can also be polymerized or copolymerized, although not as efficiently as ethylene. For example, the reaction of Me3AI and somewhat lower activities with Et3Al.

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 Me3Al is more efficient than ethylene production. Similarly, the copolymerization of ethylene (1%) in neat propylene produced small amount (15-50 turnovers) of copolymer.

The activity of the catalyst is sensitive to the amount of Me3Al used. As shown in Figure 1, polyethylene production (1 atm, 25 °C, 3 h) is maximized when approximately 3 equiv of Me3Al is used as cocatalyst. Large excesses of Me3Al lead to deactivation of the catalyst. Both observations are contrary to the behavior of apparent "soluble catalysts." Prepared from trialkylalane reagents (1 equivalent) to initiate olefin polymerization.

The presence and equilibration of both 2 and 3 in the starting solution greatly complicate mechanistic studies, but several polymerization reactions performed at -30 °C, where the equilibration of 2 and 3 is negligibly slow, indicate that the active catalyst is derived from the reaction of 2 with Me3Al. Specifically, the add of Me3Al to an ethylene-saturated solution of 2 and 3 at -30 °C initiates ethylene polymerization by slowly consuming 2, but does not affect the amount of 3 in solution. Furthermore, ethylene polymerization is only initiated when the 1°V NMR resonance for 2 is initially present.

The active polymerization catalysts in our system are (are) currently not known, and it would be inappropriate to speculate about its identity without additional data.

2D Nuclear Magnetic Resonance Study of the Structure of the Fullerenes 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. to propose that C_{60} 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 C_{60} and C_{70}. This development has sparked intense research activity in the production and characterization of these materials.

(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-C_{6}H_{11})_{7}Si_{7}O_{12}V(CH_{2}SiMe_{3})] 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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and infrared spectroscopy support the proposed C₆₀ soccer ball structure, and the single-resonance I³C NMR spectrum of C₆₀ is strong evidence for the icosahedral symmetry of this molecule.⁸,¹⁰ I³C NMR spectroscopy is a powerful probe of chemical structure.¹⁹,²⁰ I³C NMR analysis of fullerenes probes structure, and infrared spectroscopy support the proposed C₆₀ soccer ball structure, and the single-resonance I³C NMR spectrum of C₆₀ is strong evidence for the icosahedral symmetry of this molecule.⁸,¹⁰

The 1D I³C NMR spectrum for C₇₀, shown in the upper trace of Figure 1, consists of five lines with intensities in the ratio 10:20:10:20:10, as reported by Taylor et al.,⁸ which strongly supports the D₃₅ 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 carbon atoms 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.,⁸ 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.²²-²⁵ This experiment correlates the I³C 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% I³C were used to increase the probability of adjacent I³C atoms, resulting in the data acquisition time to be reduced by a factor of 10.

The enriched clusters were prepared by using cored carbon rods loaded with amorphous I³C powder (Cambridge Isotopes) in an arc fullerene generator.⁶,¹²,²₆ 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 JCC coupling constant. The D₃₅ structure of C₇₀ suggests a linear connectivity of the five carbon atoms with the polar carbons (labeled a) representing one end of the molecule 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 10:20:10:20:10, solidly supporting the D₃₅ 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 bond b. In contrast, the belt carbons c at 140.4 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),²⁸ the downfield position of e is consistent with torsional strain (e.g., the bridgehead carbons in paracyclophepane⁸ 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 polycyclic 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 z-bond orders has been observed.

References:

suggested by several groups for polycyclic aromatic compounds. A value of $\frac{1}{2}\nu_{10}$ of 45 Hz for azulene was interpreted as evidence for this bond being weak. For C$_{60}$, the 2D spectrum gives the $\nu_{1C}$ values: $\nu_{1d} = 68$, $\nu_{1e} = 55$, $\nu_{1d} = 55$, and $\nu_{1a} = 62$ Hz. These values indicate that the four bonds have substantial s character and π-bond order. Bonds d–e and a–b fuse six-membered rings and may be compared with $\nu_{1C}$ in 1-methyl- and 2-methylanthracene at 52 and 53 Hz, respectively. In analogy with cyclopropane derivatives, the larger value of $\nu_{1b}$ 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 $\nu_{1C}$ we report are evidence against proposed structures for fullerences 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 $\nu_{1C}$ 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). 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 sulfurs. 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.

Copper(I)extended X-ray absorption spectra were collected at the Stanford Synchrotron Radiation Laboratory on wiggler beam line 4-2 (unfocused) under dedicated ring conditions (30 GeV, 70–90 mA) using a Si(220) double-crystal monochromator. Protein...