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Personal history

Celebration of inorganic lives: Interview of Daryle H. Busch by Joseph A. Heppert

Fig. 1. (2008) Immediate family, 80th birthday: Jeri (middle front); Daryle behind grand daughter Sofia who wears red dress; sister, Joanna (mathematician, front row) next to husband Jack (purple heart paratrooper). Present were all four living children, Mike, Steve, Cheryl Rome and Kristina Rodriquez and their spouses (John Rome, Eric Rodriquez and Steve's wife Becky). Eight of the nine grand children were present, in descending age, Brett Rome, Lindsay Rome, Vincent Pichinini, Alex Busch, Logan Busch, Katie Rodriguez, Sofia Rodriquez, and Rachael Rodriquez, and also spouses of Lindsay, MikeBeyer, and Brett, Brooke Rome.

Professor Joseph A, Heppert, JAH: Greetings Daryle, Professor Busch, or to be more complete, the Roy A. Roberts Distinguished Professor of Chemistry, Daryle H. Busch, and congratulations on this special volume of Coordination Chemistry Reviews.

Daryle Busch, DHB: Thank you very much Joe, Professor Heppert, Chair, Department of Chemistry, University of Kansas. I do feel much honored and deeply pleased by this very special treatment.

JAH: Let's begin with your origins. Please tell us about your early family life.

DHB: Fine. It is always a pleasure to speak of those one loved. My parents and their families lived in a small town in the foothills of Southern Illinois, south of where the great ice sheet stopped creating the great plains of the corn belt, about 60 miles north of the confluence of the Mississippi and Ohio Rivers. Its name is Carterville and the population was about 2800. My mother was from gentry, a couple of generations having owned the passenger and freight franchises at the railroad and other businesses, like the hardware store and the ice and coal business. My father was one of six sons, of a foreman in a coal mine (who also had two daughters). I should emphasize the fact that coal mining dominated the economy. The Illinois Central Railroad had helped populate the region to get coal for its steam locomotives. My dad was a strapping 6 footer, at the top of his class in high school, and much liked in the town. After working more than long enough loading coal into railroad cars deep underground, Congressman C.W. "Runt" Bishop helped him get a good paying government job in the post office.

My parents married in 1926, and everything looked great even after the depression hit (1928) until President Roosevelt took office in 1933 and fired all federal employees from the "other" political party. Shortly after that, new legislation firewalled civil service jobs. Jobs were almost unavailable and those that were to be found paid poorly. Result was that both of my parents had poorly paying jobs

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for some years. We lived in a home that belonged to my maternal grandmother and raised most of our food. My family has viewed the subject with chagrin ever since then. Anyway, that is how it was when my life got started.

JAH: You surely have memories about how you responded to what must have been hard times for everyone in your family.

Fig. 2. Daryle Busch (1932), age about 4 years.

DHB: No one had anything to give to kids so I learned to raise money while I was very young. My first job was hauling waste in a toy wagon to a small city dump a few blocks from our home. I was somewhere between 6 and 8 years old. While in grade school I had many little chores and jobs, mowing lawns, cutting weeds, paper routes, picking peaches and pears. Later, in High School I worked after school and weekends at a Kroger store, mostly in the produce and meat departments. I was very lucky; my best friend's father was store manager. I bought most of my own clothing and the special things including a tennis racket and a fishing rod and reel. With the leadership of my parents, especially my mother, I learned that initiative, discipline, and reliability have value almost without limit. On the other hand, since we mostly ate what we raised and the only meat we raised was chicken; I learned to dislike that source of food. Hardship has long term consequences.

JAH: What were your experiences like in school? Was the period of time conducive to sound education?

DHB: My memories of grade school are mostly boring or even worse. The little town was by nature totally integrated and my sister and I had the problem that our mother didn't realize the extent to which she embarrassed or even endangered us by not conforming to the common dress code of most of the kids in town. She dressed me in shorts, stockings, shirts with buttoned collars and neckties, while all the other boys wore overalls and tee shirts. Since I might have tended to be a little shy, this probably served the purpose of forcing me to defend myself in the first two or three grades so that I soon adapted to my male age group. I didn't know about sports while in grade school so I missed out on basket ball.

When I started high school I took over my life. In the small school there wasn't much to learn and I was an eager student. My parents were more than busy just trying to scrape up enough money to keep the four of us alive and as a result I was on my own most of the time. In school subjects were limited. Math and physics were strong, but there was no chemistry and biology was very limited. English and writing were serious subjects but other languages were limited to Latin, German, and occasional Russian and French. No shop and no shop courses. I learned that the football team began practice in August and my best friend, Leonard, and I volunteered for the team as freshmen. In so small a town, no ambulatory male is turned down. As freshmen, they essentially made us 90 pound mascots, but we both had minutes in the games when we were sophomores. My junior and senior years, I played both corner back and tailback in football. I also ran middle distances and broad jump in track. Aside from sports I edited the school paper, instigated, produced and edited the first school yearbook, and had a couple of leading roles in stage plays and, oh yes, I played a corpse in a play as a freshman. I suppose I might have strayed into less constructive activities if I hadn't found so many interesting things to do in that small and well managed high school. The powers what be even let me stay out for basketball but I couldn't catch up with the other kids who began the sport at ages 6 or 7. The Carterville basketball team had been state champions one time. Even so, they did need a few walk-ons to fill in during practices.

JAH: It sounds like your High School was pretty special and it made a noticeable difference in your life. Did you find guidance there toward your later career in science?

DHB: The answer to that is a big no, not at all. In fact, the world was at war and there was only one possibility in the future for all young men when I was a high school student—going to war. On December 7, 1941, I was 13 years old and I had a couple of paper routes—the day of that disaster I learned about it when I picked up my papers for the afternoon delivery. My father's brothers, Jack, Bill, Gail, and Lee were either already in the military or joined shortly thereafter. Jack, the youngest and my role model, died testing the Republic P47 "thunderbolt" fighter plane. Bill's B-17 bomber was shot down over Germany and he finished the war as a German prisoner. As my father would expect—I had a plan and it involved going to war. But the war ended during my senior year in high school.

Since there was no help for me from my family and there were no grants or scholarships available that I knew of, except for veterans, I was determined to serve in the military forces to earn my college education. I wanted to fly but our impoverishment had led to neglect of my teeth and that kept me out of all air services, also out of West Point, so I enlisted in the U.S. Army. They would take any white male who could stand up and take the oath of allegiance. In my generation, the GI Bill was the source of education for many youth.

JAH: Interesting to hear you speak about this because we don't think about that source of educational support much today. In fact it seems generally true that the support of the military personnel after their service has been far from exemplary in the immediate past.

DHB: There is certainly a world of difference between then and now in the opportunities and where they might come from. But let me tell you about a very un-military military experience. Innocent young troops replaced hardened combat troops in the armies of the occupation—talent was at a premium because experience was essentially nonexistent. Enlistees were given assignments on what passed for IQ-tests, or whatever qualification seemed most appropriate. I wound up in the army of the occupation of Japan with the brightest group of people I've been privileged to meet, ever. This group was being dispersed into General MacArthur's headquarters in Tokyo, Japan, where I served as Chief Clerk, in the office of the Surgeon General, Far East Command. My job was to keep the records called *troop bases* for medical services throughout the command including hospitals and hospital ships and services—all over.

The Japanese people loved MacArthur because he brought extreme order and peace to their decimated, bombed out nation and his occupation army was a hoard of curious and friendly adolescents rather than the viciously inclined battle weary combat veterans who had been expected. For me this was the first time I had been more than a few hundred miles from my home in mid-America and I hadn't so much as fully appreciated the concept of a totally different culture. Japan was even more fun than high school, but there was a problem, or two. This business of occupying another nation was interfering with my education, and I had grown up and this wasn't where I would find my life partner. These Japanese women were unbelievably attractive, but seemingly not from the same world as I. Otherwise, time moved fairly quickly. I received promotions in weeks or months and in less than 2 years I had been promoted about as high as an enlisted man can go, sergeant first class. Actually that was almost my undoing; more on that later. I was proud of all those stripes. When discharged at age 19, I joined the inactive reserve to preserve my rank in case of national disaster. Dr. Heppert, serving in the military teaches one, at least as well as anything I can imagine, how important endings can be. I was very happy to be honorably discharged and sent home. I had only one other ending that I enjoyed as much.

JAH: Well, you did it. You earned your education. During the time in the army were you making plans so that you were prepared to move on with your education?

DHB: I have to be honest. I didn't really do any planning toward education while serving Uncle Sam. In fact, the plan I had got lost. I had wanted to go to the University of Chicago and that got lost. In Japan I studied the Japanese language and culture; read a lot of popular literature; attended a lot Japanese music, drama, and special places in that nation, and enjoyed life.

The world changed while I was gone. The depression was over; the war was over; everyone was ok; and home was very, very nice and everyone was there and happy and, just nice. I really didn't want to leave again, at least not right away. Back home in Southern Illinois in the fall of 1948, I saved my GI bill for graduate school and enrolled on a State of Illinois scholarship at Southern Illinois University, 10 miles from my parents home, where I happily set out to study everything, especially science (chemistry & physics) and math.

As time passed I made plans to marry a very nice, talented, pretty lady named Geraldine, Jeri, Barnes toward the end of my education at SIU. But, when the Korean war happened the Army called me back. I appealed and the Army decided to let me finish college before returning to active military duty—if I could graduate in a total of 3 years. I continued my undergraduate education on quarter-by-quarter military permission. Jeri and I went ahead with our plans and on March 11th of my early graduation year, 1951, we married. My dad shook his head and said "when you get on that train headed for Seattle you are going to think this is one cruel world." Remarkably just weeks before I was supposed to leave for Korea the US Army canceled my orders, and released me. They had discovered that I had less than 1 year left on my reserve enlistment. Suddenly Jeri and I were free to build out lives together. Joe, that was the luckiest day of my life. But, as happened a few other times, I didn't have any immediate plans, just a long range plan.

JAH: You do have a talent for drama. This time two graduations, your Bachelor's degree and your second honorable discharge. I suppose this opened the way to graduate school.

DHB: Yes, all of a sudden I needed to find a graduate school and I was still considering physics as well as chemistry. Fate and a friendly faculty member intervened. Professor Ken Van Lente, the physical chemistry faculty member at SIU, took me to the Chemistry Department Chairman, Jim Neckers, to see if he could help me get into a good graduate school in chemistry.

Dr. Neckers soon had John Bailar at the University of Illinois on the telephone and he indicated that he had a candidate for graduate school for Dr. Bailar to consider. Dr. Bailar obviously said "is he any good" because Dr. Neckers turned to me and said "are you any good?" With little chance to think, I replied "Darwin Davis has a little better record than I and he is a regular 4-year student. Otherwise. . .", I'm not sure exactly how I said 'otherwise my record is the best of any student you have coming out this year'—probably pretty much just that. Dr. Neckers repeated my statement, without using Darwin's name. Then he said that I was a diamond in the rough and followed up with too flattering a comment to make in front of a young man. He handed the phone to me and Dr. Bailar told me that he would like to have me come to the University of Illinois. "Would I prefer a Research Assistantship or a Teaching Assistantship?" This was a marvelous way to begin graduate school.

JAH: Perhaps I might say you tend to be lucky too. It seems clear that your Alma Mater had very good relationships with Illinois. Otherwise I don't believe this could have happened so smoothly.

DHB: You are certainly right. There was a steady stream of SIU grads going to the University of Illinois. Lucky—sometimes I have told my students that we have to be lucky, but we have to recognize luck when it is happening to us and we have to be doing the very best we can at what we are doing or we probably won't be lucky. It seems like I have always been preparing for the next stage of my life but I have never known when it was going to happen.

JAH: What was it like to be a graduate student in the early 1950s?

DHB: Thanks for asking. It was a bit different from anytime since. In 1951 Research money was very limited, there were some armed forces grants, those from Navy seemed to be best, the Navy certainly supported some basic research. Also some contracts came from industry, but the NSF didn't really exist and NIH hadn't yet discovered it's broad interests in chemistry. John Bailar, my mentor, had a small grant from International Nickel, for an electrochemical process to separate cobalt and nickel. An undergraduate in John's lab had done the first work and reported a good separation with glycine as the ligand in water. I repeated his work and it was totally wrong regardless of reaction conditions and, unfortunately, the grant expired before any positive program could be developed.

I had a much better early laboratory experience in an advanced laboratory course taught by Dr. Bailar. He suggested that we should be able to prove the tetrahedral structure of beryllium complexes by resolving the mirror image isomers of a certain neutral complex of beryllium. His neat idea was based on then recent work that suggested this could be accomplished by selective adsorption on finely ground particles made from a single crystal of quartz. Now bear in mind, this was in 1952, years before the invention of chromatography, HPLC or GC, although ion exchange separations were known. He gave me a huge quartz crystal, loaned me his big rusty old iron mortar and pestle and I was off to learn how to make bis(benzoyl-acetonato)beryllium(II). Soon I brought him a sample of the compound, and data from a polarimeter showing that the resolution was successful, along with rate data for its racemization, and that, if we must choose between possible tetrahedral and square planar structures, the structure is clearly Td. His immediate comment was "OK! Let's publish!" I was very quiet—and my mouth was probably hanging open. He said "what's the matter?" To which I stammered "I'm not sure I'm satisfied with my work, yet", and he quickly put that aside saying "Young man, do you think you will ever be satisfied with your work?" We published "The Optical Stability of Beryllium Complexes," in the Journal of the American Chemical Society.

JAH: Did Professor Bailar support your Ph.D. research?

DHB: Actually he didn't support my research after that first year and so long as a student wasn't supported by his research, Dr. Bailar was pleased to see his researchers work on their own ideas. Since I was serving as a teaching assistant during my second year in graduate school, my research proceeded accordingly. My major was inorganic chemistry with a minor in physical chemistry and a 2nd minor in math so that I was naturally focused on the chemistries of the elements and related measurements as well. The transition elements were especially attractive and chelate chemistry was a current topic when I was a student. Chelation reflected the fact that cooperative interactions are matters of consequence and this directed my attention to the chelating ligand EDTA, ethylenediaminetetraacetic acid. EDTA was designed to provide the maximum number of points of attachment to any given metal ion, six, a number corresponding to the highest common coordination number of many metal ions in individual complexes. In a visit to the U. of Illinois Dr. Bailar's former student, Professor Quagliano from Notre Dame, talked about the infrared spectra of common metal complexes, and a little later I determined the IR spectra of a couple of EDTA complexes. It had occurred to me that although EDTA can be sexadentate, (bound to all six sites) it doesn't always have to be. After all, a baseball pitcher doesn't always use all five of his fingers to grasp the ball when he throws it. With Dr. Bailar's guidance I wrote a research proposal based on that work and won a fellowship that supported my third and final year in graduate school.

JAH: Tell me about that work. I suppose you might have called it the EDTA Project.

DHB: I'm very proud of that work. The EDTA program used infrared spectroscopy to establish the following: (a) proved the sexadentate structures of certain light metal (e.g., iron, cobalt, nickel) EDTA complexes in the solid state; (b) proved pentadentate complexes are readily formed for these elements as well. (c) It showed that heavy square planar metal ions (e.g., palladium, platinum) readily form bidentate chelates with H_4EDTA and (d) those heavy metal ions also form tetradentate chelates with the anions H_2EDTA^{2-}. These demonstrations of important structural details were ground breaking; chemists were just learning how to prove structures with these tools and combine multiple spectroscopies with other tools, like magnetic moments (to count unpaired electrons, etc.), and electrochemistry to deduce complicated structural relationships. What was begun in the fifties expanded into today's enormously powerful research based on multiple experimental tools.

In the context of applying multiple physical measurements for structure demonstrations and proofs, I want to point out that the following was a very early, perhaps the first, work combining UV/vis, IR and magnetic moments, used in concert, to deduce and explain the properties of a new family of metal complexes. Krumholz, an analytical chemist in South America, had reported that biacetyl and methyl amine combine to form a ligand that could be used to detect and perform quantitative analysis for iron because of the purple color of it's complex. By analogy with the well known 1,10-phenanthroline and 2,2′-bipyridyl (phen & bipy) complexes of iron(II) I assumed this implied the presence of three bidentate ligands bound to iron, each of which is simply the bis(methylimine) of biacetyl (BMI). Such a structure would have functional groups just like the well known ligands (bipy & phen) and should give the same kinds of spectra (deep purple). I related the chromophore to a conjugated chelate ring involving the metal ion and the two imine groups; NOT to a pyridine ring, or pair of pyridine rings. On that basis, I supposed that hybrid structures between bipy complexes and those of BMI should exist and quickly produced the corresponding complexes of N-methyl pyridinaldimine, formed from methyl amine and 2-pyridinaldehyde. The work appeared in my Ph.D. thesis, but wasn't published until I had moved on to my first job as assistant professor at Ohio State University. I wasn't nearly as fascinated by the measurements as I was by the molecular structure relationships themselves and that is where my work began to move.

JAH: That sounds like a different subject. I assume you mean a different technical subject. Is that correct.

DHB: Yes Sir, I do. In those early days I developed an unending fascination with the cooperative atomic and molecular effects that underlie much of chemistry. One little event stands out in my memory. In his course on coordination compounds, professor Bailar described bidentate, tridentate, and on up to sexadentate ligand structures, some linear and some branched. I looked at the picture of a linear tetradentate ligand wrapping around three sides of a square planar metal ion and immediately asked Dr. Bailar if anyone hadn't added the missing edge to the ligand structure; i.e., does the corresponding macrocyclic ligand exist? He looked at me and said "No, why don't you make it?" With this, I began a first quest for ligands everyone calls macrocycles today. The challenge was to make molecular rings of between 9 and 18 members, not the region where ring closures are greatly favored. Also the structures must include regularly placed donor atoms, such as nitrogen, sulfur, phosphorus and oxygen. This introduced a second challenge, the usual complications associated with the synthesis of polyfunctional molecules. I spent something like a fourth to a third of my time as a graduate student on this project with only a few leads, before graduating from the University of Illinois, without producing a single proven example of a macrocyclic ligand or complex thereof. However, I had for the first time in my career defined issues of great value.

Two important concepts were contributed to chemistry by this work: (1) the idea that any combination of donor atoms might be incorporated into a macrocyclic ligand structure and enjoy advantages that are strictly of topological origin; (2) the hypothesis, labeled the template effect, that a metal ion, or some other organizing entity, might arrange precursors in such a way as to greatly favor the formation of, for example, macrocyclic ligands, and many other entropically disfavored structures, the next obvious step being molecular cages. Further, the concept has yet to be exploited to the fullest extent possible since that would involve chemists controlling molecules as freely as skilled persons can control all manner of component assemblies on macro-scales, using elements like strings and ropes. The first truly different examples came with the tying of knots in molecules by Sauvage, leading eventually to Stoddardt's synthesis of the Borromean Link.

JAH: Today's graduate students have many opportunities to attend national and international meetings and meet the famous scientists of the day. Was that the case when you were a student?

DHB: Yes. It was more the case than I would have expected. Well known scientists frequently visited my graduate school. Also, during my second summer as a grad student, a satellite conference to the International Conference on Coordination Chemistry was held not far from Urbana, IL, and Dr. Bailar took a number of his students to the meeting with him. During his talk, Dr. Bailar even set aside a few minutes when he asked me to explain to the audience how I had used infrared spectroscopy to prove the dentate number in structures of EDTA complexes. That was an awesome experience, but even more awesome was the opportunity to meet and chat with the greats of the blossoming field of chelate chemistry. I met not yet Nobel Laureate Henry Taube and commented to him that I couldn't imagine anyone so young having done so much important research. I talked to Professor Frank Dwyer from the University of New South Wales, Australia, about his remarkable work with sexadentate ligands and with transition metal ion based medicines and, also, about the possibility of joining him as a postdoc for a year. I met Professor Arthur Martell, who would later take over the chemistry department at Texas A&M and make it one of the country's best, and who was personally responsible for making equilibrium studies of coordination compound formation a routine and heavily used scientific tool. What a marvelous way to enter a booming field of intellectual growth!

Probably I was unusually well prepared for this opportunity since I had spent both of my graduate student summers editing books for Professor Bailar, first a volume of Inorganic Synthesis and then his massive monograph on Coordination Chemistry. The latter was written by his former students and my heaviest contribution was the introductory first chapter, an overview. That silent editorship produced immediate friendships with many of Professor Bailar's former Ph.D. students since these were our co-authors and I was obliged to correspond with each of them as I edited their chapters. I won't name them all, but just a few because you may know them; for example, Fred Basolo, Northwestern U., Bob Parry, University of Michigan (then), Jim Quagliano, Notre Dame, Bodie Douglas, University of Pittsburgh, Stan Kirschner, Wayne State U., Hans Jonassen, Tulane, U., Bob Brasted, U. Minnesota, Bill Cooley, Procter and Gamble, and Gunther Eichhorn, Louisiana State U. and National Institutes of Health.

JAH: You have told me how you seemed to benefit from the hardships of the depression. What were the benefits and limitations of seeking employment at the time when you completed your education?

DHB: While I was born into depression, I graduated into prosperity. I graduated in 1954 and the early fifties were great years to be looking for a job in chemistry. The Post-WWII world had rebuilt itself and industries and universities were all expanding and hiring on grand scales. Like my colleagues graduating that year, I agreed to visit and be interviewed at an embarrassingly large number of institutions, including Princeton University, University of Cincinnati, The Ohio State University, University of Pittsburgh, Wayne State University, Monsanto, Universal Oil Products (now UOP), National Lead, General Motors, Dupont, Dow, Armstrong Cork, Hercules, Esso, and others I won't recall quickly. The transportation system made it reasonable to proceed with a series of tours on the railroad and this meant a couple of extended absences from home. Mentioning home, by now, Fall of 1953, I left behind a pregnant wife and two tiny sons when touring on job interviews. On the second such tour I had just visited Ohio State and Princeton, along with Armstrong Cork, and was on my way to the University of Pittsburgh, when I got a call from my Jeri, saying that the family Dr. had just insisted that our two sons be admitted into the hospital with the flu. It turns out that was to save her life, not the boys. The next message I received, in a matter of minutes, was an extremely attractive offer from Ohio State. I accepted, canceled a small number of visits not yet made, notable among which was Dupont, and went home. I believe that action revealed my priorities pretty clearly. First consideration always goes to those most dependent on me, a duty learned in the Army and on the football field.

JAH: Today employers might have required postdoctoral experience for new hires. Obviously that was not the situation in the early to mid-1950s. Those of you who had served in the military had matured in other ways I suppose. Still one might wonder if the tenure system worked about the same then without prior postdoctoral experience.

DHB: I believe hires before World War II brought new faculty in as lecturers and that added a few years to the tenure system. However, after the war, most of the candidates were indeed older and the lecturer system seems to have been abandoned. I started as an assistant professor and OSU was an excellent place for an inorganic chemist to initiate a career, and the time was right. The OSU Chemistry Department is large with a lot of students, the warmth of a midwest community, a long standing tradition in inorganic chemistry, and supportive faculty members. Most notable for me were Professors Harry Sisler, the senior inorganic chemist who later became chair of chemistry and then dean at U. Florida, Jack Calvert, a physical chemist who became my best friend on the faculty, and Al Garrett who soon became chair at Ohio State. However, after my arrival, the number of inorganic faculty quickly diminished. I was the 4th inorganic chemist, but two of the other three retired and the third moved on to greater responsibilities in the first few years after I arrived. That opened the opportunity for a modern faculty in a field that was bubbling over with new ideas and activities. Transition metal and metallic element compound chemistry in general had received a strong boost forward during World War II. Organometallic chemistry was incubating, even though publications were being written about how metal—carbon bonds can't be stable. Physical inorganic chemistry had been seeded at the Atomic Energy Commission, as characterized by the research of Henry Taube, Fred Basolo, and others and the principles coming from their work. Equally important, Physicist Hans Bethe's ground breaking crystal field theory, had been rediscovered and interpreted by chemists, and symmetry relationships were providing growing insights into, especially, transition metal chemistry.

JAH: How about instrumentation? Was it comparable to today's laboratories? What I'm really wondering is whether OSU spent a lot of money getting your laboratories set up.

DHB: OSU bought me a state of the art optical rotary dispersion polarimeter but that was just about all. I assumed the department would have spectrophotometers and the like, but that was only marginally true. I had to build up my own instrumentation laboratory.

JAH: This is a closely related subject. What was research funding like when you were getting started at Ohio State?

DHB: In 1954, Federal money was only beginning to become broadly available. There was a little industrial money and my first grant was a small one from Barium Reductions Corporation. I had only been at OSU for a couple of years when Sputnik was launched and, with that event, science advanced to center stage. The National Science Foundation, just a few years old, became a major funding source and my program was awarded a project entitled "Stereochemistry of Transition Metal Complexes", soundly reflecting the influence of my preceptor. Also, the National Institutes of Health recognized the fundamental value of the new inorganic chemistry and I seem to have been the first inorganic chemist they funded. I was certainly the first to serve on one of their project evaluation committees. That first project, which continued with uninterrupted NIH support for 29 years, was entitled "Ligand Reactions for the Synthesis of Macrocyclic Complexes". I enjoyed continued research support by both NSF and NIH for most of my 34 years at The Ohio State University. My lab instrumentation grew, including a gem of the era, a Cary model 14 UV/vis spectrophotometer and an outstanding broad temperature range magnetic susceptibility balance built by Jim Burke as part of his Ph.D. thesis work.

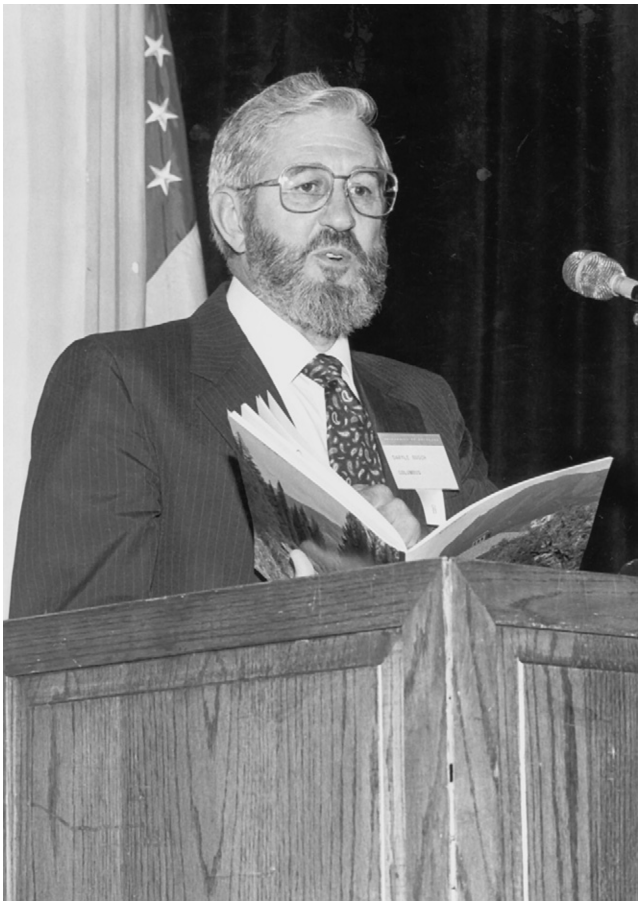

Fig. 3. (1982) Professor Busch giving the Spring Semester Graduation lecture at his university, The Ohio State University. Every generation faces its challenges – you are our gift to the future – rise above the stars.

Early on, a discovery event of a different kind was very helpful in the equipping of my OSU labs. Space was also very hard to find, and I was constantly keeping an eye out for possibilities. In exploring a particularly unattractive so-called laboratory that closely resembled my idea of a dungeon, I found a PerkinElmer Model 21 Infrared Spectrophotometer. I also found that I could easily be the sole user of the instrument and, in effect, its owner. This was a terrific break. I now had an a state of the art IR spectrometer which immediately revived my studies of the iron(II) complexes of pyridinaldimine and biacetylbismethylimine, by revealing evidence for higher order bonding between the iron(II) atom and its conjugated ligands. Remarkably, the π-interaction was so extensive that the usual C=N vibrations were difficult to detect, whereas the corresponding nickel(II) complexes showed the expected C=N stretching frequencies around 1650 cm^{-1}. The deep purple color that Krumholz put to use in the determination of iron is not dependent on an aromatic organic ring but on a five-membered aromatic ring containing a low spin iron(II) ion, two nitrogen atoms and two carbon atoms.

Foundational work for the NSF funding of our early stereochemical studies began in a paper I submitted after only a few months at OSU (1954), on an entirely new subject for me. I had begun a detailed study of the kinetics of the electron transfer racemization of optically active tris(ethylenediamine)cobalt(III), catalyzed by the corresponding cobalt(II) complex. I had to make the cobalt(III) complex and then separate it into its enantiomeric forms. However, because of the nature of the system, I could only purify the relatively insoluble diastereomeric isomer and that limited the yields to 50%, a fact I found very difficult to accept. I reasoned that since I had a reagent that precipitates the *dextro* or *d* form of the complex, I should be able to get very high yields of that enantiomer if I would simply labilize the system with my cobalt(II) catalyst and let all the cobalt(III) precipitate as the insoluble *d*-isomer. It worked and I had my first totally independent OSU publication and an early example of green chemistry in chiral synthesis, i.e., a chiral synthesis that was closer in yield to 100% than 50%. Was that a little before its time?

A bit later we expanded the project to the cobalt(III) and cobalt(II) complexes of EDTA and soon the project attracted the NSF support I mentioned. The electron transfer studies were led by Yong Ae Im, who spent most of her career at NIH, and substitution reactions were first studied in our group by Mel Morris, my first Ph.D. student. In the case of the EDTA complex, the racemization process was indeed catalyzed by the substitution labile and always racemic cobalt(II) complex. In contrast, the presence of a single methyl group on the ethylene chain that is central to the anionic ligand ethylenediaminetetracetate, EDTA^{4-}, conferred what appears to be total chiral selectivity to the resulting ligand, propylenediaminetetraacetate, PDTA^{4-}. The studies of the EDTA and PDTA complexes blossomed and ranged over other substitution reactions, including total substitution of three molecules of bidentate ethylenediamine to replace the entire sexadentate EDTA ligand; i.e., $\text{Co}^{\text{III}}(\text{EDTA})^{-}$ was converted into $\text{Co}^{\text{III}}(\text{en})_3{}^{3+}$. Dean Cooke was the key investigator during these intricate studies which were summarized at the 6th International Conference on Coordination Chemistry in Detroit, Michigan, in 1961. That meeting was organized by my graduate school classmate Professor Stanley Kirschner of Wayne State University.

JAH: You haven't talked about the NIH work. From the project title you gave us a while ago, they supported most of your work on macrocyclic ligands. Presumably that work had been going on at the same time as the works you have been talking about.

DHB: Macrocycles as a topologically benefited category of ligands. You are right. The NIH funding in the early 1950s unleashed my plan to establish macrocycles as a general class of ligands by making many of them and showing that they have special binding properties for metal ions. The strategy had three main features. It was based on *synthetic chemistry*; it focused on exploiting the concept of a *template effect*, and, finally, it used *ligand reactions* to control the macrocyclic synthesis. This plan led to the need for ligands that could chelate and donate electron pairs to metal ions and still have electron pairs to serve as nucleophiles in chemical reactions. The sulfur atoms of mercaptans and the similar oxygen atoms of alcohols and glycols were obvious candidates. Increasingly complicated mercaptoethyl derivatives of polyethylenepolyamine starting materials were studied in work initiated by Don Jicha, yielding dimeric and trimeric complexes of charming structures. Parts of this excursion served such later investigators as Dr. Marcetta Darensbourg well in her subsequent insightful studies of bioinorganic model compounds. The first intentional synthesis of a new family of macrocyclic ligands was indeed achieved by use of terminal mercaptide sulfur atoms on a tetradentate ligand that spanned three of the four edges of a square planar coordination sphere. The *kinetic template hypothesis* became a principle when, in Major Kurt Thompson's hands, α,α′-dibromo-*o*-xylene combined with the critical intermediate complex to form two new thioether linkages and a new macrocycle about a nickel(II) ion. Chemical & Engineering News summarized the first disclosure of this achievement (September 17, 1962). This was a kinetically favored process because of the adjacency of the reaction centers. Other assaults on macrocyclic ring closures were underway.

The *thermodynamic template effect* was well demonstrated when it was proven that the simple Schiff base forms of the cyclotrimeric and cyclotetrameric forms *o*-aminobenzaldehyde could not be detected except in their metal complexes. The self condensation by *o*-aminobenzaldehyde is hard to avoid and my postdoc Gordon Melson showed that the trimers and tetramers so-formed can be rearranged, in the presence of metal ions, to produce beautiful Schiff base macrocycles containing those metal ions (1963). Substantial contributions to this very interesting chemistry were also made by Sue Cummings and Larry Taylor in our labs. This realization fired our interest in using Schiff base reactions in the synthesis of many kinds and sizes of macrocyclic ligands by template effects. In ground breaking experiments in our labs, John D. Curry first explored the broader use of the Schiff base reaction. First, diethylenetriamine and triethylene tetraamine were combined with 2,6-diacetyl pyridine, forming pentadentate and sexadentate macrocycles, bound to metal ions, which were reported at the end of my first decade as a professor in 1964. Tetra-, penta-, and hexadentate macrocyclic ligands soon became easy to make by variations of John Curry's very general method. The favorite ring closure groups soon became the 2,2′-dicarboxaldehyde or 2,2′-diketones of pyridine. These and many 2,2′-dicarbonyl derivatives of pyridine and other cyclic amines and related structures have produced many, many new macrocycles with new examples appearing every year.

Requiring lone pairs on the donor atom that binds to the metal is a bit confining. A second possibility is an atom adjacent to the donor atom; i.e., an α-amino or α-hydroxo group since they also contain lone electron pairs. Recalling the Schiff base ligands formed between biacetyl and methyl amine—if the methyl amine were replaced by hydrazine, the resulting chelated hydrazone could have pairs of dangling electron rich amino groups. So we explored the chelate chemistry of various hydrazones and dihydrazones, also oximes and dioximes. Studies of pyridinal hydrazones and biacetyldihydrazone were initiated around 1955 by one of my first students, R. Carl Stoufer, who served on the faculty at the University of Florida for many years. This work was soon expanded into pyridinaldazines by Wilmer Stratton, and the 2-pyridinalhydrazones of metal ions were explored more broadly by Martin Robinson.

Oximes were particularly fascinating. It had long been known that two molecules of dimethylglyoxime will chelate to a single potentially planar nickel(II) ion, and lose just two of the four protons from the OH groups so that the two remaining acidic OH groups produce a ring-like structure by hydrogen bonding to the deprotonated oxo groups. In our view, replacing both H-bonds in some way should create a true macrocycle. Ronald Krause initiated alkylation studies on chelated oximes and then Bill Findlay and I set out to perform the ring closure. We believed that the tendency of perfluoro acetone to form its hydrate made it the ideal candidate for the job. While we were struggling with the reversibility of that reaction, researchers in two other laboratories succeeded in completing this macrocycle synthesis. Professor Gerhardt Schrauzer, succeeded by chance; he thought the lone electron pair in the $d_Z{}^2$ orbital of low spin nickel(II) in bis(dimethylglyoximato)nickel(II) might combine with boron trifluoride to form a the Lewis acid adduct. At about the same time, Thierig and Umland performed the same experiment with the same success, but having anticipated the possibility of attack on the coordinated oxime oxygen by the BF_3. With this event, template reactions clearly had moved on into the toolbox of all chemists.

JAH: To be copied is considered flattery in some circles, but I detect your realization that you had been working with expanding success in the happy situation of no visible competition. That may be more than one can expect. On the other hand, I suppose the realization did influence your work. Comment?

DHB: Yes it did and in more ways than one. Our laboratory continued to produce new macrocyclic chemistry, but in a greater variety of ways and we began to encounter much more interesting competition. Examples of variety in our labs: polydentate macrocycles containing from 3 to 8 sulfur donors, stereochemical analysis of tetraazamacrocyclic complexes having many chiral centers, chiral and achiral isomers of complexes containing two moles of the trimeric macrocycles from *o*-aminobenzaldehyde; chirality of the corresponding 1:1 complex of TRI; less common oxidation states stabilized by inert macrocyclic complexes; pairs of metal ions inside single macrocyclic rings. We continued our work on cyclic oligomers of *o*-aminobenzaldehyde, adding a bridge to the metal complex of the cyclic tetramer and producing a cup-shaped ligand. That same year, 1964, I had suggested in print that 2 such bridges provides one of two ways to produce a caged structure with a metal ion inside a three dimensional ligand. On that same subject, as Norman Rose left my group he told me of his plans to build caged structures in his new job at U. Washington, Seattle, and, soon after, he and his student, D.R. Boston reported the first such structure that was ever synthesized. There are no known naturally occurring examples of complexes of this type, ligands that encage metal ions.

Examples of important contributions came from other laboratories in these early times: Neil Curtis in New Zealand discovered and soon recognized the formation of very important families of tetraazamacrocycles by the condensation of acetone and ethylenediamine in the presence of metal ions. The previously reported simple unsubstituted tetraazamacrocycles, namely cyclen and cyclam, were rediscovered and their first metal complexes studied. Charlie Pedersen developed his macrocyclic polyethers (1967) and I had the pleasure of introducing Charlie to the broad Chemical Community. He showed me his work when I consulted with Dupont and I got him invited to an important meeting in Japan and later nominated him for his first award by the Delaware ACS Section. J.-M. Lehn added dimensions, extending Pedersen's work to the cage-like, bicyclic cryptands and their metal complexes, cryptates (1975–1980). Dale Margerum at Purdue provided a sound study of equilibrium systems showing the quantitative thermodynamic advantage of macrocyclic ligands and naming the phenomenon the *macrocyclic effect* (1970–1975). Of course the added stability of cage structures was identified by labels such as a "cryptate effect".

At this point, we had begun to broaden our interest in the structures of macrocycles including performing detailed studies to provide the tools to design macrocyclic ligands having more or less predictable capabilities, using such tools as NMR, EPR, electrochemistry, and detection of oxidation states and spin states by magnetic measurements. New principles began to emerge. Multijuxtapositional fixedness (MJF) was described as the underlying principle reflected in the extra stabilities of macrocyclic metal complexes. (Daryle H. Busch, "Metals and Enzymes—Multiple Juxtapositional Fixedness," *Chem. Eng. News*, p. 9, June 29, 1970. This principle was later referred to as preorganization in the work of UCLA's D. Cram, completing the triad, with Pedersen and Lehn, of 1987 Nobel Laureates.) This principle explains why, for example, a given metal complex of the triaxial conformer of 1,3,5-triaminocyclohexane is essentially as stable as an appropriate macrocyclic complex, such as those of TRI.

In 1972 I gave an organic chemistry seminar at UCLA laying out my perspective on macrocycles, cages, template effects, MJF, and cooperative interactions as they might evolve in the near and more distant future. A short time later I was invited to UCLA by Professor Fred Hawthorne to present a course and after investigating the possibility of a sabbatical, I accepted. When Fred invited me he indicated that Don Cram had been interested in my giving that class and that was important to me since this indicated that there was increasing communication between the inorganic and organic chemistry communities.

Some months after this, the most heart rending event of life occurred in my household. Our firstborn, our son Derek, was a fatal accident victim at the blossoming age of 22. He was a college student, a gifted musician in all respects, singing with the Columbus Symphony, leading his own pop bands over years, playing almost all instruments, with school bands and orchestras, composing and playing music for a variety of audiences. All the music at his funeral was from his compositions and was played by the distinguished OSU faculty soloist at the keyboard.

I was clouded but Jeri was in shock. She functioned with no apparent presence. Besides, in childhood she had tuberculosis and the germ that hid in a kidney cyst burst out and threatened her life. I spent my energy trying to regain her presence and save her life. With the help, often guidance, of our marvelous children Mike 22, Steve 21, Cheryl 18 and Kristina 13, we carried on with a family routine. I continued to teach and that made it easier for me. Then I remembered that in a few months I was to go to California and take Jeri and Kristina with me. I saw too much seclusion for Jeri and too much responsibility over Kristina. So I offered the options to UCLA of canceling my visit or postponing it for a year. UCLA graciously chose to postpone the course until the following year. The warmth of familiarity, close friends, and family, brought Jeri back. Many helped us so much in those difficult times, but I recall clearly two early offerings that were especially helpful. Professor Steve Lippard, then at Columbia University, wrote a very insightful letter to us shortly after the tragedy. The Lippards had suffered the loss of a child earlier and their pen wrote from real understanding. Professor Geoffrey Leigh, who I believe was at Brighton in the UK, shared a book with us, "Three Men in a Boat", that has in it a remarkable section that describes the emergence of a mourner from that thorny crown of suffering in so true a vision that we have shared it with others many times. The tuberculosis was another problem. Jeri sometimes had debilitating back pains and the first doctor thought she was a hypochondriac. I knew better; she is tough. The second doctor recognized her character and found the real problem and solved it with a trio of powerful antibiotics and she still carries the germ closeted in the cyst. The next year we had a nice time with the inorganic chemists at UCLA. Let's not talk about this anymore.

Instead—as a PI, I am not particularly happy working in a crowd. I think it is more fun to go where others haven't been, at least not in large numbers. The result is that when a field becomes too popular, I will tend to move on.

JAH: I don't think you mean that you left the subject that long ago do you? I think you must be talking more about a change in focus rather than a complete change in fields.

DHB: Right. I began to think more about our "Libraries of Macrocyclic Complexes" and just how they might be most useful. An *advantage* lay in the inventory of compounds which was especially rich in nitrogen donors, mixed nitrogen/sulfur donors and sulfur donors.

The program published detailed studies of families of macrocyclic ligands and complexes, beginning with the common templating ion, nickel(II), first expanding its oxidation states, and then proceeding to cobalt(II) and cobalt(III), and continuing on to the very difficultly handled iron complexes of saturated and variously unsaturated tetraamine macrocycles and macrocycles whose unsaturation is rearranged through control of the isomeric olefinic structure by the iron. Lovecchio, Gore and Barefield led the work on electrochemistry, electron spin resonance spectroscopy and redox reactions of macrocyclic complexes of nickel, including stable low spin Ni(III) complexes. NMR and conformational analysis of stereoisomers of macrocyclic nickel(II) complexes having as many 8 chiral centers were conducted by our colleagues Ito, Warner, and Gore. Our colleagues, Jackels, Farmery, Barefield, Tait and Rose reported on tetragonal cobalt(III) complexes with macrocyclic amine ligands having different degrees of unsaturation. Farmery, followed by Ochiai, led studies on monoalkyl and dialkyl derivatives of cobalt(I), cobalt(II) and cobalt(III) macrocyclic complexes reflective of vitamin B_{12} chemistry. Our group clearly showed the effects of ring size on electronic properties, along with consequent chemical effects on, for example, rates of substitution reactions through molecular mechanics calculations by DeHayes and electronic spectroscopic studies by Martin, Sperati, Hung, Jackels and Tait, using macrocyclic complexes of cobalt(III) and high spin 6-coordinate nickel(II) with unsubstituted tetraazamacrocycles of varying ring sizes.

The derivatives of *o*-aminobenzaldehyde are starting materials for additional exciting compounds besides the trimeric tridentate ligand (TRI) and the planar tetradentate tetrameric ligand (TAAB) and the cup-like structures mentioned above. The porphyrin molecule is aromatic, however, two electron oxidation converts it to a nonaromatic *annulene*. Correspondingly, the cyclotetramer of *o*-aminobenzaldehyde, abbreviated as TAAB, is an annulene, and 2-electron reduction produces an aromatic tetrabenzo-substituted dianionic ligand bonded to whatever metallic ion was present prior to the reduction; work reported by Katovic, Taylor, Takvoran, Farmery, Urbach, White, Lovecchio and Busch. Also working in our labs, but independent of each other, Dennis Riley, Maureen Caste and the team of Herron, Grzybowski, Matsumoto and Zimmer have produced a variety of cage structures completely encompassing the metal ions.

Looking ahead—iron complexes with tetraazamacrocycles. Because of its importance in nature, iron complexes with ligands having nitrogen donors constituted an area of much interest. Dabrowiak and Merrell made the synthetic macrocycle iron(II) complexes using the least likely ligands first, those containing four saturated nitrogen donors. Iron complexes were prepared for essentially all of the known saturated and unsaturated macrocyclic ligands and the compounds were characterized by UV/visible, infrared, NMR, and Mossbauer spectroscopies and by redox properties. New ligands were generated in situ by tautomerization and by dehydrogenation of the iron complexes, and further studies showed that the iron can control the relative locations of the olefinic groupings within certain ligand molecules. Mary Rakowski exploited the α-diimine affinity for iron to produce remarkable new iron complexes. In fact, a surprising structure was solved recently by Professor Wieghardt and collaborators (doi:10.1002/anie.200) showing a reduced TIM ligand in a dimeric structure with a moderate iron–iron bond and no bridging atoms. Returning to that earlier point in time, it seemed safe to assume that we were well positioned to exploit macrocycles for purposes that we might deem to be of considerable importance.

JAH: Today it is commonplace to build a library of compounds that can be searched for particular applications. I believe you have just told us about your library. So you were going to pick one or more specific goals. What were they and how did you go about picking them?

DHB: *Exploiting the library—synthetic O_2 carriers.* Our choice was the result of a combination of careful systematic decision making and for reasons of history. Repetitive external influence pulled the Busch group into increasing research on oxygen carriers. Years earlier, along with Professor Fred Basolo from Northwestern University, I had served as a consultant helping guide U.S. Air Force researchers as they developed a chemical based oxygen source for their aircraft. Then in the 1980s we collaborated with Air Products in research seeking industrial replacement of air distillation with a process based on a synthetic O_2 carrier. For the Air Force, the compounds of choice were simple substituent modified derivatives of the first discovered synthetic O_2 carrier, cobalt(II)salen. As you suggest, the strongest driving force toward O_2 carriers may well have been the advantage of the inventory of iron, cobalt, nickel, and manganese macrocyclic complexes.

Nature's best known O_2 carriers, and their many related biomolecules, use iron porphyrins as their macrocyclic complexes. When we chose to synthesize the first truly synthetic iron-based dioxygen carrier molecule, and announced that goal to our sponsor, our large inventory of iron macrocyclic complexes paid off beautifully. We studied the properties of the many compounds and matched the redox properties of the iron porphyrins to one of our families of ligands that is especially easy to subject to appropriate structural modifications, the so-called cyclidenes. The ligand name “cyclidene” was suggested by our crystallographer partner, Dr. Nathaniel Alcock from the University of Warwick in the UK. Not only was the Fe^{2+}/Fe^{3+} couple very similar for appropriate examples of the two families of compounds (e.g., those having N-methyl imidazole as the axial ligand), the space around the coordination site that an O_2 molecule would occupy in an iron/cyclidene complex was easily modified in order to control the environment of the bound O_2 molecule. The structure could also be designed to accommodate a potential substrate molecule in case we wanted to convert our oxygen carrier into an oxidase or oxygenase mimic. Stated very simply, our synthetic goal was to make a totally synthetic O_2 carrier, based on iron(II) that would contain a totally different ligand than that found in any known natural O_2 carrier.

JAH: You have certainly had a run through of applications of macrocyclic complexes, but somewhere along the line you seem to have become involved in the ACS, IUPAC, the AAAS and the like. Where does all of that fit in?

DHB: Now that’s a quick shift of topics, but I guess I was dwelling on chemistry a bit heavily. With regard to all of these organizations and the service they require, we can say that the inevitable caught up with me. Chemical Abstracts Service was located in Columbus, Ohio. In fact, CAS was in the older building right in the Ohio State Chemistry Department for many years. Many faculty had voluntarily helped with the business of abstracting articles for CA over its long history. When CAS was being put into computer form, the organic chemistry was handled first, then the simple inorganic chemistry and finally the coordination chemistry. At that point, I was called on as a consultant to CAS and enjoyed a long term relationship that not only involved helping CAS represent metal complexes for their computer systems, it brought me into the nomenclature of both coordination chemistry and organometallic chemistry. Completely without expectation, I found myself in a peculiar intermediary position between parts of ACS and IUPAC, at the suggestion/insistence of CAS personnel. This was because both the Chemical Abstracts Service of the American Chemical Society and the Nomenclature Commissions of the International Union of Pure and Applied Chemistry had to serve their constituents by providing definitive nomenclatures, and they did not always spontaneously produce compatible results. So, as best I remember, I became active in IUPAC at the suggestion of CAS. There were at least two more reasons. I felt that I hadn’t served the international community adequately and others told me that I had not had adequate international exposure and here was the opportunity.

After a year or so as a beginner I became a full member of the IUPAC Commission on Inorganic Nomenclature and spent time every summer for some years in that service, usually in Europe. Finally I wound up as chair of the Inorganic Nomenclature Commission, and it was my privilege to serve in that capacity during the time when the Commission produced the current volume of the ultimate nomenclature reference, the Red Book on Inorganic Nomenclature. Having successfully led the Inorganic Chemistry Division through that process I began to work my way through the officer positions of IUPAC. I was division secretary, when I was approached by the American Chemical Society with a still more challenging possibility. While these developments were going on I moved from Ohio State University to the University of Kansas. The move occurred in 1988. In all fairness, I have always been very active in the service of the professional organizations that serve our societies and communities.

I will come back to this service later. First I want to go back to the subject of oxygen carriers because this cyclidene chemistry was Ohio State Chemistry and my service history moves me to the University of Kansas at this point in time.

JAH: OK it sounds like you know where you want to take off, so proceed.

DHB: I was talking about changing subjects and focusing our work on creating the first non-porphyrin iron-based oxygen carrier. This led us to the cyclidenes and for the purposes of our discussion, the general structure of the cyclidene we sought can be thought of as involving a fusion of two perpendicular rings, one being a tetraaza macrocycle that encompasses the metal ion and the other acting as a bridge going over the top of the macrocyclic complex. We made cyclidenes with chelating macrocycles of 14-, 15-, and 16-members, and the bridge creating a cavity around one coordination site varied in length from two carbon atoms (an ethylene group) to as many as 20 methylene groups. In addition, we were able to suspend large aromatic groups above the cavity to provide a sizeable hydrophobic volume. We could also suspend polar groups such as carboxylates, hydroxyls, or amines, above the metal ion from this bridging unit. The cyclidenes were first discovered and prepared by Chris Hipp in our labs by extreme modification of a well known family of ligands. The version having the cavity, the lacunar complexes, were first prepared and characterized by Wayne Schammel as their nickel complexes and the first crystal structure was determined by Kristin Bowman-Mertes (now Kristin Bowman-James), and Gary Christoph. Remarkably, that first cyclidene compound, which had a *m*-xylylene bridging group, existed in two isomeric forms and the crystal structure was available, early on, only for the isomer that revealed the expected structure. That ligand went submissively onto cobalt(II) and Jim Stevens soon had shown that the cobalt cyclidene complex binds O_2 as well as coboglobin itself. However, attempts to synthesize the corresponding iron complex went slowly, one might say, grudgingly. The second isomer, of unknown structure, gave an iron complex that showed an interesting reaction with oxygen. Most simply stated, solutions of this complex changed colors when oxygen was bubbled through them and the color quickly reversed if nitrogen was then bubbled through the solution. While this looked like O_2 binding, that was not the case. The reaction associated with the color change is a striking example of a reversible redox reaction rather than simple O_2 binding. Fortunately, prior to any misinformed publication, Larry Zimmer solved the structure and found the complex to be the dimer with two *m*-xylylene bridges linking a pair of macrocyclic metal complexes.

In the meantime, the Busch group adopted a very unusual organizational plan (for us) which made use of all of our available resources in order to confront the issue of the monomeric iron cyclidene O_2 carrier. Everyone was encouraged to divert their attention to the problem of synthesis of that compound and demonstration of its efficacy—if they had any idea how to make and isolate a version of the iron(II) compound that actually worked. Also, we agreed that it was ok to work alone or in collaboration with any number of other group members. Overall some 18 or 19 skilled high energy scientists were all trying to make this thing work. Norman Herron solved the problem by assuming that the compound we sought would not be encountered in its optimally stable form and/or conditions during the discovery experiments. Once one has even a crudely purified reactive molecule in the lab it is soon possible to improve and optimize it. Consequently, we were soon able to make lots of the purified compounds and report on the first truly synthetic iron—based O_2 carrier, that uses a macrocyclic ligand that is very unlike the porphyrin ligand of nature.

At this point it should be emphasized that the reason these iron O_2 carriers work at all is because the cavity in which the O_2 is bound hinders autoxidation mechanisms since all O_2 carriers are subject to irreversible oxidation. The question simply is “how fast is the spontaneous intramolecular oxidation of the O_2 adduct?” Cyclidenes received substantial attention and we were asked to consider synthetic O_2 carriers for synthetic blood systems, a familiar subject, and industry inquired about the possibility of using these carriers to separate air in competition with the distillation of air. More about that later.

The new cyclidene O_2 carriers offered a unique opportunity to provide parallel studies to those already underway in the case of iron porphyrins. For example, attempts to control the space above and below nature's flat porphyrin ring have not been dramatically successful in model compounds, despite beautiful synthetic procedures and products. Early results with iron cyclidenes showed that a relatively short bridging group actually distorted the normally linear Fe–CO linkage, resulting in markedly reduced affinity for CO in that version of the cyclidene complex. The extreme variability of cavity size and character accessible to cyclidenes allowed us to expand the studies to enzyme models in which substrates were bound (for the most part hydrophobically) within the cavities in addition to the oxidant, O_2. A functional model was designed for the ternary complex of activated cytochrome P450 but with a complex having no porphyrin ligand. The essential studies were led by Ken Takeuchi and Tom Meade and contributions were made by Whei-Lu Kwik, and Norman Herron. Exciting days were many during the developing of these ground breaking new molecules.

Kristin Bowman's crystal structure that proved Wayne Schammel had a lacunar complex (1979).
The marvelous properties of Jim Steven's lacunar cobalt(II) cyclidene O_2 carrier (1980).
The day Norman Herron proved we had the first reversible fully functional truly synthetic iron-based O_2 carrier (1981).
The first proof, by NMR, that Ken Takeuchi's O_2 binding host molecule actually binds organic ligands in water solution (1981).
Tom Meade's demonstration of the ternary catalyst:oxidant:substrate complex in the cyclidene system (1987).

The catalytic oxidations were explored, but were not highly successful because of the vulnerability of the ligand to oxidation.

After proof of concept, an industrial company became interested in cyclidenes for air separation and our funding was divided with bio-inspired work continuing under federal sponsorship and the O_2 complexation diverting to industrial sponsorship. The industrial goal was simple but extremely demanding. If a homogeneous O_2 carrier could perform with a lifetime of many years, then such a separation would be competitive with the distillation of liquid air. This produced multiple research programs in our labs and those of our sponsors on the kinetics and mechanisms of decomposition of the O_2 carriers of cyclidenes, the synthesis and testing of many other families of O_2 carriers, and the redesign of cyclidenes and many other families of O_2 carriers. Recognizing that, understandably, in the case of porphyrins, four vertical posts evenly spaced about the ligand were at least as effective as the presence of a cavity at producing reversible O_2 binding, pillored cyclidenes were designed and studied, mainly by Dorai Ramprasad. Also, many of the families of macrocyclic cobalt(II) complexes that had been produced in earlier decades in our labs were again explored for O_2 binding, mostly with some, but limited success. Kim Lance explored the BF_2^+ bridged dimethylglyoxime ligands; Rita Delgado and Mark Glogowski studied the β-diketo-Schiff base ligands; Susan Ransohoff expanded work on bridged salicylidene Schiff base ligands, and Sharlene Dzugan altered the macrocycle derived from β-diketones and *o*-phenylenediamines to produce interesting O_2 carriers (1990). Success was more limited than the promise of the cyclidenes. After all, we had already used nature as the screen for O_2 binding and it had directed us to the cyclidenes.

Autoxidation behavior of the O_2 carriers. Kinetic studies of the O_2 oxidation of the iron(II) and cobalt(II) complexes gave very different results for the two metal ions using the cyclidenes (Soodan Kim, Alexandra Sauer-Masarwa, P. Richard Warburton, Carol Fendrick, Lyndel Dickerson (1993–1996).) Outer sphere electron transfer dominates the autoxidation process for the lacunar cyclidene complexes of iron(II) and the process occurs under mild conditions, so that iron(III) complex formation is competitive with O_2 adduct formation in the case of the iron cyclidene complexes. The good news is that once oxidized, the iron(III) cyclidene complex can be simply reduced back to the iron(II) form; i.e., iron(II) cyclidene autoxidation is reversible.

In contrast, the observed O_2 oxidations of cobalt(II) cyclidene complexes can be quite slow but proceed by pathways that involve proton activation and are accompanied by ligand destruction. Chemically, these oxidation processes involve extraction of the most active hydrogen atoms from the ligand. The simplest of cyclidenes contain hydrogen atoms on their amino groups. These O_2 carriers are autoxidized in minutes under operating conditions. If alkyl groups replace all amino hydrogen atoms, the half-life of the operating O_2 carrier increases by orders of magnitude. However, a few of the methyl groups in the simplest of these cyclidenes ionize to produce conjugated anions, and the hydrogen atoms associated with these ionizations are implicated in autoxidation processes. Replacing the suspected methyl groups with phenyl groups increases the half-life for operating of the O_2 carrier, again by orders of magnitude. But in the macrocycle itself, there is a methylene group that has an ionizable/extractable hydrogen and this is where we left the system. At this stage we had improved the in-service lifetime of the O_2 carrier by between 4 and 5 orders of magnitude from where we started (Sasha Kolchinski 1997).

Kinetics of the O_2 and CO binding processes. The excellent behavior of the cobalt(II) cyclidene O_2 carriers and the broad ranging structural variations available made those compounds especially useful for the study of the of O_2 binding process. Elena Rybak-Akimova led those studies, joined by Mohamad Masarwa, Keith Marek, Rebecca Roesner, William Otto, Peter Deardorf, and Richard Warburton (1997–1998). Molecular modeling by Wang Kan Lin figured strongly in these studies. The most unusual aspect of these studies was the binding of O_2 to a metal ion, cobalt(II), in a broad range of vacant sites, many of them in confined cavities. Low activation enthalpies of a few kcal/mol and sensitivity to even small steric and solvent effects are consistent with the radical nature of these processes. Theoretical studies by Elena Rybak-Akimova, Gouri S. Jas, and Yanpei Deng under the guidance of Professor Krzysztof Kuczera (1998), elucidated the varying effect of solvent on planar, saddle shaped, and lacunar cyclidenes.

Attempts to achieve similar experimental results with O_2 binding on the iron complexes were thwarted by the facile parallel autoxidation reaction and this sidetracked our attention to the reaction of the iron(II) cyclidenes with carbon monoxide. Maria Buchalova was the principal researcher, aided early by Richard Warburton, and Maria performed the pressure and temperature dependent measurements in the laboratories of Professor Rudi van Eldik in Germany (1998). In acetonitrile solution, the 5-coordinate complex, bound to one molecule of solvent, reacts with CO via an early transition state, first forming a high spin adduct in the transition sate that transforms to the low spin product. Bond breaking involves a spin state change and a late transition state.

JAH: This would be a good time to return our discussion to service to professional organizations, specifically, the ACS, AAAS, etc.

DHB: Good timing—this applies to my time at KU. My contributions to IUPAC were interrupted by an invitation from the ACS to become a candidate for the presidency. I accepted that challenge because I believe that too few in the research community are willing to lead the American Chemical Society. I quickly learned why. To begin with, one hangs one's hat with those of a very mixed group. The ACS Council is the conglomerate of all chemists and the ACS Board is selected from this diverse group. Many researchers aren't prepared to address the enormous breadth of issues that concern their profession. I loved it because I believe that each of us has a unique message to share with the rest. In the presidential succession of the American Chemical Society I had the opportunity to make contributions to our profession and even more broad contributions that otherwise wouldn't have been possible.

It was my privilege to be the main actor in securing a future for the Green Chemistry Institute, GCI, which I continue to serve in its present form as the ACS GCI. This institution is the dynamic functioning voice, conscience and vision of sustainability for our chemical profession and it belongs as it is and where it is in the heart of the American Chemical Society. Dr. Bob Peoples, its director, personifies the potential of green chemistry to stabilize this great ship, Planet Earth, in the challenging sea of our universe.

Having served Chemical Abstracts Service I also focused on the outstanding services of CAS and how and where those services are dispersed. We may all recall that industry paid much of the cost of developing the computer versions of Chemical Abstracts, search engines and all. Actually making SciFinder Scholar available and useful to all of academe became a mission to me. At every opportunity, without expressing authority, but only opinion, I harped to their leader, the highly talented Robert J. Massie until SciFinder, first became available to the large universities. He reminded me of a discussion that lasted an entire flight from Honolulu to Los Angeles. Then I pushed until Scifinder became available at a level that was actually really useful. After that the mission shifted to availability to 4-year colleges, and then to community colleges and, effectively to all in academe who need to have access to the literature of chemistry. I think of the literature as a part of my realm and I felt a deep need to solve the problem if I could. I believe everyone is at least considered now.

From childhood I have been color and gender blind. Remarkably, my little hometown had no black residents, but the nearest medical doctor was black and lived a short distance away, at the edge of a village named Colp. I could never forget my father's story about running from the scene of an auto accident in Carterville carrying my injured infant body to this Dr. in order that I might have his care. While growing up, my best friend was always my sister, Joanna. My first two graduate students were women, and my research group reflected this open and equal character. It was natural for me to strongly support ACS actions that moved any and all disadvantaged groups toward equality. I also had the opportunity to promote leadership development as an initiative that benefits all individuals, our ACS, and our profession.

Being ACS President involves being a lot of places and doing a lot of things with and for a lot of people. I really enjoyed that as well. In the year 2000, my records show that I went to the airport 50 times to fly on ACS business, most often with more than one event, occasion, and/or destination. It was a lot of fun, but, I like to joke that like the army it helped me but taught me bad habits. In the army I really learned to be independent and to take command, but I also learned to smoke and drink. As an ACS officer I learned to speak freely about subjects in which I was and am not expert. But I had a lot of backing in speech writers and the like. Let's talk about something else.

JAH: Actually you have said relatively little about the chemical industry today. Yet I remember your having told me earlier that you wouldn't have been in academia without the help of industry. How about that?

DHB: This covers a long range of time. – in response to your question – *My Dupont Story*: The simple truth is that when I started work, academic salaries were much lower than those in industry and, thinking of myself as the father of 3 children, one of the reasons I chose Ohio State was that the salary ($5400 for 9 months) was substantially higher than those at the other universities I had visited. Memories of serious hardship are not easily lost. Back to industry, in the summer before my second year at OSU (1956), I received a generous offer to serve as a consultant, solely to E.I. du Pont de Nemours & Co., Inc. I was to receive a monthly retainer of $100 per month, a daily stipend at the remarkable rate of $100 per day when consulting with their personnel at any of their locations, and all my expenses would be paid. I would be obligated to serve at least two business weeks each year with the expectation of serving substantially more, perhaps twice that amount. For the next 25 plus years I spent a week in Wilmington, Delaware, twice each year and two or three, 1 or 2 day visits consulting at other locations. The compensation equaled something like half of my annual OSU salary and that made an academic career financially viable. I was assigned to the new Polymer Intermediates Division but actually consulted with all divisions of Dupont, except Central Research. The experience was totally inspiring and should have been exhausting, but I didn't notice. I feel certain this opportunity arose because of the confidence held for me by two of the influential faculty at the University of Illinois, my Ph.D. Alma Mater, Professors Karl "Speed" Marvel and Chair Roger "The Boss" Adams. I know that they were held in the highest possible esteem at Dupont. Both had been Dupont consultants for many years. Now for contrast, or maybe payback, let me tell you about the best thing I ever did for Dupont (aside from helping Dupont share the 1987 Nobel prize). During one of those visits to Wilmington, I was invited to lunch at the Hotel Dupont with the research director of the Plastics Department, Frank McGrew. Shortly after we got acquainted, the director asked me if it was within the capabilities of the science and technology of the time to develop a process to make adiponitrile starting with butadiene and HCN. I simply replied yes sir it certainly is, and he asked the obvious question. Ok, how do you make adiponitrile starting with butadiene and HCN? I said I don't know how. At that point he wanted to know what was going on. Was I playing with him or what? I apologized and said that I had simply answered his question, but I should have expanded on my answer. Yes the science has advanced to the point where it should be possible to develop the process he wants, but no one has done so and, consequently, I don't know how to do what he wants to do. Now, please let me expand on this subject a bit further and forgive me for being very honest with you. This can be done and it could be done here, but not in the way Dupont does research in its operating divisions. There is essentially no reasonable probability of success if you assign this problem to one of your people and expect them to solve it in 90 days—or something of the sort. You will need to find a person who has an appropriate background and is sufficiently creative to do the job and, in my opinion, give that person a couple of years to come up with proof of concept. McGrew then pondered and responded very positively. "I believe you have thought about these matters a good bit and I think this is important enough and the potential value is great enough that I will take your advice, but only if I can find that person. Do we have anyone who can do the job?" I answered that there are probably many at Dupont who could achieve this challenging goal. I can think of a few and I named some. The director wrote the names down. We finished lunch talking about golf and the weather and he and I parted.

Years later a close acquaintance at Dupont told me that the purpose of the luncheon I just described was to hire me to develop the butadiene/HCN process. I find that hard to believe. Anyway, within months I learned that Bill Drinkard had been reassigned temporarily to Central Research to work on the adiponitrile project and when I next visited Dupont, some 3 months later, I spent a few hours with Bill. Dr. Drinkard and I did our Ph.D. work with the same mentor, John C. Bailar at the University of Illinois, so we were of a brotherhood from the beginning. Bill told me that when he arrived at Central Research, Director Ted Cairns greeted him kindly and said you are most welcome. You are wasting your time, but you are welcome to join us and share your learning with us. Bill Drinkard was a kind and quiet man who would not know how to be offensive. On the other hand he could not let a challenge like that rest undefeated and eventually he won overwhelmingly. There is a slight misunderstanding in the report in the Dupont book (D.A. Hounshell and J.K. Smith Jr., "Science and Corporate Strategy, Dupont R&D 1902–1980", p. 581, Cambridge University Press, NY, 1988). The initial discovery research in Central Research laboratories was expanded under Bill Drinkard's leadership, through the Plastic Department laboratories on site. Bill's leadership continued as the work moved to the Texas plant site, clear up until the plant was built and, to the best of my knowledge, on stream.

His new boss, Frank McGrew, did all that I had recommended except giving Bill only one (1) year for proof of concept. I was Bill's sounding board and he tried everything imaginable. Finally he settled on liquid HCN as the medium for the reaction and a nickel phosphine catalyst. At zero hour he had his proof of concept. What remained were such issues as identifying the best ligand, improving isomer ratios, addressing safety matters, and the like. At the end of the year Frank McGrew had moved overseas and Bill's world had changed but it mattered not. In the Plastics Department, the project blossomed, and then boomed. Plans for the first plant began. Bill and his team of approximately 30 went to Texas to build the plant and I visited them there. Finally they built two more plants, a second in Texas and one in France. Then Bill Drinkard didn't have anything to do—so he was made a manager at Central Research, CR, which he promptly renamed as Central Research and Development, CRD. And CRD became a rare organization in the chemical industry. Research and development were coordinated. Without ever having said a word about it, Bill Drinkard had noticed that Central Research had been of little practical value to Dupont over the years and now he had corrected that misuse of a powerful resource, at a time when corporate research operations were generally disappearing. In the end, finding a big enough job for Bill Drinkard was the best thing I ever did for Dupont.

Fig. 4. (1999) A proper team for the good life. Jeri, Daryle, Rhodesian Ridgeback, *Ruby*, and the Arabian horse, *Rad*, on the 23 acre Busch homeplace in Lawrence, Kansas; the cat, Samantha, chose not be participate in the photo.

For 3M—a blue dye for carbonless paper: In the mid 1980s, the 3M Company came to me saying Al Cotton isn't available, so would I help them design a certain molecule and overcome a problem that really bothered them? When they told me the problem, I understood why Al wasn't available; he never did design molecules. What they wanted was to change the color of their dye from a pale pinkish purple to deep blue or, preferably black. So why me? The dye was an insoluble nickel complex with an N-substituted dithiooxamide. There were three reasons why I should take on this problem besides the fact that I do design large molecules. I already knew about the parent compound which had been tested positive for use as a polarized colorant in lenses for sun glasses. In fact, I knew exactly the right student to work on the project, Nusrallah Jubran, and he needed support to come to Ohio State and work with me. Finally, this would be a chance to explore the controlling factors in the energetics of nickel(II) charge transfer spectra, and I had a colleague who might, later on, want to collaborate on the theory. I said yes, the student joined me in late spring, he went to work, and within weeks we had a beautiful deep blue insoluble product. I called the company contact and described our terrific early success, invited them down and offered to send samples. The samples went forward and a few days later a call came back. Yep. You solved the problem. Terrific, but we will support you anyway! Shocking thought. Too much success could mean no more money. The work went on for several years. My colleague, Professor Bruce Bursten joined me as a collaborator in theoretical work on the spectroscopy, and the product, which was the best in the field, was the result of some really good science and generated valuable collaborations.

For P&G—the exceptionally selective KU catalyst: In 1996, one of the largest manufacturers of home products asked me to consider designing a catalyst for use with H_2O_2 as a laundry bleach. After some consideration I became fascinated with the challenge. My translation of the request was "*design a first row transition metal complex that would selectively oxidize only the most vulnerable of color sources while surviving in a solution for something like an hour at a temperature somewhere around 50 °C at a pH of 10 or so*". The likely metals, from my perspective, were iron, manganese, and copper because of their rich redox chemistry and because of the range of use nature makes of their compounds in biological redox systems. However, the greatest challenge was simply that of stability of the catalyst under common laundry conditions and the vision of rust or MnO_2 deposited on white clothing; that challenge really attracted my interest. I liked manganese for the catalyst because of its many intermediate oxidation states and multiple mechanisms of oxidation. Also, manganese isn't nearly as famous for its tendency to retreat into a colorful and insoluble oxide like rust. I had just recruited a top graduate student, Tim Hubin, who was notable for being among the first "Self Fellows", a highly touted fellowship at KU. In addition our group had a bright new postdoc from Britain, Simon Collinson, who could serve as Tim's partner on this new project.

Their first task was to make what I thought was a *new* family of "cross-bridged" macrocycles, by linking a pair of *trans*-nitrogen atoms in 1,4,8,11-tetraazacyclohexadecane (cyclam) with an ethylene bridge. Then after adding the *trans*-bridge, the two remaining secondary amines in the tetradentate macrocycle were to be methylated, so that all four amino groups would be tertiary. My good researchers quickly did a thorough library search and found that the desired ligand had recently been synthesized and its metal complexes with copper(II) and zinc(II) had been published. After having tried all of the easier paths unsuccessfully, our new team followed suggestions, were soon successful, and the complexes of iron and manganese were available for their evaluation.

Fig. 5. (2001) As immediate past ACS President, Daryle presents Priestley Award to Professor Fred Basolo at the National ACS Meeting.

The compounds exceeded our expectations, performing catalytic 1-electron H_2O_2 oxidations only at extremely low energy; i.e., cleaving C–H bonds of <82 kcal/mol, so that very little radical chemistry is expected with this system. Of still more importance, the 2-electron chemistry occurs by a mechanism that is unusual for manganese: it occurs by Lewis acid activation of the hydrogen peroxide molecule by the Mn(IV) complex, rather than by the more common Groves rebound mechanism. The result is an exceptionally clean H_2O_2 catalyst for a very popular household detergent. Our work has been supported very recently by detailed theoretical studies of both mechanisms (A. Haras and T. Ziegler, Can. J. Chem. 87 (2009) 33–38).

JAH: How about the stability of the catalyst? Will it give up the metal ion to precipitate an oxide on the surface of clothing?

DHB: Thanks. I should have told you about that advantage of this catalyst. The main reason I took on this design challenge was that I was confident I could prevent that disaster. In fact the in-service life times of these catalysts can be amazing. One copper system, that we chose to study because of the lability of copper complexes, gave an improvement in half-life in strong acid from 2 s for the complex of the simple folded macrocycle to >8 years for the complex of the corresponding bridged macrocycle. Stability in base is even greater. The effect of “MJF” is profound, but all elements in the design are critical. Our manganese catalyst isn't quite that good but it functions quite a while in base at 50 °C and the fabric is safe from possible metal oxide deposits. The total story is actually fantastic and I'm not sure anyone knows it but me.

JAH: I judge that story it too long to tell here. Where do we go from here? You are more deeply involved with industry than ever today, I believe.

DHB: Our present industrial collaboration occurs on a grand scale, involving 15 members, most of them from industry's giants, but it began because my postdoc Dr. Elena Rybak-Akimova wanted to try some experiments in super critical carbon dioxide and that brought me together with Professor Bala Subramaniam in Chemical and Petroleum Engineering at the University of Kansas. Subsequently, Bala suggested that he and I might write a joint Center Proposal on catalytic oxidations in super critical CO_2 using oxygen carriers as the catalysts. It took us three tries but eventually we were funded as an NSF Engineering Research Center (NSF/ERC) with, at that time, the biggest federal grant received by the University of Kansas.

Industrial partners are a major requirement of NSF/ERCs and, under Bala's leadership as Director, our Center for Environmentally Beneficial Catalysis, CEBC, has attracted a growing membership including mostly major players from the traditional chemical industry: ArcherDanielsMidland, BASF Catalysts, BP-Amoco, ChevronPhillips, ConocoPhillips, Crititech Inc. Dupont, ExxonMobil, Eastman, KTec, Novozymes, PhamaRoundTable, Procter&Gamble, SI Group, and UOP-Honeywell. Thanks to NSF/ERC we acquired the resources and industrial backing and built facilities to perform collaborative research of a kind and on a scale that isn't usually possible for one or two faculty members in academe. During the immediate past, our Center for Environmentally Beneficial Catalysis has looked at what is happening in global industry and judged that this or that chemical process badly needs to be and can be replaced and proceeded to offer an alternative that is both economically and environmentally better. It isn't quite that simple. These “offerings” are bench scale, but complete enough to make economic and environmental assessments. To date we have earned very broad respect for our intellectual products but have not yet replaced a major industrial process. The first licensing has been achieved and the first major multiproject contracts with industry are in place and these are major steps forward.

In the beginning our chemistry was largely traceable to the petroleum industry, but major state of Kansas initiatives and specific industrial interests have enabled us to move boldly into the science of the developing biorefinery of the future and the industrial processing of biomass to produce both fuel and higher value chemicals. This is not to down-play the importance of petroleum chemistry going forward but to recognize the relative need for research in the area limited by decades of neglect. I must confess, most important to me, we have built an infrastructure and institution that we believe will be of great value to the University of Kansas and the State of Kansas for years to come.

JAH: This is all very general. Are there specific achievements in this recent work that you would care to focus on?

DHB: Personally I'm a relentless advocate of catalytic oxidations and that subject is a substantial fraction of the research at CEBC. I've told you about the catalyst we created for Procter and Gamble. I will tell you about just two more catalytic oxidation projects and then stop. The first involves one of the best catalysts ever discovered, methyl trioxorhenium, MTO, which has attracted the interests of no less than Espenson, Herrmann, Noyori, and Sharpless. This precious metal organometallic compound is the finest Lewis acid catalyst we have seen as a hydrogen peroxide activating catalyst. I share with most inorganic chemists a natural revulsion at the thought of an organometallic compound serving as an oxidation catalyst, but Jim Espenson's extremely thorough studies of MTO convinced me that I might make an exception in this case. Jim emphasized the fact that MTO is stable to air (O_2), water, and acid, although it is decomposed in base. In fact under oxidizing conditions, the destruction of MTO depends on both hydroxide and hydrogen peroxide and Jim and his students didn't work out the distinction between two possible pathways that we have concluded are critically different. Here is where we enter the picture.

Pressure intensive EO process. In performing its oxidation catalysis, MTO forms both 1:1 and 2:1 peroxo complexes and the question is whether the decomposition during oxidation by MTO + H_2O_2 occurs during formation of the monoperoxo complex or by the reaction of the monoperoxo complex with hydroxide. My former postdoc, new Asst. Prof. Guochuan Yin did the isotopic labeling experiments and proved that the destruction of MTO occurs during the formation of the monoperoxo complex. This provides the possibility of maximizing the in-service lifetime of MTO as an H_2O_2 activating catalyst by operating it in a cycle between the monoperoxo and the diperoxo complexes. For propylene oxide production, new plants were being built with cheaper catalysts based on titanium oxide on silicate supports. However insofar as we have been able to learn, only Bala's pressure intensive process offers a possible alternative to the prevailing high temperature process used for ethylene oxide production. We have shown that MTO/H_2O_2 in, for example, *t*-butyl alcohol can be used to produce ethylene oxide from ethylene with ~50% conversion and >95% selectivity at 40 °C, with zero solvent or substrate burning. In contrast, the existing EO process is among the worst industrial processes from the standpoint of CO_2 produced.

Let us spray for TPA. The other new oxidation system I want to tell you about is our absolutely flashy alternative for the Mid-Century Process, MCP, for the oxidation of *p*-xylene to terephthalic acid, TPA. (Perhaps we should call it the Millennial Process.) MCP is one of the largest manufacturing processes in the chemical industry and the product TPA is used along with a glycol, most often, ethylene glycol, to make a polyester. In oxidizing *p*-xylene to TPA, there are eight intermediates and a few of these create problems. The final product TPA is almost insoluble in the reaction solvent and precipitates as it forms even at the high temperature. *p*-Toluic acid, *p*-TA, is difficult to oxidize and does tend to accumulate. 4-Carboxybenzaldehyde, 4-CBA, is co-crystallized in the TPA, possibly as it forms, and is associated with discoloration of the product. So, these two intermediates force severe conditions on the MidCentury Process, conditions so severe that the contents of the reactor are beat into a froth by the plunging air and vigorous stirring and a very substantial fraction of the reactor volume must be reserved for the turbulence and foam, 30–33%.

Suspecting that the problem is that the high temperature overcomes activation barriers but obviates gas solubility so that optimization dictates maximum gas/liquid interface, Bala proposed experiments with a simple spray apparatus because tiny droplets maximize that surface/interface area. This simple, seemingly peculiar treatment may turn out to be an alternative way of introducing the reacting solution into the existing huge reactor. If that were followed by no change in the solids management, but with the advantage that no follow-up chemical treatment were necessary, and, also, much decreased contact time and decreased solvent burning, the benefits are enormous. Results to date are amazing and patent has been filed.

Expanding into biomass. At the present time, much of the effort of CEBC is directed toward new programs in biomass conversion, a realm crying for creativity on the part of today's chemists. Ozone looks great and in liquid CO_2 it seems to focus on 2-electron chemistry. Also O_3 plus CO_2 provides a great opportunity for selectivity because ozone doesn't attack that solvent whereas it reacts with most organic solvents; patent filed. The production of alternative intermediates from biomass is a broad area with many neat subjects, and we are focusing our expertise on some of industry's favorite processes there as well. Our first publications and patent applications are, as indicated, in process. We are teaming with industrial partners in some of these endeavors. Substantial new funding for research in this area has been established for CEBC and its members, but this is still early in view of our limited visibility in the field. Our center continues to enjoy the support of a powerful array of industrial partners and has been recognized as a Center of Excellence by the University of Kansas. With the latter recognition comes a modest but sound level of support from industrial, university and State of Kansas sources. Chemical research is as exciting and as important as it ever was. I guess that pretty well tells you where we are today.

Fig. 6. (2009) Immediate past ACS President Bruce Bursten recognizes Daryle as one of the 0.1% of the members of the ACS who were named in the Inaugural Class of American Chemical Society Fellows. Years earlier Daryle led in hiring Bruce at Ohio State and Bruce lived with Jeri, Daryle and family until his home became available. Bruce responded by, unannounced, asking Daryle to speak for the Fellows at the inaugural ceremony.

JAH: It is difficult bringing this discussion to an end. That is consistent with my next question. How do you plan to end your career? I will take advantage of my position and not give you first comment. I predicted that you would never retire.

DHB: In the past I could only have said I have no plans. This summer and last, I did very little work, just attended my regularly scheduled meetings and looked after a few critical matters.

I love people and science and will probably find a way to continue to aid CEBC as long as I'm genuinely useful. Also it is difficult to abandon the ACS Green Chemistry Institute.

I want to take this opportunity to thank everyone who has contributed to this volume. First I thank our editor Barry Lever for the invitation to experience this happy event, and, I trust, my inseparable family and students, at all levels of seniority, are also grateful. Second, I hasten to thank Professor Elena Rybak-Akimova and Professor Becky Roesner for organizing and editing this special volume. Although it would go without saying, that isn't good enough. Thank you Joe, Professor Joseph A. Heppert for guiding this session. Most important of all I must thank our colleagues who have contributed their valuable manuscripts to this volume. Our international chemical community has always been both marvelously warm and friendly. I am always happy about our friendships and the sharing of the excitement of chemistry which will be forever young. It has been a great privilege and joy, being a member of the research and teaching community in the profession of chemistry.

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