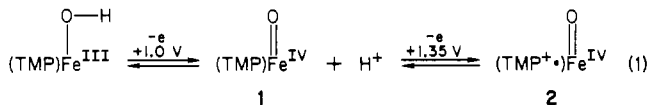


Proton NMR spectra of solutions of **1** in  $\text{CH}_2\text{Cl}_2$  at  $-50^\circ\text{C}$  derived from  $(\text{TMP}^+)\text{Fe}^{\text{III}}(\text{OClO}_3)_2$  and  $(\text{TBA})\text{OH}$  or  $(\text{TMP})\text{Fe}^{\text{III}}\text{OH}^9$  and iodobenzene show resonances only in the 0–8 ppm range. It is apparent from the nonequivalent meta hydrogen resonances at  $\delta$  6.2 and 6.7 and the para methyl resonance at  $\delta$  2.8 that **1** is similar to the oxoiron(IV) complex  $(\text{TMP})\text{Fe}^{\text{IV}}\text{O}$ , described by Balch.<sup>1,9b</sup>

Taken together, these results indicate that the reversible one-electron oxidation observed at +1.0 V vs.  $\text{Hg}/\text{HgO}$  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).<sup>10</sup>



Constant-potential electrolysis of a solution of  $(\text{TMP})\text{Fe}^{\text{III}}\text{OH}$  at +1.18 V in the presence of olefins was found to produce epoxides.<sup>11</sup> Electrolyses of solutions containing styrene, *cis*- or *trans*- $\beta$ -methylstyrene, cyclododecene, cyclooctene, or norbornene were found to give an average of 15 equiv of the corresponding epoxide after 4 h.<sup>12</sup> Blank experiments in the absence of the iron porphyrin produced negligible quantities of epoxides. A 24-h electrolysis of a  $4.8 \times 10^{-6}$  M  $\text{CH}_2\text{Cl}_2$  solution of  $(\text{TMP})\text{Fe}^{\text{III}}\text{OH}$  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<sup>13</sup> 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*- $\beta$ -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  $(\text{TMP})\text{FeOH}$ . 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  $\text{Fe}^{\text{IV}}$  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  $(\text{TMP})\text{Fe}^{\text{IV}}\text{O}$  could contain as much as 0.1%  $(\text{TMP})\text{Fe}^{\text{III}}\text{OH}$  and 0.1%  $(\text{TMP}^+)\text{Fe}^{\text{IV}}\text{O}$  (**2**) at equilibrium. The availability of protons at the anode could make the production of **2** facile by providing a source of  $(\text{TMP}^+)\text{Fe}^{\text{III}}$ .<sup>14</sup>

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

**Acknowledgment.** Financial support of this work by the National Institutes of Health (Grant GM 25923) is gratefully acknowledged.

- (15) (a) Data characterizing the  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{IV}}$  redox couple have been described recently by: Lee, W. A.; Calderwood, T. S.; Bruce, 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  $\text{Na}_2\text{CO}_3$  and presence of chloride; cf. ref 5 and 8.  
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Received August 2, 1985

### Preparation and Structure of $\text{W}(\text{CO})_5\text{OPPh}_2\text{NPPH}_3$ , a Novel Complex Containing a Ligand Derived from the Bis(triphenylphosphine)nitrogen(1+) Cation

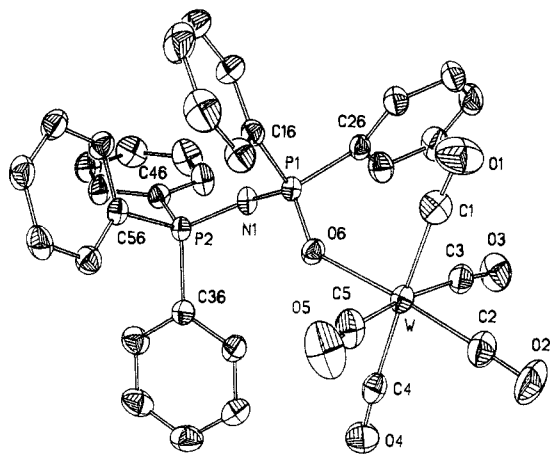
Sir:

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

Our current interest in low-valent  $[\text{M}]\text{OCH}_3^-$  and  $[\text{M}]\text{C}(\text{O})\text{OCH}_3^-$  species, namely where  $[\text{M}] =$  group 6 pentacarbonyls or  $\text{Ru}_3(\text{CO})_{11}$ , as possible intermediates in methanol carbonylation processes to provide methyl formate prompted us to attempt preparation of the  $[\text{PNP}]\text{OMe}$  salt.<sup>5–7</sup> The reaction of  $[\text{PNP}]\text{Cl}$

- (9) (a) Preliminary Mössbauer data on  $^{57}\text{Fe}$ -enriched **1** indicate a quadrupole doublet centered at 0.04 mm/s ( $\Delta E_Q = 2.3$  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 ( $\delta$  8.5) and one ortho methyl resonance ( $\delta$  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**, *107*, 3855–3864 and references therein.  
 (11) A quasi-reversible CV wave at +0.68 V for  $(\text{TPP})\text{Fe}(\text{F}_2)^-$  has been suggested to be that of an  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{IV}}$  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.  
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**Figure 1.** Molecular structure and labeling diagram for  $W(CO)_5OPPh_2NPPh_3$ . Distances (Å) and angles (deg): W–C(1), 2.037 (7); W–C(2), 1.946 (5); W–C(3), 2.028 (5); W–C(4), 2.034 (7); W–C(5), 2.040 (5); W–O(6), 2.220 (2); C(1)–O(1), 1.146 (9); C(2)–O(2), 1.165 (6); C(3)–O(3), 1.140 (7); C(4)–O(4), 1.135 (9); C(5)–O(5), 1.138 (7); O(6)–P(1), 1.510 (3); P(1)–N(1), 1.589 (3); N(1)–P(2), 1.576 (4); W–O(6)–P(1), 141.8 (2); O(6)–P(1)–N(1), 115.4 (2); P(1)–N(1)–P(2), 138.0 (2).

**Table I.** Comparison of Distances (Å) and Angles (deg) for the  $Ph_2P(O)NPPh_3$  Ligand and  $PNP^+$  Cation

compd	av P–N bond	P–N–P angle	av N–P–C- (phenyl) angle	ref
$Ph_3PNP(Ph_2)OW(CO)_5$	1.582	138.0	111.8 <sup>a</sup>	this work
$PNP[Cr_2(CO)_{10}I]$	1.58	142.0	111	13
$PNP[Cr(CO)_3(OSCH)]$	1.581	140.1	111.5	14
$PNP[\mu-HCO_2Ru_3(CO)_{10}]$	1.565	151.3	111.6	2c

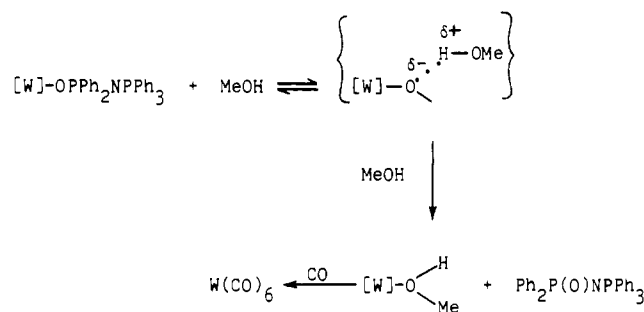
<sup>a</sup> Without the N(1)–P(1)–C(26) angle; with this angle included the average N–P–C angle is 110.5°.

with NaOMe in methanol led instead to the isolation of the novel ligand  $Ph_2P(O)NPPh_3$ , presumably resulting from nucleophilic attack at the phosphorus atom by methoxide or hydroxide.<sup>8</sup> In this communication we wish to describe the X-ray structure of the tungsten(0) complex derived from the addition of this unique ligand to  $W(CO)_5THF$ .<sup>9</sup>

A perspective view of the title complex is depicted in Figure 1, where the atomic numbering scheme is defined as well.<sup>10</sup> The

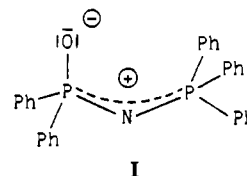
- (8)  $[PNP]Cl$  and an excess of NaOMe were refluxed under nitrogen in dry methanol for 4 h (hydroxide ions may arise either as impurities in NaOMe or from trace quantities of water in MeOH). The resulting clear, colorless reaction mixture was filtered through Celite at ambient temperature. At this stage the reaction solution revealed by  $^{31}P$  NMR spectroscopy the presence of  $PNP^+$  (singlet at 22.9 ppm, 88%),  $Ph_3PO$  (singlet at 33.9 ppm, 5.3%),  $Ph_2P(O)NPPh_3$  (two doublets, 15.8 and 18.3 ppm ( $J = 3$  Hz), 3.5%), and a trace of unidentified phosphorus-containing material with a signal at 123.9 ppm. During the removal of the solvent under reduced pressure at ca. 30 °C, the reaction ensued with production of  $Ph_2P(O)NPPh_3$  reaching 81%; the remaining phosphorus-containing materials were  $Ph_3PO$  (15%) and unreacted  $PNP^+$ , as indicated by  $^{31}P$  NMR spectroscopy. The residue was recrystallized from acetone/ $Et_2O$  to afford an off-white amorphous solid in varying yields.  $^{31}P$  NMR of  $Ph_2P(O)NPPh_3$  in THF or acetone: two equal-intensity singlets at 12.8 and 13.4 ppm. A small quantity of  $Ph_3PO$  has previously been reported during the preparation of  $[PNP]CN$  from  $[PNP]Cl$  and KCN in methanol, presumably resulting from attack on  $PNP^+$  by hydroxide ions.<sup>4</sup>
- (9) The complex was prepared from the reaction of photochemically produced  $W(CO)_5THF$  and  $Ph_2P(O)NPPh_3$  in THF. Crystals suitable for X-ray structural analysis were obtained from THF/hexane. Infrared  $\nu_{CO}$  region: 2066 (w), 1966 (w, br), 1917 (vs), 1866 (m)  $cm^{-1}$ . A peak at 1170  $cm^{-1}$  in  $Ph_2P(O)NPPh_3$  that is shifted to 1125  $cm^{-1}$  upon complexation is assigned to the PO stretching vibration. This is similar to the shift observed in  $\nu_{PO}$  in  $Ph_3PO$  upon complexation to  $[W(CO)_6]$ , from 1190 to 1146  $cm^{-1}$ .  $^{31}P$  NMR (THF): two resonances of equal intensity at 15.1 and 25.3 ppm. Presumably the latter signal is due to  $Ph_2P(O)NPPh_3$ , since it is shifted the most upon complexation.<sup>3</sup>

## Scheme I



arrangement of the ligands around the central tungsten atom closely defines a regular octahedron. The average  $W-CO_{eq}$  bond length is 2.035 (6) Å while that of  $W-CO_{ax}$  is 0.089 Å shorter (1.946 (5) Å). Thus, the  $Ph_2P(O)NPPh_3$  ligand displays a significant trans effect, much like that of anionic oxygen donor ligands.<sup>18,11</sup> The O(6)–W–C(1), O(6)–W–C(3), and O(6)–W–C(5) angles are all greater than 90° (94.6 (2), 95.0 (1), and 93.4 (2)°, respectively), indicative of some steric repulsion from the non-carbonyl ligand. The latter ligand is situated 2.220 (2) Å from the tungsten center.

Interestingly, the structural features common to the  $PNP^+$  cation and its  $Ph_2P(O)NPPh_3$  derivative are not greatly different (Table I).<sup>12,13</sup> For example, the two phosphorus nitrogen bonds are almost equal and average 1.582 Å, and the P(1)–N(1)–P(2) angle is 138°, which is well within the range reported for the bis(triphenylphosphine)nitrogen(1+) cation. In other words, the  $Ph_2P(O)NPPh_3$  species (I) is best viewed as containing a very



negative oxygen center with the  $PNP$  network delocalizing the cationic component of the zwitterion and maintaining its identity with the  $PNP^+$  cation.<sup>12,14</sup> Spectral and reactivity studies (vide infra) are supportive of this interpretation in that the W–O bond resembles that of anionic oxygen donor ligands as opposed to neutral oxide donors.<sup>15</sup> Although the proximity of the bulky  $Ph_2P(O)NPPh_3$  ligand has an effect on bond angles within the octahedron around tungsten, these steric interactions are not sufficient to notably modify the disposition of the phenyl rings about the phosphorus atoms. The only exception is the N(1)–P(1)–C(26) angle of 105.5 (2)°, which is the smallest among those reported and compared in Table I. The other pertinent bond distances and angles are listed in Figure 1.

Dissolution of  $W(CO)_5OPPh_2NPPh_3$  in the protic solvent methanol results in rapid replacement of  $Ph_2P(O)NPPh_3$  by MeOH with formation of  $W(CO)_5MeOH$ .<sup>16</sup> This process is

- (10) Crystal data:  $WC_35H_{25}NO_6P_2$ , triclinic  $P\bar{1}$ ; 22 °C;  $a = 11.248$  (2) Å,  $b = 12.434$  (3) Å,  $c = 13.353$  (3) Å,  $\alpha = 75.07$  (2)°,  $\beta = 80.84$  (2)°,  $\gamma = 63.85$  (2)°,  $V = 1622.8$  (6) Å<sup>3</sup>,  $Z = 2$ ,  $\mu = 39.1$   $cm^{-1}$  (Mo  $K\alpha$ ); heavy-atom solution, blocked-cascade refinement using 5099 absorption-corrected, observed reflections,  $F_o \geq 3\sigma(F_o)$ ,  $4^\circ \leq 2\theta \leq 48^\circ$ ;  $R_F = 0.029$ ,  $R_w = 0.031$ , GOF = 1.034; phenyl rings constrained as rigid hexagons. The structural details will be published separately.
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- (15) More detailed  $\nu_{CO}$ ,  $^{13}C$  NMR, and ligand substitution reaction kinetic measurements are in progress in our laboratories involving  $W(CO)_5OPR_3$  derivatives for comparison with this unique  $Ph_2P(O)NPPh_3$  ligand.
- (16)  $W(CO)_5MeOH$  has  $\nu_{CO}$  absorptions in methanol at 2074 (w), 1975 (sh), 1932 (vs), and 1888 (m)  $cm^{-1}$ . This species has been independently prepared by photolysis of  $W(CO)_6$  in methanol.

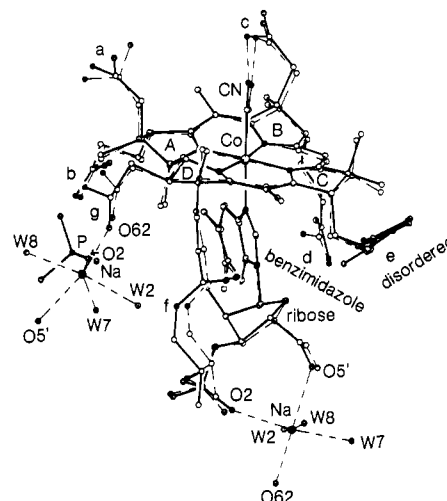
represented in Scheme I. Reversible hydrogen-bonding interactions of the type depicted have been observed spectroscopically for similar, more tightly bound, anionic ligands.<sup>17</sup> Displacement of MeOH from the tungsten's coordination sphere is observed, as would be expected,<sup>18</sup> to be dependent on the concentration of the incoming CO ligand.<sup>19</sup>

In the absence of this solvent-assisted ligand substitution process, that is when the reaction is carried out in aprotic solvents, displacement of the  $\text{Ph}_2\text{P}(\text{O})\text{NPPH}_3$  ligand is much less facile. For example, in THF at atmospheric CO pressure, substitution of  $\text{Ph}_2\text{P}(\text{O})\text{NPPH}_3$  occurs without any buildup of  $\text{W}(\text{CO})_5\text{THF}$  at a rate at least 50 times slower than the displacement of methanol in  $\text{W}(\text{CO})_5\text{MeOH}$ . Therefore dissociative ligand loss of  $\text{Ph}_2\text{P}(\text{O})\text{NPPH}_3$  from  $\text{W}(\text{CO})_5\text{OPPh}_2\text{NPPH}_3$ , a process directly related to the  $[\text{W}]-\text{O}$  bond strength, is much slower than the analogous processes involving the neutral O-bonded ligands THF and MeOH.

In conclusion, the observation of nucleophilic attack at the electrophilic phosphorus atoms of the  $\text{PNP}^+$  cation by  $\text{OMe}^-$  and/or  $\text{OH}^-$  reported herein might be more widespread for good nucleophiles (including, e.g., the hydride ligand)<sup>20</sup> and hence needs to be considered when  $\text{PNP}^+$  salts are used in organometallic chemistry.

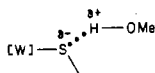
**Acknowledgment.** The financial support of this research by the National Science Foundation (Grant CHE 83-08281) is greatly appreciated.

**Registry No.**  $[\text{PNP}]\text{Cl}$ , 21050-13-5;  $\text{NaOMe}$ , 124-41-4;  $\text{Ph}_2\text{P}(\text{O})\text{NPPH}_3$ , 2156-69-6;  $\text{W}(\text{CO})_5\text{OPPh}_2\text{NPPH}_3$ , 99618-35-6;  $\text{W}(\text{CO})_5\text{THF}$ , 36477-75-5.



**Figure 1.** View of the structures of vitamin  $\text{B}'_{12}$  (solid lines) superimposed, via the four pyrrole nitrogen atoms, on the structure of air-dried vitamin  $\text{B}_{12}$  (broken lines). Broken lines are also used to show the coordination to the sodium ions (one per vitamin  $\text{B}'_{12}$ ) and the internal hydrogen bond from the cyanide group to the c side chain. The e side chain is disordered in vitamin  $\text{B}'_{12}$ . P and N are denoted by solid circles, O is shown by stippled circles, and Co and C are depicted by open circles. Hydrogen atoms are not included. Note the great similarities in the two structures. Sodium ions and phosphate groups from two different asymmetric units are shown. Water molecules are designated W.

(17) A reversible interaction of this type



has been observed for the  $\text{W}(\text{CO})_5\text{SH}^-$  and  $\text{W}(\text{CO})_5\text{SPh}^-$  derivatives: unpublished results of Kathryn Summers from our laboratories.

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 (19) An increase in CO pressure from atmospheric to 110 psi resulted in an increase in the rate of MeOH displacement in  $\text{W}(\text{CO})_5\text{MeOH}$  by a factor of 7.9.  
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## The Principal Components of Synthetic Vitamin $\text{B}'_{12}$

Sir:

An extensive literature indicates that commercial sources of  $\text{B}_{12}$  compounds contain impurities with potential health consequences.<sup>1</sup> Nath<sup>1-5</sup> has investigated these impurities and has concluded that an isomeric modification of  $\text{B}_{12}$  is present on the basis of synthetic materials having properties similar to those of the impurities. The synthetic materials also have properties very

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**Figure 2.** Traces from the HPLC experiments using  $\text{CH}_3\text{CN}$  (left) or  $\text{CH}_3\text{OH}$  (right) as solvent: (top) noncrystalline  $\text{B}'_{12}$ ; (middle) crystalline  $\text{B}'_{12}$ ; (bottom) mixture of d-, b-, and e-monocarboxylic acids. The vertical bar corresponds to 0.01 absorbance unit. HPLC separation conditions:  $4.6 \times 250$  mm Microsorb  $\text{C}_{18}$  ( $5 \mu\text{m}$ ) column; 15–20- $\mu\text{L}$  injections of 0.34 mg/mL solutions (except for the crystalline  $\text{B}'_{12}$ , which was available in insufficient quantity for weighing); absorbance at 260 nm, 0.2 AUFS; flow rate 1.5 mL/min; 30-min gradients; solvent 0.1 M triethylamine/acetate buffer (pH 7.0); gradients from 10 to 15%  $\text{CH}_3\text{CN}$  (left) and from 20 to 25%  $\text{CH}_3\text{OH}$  (right). Separations were optimized by starting from conditions outlined by Jacobsen.<sup>11</sup>

similar to those of the  $\text{B}_{12}$  analogues and thus have been called  $\text{B}'_{12}$ . However, the evidence suggests that  $\text{B}'_{12}$  contains a negatively charged group since, for example, the aquocobalamin ( $\text{B}_{12a}$ ) is positively charged whereas  $\text{B}'_{12a}$  is not retained by cation-exchange resins.<sup>1</sup>

Slow hydrolysis of the amide functions in  $\text{B}_{12}$  compounds could account for (a) the slow changes in  $\text{B}_{12}$  species that lead to the corresponding  $\text{B}'_{12}$  and (b) the occurrence of a negatively charged group (i.e. an ionized carboxylic acid). Therefore, we utilized the method of Hogenkamp<sup>6</sup> to acid hydrolyze vitamin  $\text{B}_{12}$ . The three

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 (b) Anton, D. L.; Hogenkamp, H. P. C.; Walker, T. E.; Matwiyoff, N. A. *J. Am. Chem. Soc.* **1980**, *102*, 2215.