

Figure 1. Electron micrograph of a Pd/C model catalyst. The amount of the incident palladium atoms measured by the quartz thickness monitor was 1.6×10^{15} atoms cm^{-2} . The mean diameter of palladium particles, \bar{d} , is 1.2 nm; bright field.

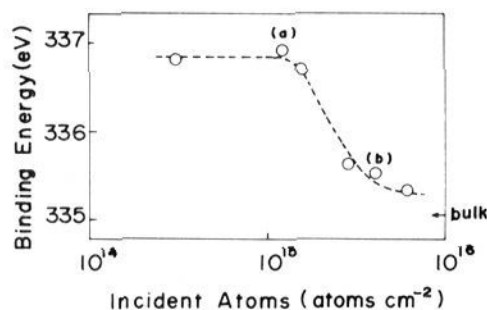


Figure 2. Binding energy of the peak energy of Pd $3d_{5/2}$ level of the Pd/C model catalyst system measured by XPS. The mean diameter of palladium particles, \bar{d} , is (a) 1.0 nm and (b) 1.8 nm.

The mean diameter of the palladium particles, \bar{d} , was controlled by varying the total amount of palladium deposited. The average particle size determined by electron microscopy was found to correlate with electronic energy levels of the particles as determined by X-ray photoelectron spectroscopy (VG, EXCA-3 Spectrometer, Mg $K\alpha$). In Figure 2 we show the binding energy of the $3d_{5/2}$ electrons as a function of the number of palladium atoms per unit area deposited. In the range 10^{15} – 10^{16} atoms cm^{-2} , the binding energy decreases rapidly and approaches that of bulk palladium. The energy of the valence band in the palladium particles is thought to shift with that of the $3d_{5/2}$ band.⁴ It is not known whether this energy shift originates in the interaction between the metal particles in the support or is a property of the metal particles themselves. Tauster et al.⁹ have recently described alterations in the electronic structure of small metal particles that are attributable to strong metal-support interactions.

Rates of the H_2 - D_2 exchange reaction were measured over a temperature range of 0–30 °C, in the presence of H_2 and D_2 pressures of 2.8×10^{-2} torr. The reaction chamber volume was 166 cm^3 . Attempts to determine the specific activity of the catalyst are hampered by difficulty in estimating the surface area. If a hemisphere model is used to estimate the surface area, the specific activity appears to exhibit a maximum at a particle size of $\bar{d} = 1.3$ nm at a rate of $k_m = 3 \times 10^{17}$ molecules $\text{cm}^{-2} \text{s}^{-1}$. At higher and lower average particle size, specific activities estimated from the hemisphere model decline by a factor of about 3 from the maximum value. Further studies of the meaning of this activity maximum are in progress. The principal result of our studies so far concerns the variation of the activation energy for the catalyzed reaction, which is not affected by problems in determining the surface area of the catalyst. In Figure 3, we show the phenomenological activation energy, as a function of mean particle diameter in the range from 1–2 nm. This is the same range of average particle size in which the $3d_{5/2}$ energy level of palladium was observed to shift by about 1.5 eV. As the average particle diameter increases in this range, the activation energy for the catalyzed exchange reaction declines from about 50 kJ mol^{-1} at

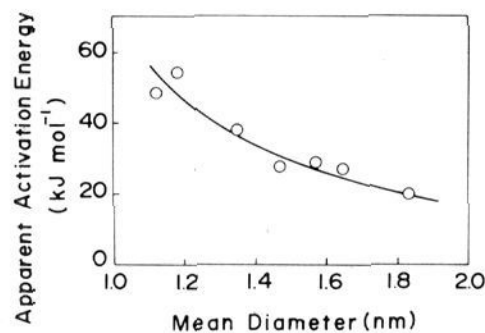


Figure 3. Apparent activation energy for the H_2 - D_2 exchange reaction, catalyzed by the Pd/C model catalyst, as a function of mean palladium particle diameter \bar{d} . The temperature range was 0–30 °C.

$\bar{d} = 1.1$ nm to 20 kJ mol^{-1} at $\bar{d} = 1.8$ nm. We postulate that as the particle size decreases and the binding energy of the core and valence electrons within the palladium particles increases, the adsorption energy of hydrogen on the palladium particles decreases. If this is the case, then the increase in the apparent activation energy for the H_2 - D_2 exchange reaction with decreasing particle size is likely to be caused by a decrease in the rate of dissociation of the adsorbed hydrogen.

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Registry No. Palladium, 7440-05-3; carbon, 7440-44-0; hydrogen, 1333-74-0; deuterium, 7782-39-0.

Asymmetric Induction in Reactions Employing Enolates Generated from Cyclic Organo Transition-Metal Acyl Complexes

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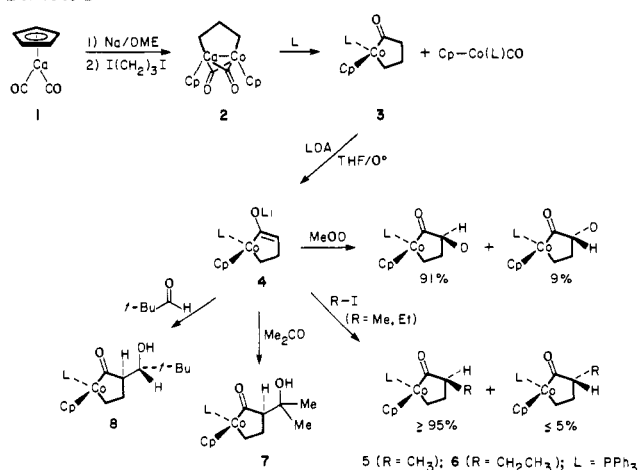
Organo transition-metal acyls comprise a ubiquitous class of complexes made easily by acylation at nucleophilic metal centers, migratory insertion in alkylcarbonylmetal complexes, or attack by nucleophilic carbon reagents at metal-bound CO.¹ Because of the electron-donating properties of the low-valent metal centers in acylmetal complexes, they can be viewed as close relatives of ketones or esters. This analogy has been utilized in developing much of their chemistry (especially reduction and alkylation²). However, one esterlike property that should be characteristic of acyls—the ability to activate α hydrogens toward reaction with basic reagents, leading to alkali metal salts of enolate anions (eq

(1) (a) Coates, G. E.; Green, M. L. H.; Wade, K. "Organometallic Compounds"; Methuen: London, 1968; Vol. 2, pp 257–63. (b) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87. Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299. (c) Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195. (d) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; pp 80–81. (e) Ellis, J. E. *J. Organomet. Chem.* **1975**, *86*, 1. (f) King, R. B. *Acc. Chem. Res.* **1970**, *3*, 417.

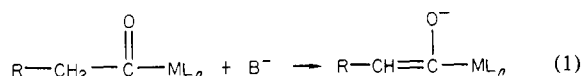
(2) See, for example: (a) Van Doorn, J. A.; Masters, C.; Volger, H. C. *J. Organomet. Chem.* **1976**, *105*, 245. (b) Gladysz, J. A.; Selover, J. C.; Strouse, C. E. *J. Am. Chem. Soc.* **1978**, *100*, 6766. (c) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1. (d) Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1.

(9) S. J. Tauster, S. C. Fung, R. T. K. Baker, and J. A. Horsley, *Science (Washington, D.C.)* **211**, 1121 (1981).

Scheme I



1)—has not been extensively investigated, despite the immense utility of enolates in many areas of organic chemistry.



We report here the successful conversion of two cyclic organo transition-metal acyl complexes to the corresponding lithium enolates and preliminary observations on their alkylation and aldol reactions.³ Specifically, we have found it possible to convert cobaltacyclopentanones of general structure **3** into the corresponding enolates **4** (Scheme I). Enolate **4** reacts rapidly with electrophilic reagents and gives products typical of alkylation with organic halides and aldol condensations with aldehydes. The chirality of the metal center results in a significant amount of asymmetric induction in these reactions, at both the five-membered ring and the reacting carbon atom of the aldehyde.

We reported earlier⁴ the reaction of dinuclear metallacycle **2** with phosphines to give metallacyclopentanones **3**. Slow addition of the air-stable triphenylphosphine complex **3** to a solution of the strong, hindered base lithium diisopropylamide (LDA) in THF at 0 °C under nitrogen generates a red solution of the enolate **4** (IR 1550 cm⁻¹; NMR (THF-*d*₆) δ 7.97 (m, 6 H), 7.23 (m, 9 H), 4.41 (s, 5 H), 4.07 (br, 1 H), 2.39 (br, 1 H), 2.13 (br, 1 H), 1.64 (br, 1 H), 1.46 (br, 1 H)). The first indication as to the diastereoface selectivity in reactions of **4** was provided by cooling the enolate to -78 °C and quenching it with CH₃OD. In the ¹H NMR, diastereotopic α protons in recovered **3** integrated to 0.87 and 0.08 hydrogens, showing that the two possible diastereomers of **3-*d*₁** (Scheme I) were formed in a ratio of 11:1.

Encouraged by this result, we carried out the reactions of enolate **4** with various carbon electrophiles. In all cases high diastereoface selectivity resulted; in each instance the small amount of "unfavored" product was estimated by high-field NMR. The results are summarized in Scheme I. On the basis of examination of models and by analogy to the results of the conversion of **10** to **11** in which the stereochemistry of the product was established by an X-ray diffraction study (see below), we judge that approach of the electrophile syn to the Cp ring is preferred, leading to the geometry of the products shown in the scheme.

Alkyl halides and symmetrical ketones are the simplest substrates, since only one new asymmetric center is generated in these reactions. Primary iodides MeI and EtI show roughly twice the diastereoface selectivity observed with MeOD. Reaction with acetone leads to only one observable product (**7**), and thus aldol

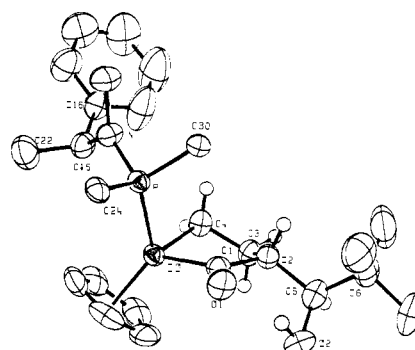
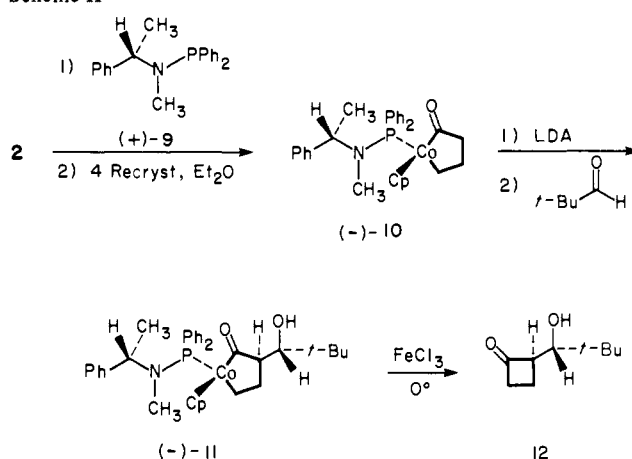


Figure 1. ORTEP diagram of complex **11**. Two phenyl rings on phosphorous and the hydrogen atoms have been eliminated for clarity. Selected angles (deg): C₁-Co-C₄, 84.22 (10); C₂-C₅-C₆, 115.34 (24). Selected bond distances (Å): Co-P, 2.164 (1); Co-C₁, 1.914 (2); Co-C₄, 2.004 (2); O₁-H(O₂), 1.75; O₂-H(O₂), 1.18 (H(O₂) was located but not refined).

Scheme II



condensation is completely face selective within the limits of detection by high-field ¹H NMR (ca. 3%). The use of prochiral ketones or aldehydes in this reaction generates two chiral centers, leading to threo and erythro aldol products. The possible number of racemic diastereomers is thus increased to four. However, no more than two isomers are ever detected, consistent with the high diastereoface selectivity observed with acetone. With respect to threo/erythro selectivity, **4** is a trans enolate and thus should favor formation of threo product on the basis of the transition-state structure suggested for organic systems by Zimmermann and Traxler.⁵ This is again in accord with the X-ray structure study summarized below, and by analogy we assign the threo structure⁶ to the major isomers formed in reactions of **4** with various aldehydes. The threo/erythro selectivity is only moderate with use of acetaldehyde (3.51:1) and 2-methylpropionaldehyde (3.0:1) but appears to be complete for pivaldehyde, leading only to **8**.

The applicability of this chemistry to the preparation of optically active materials was investigated by using the sequence summarized in Scheme II, involving the chiral phosphine **9**. This phosphine was prepared in a straightforward manner from (*S*)-(-)-α-methylbenzylamine by literature procedures.⁷

(5) Zimmerman, H. E.; Traxler, M. *J. Am. Chem. Soc.* **1957**, *79*, 1920.

(6) The ¹H NMR vicinal coupling constant between the protons attached to the adjacent chiral centers is commonly used to determine the relative stereochemistry of the aldol product, with *J*_{AB}(threo) > *J*_{AB}(erythro). In our systems examination of these coupling constants did not facilitate unambiguous assignment of stereochemistry. Other exceptions to this pattern have been noted; cf.: Heng, K. K.; Simpson, J.; Smith, R. A. *J. Org. Chem.* **1981**, *46*, 2932.

(7) (a) Brunner, H.; Rambold, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 1013. (b) Brunner, H.; Doppelberger, J. *Chem. Ber.* **1978**, *111*, 673.

(8) (a) Bush, M. A.; Dullforce, T. A.; Sim, G. A. *J. Chem. Soc., Chem. Commun.* **1969**, 1491. (b) Klyne, W.; Buckingham, J. "Atlas of Stereochemistry"; Oxford University Press: New York, 1974; p 23.

(3) (a) Meyers, A. I. *Pure Appl. Chem.* **1979**, *51*, 1255. (b) Heathcock, C. H. *Acc. Chem. Res.*, in press. (c) Evans, D. A.; Bartroli, J.; Shih, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 2127. (d) Noyori, R.; Nishida, I.; Sakata, J. *Ibid.* **1981**, *103*, 2106. (e) Bartlett, P. A. *Tetrahedron* **1980**, *36*, 2. (f) Yamamoto, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1982**, *104*, 2330.

(4) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 5694; *Organometallics*, in press.

Treatment of metallacycle **2** with this phosphine and purification by column chromatography gave a 78% yield of **10** and its diastereomer having the opposite configuration at cobalt, as an air-stable orange paste. The Cp resonances of the two diastereomers were easily distinguishable by ^1H NMR (δ 4.42 and 4.49); this showed that they were formed in approximately equivalent amounts. Four recrystallizations from diethyl ether gave the less-soluble diastereomer (**10**; absolute configuration assigned by chemical correlation to **11**; see below) in 60% recovery and optically pure form as determined by NMR and by unchanged optical rotation upon further recrystallization. Treatment of this material with LDA followed by pivaldehyde as described above gave aldol **11** in 98% isolated yield. Inspection of the 250-MHz ^1H NMR spectrum of **11** showed only a single Cp resonance, again indicative of high diastereoface selectivity at the reacting ring carbon and high three/erythro selectivity, as observed with this aldehyde in experiments with **3** and **4**.

In order to obtain a completely secure assignment of the absolute stereochemistry of **11** and therefore of the sense of the asymmetric induction observed in its formation, we determined its structure by X-ray diffraction. Details of the structure study are provided as supplementary material; an ORTEP drawing of the molecule, illustrating the absolute configuration at all chiral centers, is shown in Figure 1. As indicated in the drawing and assumed in the previous discussion, the aldol product is the three isomer, and the hydroxyalkyl chain and the Cp ring are related in a cis manner.

We have carried out preliminary experiments aimed at developing ways to remove the metal moiety. Thus far we have found one efficient method, which involves oxidatively induced reductive elimination to cyclobutanone derivatives. For example, reaction of racemic **11** with 2 equiv of FeCl_3 afforded pure 2-(1-hydroxy-2,2-dimethylpropyl)cyclobutanone (**12**) in 70% yield. Carrying out this reaction on optically active **11** gave cyclobutanone **12**, optically pure by NMR analysis using chiral shift reagents.⁹

Our results suggest that other organo transition-metal acyl complexes should be similarly reactive, and we are planning to investigate a range of such systems. Experiments aimed at removing the cobalt from the complexes described in this paper to give acyclic, rather than cyclic, systems are also under way.

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Registry No. **2**, 74656-84-1; **3**, 74656-85-2; **3-d₁(R*,R*)**, 82837-81-8; **3-d₂(R*,S*)**, 82837-82-9; **4**, 82783-72-0; **5(R*,R*)**, 82783-73-1; **5(R*,S*)**, 82837-83-0; **6(R*,R*)**, 82783-74-2; **6(R*,S*)**, 82837-84-1; **7**, 82783-75-3; **8**, 82783-76-4; (+)-**9**, 2627-86-3; (-)-**10**, 82783-77-5; **10** diastereomer, 82837-85-2; (-)-**11**, 82783-78-6; **12**, 82783-79-7; MeOD, 1455-13-6; MeI, 74-88-4; EtI, 75-03-6; Me₂CO, 67-64-1.

Supplementary Material Available: Details of the preparation of metallacyclopentanones **3** from CpCo(CO)₂ (**1**), spectral and analytical data on metallacyclic products formed from enolate **4**, details of the structure determination of optically active metallacyclopentanone **11**, including atomic numbering scheme, crystal and data collection parameters, positional and thermal parameters, selected interatomic distances, selected interatomic

angles, selected torsional angles, general temperature factor expressions, crystal and orthonormal and least-squares planes, and observed and calculated data points (38 pages). Ordering information is given on any current masthead page.

Experimental Probe of Nonadiabatic Effects in Simple Electron-Transfer Reactions¹

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It has long been postulated that purely electronic or nonadiabatic effects (such as orbital symmetries, changes in spin multiplicity, donor-acceptor separation, etc.) play a significant role in determining the rates of electron-transfer reactions.² However, the predominant features of electron-transfer reaction patterns seem best attributable to Franck-Condon factors,³⁻¹⁵ but the precise values of these factors have proved elusive.¹⁶ The actual significance of purely electronic contributions has therefore remained equivocal.^{15,16}

Recent studies of the quenching of electronically excited transition-metal complexes¹⁷⁻¹⁹ have led us to an experimental

(1) Partial support of this research by the National Institute of Health (Grant AM 14341) and by the National Science Foundation (Grant CHE 80-05497) is gratefully acknowledged.

(2) Orgel, L. E. Tenth Solvay Conference, Brussels, May, 1956.

(3) For reviews see: (a) Cannon, R. D. "Electron Transfer Reactions"; Butterworths: London, 1980. (b) Taube, H. "Electron Transfer Reactions of Complex Ions in Solution"; Academic Press: New York, 1970. (c) Linck, R. G. *MTP Int. Rev. Sci.: Inorg. Chem. Ser. One* **1971**, *9*, 303. (d) Cannon, R. D. *Inorg. Reaction Mech.* **1978**, *3*, 3. (e) *Ibid.* **1979**, *6*, 3.

(4) (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155; (b) *J. Phys. Chem.* **1963**, *67*, 853; (c) *Discuss. Faraday Soc.* **1960**, *29*, 21.

(5) (a) Hush, N. S. *Electrochim. Acta* **1968**, *13*, 1005; (b) *Prog. Inorg. Chem.* **1967**, *8*, 391; (c) *Trans. Faraday Soc.* **1961**, *57*, 557.

(6) (a) Levich, V. G.; Dogonadze, R. R.; Kuznetsov, A. M. *Electrochim. Acta* **1968**, *13*, 1025. (b) Levich, V. G.; Dogonadze, R. R.; German, E. D.; Kuznetsov, A. M.; Kharkats, Yu. T. *Electrochim. Acta* **1970**, *15*, 353.

(7) Kestner, N. R.; Logan, J.; Jortner, J. *J. Phys. Chem.* **1974**, *78*, 2148.

(8) (a) Jortner, J. *J. Chem. Phys.* **1976**, *64*, 4860; (b) *J. Am. Chem. Soc.* **1980**, *102*, 6676. (c) Buhks, E.; Bixon, M.; Jortner, J.; Navon, G. *Inorg. Chem.* **1979**, *18*, 2014.

(9) (a) Ulstrup, J.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 4358. (b) Jortner, J.; Ulstrup, J. *J. Am. Chem. Soc.* **1979**, *101*, 3744.

(10) (a) Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883. (b) Brunshwig, B. S.; Logan, J.; Newton, M. D.; Sutin, N. *Ibid.* **1980**, *102*, 5798. (c) Chou, M.; Creutz, C.; Sutin, N. *Ibid.* **1977**, *99*, 5615.

(11) Newton, M. D. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1980**, *14*, 364.

(12) (a) Efrima, S.; Bixon, M. *J. Chem. Phys.* **1976**, *64*, 3639; (b) *Chem. Phys.* **1976**, *13*, 447.

(13) (a) Van Duyne, R. P.; Fischer, S. F. *Chem. Phys.* **1974**, *5*, 183. (b) Fischer, S. F.; Van Duyne, R. P. *Ibid.* **1977**, *26*, 9.

(14) (a) Hopfield, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3640. (b) Potasek, M. J.; Hopfield, J. J. *Ibid.* **1977**, *74*, 3817.

(15) (a) Endicott, J. F.; Durham, B.; Glick, M. D.; Anderson, T. J.; Kuszaj, J. M.; Schmonsees, W. G.; Balakrishnan, K. P. *J. Am. Chem. Soc.* **1981**, *103*, 1431. (b) Endicott, J. F.; Durham, B.; Kumar, K. *Inorg. Chem.* **1982**, *21*, 2437. (c) Endicott, J. F.; Kumar, K.; Ramasami, T.; Rotzinger, F. P. *Prog. Inorg. Chem.*, in press. (d) Endicott, J. F.; Kumar, K.; Brubaker, G. R.; Dwarakanath, K.; Cassel, J., submitted for publication in *Inorg. Chem.*

(16) Franck-Condon factors based on experimental structural parameters seem consistently a little too small to account for the large barriers observed for Co(II)-Co(II) electron-transfer self-exchange.¹⁵ However, uncertainties in the knowledge of bond lengths, $\sim \pm 1$ pm in the best documented cases, lead to very large uncertainties in ΔG^{\ddagger}_{in} , since $\Delta G^{\ddagger}_{in} \propto \Delta X^2$. In a typical Co(II)-Co(II) couple, $\Delta X = 20 \pm 2$ pm, and this results in $\Delta G^{\ddagger}_{in} \approx 60 \pm 12$ kJ mol⁻¹.^{15,c} Calculated values of ΔG^{\ddagger} run 5-30 kJ mol⁻¹ smaller than $\Delta G^{\ddagger}_{obsd}$, with the discrepancy similar in magnitude to the uncertainty in ΔG^{\ddagger}_{in} . In view of such large uncertainties, the differences between $\Delta G^{\ddagger}_{obsd}$ and $\Delta G^{\ddagger}_{calcd}$ (Franck-Condon terms) cannot be an accurate measure of the contribution of purely electronic factors. Even an electronic contribution of 10^4 to the observed rate constant could not be clearly defined by this approach.

(9) (a) Whitesides, G. M.; Lewis, D. W. *J. Am. Chem. Soc.* **1970**, *92*, 6979. (b) Goering, H. L.; Eikenberry, J. N.; Koerner, G. S. *Ibid.* **1971**, *93*, 5913. (c) McCreary, M. D.; Lewis, D. W.; Wernick, D. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 1038.