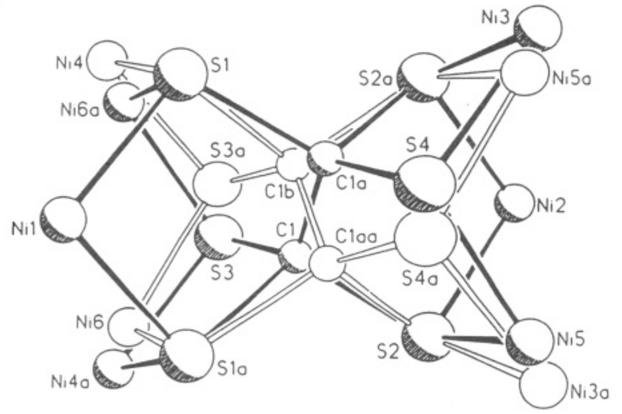

Figure 5. Ball–stick representation of the crystal-disordered $Ni_6(C_2S_6)$ core of $[Ni_3Cp_3]_2(C_2S_6)$ (**1a**) modeled as two half-weighted orientations related by a crystallographic mirror plane. The close conformity of the aggregate of these two orientations to the experimental atomic thermal ellipsoids of the "averaged structure" given in Figure 4 provides convincing evidence for the reconstitution of the crystal-disordered **1a** as a cyclopentadienyl analogue of the crystal-ordered 1.

by the crystallographic mirror plane under the orthorhombic space group *Pbcm*.

Maj et al.[2] recognized that the presence of a crystal disorder was consistent with the centrosymmetric structural solution of **1a** but attributed the crystal disorder in the "ethylene" carbon atoms to nonbonding instead of bonding interactions with the "bare" sulfur atoms. From a comparison of the $Ni_6(C_2S_6)$ core of 1 (Figure 3) with the corresponding core of **1a** (Figure 4), it is not difficult to see the relationship between the X-ray results of the Cp′ structure and its unsubstituted Cp analogue. To obtain the structure of 1 from **1a**, the two carbon atoms (C′ and C′a) in **1a** need only be moved in opposite directions parallel to the crystallographic mirror plane in accordance with their elongated thermal ellipsoids. The thermal parameters of the S(3) and S(4) atoms are elongated (due to the crystal disorder) perpendicular to the mirror plane. Moving these two sulfur atoms off their positions on the mirror plane in opposite directions to form bonds with the approaching carbon atoms gives the actual molecular structure of 1.

Nevertheless, we consider that the previous description[2] for the formation of **1a** is still valid and can be applied to 1 as well. The cycloaddition of a $(CpNi)_2S$ fragment across each of the two pairs of sulfur-chelating atoms of the planar tetrathiolene-like $Ni_2Cp_2(C_2S_4)$ precursor is accompanied by a marked distortion of the molecule that completely disrupts the delocalized π-system. The revised connectivity in **1a** additionally requires concomitant bonding of the sulfur atom in each of the $(CpNi)_2S$ fragments to one of the carbon atoms of the C_2S_4 ligand, thereby forming the hexathioethane C_2S_6 ligand.

The crystal-disordered structure of **1a** can be successfully described by modeling the average atomic positional parameters of the $Ni_6(C_2S_6)$ core to those obtained from the triclinic structure solution of 1. The resulting parameters of **1a** were then refined under *Pbcm*. By averaging the atomic positions for the two disordered orientations given in Figure 5, the abnormal shapes of the atomic thermal ellipsoids of **1a** (Figure 4) can be accounted for. Our ability to reproduce the discrepancy *R* values obtained in the original refinement of the "averaged structure" provides an equally plausible molecular configuration that permits the reformulation of $[Ni_3Cp_3(\mu_2\text{-}S)]_2(C_2S_4)$ as $[Ni_3Cp_3]_2(C_2S_6)$, consistent with the molecular configuration of 1.

It is ironic that the incorrect molecular connectivity of the crystal-disordered **1a** provided the insight and hence the stimulus for the subsequent synthetic–stereochemical–bonding studies in our laboratories on the tetrathiolate-bridged dimetal complexes of nickel, cobalt, iron, and titanium formed via the reductive head-to-head dimerization of CS_2. Whether the actual molecular configuration of **1a** presented herein would have provided the impetus for further work remains unclear.

Acknowledgment. This research was generously supported by the National Science Foundation. We are particularly grateful to EXTREL FTMS (6416 Schroeder Road, Madison, WI) for the use of a FTMS-2000 mass spectrometer.

Supplementary Material Available: Tables of positional parameters, anisotropic thermal parameters, bond angles for the non-hydrogen atoms, and coordinates and isotropic temperature factors for the hydrogen atoms for $[Ni_3Cp'_3]_2(C_2S_6)$ (1) and positional and thermal parameters for the non-hydrogen atoms and interatomic distances for $[Ni_3Cp_3]_2(C_2S_6)$ (**1a**) (9 pages). Ordering information is given on any current masthead page.

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Notes

Crystal and Molecular Structure of $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{\equiv}CCH_2OMe)][Na(15\text{-crown-}5)]$

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The transformations of hydrogen-poor hydrocarbyls (C_nH_x, $x \leq n$) on multimetallic sites are of interest in connection with the study of surface "cokes" and "carbides" formed during catalytic reactions of hydrocarbons or CO on metal surfaces.[1–6] A facile route to multimetallic carbon-rich, hydrogen-poor complexes is through the reactions of alkynes or acetylides with metal–metal dimers

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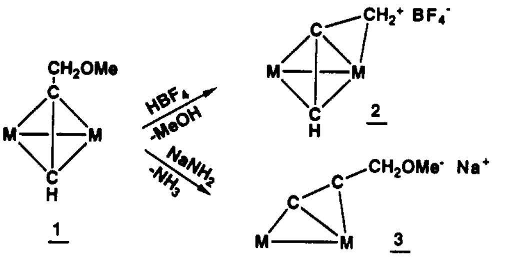
(1) Thompson, S. J.; Webb, G. *J. Chem. Soc., Chem. Commun.* **1976**, 526.

Scheme I



or clusters.[7,8] Dimetallic acetylene and acetylide complexes undergo interesting reactions, e.g., protonation,[9,10] coupling,[11-13] Diels–Alder additions,[14] metathesis,[7g] and deprotonation/realkylation to give μ-vinylidene structures.[15]

We have shown previously that the α-substituted alkyne complex, 1 (Scheme I), is a convenient precursor to the metal-stabilized carbo-cation 2 upon reaction with protic acids.[16] During our studies of the deprotonation reactions of dimolybdenum alkyne complexes, Green et al.[15] published the results of their thorough investigation on this topic.[15] In this paper, we report on the structure and fluxional behavior of the σ,π-acetylide, 3 (Scheme I), formed by the deprotonation of 1. The structure features an interesting chelate-type coordination of the counterion, Na(15-crown-5)$^+$, and the diasteriotopic methylene protons in 3 gives additional information on the nature of the fluxional process that these complexes exhibit.

Experimental Section

All reagents and solvents were handled under an atmosphere of dry N_2 using standard Schlenk or drybox techniques. Drying and removal of molecular oxygen from solvents was accomplished by distillation from sodium benzophenone ketyl (THF, Et_2O). Methylene chloride was dried by distillation from P_4O_{10} and degassed prior to use. Organic reagents were purchased from Aldrich. Infrared spectra were collected on a Perkin-Elmer 257 spectrometer (compensation method). Both ^1H and ^{13}C NMR spectra were recorded on a Bruker WT360 FT spectrometer. X-ray diffraction data were collected on a Syntex $P2_1$ automated four-circle diffractometer. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN. Preparation of $Cp_2(CO)_4Mo_2(HC{\equiv}CCH_2OCH_3)$ (1) was accomplished by the literature method.[16]

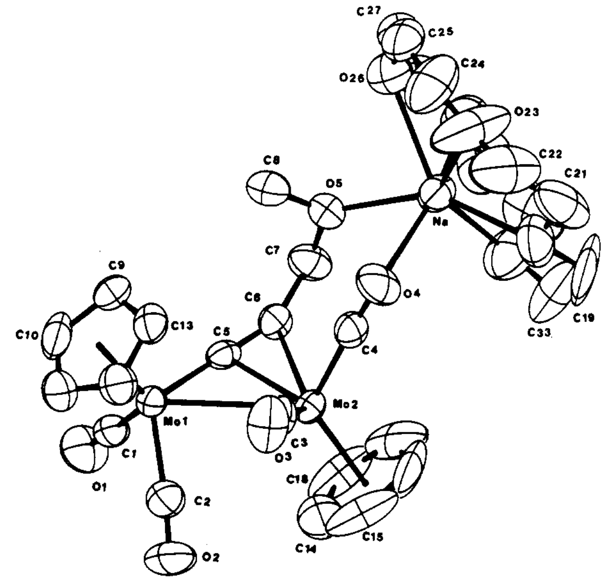


Figure 1. ORTEP plot (50% thermal ellipsoids) of 3 showing the atomic numbering scheme and the coordinate bonding between the anion and cation.

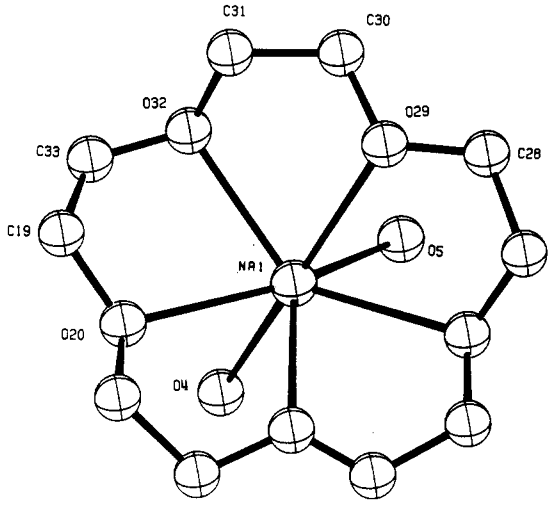


Figure 2. Detail of the coordination about the sodium atom.

$[Cp_2(CO)_4Mo_2(\mu_2\text{-}\eta^1{:}\eta^2\text{-}CCCH_2OCH_3)][Na(15\text{-}crown\text{-}5)]$ (3). A suspension of $NaNH_2$ (0.050 g, 1.28 mmol) in 10 mL of THF was added at room temperature to $Cp_2(CO)_4Mo_2(HC{\equiv}CCH_2OCH_3)$ (0.600 g, 1.13 mmol) dissolved in 15 mL of THF. An excess of 15-crown-5 (1.0 mL, 5 mmol) was added. This solution was stirred at 25 °C for 48 h during which time the solution turned from dark red to violet. The solution was filtered, and the THF was stripped from the filtrate under vacuum. The residue was dissolved in CH_2Cl_2 (40 mL), and Et_2O (160 mL) was slowly added until the product crystallized. The violet crystals were collected, washed with Et_2O (2 × 5 mL), and dried under vacuum. IR (THF): 1900 (m), 1850 (s), 1795 (m), 1773 (m) cm^{-1}. ^1H NMR (CD_3CN, δ): 4.99, s, 10 H (Cp); 4.66, d, 1 H; 4.41, d, 1 H (J_{AB} = 14.2 Hz) (CH_2); 3.62, s, 20 H (15-crown-5); 3.29, s, 3 H (OCH_3). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 236.5 (CO), 186 (C≡), 118.2 (Cp), 102 (≡C), 87.0 (CH_2O); 70.5 (OCH_3) 69.5 (15-crown-5). A satisfactory elemental analysis was not obtained due to apparent oxidation of the sample.

X-ray Crystal Structure. Single crystals of 3 were grown from a methylene chloride/diethyl ether solution and mounted on the diffractometer. A summary of data collection conditions and results is provided as supplementary material. Lattice parameters were determined from a least-squares refinement of 15 reflection settings obtained from an automatic centering routine. Intensity data were obtained using Mo Kα radiation monochromatized from a graphite crystal whose diffraction vector was parallel to the diffraction vector of the sample. Three standard

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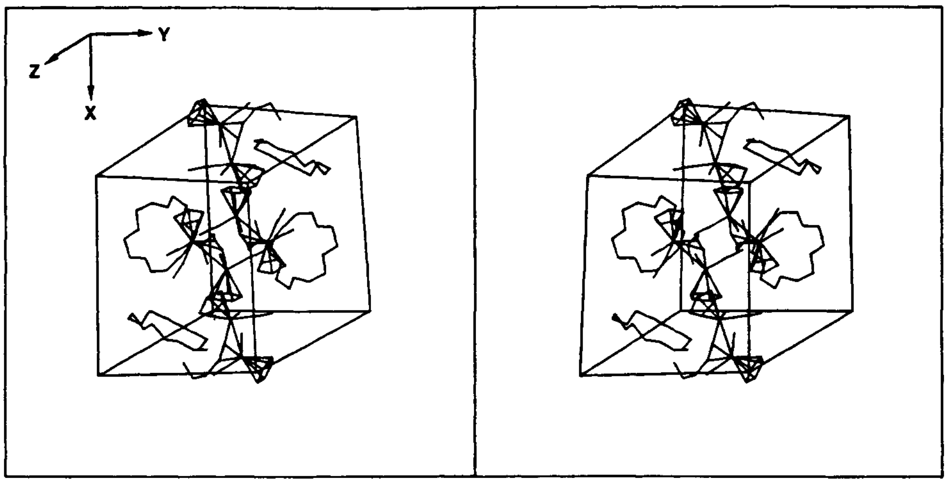


Figure 3. Stereoscopic view of the unit cell showing the alternating layers of anions and cations.

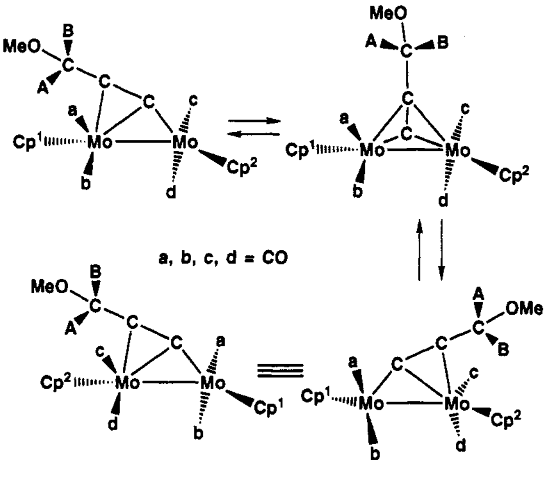
Table I. Selected Bond Distances and Angles in $[Cp_2Mo_2(CO)_4(\mu\text{-}CCCH_2OMe)][Na(15\text{-}crown\text{-}5)]$

atoms	distances (Å)	atoms	distance (Å)
Mo1-Mo2	3.127 (1)	Mo2–C5	2.284 (6)
Mo1–C5	2.030 (7)	Mo2–C6	2.319 (6)
Mo–CO	1.930 [8][a]	Mo–Cp[b]	2.34 [3][a]
C–C(Cp)[b]	1.37 [5][a]	C–O(Crn)[c]	1.36 [6][a]
C–C(Crn)[c]	1.43 [6][a]	C–O[d]	1.169 [8][a]
Na–O20	2.470 (7)	Na–O29	2.464 (7)
Na–O23	2.442 (8)	Na–O32	2.412 (7)
Na–O26	2.537 (6)	Na–O4	2.561 (6)
Na–O5	2.456 (6)		

atoms	angle (deg)	atoms	angle (deg)
Mo1–C5–C6	161.4 (6)	C5–C6–C7	153.1 (7)
Mo2–Mo1–C5	46.8 (2)	C6–C7–O5	113.0 (6)
Mo1–Mo2–C5	40.4 (2)	C7–O5–C8	111.9 (6)
Mo1–Mo2–C6	71.4 (2)	Mo–C–O[d]	176 [2][a]
Mo1–Mo2–C3	72.1 (2)	Mo2–Mo1–C1	113.5 (2)
Mo1–Mo2–C4	113.3 (2)	Mo2–Mo1–C2	79.8 (2)
Mo1–C5–Mo2	92.7 (2)	Mo2–C5–C6	75.7

[a] Average value; standard deviations in parentheses are from the variance covariance matrix while those in brackets are calculated from the formula, $\sigma = \{\sum(x_i - \bar{x})^2/(n-1)\}^{1/2}$. [b] C_5H_5 carbon. [c] 15-Crown-5 bond. [d] Carbonyl.

Scheme II



reflections were measured every 50 reflections. The data were reduced and corrected for absorption.[17] The structure was solved using MULTAN. In the subsequent refinement the function $\sum w(|F_o| - |F_c|)^2$ was minimized where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The agreement indices $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ were used to evaluate the results. The atomic scattering factors are from the *International Tables for X-ray Crystallography*.[18] Positions of all hydrogen atoms were calculated but not refined. All hydrogen atoms were given fixed U values (isotropic temperature factors) of 0.05. Tables listing the final positional parameters, anisotropic thermal parameters and a complete set of bond distances and angles are deposited as supplementary material (see below). Selected distances and angles are given in Table I. Figure 1 shows the structure of 3 with the atomic numbering scheme, Figure 2 is a view of the coordination sphere of the sodium ion, and Figure 3 is a stereoscopic view of the unit cell. Crystal data: a = 16.506 (8) Å, b = 12.566 (6) Å, c = 15.681 (5) Å, β = 106.96 (3)°, V = 3111 (2) Å^3, z = 4, μ = 8.50 cm^{-1}, space group = $P2_1/a$ (nonstandard setting of $P2_1/c$), ρ(calcd) = 1.59 g/cm^3, R = 0.040, R_w = 0.039 based on 3134 intensities with $I \geq 3\sigma(I)$.

Results and Discussion

The acetylenic proton of 1 is removed by $NaNH_2$ in THF to give an exceedingly air-sensitive, purple solution. The addition of 15-crown-5 (1,4,7,10,13-pentaoxyacyclopentadecane) to this solution allows for the isolation of the purple, crystalline complex 3. The IR spectrum of 3 displays four ν_{CO} bands at 1900 (m), 1850 (s), 1795 (m), and 1773 (m) cm^{-1}. The two low-frequency bands may be due to a semibridging carbonyl (C3–O3) and/or ion pairing with the sodium counterion (see below). At room temperature, the ^{1}H NMR spectrum shows single peaks for the Cp, crown, and methoxy protons at δ 4.99, 3.62, and 3.29 ppm, respectively. The crown ether protons are approximately 0.1 ppm downfield of the free ether, suggesting that the sodium ion remains coordinated in the CD_3CN solvent.[19] The methylene protons appear as an AB quartet (Δδ = 48 Hz, J_{AB} = 14.2 Hz) centered at δ 4.54.

At room temperature, only one peak for the Cp carbon atoms is observed at δ 118.2, and two other singlets at δ 186 and 102 ppm are assigned to C_α and C_β (C5, C6 in Figure 1) of the acetylide moiety.[15,20] One peak assignable to the CO group was observed at δ 236.5, but the signal

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(17) Computations were carried out on an Amdahl 5860 computer. Computer programs used during the structural analysis were from the SHELX program package by George Sheldrick, Institute Fur Anorganische Chemie der Universitat Gottingen, Federal Republic of Germany. Other programs used include ORTEP, a thermal ellipsoid drawing program by C. K. Johnson, and the direct methods program MULTAN78 by Peter Main.

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to noise ratio was poor and a second peak may not have been observed (see below).

At −55 °C, the Cp protons give rise to two peaks δ 4.95 and 4.94, while the remaining peaks in the ^{1}H NMR spectrum are invariant with temperature. A "windshield wiper" motion is common for σ,π-complexes similar to 3.[21-24] The anion in $[Cp_2Mo_2(CO)_4(\mu\text{-}CCPh)][PPN]$ (4) was also observed to be fluxional and showed four resonances due to CO carbon atoms at −60 °C that coalesce to two peaks at room temperature.[15]

The observation that the diasteriotopic methylene protons in 3 are not interchanged on the NMR time scale places additional restraints on the fluxional process; namely, a time-average mirror plane containing the μ-acetylide cannot be generated. Hence, the Cp groups must be related by a time average C_2 axis in the high temperature limit. The process shown in Scheme II generates such an axis wherein the two Cp group environments are interchanged, the carbonyl group environments are interchanged pairwise (a = c, b = d), but enantiomers are not interchanged so that $A \neq B$ (the AB quartet is preserved). The "cis–cis" isomerization common to CpM(CO)$_2$XY species[25] that would cause all CO group environments to become equivalent must have higher activation energy than the process shown in Scheme II. A cis–cis isomerization in a dimeric structure, e.g. 3, would also cause the interconversion of enantiomers and the collapse of the AB quartet.[26]

The solid-state structure of the anion in 3 is very similar to that in 4. Thus, the Mo1–Mo2 distance, 3.127 (1) Å, is appropriate for a Mo–Mo single bond, the Mo1–C5 distance, 2.03 (1) Å, approaches the value expected for a Mo=C double bond, while the Mo2–C5,C6 distances of 2.28 (1) and 2.32 (1) Å are normal for Mo bonded to a π-system. The C5–C6 distance (1.26 (1) Å) is only slightly longer than that in free acetylenes (ca. 1.18 Å).[27] These values compare well with those found for 4.[15]

An interesting feature of the structure of 3 is the cation–anion interaction and the packing arrangement. The sodium ion is encapsulated in the 15-crown-5 ring but forms two addition bonds to the oxygen atoms of one of the carbonyl groups (O4) and the methoxy group (O5) (Figure 2). The average of the Na–O (crown) distances is 2.465 ± 0.046 Å (range 2.54 (1)–2.41 (1)). The Na–O bond lengths to the carbonyl and methoxy oxygen atoms are 2.46 (1) and 2.56 (1) Å, respectively. Several structures of metal carbonyl anions with Na(crown)$^+$, K(crown)$^+$, or Na(crypt)$^+$ counterions have been determined.[28-30] Coordination of a carbonyl oxygen to the alkali metal ion is not unusual in these structures, but in most cases, bonds are formed from both sides of the crown ring rather than in a chelate-type structure as found here.[29,30] The Na–O bond distances determined here fall within the range of distances found in previous work.[28-30]

Interest in solid-state materials based on organometallic compounds has spurred new work on the extended structures of ionic organometallics. Braga and Grepioni found that large cluster anions form columnar stacks around which the cations form a sheath.[31] As Figure 3 shows, the dimolybdenum anions of 3 crystallized in a 2-dimensional sheet parallel with the 011 planes, and the Na(crown)$^+$ cations are layered on either side of the anion sheet. Apparently, the negative charge in the large anions is sufficiently delocalized that their packing more closely resembles that of neutral complexes, and the result is a structure featuring layers of alternating charge.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE-8305235) for support. We also thank Dr. D. J. McCabe for assistance in preparing the manuscript.

Supplementary Material Available: Tables of crystallographic statistics, positional coordinates, thermal parameters, and bond lengths and angles (5 pages). Ordering information is given on any current masthead page.

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Carbon–Hydrogen Coupling Constants ($J(^{13}C-^{1}H)$) in Icosahedral Carboranes[1]

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Summary: Carbon–hydrogen coupling constants ($J(^{13}C-^{1}H)$) are measured for *o*-carborane, *m*-carborane, *p*-carborane, and various carbon- and boron-substituted *o*-carboranes. The values cluster about 190 Hz, implying approximately 38% s character in the C–H bond, or a hybridization of roughly sp$^{1.6}$.

Although the structures and bonding of the icosahedral carboranes have been reviewed many times,[2] little attention has been paid to a technique available for determining the hybridization at the hexacoordinate carbons, mea-

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[1] Support for this work by the National Science Foundation through Grant CHE-9024996 is gratefully acknowledged.

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