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$_3$SiO)$_2$VO and (n-Pr$_3$O)$_2$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. We have not extensively explored the use of other cocatalysts with EtAl, but we have observed similar activities with Me$_3$SiCH$_2$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). One olefin that is similarly, the copolymerization of ethylene (1%) in neat propylene contained 5-10% propylene (by $^{13}$C NMR).9 One olefin that is polymerized well by our catalyst is 1,3-butadiene; an ampule containing 50 mL of neat butadiene (bp -4.5 °C) completely solidifies within 30 min to create a partial vacuum inside the ampule. $^1$H and $^{13}$C NMR spectroscopy$^{10}$ indicated that the resulting product was >95% trans-1,4-polybutadiene.$^{11}$

The activity of the catalyst is sensitive to the amount of Me$_3$Al 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. Larger excesses of Me$_3$Al lead to deactivation of the catalyst. Both observations are contrary to the behavior of typical "soluble catalysts"$^{12}$ prepared from trialkylalanes, which typically require large excesses of alkylaluminum reagents (15-50 equiv) to initiate olefin polymerization.$^{13}$ In light of the narrow polydispersity measured for our polyethylene sample (2.28), these results suggest that a well-defined catalyst is being formed$^{14}$ and that this catalyst is fundamentally different from these conventional soluble V catalysts.

The presence and equilibration of both 2 and 3 in the starting solution greatly complicate mechanistic studies, but several polymers have been polymerized 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 Me$_3$Al. Specifically, the addition of Me$_3$Al to an ethylene-saturated solution of 2 and 3 (~10:90 by $^{51}$V NMR) 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 $^{51}$V NMR resonance for 2 is initially present. The active polymerization catalyst(s) in our system is (are) currently not known, and it would be inappropriate to speculate about its identity without additional data.$^{15}$ It is, however, important to note that this POMSS-based catalyst is capable of polymerizing olefins when stoichiometrically similar complexes (e.g., (Ph$_3$SiO)$_2$VO and (n-Pr$_3$O)$_2$VO) show little or no reactivity. Since our understanding of surface catalysis is based upon and inherently limited by known reaction chemistry of solution complexes, the unique chemistry of V-containing POMSS may provide new insights into the chemistry of silica-supported vanadium catalysts. Efforts to elucidate the active polymerization catalyst(s) in this interesting system are currently in progress.

Acknowledgment. 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$_{70}$

Robert D. Johnson,* Gerard Meijer,† Jesse R. Salem, and Donald S. Bethune

IBM Research Division, Almaden Research Center
650 Harry Road, San Jose, California 95120-6099
Received January 10, 1991

Geodesic structures were developed by R. Buckminster Fuller$^2$ on the basis of his insight into their structural economy and stability. In 1985, similar considerations led Smalley, Kroto, et al.$^1$ to propose that C$_{60}$, observed in carbon cluster beam experiments,$^3$ 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}$$^4$-$^5$. This development has sparked intense research activity in the production and characterization of these materials.$^6$-$^9$ Raman$^{10}$

(1) Present address: Department of Molecular and Laser Physics, Catholic University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands.
(2) Fuller, R. B. Ideas and Integrities; Collier Books: New York, 1943.
The resonance position for Cm is in excellent accord with 512 scans/block. with a refocusing delay of 5 ms, a sweep width of 7779 ppm, and a sweep width of 7779 ppm, allowing the assignment of polar end cap carbon a and the remaining carbons. The spectrum was obtained in the presence of Cr(ac),, by using the pulse sequence of Mareci and Freeman25 with a 2D INADEQUATE NMR spectrum of C70. Doublets (circled) are obtained at a common double quantum frequency for the two resonances of a bonded carbon pair. The connectivity obtained is linear and highlighted by lines; the asymmetrical intensity string of 10:10:20:20:10, as reported by Taylor et al.,8 which strongly supports the proposed Cm soccer ball structure, and the single-resonance 13C NMR spectrum of C70. The I3C 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 1JC coupling constant. The D2 structure of C70 suggests a linear connectivity of the five carbon type-bonds 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 10:10:20:20:10, solidly supporting the D2 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.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 paracyclophane18 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.9,20

One-bond carbon–carbon coupling constants (1JC) 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 1JC and decreasing bond lengths or increasing z-bond orders has been the NMR lines are critical for their interpretation. An assignment of the resonances of C60 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 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. C60 samples enriched to ~20% 13C were used to increase the probability of adjacent 13C atoms, resulting in the data acquisition time of the experiment. The enriched clusters were prepared by using cored carbon rods loaded with amorphous 13C 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 1JC coupling constant. The D2 structure of C70 suggests a linear connectivity of the five carbon type-bonds 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 10:10:20:20:10, solidly supporting the D2 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.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 compared 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 paracyclophane18 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.9,20

One-bond carbon–carbon coupling constants (1JC) 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 1JC and decreasing bond lengths or increasing z-bond orders has been
suggested by several groups for polycyclic aromatic compounds. A value of 1 for azulene was interpreted as evidence for this bond being weak. For C60, the 2D spectrum gives the J values: Jab = 68, Jbd = 55, Jcd = 55, and Jde = 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 Jbc in 1-methyl- and 2-methylnaphthalene at 52 and 53 Hz, respectively. In analogy with cyclopropane derivatives, the larger value of Jbc 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 in a five-membered ring. We note that the large values for Jbc we report are evidence against proposed structures for fullerene 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 C70 yields bonding topology, coupling constants, and a definitive assignment of the 13C NMR spectrum. The bonding topology and coupling constants solidly support the “rugby ball” D3h structure for this molecule. The resonance assignments confirm those previously proposed. The J values are relevant to investigations of reactivity and bonding in fullerenes.

Acknowledgment. We gratefully acknowledge stimulating discussions with C. S. Yannoni, F. A. L. Anet, G. M. Wallraff, and C. G. Wade, and we thank C. R. Moylan for a critical reading of the manuscript.

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

Kent H. Nakagawa, Carla Inouye, Britt Hedman, Michael Karin, Thomas D. Tullius, and Keith O. Hodgson*†

Department of Chemistry, Stanford University
Stanford, California 94305-5080
Department of Pharmacology, M-036, School of Medicine
University of California, San Diego
La Jolla, California 92037
Stanford Synchrotron Radiation Laboratory
Stanford University, SLAC, Bld 69, P.O. Box 4349
Stanford, California 94309
Department of Chemistry, The Johns Hopkins University
Baltimore, Maryland 21218

Expression of yeast metallothionein, which binds copper specifically, is regulated by the protein CUP2 (also known as AEC1). CUP2 itself is activated for binding to DNA by copper(1). Yeast metallothionein contains a cluster of eight copper 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(1) 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 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 structure demonstrates that the couplers in CUP2 are in the +1 oxidation state and furthermore indicates that their electronic environment is closest to 3-fold coordination.

Copper K-edge X-ray absorption spectra were collected at the Stanford Synchrotron Radiation Laboratory on wiggler beamline 4-2 (unfocused) under dedicated ring conditions (3 GeV, 70–90 mA) using a Si(220) double-crystal monochromator. Protein