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EARL LEONARD MUETTERTIES

1927—1984

A Biographical Memoir by

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Biographical Memoir

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Earl L. Muttler

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June 23, 1927–January 12, 1984

BY R. G. BERGMAN, G. W. PARSHALL,
AND K. N. RAYMOND

EARL MUETTERTIES, Professor of Chemistry at the University of California, Berkeley, died of cancer on January 12, 1984, at the age of fifty-six. He was a major figure in American inorganic chemistry and contributed in almost every area of this discipline. He made important contributions in the structure and bonding of clusters, in reaction dynamics of both main-group and transition-metal compounds, and in both homogeneous and heterogeneous catalysis.

Earl Muetterties was an internationally recognized scientist whose career—first at Du Pont Central Research, later at Cornell, and finally at Berkeley—had a major impact in virtually every area of inorganic chemistry. His work extended into chemical bonding theory, fundamental chemical reaction dynamics, NMR spectroscopy, surface chemistry, applications of topology to chemistry, and stereochemical theory. Because of this wide range of fields in which he made major research contributions, Earl Muetterties emerges as a unique individual who during the last three decades

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had a major impact on the development of modern inorganic chemistry as we know it today.

A hallmark of Muetterties' research was the intellectual elegance of his papers and the rigor of his approach. For example, he was among the first to apply topological arguments to the analysis of intramolecular exchange phenomena and was a pioneer in applying permutation analysis to NMR data in distinguishing reaction pathways. In his organometallic research, he discovered the unique regioselective reduction of aromatic hydrocarbons to give all-cis addition of hydrogen and characterized the mechanistic aspects of this reaction. He demonstrated nucleophilic attack at the carbon atom of coordinated carbon monoxide in metal carbonyls by looking at labeled oxygen exchange between $\text{Re}(\text{CO})_6^+$ and ^{18}O -labeled water. In his metal cluster chemistry, Muetterties was among the first to develop and articulate the cluster-surface analogy for surface chemisorption states. He discovered a new class of metal clusters that are coordinately unsaturated and that consequently are extremely active catalysts for hydrogenation reactions. In his coordination chemistry, Muetterties investigated the structural systematics and interrelationships between coordination complexes and clusters. Finally, in his latest field of research, Muetterties had begun a concerted effort to compare the bonding of adsorbed monolayers of molecules on surfaces with the structures of metal clusters. Using adsorbed molecules on crystal surfaces, his approach has promise of producing new advances in our ability to correlate heterogeneous and homogeneous catalytic systems.

Earl was born in Elgin, Illinois, on June 23, 1927. Instead of following his family's wishes that he take over his grandfather's bakery, he earned a bachelors degree in chemistry at Northwestern University in 1949. He did his doc-

toral thesis in boron–nitrogen coordination chemistry under Charles Brown and Eugene Rochow. He received his Ph.D. from Harvard in 1952 and joined the Chemical Department, the predecessor of the Central Research Department, at Du Pont. Earl's abilities were soon apparent, and he was promoted to research supervisor extraordinarily rapidly in 1955. He formed a very productive partnership with another rising star, William D. Phillips. Between them, they effectively exploited the new tool of nuclear magnetic resonance spectroscopy for study of dynamic processes in inorganic compounds. In an elegant series of papers, they established the stereochemistry of main-group fluorides such as PF_5 .

Earl's research group carried out pioneering work on new processes for synthesis of fluorocarbons and the main-group hydrides, particularly SiH_4 and B_2H_6 . The emphasis was on synthesis of these compounds from basic raw materials, such as calcium fluoride, which was explored as a fluorinating agent for chlorocarbons. The hydride synthesis employed aluminum and hydrogen as reducing agents for SiO_2 or B_2O_3 suspended in an aluminum chloride melt.

The boron hydride work led into one of the most exciting periods of Earl's career, the discovery of polyhedral borane anions such as $\text{B}_{12}\text{H}_{12}^{2-}$. Walter Knoth, who was exploring decaborane chemistry in Earl's group, discovered that the dimethyl sulfide complex $\text{B}_{10}\text{H}_{12}(\text{SMe}_2)_2$ was easily converted to the $\text{B}_{10}\text{H}_{10}^{2-}$ ion. The most exciting aspect was that $\text{B}_{10}\text{H}_{10}^{2-}$ displayed a substitution chemistry like that of aromatic hydrocarbons. It was like rediscovering benzene in the richness of its chemistry. A six-to-eight-man task force was assembled to exploit this discovery. Some explored the "aromatic substitution" chemistry and sought practical applications while others attempted direct syn-

thesis of $B_{10}H_{10}^{2-}$ from simple reagents like $NaBH_4$ and B_2H_6 . The synthesis group uncovered a family of polyhedral borane anions beginning with $B_{11}H_{14}^-$ and $B_{12}H_{12}^{2-}$. The work proceeded at a breakneck pace to obtain broad patent coverage. The urgency was maintained by the fact that Fred Hawthorne's research group at the Redstone Arsenal in Alabama had discovered these same materials independently. There were also rumors that Russian scientists were developing high-energy rocket fuels based on boron hydrides, including apocryphal stories of Russian jets belching green flames from their tailpipes.

The late 1950s and early 1960s were a golden era in Earl's group, just as in chemistry as a whole. The intellectual vitality of the group was amazing. Earl led study projects in which the group worked through texts on group theory, ligand field theory, and biochemistry. The study of symmetry and topology stimulated by the polyhedral borane research provided two intellectual themes that persisted throughout Earl's research career, namely, exploration of cluster compounds and delineation of coordination geometries of metal ions. He initiated preliminary attempts to generate polyhedral aluminanes and explored molybdenum cluster chemistry. Even though the results of these programs were disappointing, they laid the foundations for more successful programs in the future.

In addition to the polyhedral borane work, the late 1950s and early 1960s saw the beginning of transition-metal organometallic chemistry in Earl's group. Some pioneering work was done on π -allyl, fluoroalkyl, and boron hydride complexes of the transition metals. Earl's own research diversified to exploration of high coordination number (7-11) complexes.

A major inflection point in Earl's career came in 1965 when he was appointed associate director of the Central

Research Department with a charter to reestablish catalysis as a major discipline in the department. He set up groups in homogeneous and heterogeneous catalysis and in the synthesis and spectroscopy of organometallic compounds. In spite of the administrative responsibility of his new position, he maintained active laboratory research and participated in a variety of new intellectual activities. He edited volume 10 of *Inorganic Syntheses*, published in 1967, and played a major role in revitalizing the *Inorganic Syntheses* organization. Earl edited books on boron chemistry and transition-metal hydrides and wrote a number of reviews on complexes with unusual coordination numbers. Along with Alan MacDiarmid at the University of Pennsylvania and Neil Bartlett, then at Princeton, he set up the Penn-Princeton-Du Pont seminar series that met monthly for discussions of research in inorganic chemistry.

Earl's research interests continued to diversify, even to the extent of research on mammalian pheromones. His technician spent many redolent hours extracting various monkey excretions. The venture into pheromone research was formalized by participation in the Monell Chemical Senses Center of the University of Pennsylvania. His formal academic ties included adjunct professorships in chemistry at Princeton (1967-1969) and at the University of Pennsylvania (1969-1973). He and Alan MacDiarmid shared supervision of a graduate student working in organometallic chemistry.

After a two-month lectureship at Cambridge University in 1972, Earl decided to pursue an academic career. He assumed a professorship in chemistry at Cornell in 1973. A major attraction of Cornell was the potential for interaction with outstanding faculty colleagues. Earl and Roald Hoffmann had a particularly good collaboration during this period when Roald was becoming involved in organome-

tallic chemistry. Although Earl continued research in chemical anthropology and in coordination chemistry, his major research theme was organometallic chemistry and homogeneous catalysis. He was associated with some outstanding graduate students and postdoctoral fellows who are now distinguishing themselves in academic and industrial careers—Patricia Watson, David Thorn, Bill Evans, Mary Rakowski, and Marcetta Darensbourg, to name a few. One of the more productive research themes of this period was the exploration of labile allyl and phosphite complexes of cobalt and rhodium that were among the first well-characterized soluble catalysts for the hydrogenation of benzene.

During his years at Cornell (1973-1978) Earl renewed his enthusiasm for cluster chemistry and expounded the analogy between transition-metal cluster compounds and the surface structures of metallic catalysts. A desire to explore this relationship in rigorous fashion was a major driving force for a move to the University of California at Berkeley, which has long been a center of surface science research.

Upon arriving at Berkeley, Earl set up his research in organometallic catalysis and cluster chemistry in the chemistry department at the university and began work on surface science in his new facility at the Lawrence Berkeley Laboratory, which adjoins the Berkeley campus. His perception was that much new understanding of surface-catalyzed reactions could be obtained by applying the principles and ideas of inorganic solution chemistry to this area. He liked to describe his heterogeneous catalysis work as experiments on the coordination chemistry of metal surfaces, but he also focused attention on reactive surface-bound organic species. During this period his organometallic group synthesized and studied the chemistry of a number of in-

teresting complexes, such as reactive carbide clusters and very temperature- and air-sensitive anionic dinuclear rhodium complexes. They also uncovered a reaction in which a dinuclear complex reduces an alkyne with specifically trans stereochemistry. At the same time his surface science group was applying Earl's earlier findings on arene activation to his heterogeneous work. They obtained important information about how aromatic organic molecules are bound to surfaces and how carbon-hydrogen bonds are broken in reactions of these molecules. He combined his major areas of research especially well in his parallel studies of the reactions of small coordinating molecules such as CH_3CN and CH_3NC with metal surfaces, metal cluster compounds, and monomeric metal complexes.

Earl's establishment of these parallel efforts had a major impact on the nature of research and the intellectual atmosphere at Berkeley. Because of his conviction that the fundamental chemical processes in heterogeneous and homogeneous metal-based chemistry were closely related, the presence of his group did a great deal to increase the interaction between surface scientists and inorganic chemists at Berkeley. This trend fit in well with Earl's growing conviction that chemistry departments in general were too divisionalized and interdisciplinary research was likely to be of growing importance in the future. This was an attitude that undoubtedly germinated at Du Pont and was reinforced by Earl's experience in the small, interactive department at Cornell. He believed strongly that if the Cornell-style interactive atmosphere and the physical and intellectual resources of the university and Lawrence Berkeley Laboratory could be combined, his new environment could be truly unique and scientifically powerful. He worked hard—and successfully—to establish that combination.

Earl's dedication to all phases of the education process were evident early in his career, when he played a major role in the establishment of the ACS journal *Inorganic Chemistry*. After moving to Berkeley, he perceived a need for a focused journal in the area of organometallic chemistry. He worked hard to determine whether there was a solid demand for such a journal and, after being convinced of this, played a singularly effective role in getting the new journal *Organometallics* established. He was instrumental in attracting Dietmar Seyferth and Richard Schrock to their current editorial positions at the journal. Educational policies and processes, at both the graduate and undergraduate levels, were also an important part of Earl's vision of Berkeley's growing excellence in inorganic chemistry. His terms as graduate inorganic advisor were marked by successful efforts to provide students with new flexibility in designing their course programs. Shortly after arriving at Berkeley he instituted a new advanced inorganic course, emphasizing modern structural and mechanistic principles, and taught the course himself for several years. Dedicated to attracting the best faculty and graduate students to the department, he expended much effort explaining his goals and ideas to potential students and faculty. At the time of his death, he was chairing a committee charged with revising the first-year chemistry curriculum. The committee continued his work on this project, and several of Earl's ideas have been incorporated into a new freshman chemistry program that was instituted this year.

Earl's personality reflected and reinforced much of the character of his scientific work. He gave the impression of being rather reserved, placing great importance on interacting with others with calm and dignity; he almost never raised his voice or became outspoken in public. However,

his friends, family, and colleagues realized that he was a deeply caring and emotional person and understood the powerful drive and intensity that motivated him. This intensity affected everyone who knew him. Although in some cases his work provoked controversy, everyone acknowledged his dedication to research and education, the unique breadth of his scientific vision, and the major contributions he made to chemistry during his lifetime.

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