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$_2$SiO)$_2$VO and (n-Pro$_2$O)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. 7,8,9 We have not extensively explored the use of other cocatalysts with $M_n$ but we have observed similar activities with Et$_3$Al and somewhat lower activities with (Me$_2$SiCH$_2$)$_2$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 (5~125 turnovers) of atactic polypropylene 9 ($MW < 10,000$). Similarly, the copolymerization of ethylene (1%) in neat propylene produced small amounts (5~200 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-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. 1,5 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 (15~500 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 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 Me$_3$Al. Specifically, the addition of Me$_3$Al to an ethylene-saturated solution of 2 and 3 (~10:90 by $^{13}$C 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 $^{13}$C NMR resonance for 2 is initially present.

The active polymerization catalysis(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$_2$SiO$_2$VO and (n-Pro$_2$O)VO show little or no reactivity. Since our understanding of surface catalysis is both 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 catalysis(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 Fullerenes

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. 3 to propose that C$_{60}$, observed in carbon cluster beam experiments, 4 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$_{70}$. 5,4 This development has sparked intense research activity in the production and characterization of these materials. 5-8 Raman 9 and $^{13}$C NMR 10 spectroscopy have been key tools in the study of fullerenes.

(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$_{5}$(CH$_{3}$)$_{5}$)SiO$_{2}$V(C$_{6}$H$_{5}$SiMe$_{3}$)] 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 catalysis(s) will be reported in a subsequent article.

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The resonance position for C\text{m} is in excellent accord with similar carbons\textsuperscript{19} in azulene (140.2 ppm), fluorene (141.6 ppm), C\text{a} (146.8 ppm), and 143.2 ppm), and this is consistent with the soccer ball structure for C\text{60} (Figure 1). This structure of C\text{70} suggests a linear connectivity of the five carbon rods loaded with amorphous 13C powder (Cambridge Isotopes) in an arc fullerene generator.\textsuperscript{6,12,26}

The 2D INADEQUATE NMR spectrum of C\text{70} 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 J\text{CC} coupling constant. The D\text{4h} structure of C\text{70} suggests a linear connectivity of the five carbon rods (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 D\text{4h} 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 a-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 c at 138.8 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.\textsuperscript{27} These results confirm the assignments of ref 8.

Taylor et al.\textsuperscript{8} noted that the C\text{70} chemical shifts indicated torsional strain. Belt carbon e resonating at 138.8 ppm can be contrasted to similar carbons in benzo[7]pyrene (125.5 and 123.8 ppm);\textsuperscript{28} the downfield position of e is consistent with torsional strain (e.g., the bridgehead carbons in paracyclophane\textsuperscript{48} resonate at 140.4 ppm). However, while carbon a has a similar structural environment to those in C\text{60}, 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.\textsuperscript{29,30}

One-bond carbon-carbon coupling constants (J\text{CC}) in polyyclic aromatic compounds generally range from 53 to 63 Hz.\textsuperscript{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 J\text{CC} and decreasing bond lengths or increasing 3z-bond orders has been
suggested by several groups for polycyclic aromatic compounds.\textsuperscript{38,39} A value of $J_{d,e}$ of 45 Hz for azulene was interpreted as evidence for this bond being weak.\textsuperscript{35} For C\textsubscript{60}, the 2D spectrum gives the $J_{CC}$ values: $J_{d,b} = 68$, $J_{b,c} = 55$, $J_{c,d} = 55$, and $J_{d,e} = 62$ Hz. These values indicate that the four bonds have substantial $s$ character and $\sigma$-bond order. Bonds $d\rightarrow c$ and $a\rightarrow b$ fuse six-membered rings and may be compared with $J_{d,c}$ in 1-methyl- and 2-methylnaphthalene at 52 and 53 Hz, respectively.\textsuperscript{33} In analogy with cyclopropane derivatives,\textsuperscript{36,37} the larger value of $J_{d,b}$ may arise from both carbons in bond $a\rightarrow b$ belonging to five-membered rings, whose bonds have greater $p$ character due to smaller internal angles. This should increase the $s$ character of the $a\rightarrow b$ bond and hence the coupling constant; this effect should be less for bond $d\rightarrow e$, 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,\textsuperscript{38} as by analogy with cyclopropane derivatives\textsuperscript{36,37} these rings would be expected to have markedly small coupling constants.

The 2D NMR spectrum of C\textsubscript{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.\textsuperscript{39} The $J_{CC}$ 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.

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

Kent H. Nakagawa,\textsuperscript{a} Carla Inouye,\textsuperscript{1} Britt Hedman,\textsuperscript{1} Michael Karin,\textsuperscript{1} Thomas D. Tullius,\textsuperscript{1} and Keith O. Hodgson\textsuperscript{1,2}

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 92033

Stanford Synchrotron Radiation Laboratory
Stanford University, SLAC, P.O. Box 4349
Stanford, California 94309

Department of Chemistry, The Johns Hopkins University
Baltimore, Maryland 21218

Received December 10, 1990

Expression of yeast metallothionein, which binds copper specifically, is regulated by the protein CUP2 (also known as ACE1).	extsuperscript{1,2} CUP2 itself is activated for binding to DNA by copper\textsuperscript{1}. Yeast metallothionein contains a cluster of eight copper\textsuperscript{1} ions bridged by thiolate ligands that are likely provided by the 12 cysteines of the protein.\textsuperscript{4} How copper is bound to CUP2 is unknown, however. Since stimulation by copper\textsuperscript{1} of CUP2 binding to DNA is a cooperative process,\textsuperscript{5} and the DNA binding domain of CUP2 contains 12 cysteines,\textsuperscript{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 copper in CUP2 are sulfur-coordinated and in close proximity to each other, most likely bridged by thiolate sulfur. The Cu-K-edge X-ray absorption edge structure 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.

Copper cluster in CUP2 is also likely. Here we report that Cu-K-edge X-ray absorption fine structure (EXAFS) gives strong evidence that the copper in CUP2 are sulfur-coordinated and in close proximity to each other, most likely bridged by thiolate sulfur. The Cu-K-edge X-ray absorption edge structure 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.

Cup 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...