

The intercalation reaction reported here using layered $V_2O_5 \cdot nH_2O$ xerogels is general. We have produced stable free standing films containing a variety of other important conducting polymers such as polypyrrole, polythiophene, and their derivatives.¹⁸ It should be noted that this class of materials can be viewed not only as conducting polymer intercalation compounds but also as bronzes. 1 could be characterized as a *polymer bronze* by analogy to alkali metal¹⁹ or molecular^{5d,e} bronzes. It is conceivable that in molecular scale organic/inorganic composites the otherwise independent band structures of each component can interact/overlap, thus giving rise to a new set of properties not possible from either component separately.²⁰ They may provide theoretical models for oriented polymers and also be of potential value for uses as electrode materials. Work on the characterization and development of these materials is underway.

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(17) (a) Bullot, J.; Gallais, O.; Gauthier, M.; Livage, J. *Appl. Phys. Lett.* **1980**, *36*, 986-988. (b) Sanchez, C.; Babonneau, F.; Morineau, R.; Livage, J.; Bullot, J. *Philos. Mag. [Part B]* **1983**, *47*, 279-290. (c) Bullot, J.; Cordier, P.; Gallais, O.; Gauthier, M.; Livage, J. *J. Non-Cryst. Solids* **1984**, *68*, 123-134.

(18) Wu, C.-G.; Kanatzidis, M. G., manuscript in preparation.

(19) (a) Hagemuller, P. In "Non-Stoichiometric Compounds, Tungsten Bronzes, Vanadium Bronzes and Related Compounds; Bevan, D. J., Hagemuller, P., eds.; Pergamon Press: Oxford, 1973; Vol. 1.

(20) This point has been raised previously by Peter Day who attempted to prepare such materials via photopolymerization of appropriate intercalated monomers. The resulting materials however were nonconductive. See: Day, P. in ref 1, pp 117-131, and ref 6.

The Preparation of Large Semiconductor Clusters via the Pyrolysis of a Molecular Precursor

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The systematic preparation of nanometer size semiconductor clusters represents a significant challenge to synthesis chemistry. Recent efforts have included aqueous arrested precipitation,¹ organic² and inorganic³ polymer-stabilized arrested precipitation, and precipitation in organized media such as zeolites,⁴ lipid

(1) Rosetti, R.; Hull, R.; Gibson, J. M.; Brus, L. E. *J. Chem. Phys.* **1984**, *82*, 552.

(2) (a) Meissner, D.; Memming, R.; Kastening, B. *Chem. Phys. Lett.* **1983**, *96*, 34. (b) Mau, A. W. H.; Huang, C. B.; Kakuta, N.; Bard, A. J.; Campion, A.; Fox, M. A.; White, M. J.; Webber, S. E. *J. Am. Chem. Soc.* **1984**, *106*, 6537. (c) Kuczynski, J. P.; Milosavljevic, B. M.; Thomas, J. K. *J. Phys. Chem.* **1984**, *88*, 980. (d) Tien, H. T.; Bi, Z. C.; Tripathi, A. K. *Photochem. Photobiol.* **1986**, *44*, 779. (e) Wang, Y.; Mahler, W. *Opt. Comm.* **1987**, *61*, 233. (f) Wang, Y.; Suna, A.; Mahler, W.; Rasowski, R. *J. Chem. Phys.* **1987**, *87*, 7315. (g) Mahler, W. *Inorg. Chem.* **1988**, *27*, 435.

(3) Fojtik, A.; Weller, H.; Koch, U.; Henglein, A. *Ber. Bunsenges. Phys. Chem.* **1984**, *88*, 969.

(4) Wang, Y.; Herron, N. *J. Phys. Chem.* **1987**, *91*, 257.

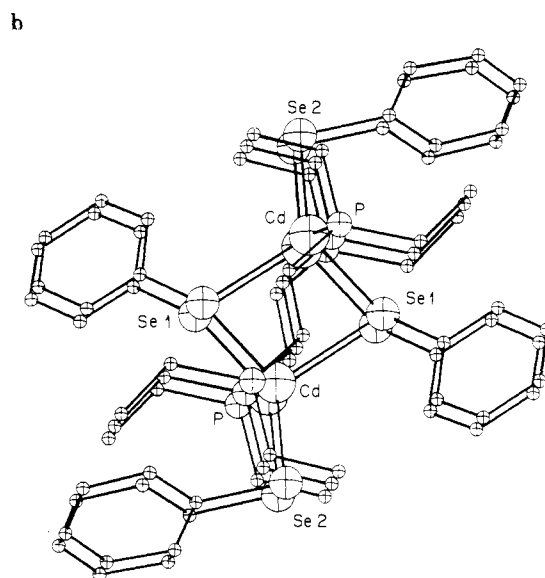
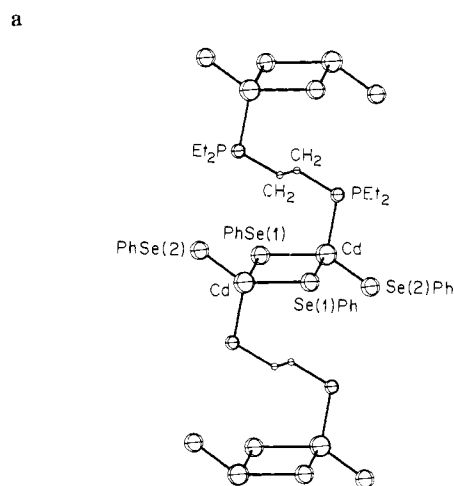


Figure 1. (a) ORTEP drawing of the backbone of $[Cd(SePh)_2]_2 \cdot [Et_2PCH_2CH_2PEt_2]$, with the phenyl and ethyl groups removed for clarity. Significant distances are as follows: Cd-Se(1), 2.735 (3) Å; Cd-Se(1a), 2.678 (3) Å; Cd-Se(2), 2.564 (3) Å; Cd-P, 2.582 (7) Å. Significant angles are as follows: Cd-Se(1)-Cd, 83.55 (9)°; Se(1)-Cd-Se(1a), 96.45 (10)°; Se(1)-Cd-Se(2), 114.02 (11)°; Se(1)-Cd-P, 99.59 (17)°; Cd-Se(1)-C(Ph), 104.2 (7)°; Cd-Se(2)-C(Ph), 97.5 (7)°. (b) View of the polymer down the *c*-axis, illustrating the stacking of the Cd_2Se_2 cores.

membranes,⁵ vesicles,⁶ and micelles.⁷ Since molecular precursors have been used to prepare bulk solid-state compounds,⁸ it seemed reasonable that the solution-phase thermolysis of the appropriate precursors would be an independent synthesis route to large clusters. In this communication we describe the preparation of nanometer-sized clusters of CdSe starting from either $Cd(SePh)_2$, **1**, or $[Cd(SePh)_2]_2[Et_2PCH_2CH_2PEt_2]$, **2**. We report the molecular structure of **2**, and we show that the mild solid-state pyrolysis of

(5) Zao, X. K.; Baral, S.; Rolandi, R.; Fendler, J. H. *J. Am. Chem. Soc.* **1988**, *110*, 1012.

(6) Youn, H. C.; Tricot, Y.-M.; Fendler, J. H. *J. Phys. Chem.* **1985**, *89*, 1236 and references therein.

(7) (a) Meyer, M.; Wallberg, C.; Kurihara, K.; Fendler, J. H. *J. Chem. Soc., Chem. Commun.* **1984**, 90. (b) Lianos, P.; Thomas, J. K. *J. Coll. Surf. Sci.* **1986**, *117*, 505. (c) Daunhauser, T.; O'Neil, M.; Johansson, K.; Witten, D.; McLendon, G. *J. Phys. Chem.* **1986**, *90*, 6074. (d) Fendler, J. H. *Chem. Rev.* **1987**, *87*, 877. (e) Petit, C.; Pileni, M. P. *J. Phys. Chem.* **1988**, *92*, 2282. (f) Steigerwald, M. L.; Alivisatos, A. P.; Gibson, J. M.; Harris, T. D.; Kortan, R.; Muller, A. J.; Tayer, A. M.; Duncan, T. M.; Douglass, D. C.; Brus, L. E. *J. Am. Chem. Soc.* **1988**, *110*, 3046.

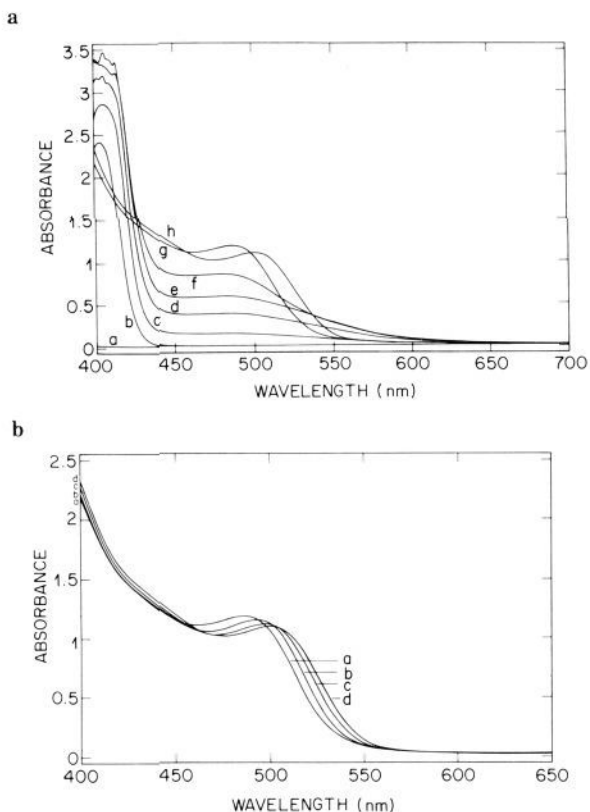


Figure 2. (a) Evolution of the visible absorption in the thermolysis of Cd(SePh)₂ (5×10^{-2} M in refluxing 4-ethylpyridine) showing the increasing concentration of CdSe particles. Trace a is starting material. Traces b (4 min), c (25 min), d (1 h), e (2 h), and f (5.5 h) show the initial formation of a small CdSe cluster with $\lambda_{\max} = 410$ nm. By the time of trace g (9 h), the concentration of 410 species is exhausted. The final trace h (84 h) shows sharpening of the cluster absorption and a shift toward the red. This implies the formation of larger clusters, the ensemble having a narrower size distribution. (b) A more detailed view of the cluster "ripening" process, after the disappearance of the 410-nm species. Spectra were recorded after 9 (a), 26 (b), 50 (c), and 84 (d) h.

each complex gives predominantly zinc-blende CdSe, a phase previously reported⁹ only from high-pressure reactions.

The reaction¹⁰ of benzeneselenol with dimethylcadmium gives oligomeric Cd(SePh)₂, **1**, in high yield. The compound is insoluble in hydrocarbons, slightly soluble in tetrahydrofuran or acetonitrile, and very soluble in tertiary phosphine/toluene mixtures or in pyridine. When this reaction is conducted in the presence of Et₂PCH₂CH₂PEt₂, a compound, **2**, having the stoichiometry [Cd(SePh)₂]₂[Et₂PCH₂CH₂PEt₂] can be isolated in 60–70% yields.¹¹ Recrystallization from pyridine/heptane gives colorless needles which have been characterized by single-crystal X-ray diffraction. The structure is polymeric,¹² with planar (CdSePh)₂ units connected to one another by a bridging phosphine (Figure 1). The Cd₂Se₂ core is planar with phenyl groups of the μ -Se atoms above and below the plane. Significant distances and angles are given in Figure 1. The Cd–P and Cd–Se distances are similar to previously reported values.¹⁴

Pyrolysis of either **1** or **2** in vacuo in the solid state gives bulk CdSe in essentially quantitative yield,¹⁵ the volatile products being Ph₂Se and the phosphine. This process is directly analogous to the formation of ME (M = Zn, Cd; E = S;^{16a} M = Cd, Hg; E = Te^{16b}) from the corresponding complexes, M(ER)₂. When **1** is heated in refluxing 4-ethylpyridine, the optical homogeneity of the solution is maintained, while its UV-vis absorption spectrum changes as shown in Figure 2a. (At any point in the reaction the species responsible for the absorption can be isolated as powders by the addition of petroleum ether to the cooled solution. The isolated red powder redissolves in pyridine to give UV-vis spectra identical with that of the mixture prior to precipitation).

We believe that the UV-vis absorptions are due to electronic transitions in nanometer-scale fragments of the CdSe lattice. We have previously observed that surface-derivatized clusters of CdSe^{7f} show a similar variation in optical absorption, with larger clusters absorbing to the red of smaller clusters.¹⁷

Some features of Figure 2a are particularly noteworthy: (1) The molecular starting material is converted to an as yet unidentified complex having an absorption maximum at approximately 410 nm. We believe that this species is a small CdSe cluster of particular kinetic stability. (2) The disappearance of the 410-nm species coincides with a leveling of the absorption intensity due to the larger CdSe clusters. Upon heating, the exciton absorption both sharpens (Figure 2a, traces f and g) and shifts to the red (Figure 2b). These data indicate a narrowing cluster size distribution^{17,18} and an increase in average cluster size.¹⁷

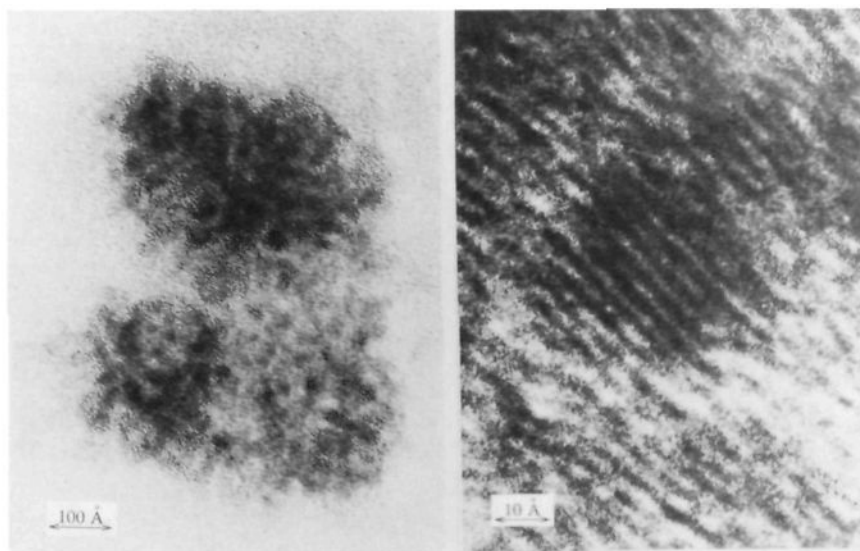


Figure 3. Transmission electron micrographs (JEOL 2000FX, 500 000 \times , 200KV) of the ca. 30 Å diameter CdSe clusters formed in the thermolysis of [Cd(SePh)₂]₂[Et₂PCH₂CH₂PEt₂]. Micrograph on the left shows a collection of particles. Micrograph on the right shows a single particle.

UV-vis spectroscopy is not sufficient to characterize the highly colored, soluble intermediates in the pyrolysis of **1**, particularly since any sort of "quantum confinement" (one-, two-, or three-dimensional) would lead to the observed changes in absorption. Transmission electron microscopy provides more definite structural assignment since it allows the imaging of distinct particles. The micrograph shown in Figure 3 indicates that the soluble intermediates in the pyrolysis of Cd(SePh)₂ are nanoclusters of CdSe. The electron diffraction pattern of this material is consistent with that of CdSe. These clusters are structurally similar to those previously prepared by arrested precipitation and organic capping,^{7f} although chemically they are different in being slightly air sensitive.

In this report we have shown that nanoscale compounds can be prepared by the solution phase thermolysis of molecular precursor compounds. This technique is a valuable complement to the now familiar arrested precipitation and offers the chance to prepare nanoclusters of materials which cannot easily be formed by simple precipitation. This work also directly demonstrates the intermediacy of large clusters in the formation of solid-state compounds by the precursor method.

Supplementary Material Available: Tables listing positional and thermal parameters, significant distances and angles, and X-ray powder patterns of the products of the thermolysis reactions and an electron diffraction pattern of the TEM sample (15 pages); table of calculated and observed structure factors (34 pages). Ordering information is given on any current masthead page.

(8) (a) West, A. R. *Solid State Chemistry and Its Applications*; Wiley and Sons: New York, 1984; pp 16-31. (b) Rao, C. N. R.; Gopalakrishnan, J. *New Directions in Solid State Chemistry*; Cambridge University Press: Cambridge, UK, 1986; pp 116-24. (c) Foise, J.; Kim, K.; Covino, J.; Dwight, K.; Wold, A.; Chianelli, R.; Passaretti, J. *Inorg. Chem.* **1984**, *23*, 872-4. (d) Jensen, J. A.; Gozum, J. E.; Pollina, D. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 1643-4. (e) Nanjundswamy, K. S.; Vasanthacharaya, N. Y.; Gopalakrishnan, J.; Rao, C. N. R. *Inorg. Chem.* **1987**, *26*, 4286-8.

(9) Rooymans, C. J. M. *Phys. Lett.* **1963**, *4*, 186.

(10) All reactions were done under inert atmosphere using dry, degassed solvents. To Me₂Cd (Alfa, 0.15 g, 11 mmol) in toluene (10 mL) was added HSePh (Aldrich 0.34 g, 22 mmol) in toluene (5 mL). A white solid formed immediately. The reaction mixture was stirred for 4 h, and the white precipitate was collected, washed repeatedly with heptane, and dried in vacuo to give a white solid (0.38 g, 80%); mp > 304 °C; ¹H NMR (pyr-*d*₅, 30 °C) 8.03 (2 H), 7.00 (3 H); visible spectrum (HP-8451A) λ_{max} = 315 nm. Anal. Calcd for C₁₂H₁₀CdSe₂: C, 34.2; H, 2.37. Found (Schwarzkopf): C, 34.6; H, 2.54.

(11) To a solution of Me₂Cd (0.15 g, 11 mmol) and Et₃PCH₂CH₂PEt₂ (Strem, 0.18 g, 9 mmol) in toluene (10 mL) was added HSePh (0.34 g, 22 mmol) in a dropwise fashion. After a period of minutes to hours, a white precipitate formed (0.45 g, mp 162-3 °C). Recrystallization from pyridine/heptane (1:8) gave colorless needles (0.17 g, 28%); mp 158.6-159 °C; ¹H NMR (pyr-*d*₅, 30 °C) 8.06 (4 H), 7.04 (6 H), 1.67 (2 H), 1.46 (4 H), 1.02 (6 H). Anal. Calcd for C₁₇H₂₂CdPS₂: C, 38.6; H, 4.49; P, 5.85. Found: C, 38.9; H, 4.27; P, 5.88.

(12) Refinement procedures were as described elsewhere.¹³ The complex crystallizes in the monoclinic space group *P*2₁/*c* with *a* = 21.867 (8) Å, *b* = 22.261 (8) Å, *c* = 8.131 (2) Å, β = 100.08 (5)°, *V* = 3896.92 Å³, *Z* = 8, *d*(calcd) = 1.733 g/cm³, and μ (Mo Kα) = 4.89 mm⁻¹. A CAD4 diffractometer was used to collect 8429 reflections (5092 unique) in the range 5 < 2θ < 45° at 28 °C. Data (3785) with *I*_{net} > 2.5σ(*I*_{net}) were used in refinement. Refinement of 380 parameters gave residuals of *R*₁ = 0.091 and *R*_w = 0.075. The goodness of fit index was 7.659, and the largest shift/esd = 0.156.

(13) Siegrist, T.; Schneemeyer, L. F.; Sunshine, S. A.; Waszczak, J. V. *Mat. Res. Bull.* **1988**, *23*, 1429.

(14) (a) Dean, P. A. W.; Vittal, J. J.; Payne, N. C. *Inorg. Chem.* **1987**, *26*, 1683. (b) Allman, T.; Goel, R. C.; Jha, N. K.; Beauchamp, A. L. *Inorg. Chem.* **1984**, *23*, 914. (c) Goel, R. G.; Henry, W. P.; Olivier, M. J.; Beauchamp, A. L. *Inorg. Chem.* **1981**, *20*, 3924.

(15) Both compounds were sealed in Pyrex under vacuum. Compound **1** (95 mg) was brought initially to 400 °C and then held at 350 °C for 24 h to give CdSe (40 mg, 97%). Compound **2** (72 mg) was brought to 350 °C and then held at 320 °C for 24 h to give CdSe (24 mg, 90%). X-ray powder patterns (Rigaku Miniflex, λ = 1.5418 Å) of both reaction products are included in the Supplementary Material.

(16) (a) Osakada, K.; Yamamoto, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1117. (b) Steigerwald, M. L.; Sprinkle, C. R. *J. Am. Chem. Soc.* **1987**, *109*, 7200.

(17) Brus, L. *Nouv. J. Chem.* **1987**, *11*, 123.

(18) Alivisatos, A. P.; Harris, A. L.; Levinos, N. J.; Steigerwald, M. L.; Brus, L. E. *J. Chem. Phys.* **1988**, *89*, 4001.

Determination of Homolysis Energies in Solution from Heterolysis Enthalpies and Electron-Transfer Energies

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During the past 5 years we have developed a method for determining heats of heterolysis (ΔH_{het}) from the calorimetric heats of reaction ($\Delta H_{\text{het}} = -\Delta H_{\text{reaction}}$) of carbocations with carbanions, phenoxide, imide, and thiolate anions in solution.¹ Well over 100 values have been determined by this method for C-C, C-O, C-N, and C-S bonds from resonance-stabilized precursors and the ΔH_{het} 's are related in a remarkably simple manner to the pK_{R^+} of the carbocation and the pK_{a} of the conjugate acid of the anion.¹⁻³

We now show that by combining the ΔH_{het} 's with the redox potentials of the cations and anions through a simple thermodynamic cycle, heats of homolysis (ΔH_{homo}) may be calculated, and the complete set of energetics for homolytic, heterolytic, and electron-transfer reactions related to each other. These data provide the first available quantitative criteria for the selective cleavage of such bonds in macromolecules to give resonance-stabilized cations, anions or radicals. Our method is closely analogous to Bordwell's approach^{4,5} for the determination of bond dissociation energies for C-H bonds ($\text{BDE}_{\text{C-H}}$) but differs in that a variety of carbocations take the place of the proton.

Scheme I combines the redox potentials of the separate cationic and anionic species with the heats of heterolysis referred to above. The difference between the heterolysis and homolysis energies is the Gibbs free energy of electron transfer, ΔG_{ET} , obtained from the redox potentials of the cation and anion.

Two obstacles might stand in the way of applying this approach. First is the difficulty of obtaining reversible redox potentials for the carbocations and carbanions using ordinary cyclic voltammetry (CV). We have applied second harmonic AC voltammetry (SHACV)⁶ to successfully determine reversible potentials which confirm Bordwell's irreversible CV values for a number of anions.

The second problem is more fundamental—the mingling of ΔH_{het} enthalpic measurements with redox free energy terms. Application of Scheme I requires that the entropy terms associated with electron transfer will have a negligible effect on combining the ΔG_{ET} terms with ΔH_{het} . If $\Delta S_{\text{ET}} = 0$, then $\Delta G_{\text{ET}} = \Delta H_{\text{ET}}$. Various arguments and several published reports^{4,7,8} support this assumption, but a more compelling argument is our demonstration that the temperature coefficients of the redox potentials, $-(\partial \Delta G_{\text{redox}} / \partial T) = \Delta S_{\text{redox}}$, are small for relevant ions.

Table I presents data for trityl and triphenylcyclopropenium cations which represent the extremes of the stability range of ten carbocations that we have studied with a variety of anion types. The family of substituted fluorenyl anions shown here duplicates, for the most part, the studies by Bordwell's group.^{4,5,9} Stein's estimate¹⁰ of less than 15 kcal/mol for the trityl-trityl bond in hexaphenylethane corresponds well with our determined value of 13 ± 3.5 kcal/mol for ΔH_{homo} for the trityl-9-phenylfluorenyl bond.

Several trends and correlations are noteworthy that are established with the full data set which is presently being prepared for publication. Properties which involve the conversion of a neutral species to an ion or vice versa (e.g., pK_{a} , pK_{R^+} , ΔH_{het} , ΔG_{ET} , and redox potentials) all correlate quite well with each other.¹⁻³ The overwhelming factor in such cases is the distribution of charge

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(1) Arnett, E. M.; Chawla, B.; Molter, K. E.; Amarnath, K.; Healy, M. *J. Am. Chem. Soc.* **1985**, *107*, 5288.

(2) Arnett, E. M.; Chawla, B.; Amarnath, K.; Whitesell, L. G., Jr. *Fuel Energy* **1987**, *1*, 17.