leads to deactivation of the system.GPC analysis of the polymer indicated $M_n$ and $M_w$ 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 (Ph$_3$Si)$_2$ VO and (n-Pro)$_3$ VO under identical conditions gave no polyethylene; the only observable reaction (by $^{13}$C NMR) was metathesis of alkyl ligands on Al for alkoxide ligands on V. 6 We have not extensively explored the use of other cocatalysts with 2, but we have observed similar activities with Et$_3$Al and somewhat lower activities with (Me$_5$SiCH$_2$)$_3$ Al. 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 Me$_3$ Al (3 equiv) in propylene (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 $^{13}$C NMR). 9 One olefin that is polymerized well by our catalyst is 1,3-buta diene; an amouple containing 50 mL of neat butadiene (bp -4.5 °C) completely used. As shown in Figure 1, polyethylene production (1 atm, 25 °C, 3 h) is maximized when approximately 3 equiv of Me$_3$ Al is used as cocatalyst. 3 Large excesses of Me$_3$ Al lead to deactivation of the catalyst. 3 Both observations are contrary to use of other cocatalysts with 2, and we have prepared [(c-C$_6$H$_5$)$_7$ Si$_7$ O$_{12}$ V(CH$_2$ SiMe$_3$)$_4$ ] as a discrete solvent system that appears to remain homogeneous. 13b In many instances, serious problems arise in the production of macroscopic amounts of C$_{60}$ and C$_{70}$. 13c, d These studies were supported by the National Science Foundation (CHE-8703016 and CHE-9011593) and an NSF Presidential Young Investigator Award (CHE-8657262). Acknowledgement is also made to the Chevron Research Company and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research (22376-AC3). F.J.F. gratefully acknowledges financial support from an Alfred P. Sloan Foundation Research Fellowship.

2D Nuclear Magnetic Resonance Study of the Structure of the Fullerene C$_{70}$

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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. 10 to propose that C$_{60}$, observed in carbon cluster beam experiments, 11 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 C$_{60}$ and C$_{70}. 12$ This development has sparked intense research activity in the production and characterization of these materials. 13

(15) A referee has suggested that a V(V) species might be the active catalyst. This is clearly a reasonable hypothesis, but we have prepared [(c-C$_6$H$_5$)$_7$Si$_7$O$_{12}$ V(CH$_2$ SiMe$_3$)$_4$ ] and found that it does not initiate ethylene polymerization. The synthesis of this complex and the results from other efforts to elucidate the identity of the polymerization catalyst(s) will be reported in a subsequent article.
equivalent. The resonance position for Cm is in excellent accord to the c60 structure with the insertion of 10 carbons forming a molecule. I3C NMR analysis of fullerenes probes structure, and infrared spectroscopy support the proposed C60 soccer ball structure, and the single-resonance 13C NMR spectrum of C60 is strong evidence for the icosahedral symmetry of this molecule. NMR spectroscopy is a powerful probe of chemical structure. 13C NMR analysis of fullerenes probes structure, torsional strain, and bonding in these molecules. The 13C NMR spectrum of C60 is a single line at 143 ppm (in both liquids and solids), showing that all carbons in the molecule are chemically equivalent. The resonance position for C60 is in excellent accord with similar carbons in azulene (140.2 ppm), fluorene (141.6 and 143.2 ppm), and 3,5,8-trimethylaceheptylene (146.8 ppm); this is consistent with the soccer ball structure for C60 (Figure 1).

The 1D 13C NMR spectrum for C70, shown in the upper trace of Figure 1, consists of five lines with intensities in the ratio 10:10:10:10:10, as reported by Taylor et al., which strongly supports the D4h structure shown in Figure 1. This structure has five chemically distinct kinds of carbon atoms and is similar to the C60 structure with the insertion of 10 carbons forming a belt around the molecule. Characterization of the bonding of C70 is important for understanding its structure, and assignment of the NMR lines is critical for their interpretation. An assignment of the resonances of C70 was proposed by Taylor et al. based on model compounds and relative strain in the molecule. However, unequivocal experimental assignment of the lines is clearly desirable.

In this communication we show that it is possible to map the bonding connectivities of C70 and obtain definitive resonance assignments by the 2D INADEQUATE NMR experiment. This experiment correlates the 13C NMR line of a carbon to that of its bonded neighbor by excitation of a shared double quantum coherence via scalar J coupling, thus yielding the carbon connectivity map of the molecule. C70 samples enriched to ~20% 13C were used to increase the probability of adjacent 13C atoms, resulting in the data acquisition time to be feasible and low solubility. The enriched clusters were prepared by using cored carbon rods loaded with amorphous 13C powder (Cambridge Isotopes) in an arc fullerene generator.

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 D4h structure of C70 suggests a linear connectivity of the five carbon rods 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 10:10:20:10:10, solidly supporting the D4h 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 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.

These results confirm the assignments of ref 8.

Taylor et al. noted that the C70 chemical shifts indicated torsional strain. Belt carbon e resonating at 130.8 ppm can be contrasted to similar carbons in benz[a]pyrene (125.5 and 123.8 ppm); 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.

One bond-carbon coupling constants (JCC) in polycyclic aromatic compounds generally range from 53 to 63 Hz. 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 x-bond orders has been

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suggested by several groups for polycyclic aromatic compounds. A value of $J_{ab}$ of 45 Hz for azulene was interpreted as evidence for this bond being weak. For C$_{60}$, the 2D spectrum gives the $J_{CC}$ values: $J_{ab} = 68$, $J_{bc} = 55$, $J_{cd} = 55$, and $J_{de} = 62$ Hz. These values indicate that the four bonds have substantial single character and π-bond order. Bonds d–e and a–b fuse six-membered rings and may be compared with $J_{10}$ in 1-methyl- and 2-methylnaphthalene at 52 and 53 Hz, respectively. In analogy with cyclopropane derivatives, the larger value of $J_{ab}$ may arise from both carbons in bond a–b belonging to five-membered rings, whose bonds have greater π 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 are evidence against proposed structures for fullerenes involving three-membered rings, as by analogy with cyclopropane derivatives these rings would be expected to have markedly small coupling constants.

The 2D NMR spectrum of C$_{70}$ yields bonding topology, coupling constants, and a definitive assignment of the $^{13}$C NMR spectrum. The bonding topology and coupling constants solidly support the “rugby ball” $D_{5h}$ structure for this molecule. The resonance assignments confirm those previously proposed. The $J_{CC}$ values are relevant to investigations of reactivity and bonding in fullerenes.

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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).** CUP2 itself is activated for binding to DNA by copper(I). Yeast metallothionein contains a cluster of eight copper(I) ions bridged by thiolate ligands that are likely provided by the 12 cysteines of the protein. How copper is bound to CUP2 is unknown, however. Since stimulation by copper(I) of CUP2 binding to DNA is a cooperative process, and the DNA binding domain of CUP2 contains 12 cysteines, 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 copper ions bound to CUP2 are sulfur-coordinated and in close proximity to each other, most likely bridged by thiolate ligands. The Cu K-edge X-ray absorption edge structure demonstrates that the copper ions 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. Protein

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**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, with 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.