Scheme I whereby oxygen and catechol are converted to water and benzoquinone through a series of well-characterized Mo complex intermediates.

Department of Chemistry   **Marion E. Cass**
University of Colorado   **Cortlandt G. Pierpont***
Boulder, Colorado 80309

Electrochemical Generation of an Iron(IV) Porphyrin

Sir:

A variety of recent investigations has revealed a rich redox chemistry present in iron porphyrin systems. The oxidation of simple iron(III) porphyrins by one or two electrons is known to occur, and examples of Fe^{IV},[1] $Fe^{III}P^+$,[2] and $Fe^{IV}P^+$.[3] (where P$^+$.

(6) Hursthouse, M. B.; Fram, T.; New, L.; Griffith, W. P.; Nielson, A. J. *Transition Met. Chem. (Weinheim, Ger.)* **1978**, *3*, 255.
(7) Pierpont, C. G.; Buchanan, R. M. *Inorg. Chem.* **1982**, *21*, 652.

(1) (a) Groves, J. T.; Quinn, R.; McMurry, T. J.; Nakamura, M.; Lang, G.; Boso, B. *J. Am. Chem. Soc.* **1985**, *107*, 354–360. (b) Chin, D.-H.; Balch, A. L.; La Mar, G. N. *J. Am. Chem. Soc.* **1980**, *102*, 1446–1447. (c) Balch, A. L.; Chan, Y.-W.; Cheng, R.-J.; La Mar, G. N.; Latos-Grazynski, L.; Renner, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7779–7785.
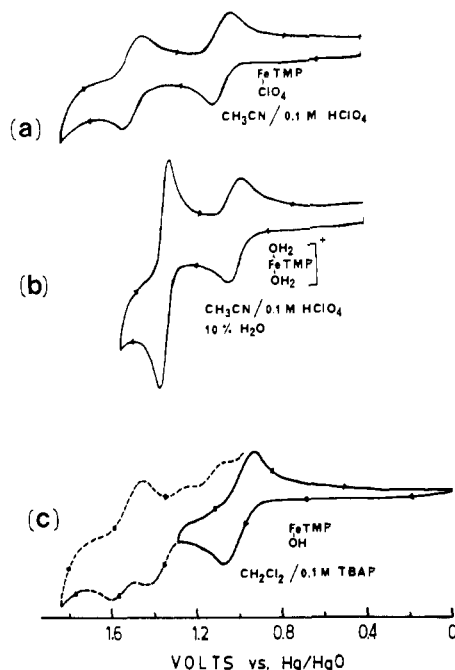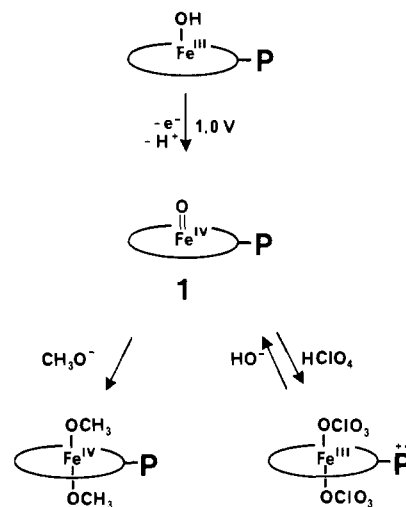
Figure 1. Cyclic voltammograms of iron(III) tetramesitylporphyrins: (a) (TMP)Fe(ClO$_4$) in CH$_3$CN containing 0.1 M HClO$_4$; (b) [(TMP)Fe-(H$_2$O)$_2$]$^+$[ClO$_4$$^-$] in 9:1 CH$_3CN/H_2$O containing 0.1 M HClO$_4$; (c) (TMP)Fe(OH) in moist CH$_2$Cl$_2$ containing 0.1 M TBAP and saturated with Na$_2$CO$_3$; (---) voltage sweep reversed at +1.3 V.

denotes a porphyrin π cation radical, a monoanion overall) have been reported. Furthermore, the oxidation of Fe(III) porphyrins by peroxidic oxidants is known to generate an active oxo species that mimics the reactivity of cytochrome P-450.[4] In order to establish the redox potentials of oxidized iron porphyrins and to understand the thermodynamic factors which govern metal vs. ligand and one- or two-electron oxidations, we have investigated the electrochemical behavior of some iron porphyrin complexes. We report here (i) the elctrochemical generation of iron(IV) porphyrins where the site of oxidation is dictated by changing the axial ligand, (ii) the direct measurement of an Fe(III)/Fe(IV) redox potential, and (iii) the iron porphyrin mediated electrocatalytic epoxidation of olefins *in the absence of oxygen-donating oxidants*.

Cyclic voltammetry of (TMP)Fe^{III}Cl in CH$_2$Cl$_2$/0.1 M tetra-butylammonium perchlorate (TBAP) in the range 0.0 to +1.8 V revealed two quasi-reversible waves at +1.15 and +1.5 V.[5] Analogous behavior has been reported for (TPP)Fe^{III}Cl.[2a,6] Bulk electrolysis of a solution of (TMP)Fe^{III}Cl at +1.3 V produced a species with a UV–visible spectrum similar to that reported previously for the one-electron-oxidized form of (TPP)Fe^{III}Cl formulated as a π cation radical species.

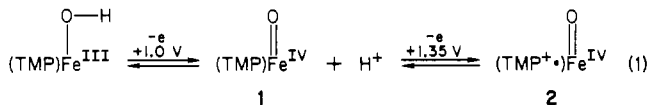Cyclic voltammetry of (TMP)Fe^{III}ClO$_4$ in CH$_2$Cl$_2$ or CH$_3$CN

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(2) (a) Phillipi, M. A.; Goff, H. M. *J. Am. Chem. Soc.* **1982**, *104*, 6026–6034. (b) Scholz, W. F.; Reed, C. A.; Lee, Y. J.; Scheidt, W. R.; Lang, G. *J. Am. Chem. Soc.* **1982**, *104*, 6791–6793; we thank C. A. Reed for a recent preprint. (c) Buisson, G.; Deronzier, A.; Duee, E.; Gans, P.; Marchon, J. C.; Regnard, J.-R. *J. Am. Chem. Soc.* **1982**, *104*, 6793–6796. (d) Kadish, K. M.; Boisselier-Cocolios, B.; Simonet, B.; Chang, D.; Ledon, H.; Cocolios, P. *Inorg. Chem.* **1985**, *24*, 2148–2156.
(3) Groves, J. T.; Haushalter, R. C.; Nakamura, M.; Nemo, T. E.; Evans, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 2884–2886.
(4) See: Groves, J. T.; Subramanian, D. V. *J. Am. Chem. Soc.* **1984**, *106*, 2177–2181 and references therein.
(5) All potentials reported were measured vs. an Hg/HgO electrode using 0.1 M NaOH as the filling solution. Chloride contamination of the iron porphyrin solution resulted in a large interfering CV wave at +1.15 V due to (TMP)FeCl. The reference potential of this electrode is +0.234 V vs. NHE. The reported potentials may be converted to SCE by subtracting 0.007 V. A cyclic voltammogram of ferrocene in CH$_3$CN/0.2 M NaClO$_4$ gave an $E_{1/2}$ value of +0.31 V vs. Hg/HgO.
(6) Felton, R. H.; Owen, G. S.; Dolphin, D.; Forman, A.; Borg, D. C.; Fajer, J. *J. Am. Chem. Soc.* **1971**, *93*, 6332–6334.

Scheme I

1

(Figure 1a) revealed two reversible redox processes at +1.06 and +1.48 V, completely analogous to the case of the chloro complex. However, in a mixture of 90% acetonitrile/10% water containing 0.1 M HClO$_4$, the waves shifted to +1.01 and +1.34 V and the second process became a two-electron wave (Figure 1b). Reed et al. have previously demonstrated that (TPP)Fe(ClO$_4$) becomes (TPP)Fe(OH$_2$)$_2$$^+$ upon addition of aqueous acid.[7] Thus, the voltammogram in CH$_3$CN/H$_2$O probably represents an aquated complex. Bulk electrolysis of a solution of (TMP)Fe(OH$_2$)$_2$$^+$ at +1.2 V produced a species with a UV–visible spectrum very similar to that of the π cation radical complex (TMP$^+$·)Fe^{III}(ClO$_4$)$_2$, indicating that the first wave represents oxidation of the porphyrin ring. Rotated-disk voltammograms verified that the second process removed twice as many electrons from the complex as the first. Significantly, these results suggest that *coordination of a water molecule allowed the iron porphyrin to access an additional redox state*. With these results in mind, the electrochemistry of (TMP)FeOH was investigated.

The cyclic voltammogram of the hydroxide complex (TMP)-Fe^{III}OH[8] (Figure 1c) shows a reversible wave at +1.0 V. In addition, a second broad, irreversible wave occurs with $E_{p,a}$ = +1.4 V and $E_{p,c}$ = +1.25 V. A third wave is present at +1.55 V.

Attempts to generate the one-electron-oxidized form of Fe^{III}OH at room temperature by controlled-potential electrolysis were unsuccessful. However, oxidation at +1.2 V in CH$_2$Cl$_2$/0.05 M TBAP at –40 °C saturated with tetrabutylammonium hydroxide ((TBA)OH) resulted in the formation of a bright red-orange species (1). This species reacted with solvent at room temperature to yield (TMP)Fe^{III}Cl and (TMP)Fe^{III}OH. The UV–visible spectrum of 1 [λ$_{max}$ 414 nm (ε 102), 545 (12.7)] lacked the characteristic long-wavelength bands of a porphyrin cation radical. No more than 5% (TMP)Fe^{III}OH was present in samples of 1, as judged by the weak shoulder at 580 nm. An identical spectrum could be obtained by the addition of excess iodosylbenzene to a solution of (TMP)Fe^{III}OH in CH$_2$Cl$_2$ containing aqueous (TBA)OH at –30 °C. Chemical oxidation carried out in ethyl acetate produced a very similar UV–visible spectrum, ruling out the possibility of a halogen-containing species. Addition of methanolic (TBA)OH to a solution of 1 led to a visible spectrum identical with that of (TMP)Fe^{IV}(OCH$_3$)$_2$,[1a] whereas addition of aqueous HClO$_4$ generated a spectrum identical with that of the cation radical specied (TMP$^+$·)Fe^{III}(OClO$_3$)$_2$[1a] (Scheme I). These observations indicate that 1, (TMP)Fe^{IV}(OCH$_3$)$_2$, and (TMP$^+$·)Fe^{III}(ClO$_4$)$_2$ are at the same formal oxidation state.

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(7) Kastner, M. E.; Scheidt, W. R.; Mashiko, T.; Reed, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 66–667.
(8) Cheng, R.-J.; Latos-Grazynski, L.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 2412–2418; this preparation often yielded samples that were contaminated with unreacted (TMP)Fe^{III}Cl. Purer samples were prepared by chromatography on basic alumina.

Proton NMR spectra of solutions of **1** in CH_2Cl_2 at –50 °C derived from $(TMP^+\cdot)Fe^{III}(OClO_3)_2$ and (TBA)OH or (TMP)-$Fe^{III}OH^9$ and iodosylbenzene show resonances only in the 0–8 ppm range. It is apparent from the nonequivalent meta hydrogen resonances at δ 6.2 and 6.7 and the para methyl resonance at δ 2.8 that **1** is similar to the oxoiron(IV) complex $(TMP)Fe^{IV}O$, described by Balch.[1,9b]

Taken together, these results indicate that the reversible one-electron oxidation observed at +1.0 V vs. Hg/HgO represents an iron(III)/iron(IV) couple and that the second wave at +1.35 V corresponds to the porphyrin ring oxidation interconverting **1** and **2** (eq 1).[10]

$$(TMP)Fe^{III} \overset{-e}{\underset{+1.0\ V}{\rightleftharpoons}} (TMP)Fe^{IV} + H^+ \overset{-e}{\underset{+1.35\ V}{\rightleftharpoons}} (TMP^+\cdot)Fe^{IV} \quad (1)$$

Constant-potential electrolysis of a solution of $(TMP)Fe^{III}OH$ at +1.18 V in the presence of olefins was found to produce epoxides.[11] Electrolyses of solutions containing styrene, *cis-* or *trans-β*-methylstyrene, cyclododecene, cyclooctene, or norbornene were found to give an average of 15 equiv of the corresponding epoxide after 4 h.[12] Blank experiments in the absence of the iron porphyrin produced negligible quantities of epoxides. A 24-h electrolysis of a 4.8×10^{-6} M CH_2Cl_2 solution of $(TMP)Fe^{III}OH$ containing 0.25 M norbornene yielded 71 equiv of epoxide and 11 equiv of other products. A current efficiency of 74% was calculated on the basis of only the norbornene oxide yield. Finally, the selectivity previously demonstrated for iron porphyrins[13] occurred in the electrochemical experiments as well. For all of the olefins studied, the epoxide was the major product. Furthermore, an electrolyzed solution containing equal amounts of *cis-* and *trans-β*-methylstyrene was found to yield 12.6 equiv of the cis epoxide and 4.6 equiv of the trans epoxide.

Significantly, the electrocatalytic epoxidation observed here occurred at an anodic potential below the second oxidation wave of (TMP)FeOH. The positions of the two waves obtained from the CV experiments indicate that the potential of the two-electron-oxidized species (**2**) is +1.2 V or the average of the two one-electron-redox potentials. Furthermore, from the difference in the two redox couples of 0.35 V, the equilibrium constant for the disproportionation of the Fe(IV) complex can be calculated. Using the expression $K_d = 10^{-\Delta E/0.059}$, one obtains a value of 1.17 $\times$ 10^{-6}. Accordingly, it is expected that although disproportionation is not favored, a solution of $(TMP)Fe^{IV}O$ could contain as much as 0.1% $(TMP)Fe^{III}OH$ and 0.1% $(TMP^+\cdot)Fe^{IV}O$ (**2**) at equilibrium. The availability of protons at the anode could make the production of **2** facile by providing a source of $(TMP^+\cdot)Fe^{III}$.[14]

The electrochemical characterization of iron(IV) porphyrins and the application of this technique to the electrocatalytic oxidation of substrates is under further investigation.[15]

(9) (a) Preliminary Mössbauer data on ^{57}Fe-enriched **1** indicate a quadrupole doublet centered at 0.04 mm/s (ΔE_Q = 2.3 mm/s), also characteristic of iron(IV) (see ref 1a). We thank Dr. G. Gupta and Professor G. Lang, Department of Physics, Pennsylvania State University, for the Mössbauer data, the details of which will appear elsewhere. (b) The pyrrole proton resonance (δ 8.5) and one ortho methyl resonance (δ 3.0) were apparent in toluene-d_8.
(10) The proton loss upon formation of **1** is similar to the redox behavior of hydroxoruthenium(III) species: Gilbert, J. A.; Eggleston, D. S.; Murphy, W. R., Jr.; Geselowitz, D. A.; Gersten, S. W.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, *197*, 3855–3864 and references therein.
(11) A quasi-reversible CV wave at +0.68 V for $(TPP)Fe(F_2)^-$ has been suggested to be that of an Fe(III)/Fe(IV) couple. Cyclohexene oxidation was detected with this system: Goff, H. M.; Hickman, D. L. *Inorg. Chem.* **1983**, *22*, 2787–8789.
(12) Product epoxides were identified by comparing GLPC retention times with those of authentic samples. Turnover numbers were estimated by adding a known amount of norcamphor to the solution after the electrolysis was stopped. No corrections were made for differences in relative molar responses.
(13) Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1983**, *105*, 5786.
(14) Balch, A. L.; Latos-Grazynski, L.; Renner, M. W. *J. Am. Chem. Soc.* **1985**, *107*, 2983–2985.

(15) (a) Data characterizing the Fe(III)/Fe(IV) redox couple have been described recently by: Lee, W. A.; Calderwood, T. S.; Bruice, T. C. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 4301–4305. (b) Similar data are obtained in our system in the absence of Na_2CO_3 and presence of chloride; cf. ref 5 and 8.
(16) Current address: Department of Chemistry, Princeton University, Princeton, NJ 08544.

Department of Chemistry   **John T. Groves*[16]**
The University of Michigan   **John A. Gilbert**
Ann Arbor, Michigan 48109

Preparation and Structure of W(CO)₅OPPh₂NPPh₃, a Novel Complex Containing a Ligand Derived from the Bis(triphenylphosphine)nitrogen(1+) Cation

Sir:

Bis(triphenylphosphine)nitrogen(1+) (hereafter abbreviated PNP⁺) is widely used in organometallic chemistry. Due to the high solubility of [PNP]⁺ salts in aprotic solvents, e.g., tetrahydrofuran, acetone, and dichloromethane, these salts serve as convenient sources of anions in substitution reactions.[1] Furthermore, the PNP⁺ cation stabilizes highly reactive organometallic anions both in the solid state[2] and in solution.[3] In general it is possible to prepare a large variety of PNP⁺ salts by the metathesis reaction of readily obtainable [PNP]Cl with alkali-metal salts (MX) in water or methanol where [PNP]X is usually insoluble.[4]

Our current interest in low-valent [M]–OCH₃⁻ and [M]–C-(O)OCH₃⁻ species, namely where [M] = group 6 pentacarbonyls or Ru₃(CO)₁₁, as possible intermediates in methanol carbonylation processes to provide methyl formate prompted us to attempt preparation of the [PNP]OMe salt.[5-7] The reaction of [PNP]Cl

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(2) (a) Walker, H. W.; Ford, P. C. *J. Organomet. Chem.* **1981**, *214*, C43. (b) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc.* **1978**, 920. (c) Eady, C. R.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C.; Machin, P.; McPartlin, M. *J. Chem. Soc., Chem. Commun.* **1976**, 945. (d) Walker, H. W.; Pearson, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1983**, *105*, 1179. (e) Smith, M. B.; Bau, R. *J. Am. Chem. Soc.* **1973**, *95*, 2388. (f) Wilson, R. D.; Bau, R. *J. Am. Chem. Soc.* **1974**, *96*, 7601. (g) Handy, L. B.; Ruff, J. K.; Dahl, L. F. *J. Am. Chem. Soc.* **1972**, *92*, 7312. (h) Handy, L. B.; Treichel, P. M.; Dahl, L. F.; Hayter, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 366. (i) Wilson, R. D.; Graham, S. A.; Bau, R. *J. Organomet. Chem.* **1975**, *91*, C49.
(3) Darensbourg, M. Y.; Barros, H.; Borman, C. *J. Am. Chem. Soc.* **1977**, *99*, 1647.
(4) Martinsen, A.; Songstad, J. *Acta Chem. Scand., Ser. A* **1977**, *A31*, 645.
(5) Darensbourg, D. J.; Gray, R. L.; Ovalles, C.; Pala, M. *J. Mol. Catal.* **1985**, *29*, 285.
(6) Darensbourg, D. J.; Gray, R. L.; Pala, M. *Organometallics* **1984**, *3*, 1928.
(7) Anstock, M.; Taube, D.; Gross, D. C.; Ford, P. C. *J. Am. Chem. Soc.* **1984**, *106*, 3696.