leads to deactivation of the system. GPC analysis of the polymer indicated $M_0$ and $M_n$ values of 21,000 and 47,900 daltons (Da), respectively, and a DSC curve for the polymer exhibited no detectable exotherm prior to the onset of crystalline melting at 131.6 °C. In contrast, the reactions of (Ph₃SiO)₂VO and (n-Pro₃O)VO under identical conditions gave no polyethylene; the only observable reaction (by ⁵¹V NMR) was metathesis of alkyl ligands on AI for alkoxide ligands on V.⁶⁸ We have not extensively explored the use of other cocatalysts with 2, but we have observed similar activities with Et₃AI and somewhat lower activities with (Me₂SiCH₂)₃AI.

A survey of the catalyst’s reactivity indicates that other olefins can also be polymerized or copolymerized, although not as efficiently as ethylene. For example, the reaction of 2 and Me₃Al (3 equiv) in propanol (25 °C, ~8 atm, 3 h) gave a small amount (~125 turnovers) of atactic polypropylene (MW < 10,000). Similarly, the copolymerization of ethylene (1%) in neat propylene produced small amounts (~350 turnovers) of copolymer, which contained 5-10% propylene (by ¹³C NMR).⁹ One olefin that is polymerized well by our catalyst is 1,3-butadiene; an ampule of Me₃Al lead to complete deactivation of the system. GPC analysis of the polymer provides new insights into the chemistry of silica-supported vanadate catalysts. Efforts to elucidate the active polymerization catalyst(s) in this interesting system are currently in progress.

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(15) A referee has suggested that a V(IV) species might be the active catalyst. This is clearly a reasonable hypothesis, but we have prepared [c-(C₆H₅),SiO],V(CH₂SiMe₃)] and found that it does not initiate ethylene polymerization. The synthesis of this complex and the results from our other efforts to elucidate the identity of the polymerization catalyst(s) will be reported in a subsequent article.

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**2D Nuclear Magnetic Resonance Study of the Structure of the Fullerenes C₇₀**

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Geodesic structures were developed by R. Buckminster Fuller on the basis of his insight into their structural economy and stability. In 1985, similar considerations led Smalley, Kroto, et al. to propose that C₇₀, observed in carbon cluster beam experiments, possessed the geometry of a soccer ball, and they named it "Buckminsterfullerene." Their prediction of the stability of this molecule, as well as other fullerenes, has been stunningly verified by the recent synthesis of macroscopic amounts of C₇₀ and C₇₆⁷⁻⁸ This development has sparked intense research activity in the production and characterization of these materials.⁸⁻¹⁰ Raman⁶⁻¹⁸

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equivalent. The resonance position for Cm is in excellent accord with the proposed Cm soccer ball structure, and the single-resonance 13C NMR spectrum of C70 shows that all carbons in the molecule are chemically equivalent. The spectrum was obtained in the presence of Cr(acac)3, by using the pulse sequence of Mareci and Freeman, ref 21 with a refocusing delay of 5 ms, a sweep width of 13000 Hz digitized into 8K-work datasets for the horizontal dimension, and a sweep width of 7000 Hz for the double quantum dimension digitized into 512 blocks, with 512 scans/block. One and Two Dimensions, McGraw-Hill: New York, 1983, pp 1-265.

The 2D INADEQUATE NMR spectrum of C70 is shown in Figure 1. For this experiment, two bonded carbons share a double quantum frequency in the vertical dimension, and peaks occur at the two respective chemical shifts in the horizontal dimension, allowing the correlation to be made. In addition, each peak will be split into a doublet by the relevant 13C coupling constant. The D2q structure of C70 suggests a linear connectivity of the five carbon types with the polar carbons (labeled a) representing one end of the connectivity and the belt carbons (e) representing the other. The 2D spectrum reveals the four connectivities, showing a single string of connected resonances, with respective intensities 10:10:20:10, solidly supporting the D2q structure. The crucial connectivity is obtained between the two intensity 10 lines at 150.8 ppm and 147.8 ppm, forcing the assignment of the line at 150.8 ppm to the polar end cap carbon a, and hence the remaining assignments. We note that the resonances correlating to b are the least intense, as only one out of the three bonds of an end cap carbon a connects to a carbon b. In contrast, the belt carbons a at 130.8 ppm are each bonded to two type-d carbons at 144.4 ppm, giving cross peaks twice as intense as those revealing the a-b connectivity. The small separation between resonances b and c gives rise to second-order effects in the cross peaks, reducing the outer line of each multiplet.27 These results confirm the assignments of ref 8.

Taylor et al.8 noted that the C70 chemical shifts indicated torsional strain. Belt carbon e resonating at 130.8 ppm can be contrasted to similar carbons in benzo[a]pyrene (125.5 and 123.8 ppm), but the downfield position of e is consistent with torsional strain (e.g., the bridgehead carbons in paracyclophane resonate at 140.4 ppm). However, while carbon a has a similar structural environment to those in C60, it resonates 7 ppm further downfield. The origin of this relative shift is not clear, but may be due to differences in ring currents or aromaticity between the two molecules.29,30

One-bond carbon-carbon coupling constants (JCC) in polyyclic aromatic compounds generally range from 53 to 63 Hz.31 It has been concluded that the size of the coupling is related to the s character of the bond, and a linear correlation between JCC and decreasing bond lengths or increasing n-bond orders has been.
suggested by several groups for polycyclic aromatic compounds.38,39 A value of $J_{10}$ of 45 Hz for azulene was interpreted as evidence for this bond being weak.39 For C$_{60}$, the 2D spectrum gives the $J_{CC}$ values: $J_{4a} = 68$, $J_{4e} = 55$, $J_{4d} = 55$, and $J_{4e} = 62$ Hz. These values indicate that the four bonds have substantial $s$ character and $\pi$-bond order. Bonds $d$–$e$ and $a$–$b$ fuse six-membered rings and may be compared with $J_{10}$ in 1-methyle- and 2-methylnaphthalene at 52 and 53 Hz, respectively.33 In analogy with cyclopropane derivatives,36,37 the larger value of $J_{4a}$ may arise from both carbons in bond $a$–$b$ belonging to five-membered rings, whose bonds have greater $p$ character due to smaller internal angles. This should increase the $s$ character of the $a$–$b$ bond and hence the coupling constant; this effect should be less for bond $d$–$e$, as this bond has only carbon $d$ in a five-membered ring. We note that the large values for $J_{CC}$ we report for five-membered rings, whose bonds have greater $p$ character solidly support the “rugby ball” $D_{5h}$ structure for this molecule. The resonance assignments confirm those previously proposed.4 The $J_{CC}$ values are relevant to investigations of reactivity and bonding in fullerences.

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Evidence from EXAFS for a Copper Cluster in the Metalloregulatory Protein CUP2 from Yeast

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Expression of yeast metallothionein, which binds copper specifically, is regulated by the protein CUP2 (also known as ACE1).1,2 CUP2 itself is activated for binding to DNA by copper(1).3 Yeast metallothionein contains a cluster of eight copper(1) ions bridged by thiolate ligands that are likely provided by the 12 cysteines of the protein.4 How copper is bound to CUP2 is unknown, however. Since stimulation by copper(1) of CUP2 binding to DNA is a cooperative process,5 and the DNA binding domain of CUP2 contains 12 cysteines,6 the presence of a copper cluster in CUP2 is also likely. Here we report that Cu K-edge extended X-ray absorption fine structure (EXAFS) gives strong evidence that the couplers bound to CUP2 are sulfur-coordinated and in close proximity to each other, most likely bridged by thiolate sulfurs. The Cu K-edge X-ray absorption edge demonstrates that the copper in CUP2 are in the +1 oxidation state and furthermore indicates that their electronic environment is closest to 3-fold coordination.

Cu K-edge X-ray absorption spectra were collected at the Stanford Synchrotron Radiation Laboratory on wiggler beam line 4-2 (unfocused) under dedicated ring conditions (3.0 GeV, 70–90 mA) using a Si(220) double-crystal monochromator. Protein7

Figure 1. EXAFS data for CUP2. The solid line is the raw data. The dashed line is the data obtained by Fourier transforming the data into $R$ space, applying a filter from 0.80 to 3.35 Å, and back-transforming. The dotted line is the calculated EXAFS from two-shell fits described in the text and reported in Table I.

Figure 2. Comparison of the Fourier transform on filtered EXAFS data ($R = 0.80–3.35$ Å, $k$ range of 3.0–10.0 Å$^{-1}$) from CUP2 (solid line) with transforms of a one-shell fit containing S (dashed line) and a two-shell fit containing S and Cu (dotted line). Notice the excellent agreement between the fit and data for the first shell in both cases. However, while the second peak is not reproduced by a single S shell, it is well reproduced with the presence of a second shell of Cu.