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Celebration of inorganic lives
Interview with Fausto Calderazzo
(University of Pisa)

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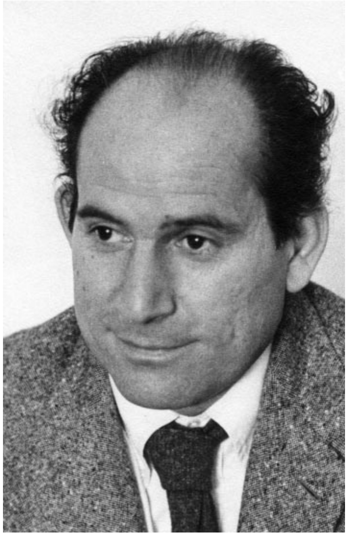

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1. Brief biographical sketch

Fausto Calderazzo was born in Parma, Italy, on March 8th 1930. He graduated in Chemistry from the University of Firenze (supervisor: Professor Luigi Sacconi, thesis on coordination compounds of nickel(II)) in July 1952 and, after the compulsory military service, he joined the research group of Professor Giulio Natta, Piero Pino and Raffaele Ercoli, Institute of Industrial Chemistry, Polytechnic of Milan, in January 1954. This collaboration continued until the end of 1962, with an interruption of about 14 months in 1960–61, when he was a recipient of an A.P. Sloan Foundation fellowship at Massachusetts Institute of Technology within the research group of Professor F.A. Cotton. Back in Italy and at the Polytechnic Institute of Milan for about a year he finally joined the Cyanamid European Research Institute, initially as Research Associate (1963–1965) and then as Leader of the Synthetic Inorganic Chemistry Group for the about 3 years until the end of 1968. From then on he has been Professor of General and Inorganic Chemistry at the University of Pisa, Italy; he has also taught advanced courses of inorganic chemistry at the Scuola Normale Superiore of Pisa. Calderazzo is or has been a member of the editorial or advisory boards of several international scientific journals (Journal of Organometallic Chemistry, Inorganic Chemistry, Dalton Transactions, Organometallics); he is a Foreign Associate of Inorganic Syntheses (1982) and has served as editor of Gazzetta Chimica Italiana from 1985 to its merging with other European journals. He is or has been a member of some international conference committees, such as the International Conferences on Organometallic Chemistry (ICOMC), and has chaired the 1988 ICOMC in Torino, Italy. He is an honorary member (1987) of the Société Royale de Chimie (formerly Société Chimique de Belgique) and of the Società Chimica Italiana (1991); he is a non-resident member of the Istituto Lombardo, Accademia di Scienze e Lettere (Milano, 1986) and a corresponding member of the Accademia Nazionale dei Lincei (1989). He is President of the Interuniversity Consortium on Chemical Reactivity and Catalysis; he has received the A. Miolati Award in Inorganic Chemistry (1988), the GICO (Gruppo Interdivisionale di Chimica Organometallica) 1994 Award, and was the first recipient of the L. Sacconi medal in June 1998. The scientific activity of Professor Calderazzo has produced about 250 papers on several areas of inorganic chemistry. About one half of his papers deal with the properties of metal carbonyls; particularly relevant in this area are the studies on hexacarbonylvanadium and on the carbonyl derivatives of Groups 4 and 5, and on carbonyl complexes of late transition metal cations, in addition to the investigations on the mechanism of the carbon monoxide insertion reaction. Metal–arene and metal–cyclopentadienyl derivatives have also been investigated. In recent years, within the domain of organometallic complexes, particular attention has been payed to the study of the change of properties within vertical sequences of transition elements, in an attempt to find trends of common behaviour. Furthermore, efforts have been dedicated to the reactions of metal-centered and ligand-centered reactions with chemical elements, such as iodine and chalcogens, respectively. Among the recent acquisitions carried out at the University of Pisa, mention should be made of the studies on dialkylcarbamato derivatives of transition and nontransition elements and the use of these relatively new species for the implantation of metal cations in inorganic matrices.

2. Interview of Fausto Calderazzo—Interviewer, Rinaldo Poli

Dijon, November 13, 1998

R.P. Can you recall what stimulated your initial interest in science and particularly in chemistry?

I had to decide at the age of 17 at the end of my high-school education; I remember that I wanted to work in a scientific or technological field, but I was uncertain between chemistry and medicine. Finally, I decided on chemistry; I don't remember for certain what made me decide on chemistry, probably the idea that it would be easier later to find a job in industry than in a hospital. I always thought that if I had studied medicine, I could have been a good surgeon.

R.P. What made you chose the University of Florence for your advanced studies and in particular Luigi Sacconi as your research advisor?

The University of Florence was the easiest choice since I lived in Florence and the University had good teachers. However, I did consider the possibility of studying in Bologna, which is about 80 km away from Florence and can be easily reached by train. Presumably I had considered commuting between Florence and Bologna without much of a problem. I even remember of visiting the Student Office of the University of Bologna where I asked silly questions of one of the employees there who could not answer properly. Once I became a student of the University of Florence I passed my exams and by the end of the fourth year I had finished all my exams. I therefore had time to spare and I asked Professors Musante and Parrini if I could attend their research laboratory, which was a laboratory of organic chemistry, in order to become acquainted with the current experimental operations, which would have increased my normal curriculum. At the beginning of the fifth academic year, after the experience I had in that laboratory, the obvious choice for the experimental thesis was to remain in that laboratory. As a matter of fact I was accepted as a student, the project being that a research subject would have been assigned to me, presumably on synthetic organic chemistry. However, as far as I recall my activity in that laboratory did not last for more than one morning. During that first morning I saw Professor Sacconi, who at that time was assistant Professor of Physical Chemistry, coming into the laboratory and speaking with Professor Musante. I suspect that I was the reason for the discussion: as a matter of fact, in the afternoon of the same day I was transferred to the laboratory of Professor Sacconi. I can only guess that Professor Sacconi was shorter of students than Professor Musante and Parrini; I have always forgotten to ask Professor Sacconi what exactly happened on that morning. Of course, this short talk that morning between supervisors considerably changed the future developments of my scientific career. I started to work with Sacconi on nickel complexes of hydrazides. Sacconi was a good teacher and an excellent organizer of research; last but not least he had an outstanding intuition for prominent projects of research. His research projects were relevant and long-range. Also, he was quite aware of the fact that publication of results, and the journal in which they are published are as important as the quality of the research. As early as 1952 Sacconi had published some outstanding results in the Journal of the American Chemical Society. Also, Sacconi was a person with wide cultural interests and he liked to talk to his students about cultural matters aside from chemistry, such as, for example, recent movies. I successfully concluded my laboratory training with reciprocal satisfaction at the end of July 1952. I came out of University with a degree in Chemistry, ready to go and spend a year and half in the Army. I only had about a week to recover from the effort of writing the thesis and defending it when I left to go to the deep south of Italy for the usual training. I had no idea exactly what military life would be like and very quickly I discovered the good and not so good aspects of it.

R.P. In perspective, how do you compare teaching and research during those years with the present situation?

When I entered the University of Florence in November 1947, the war had been over a little more than 2 years and life was still very difficult for everybody. However, things were always reduced to the essential. Teaching laboratories at the University dealt with simple experiments, carried out with rather inexpensive materials; perhaps this was in a sense an advantage because we, as students, were able to grasp more easily the significance of certain experiments. This is sometimes more difficult now for our students than for us at that time. Our teaching has certainly become more sophisticated but not necessarily more effective.

R.P. Tell us what led to your first employment at the Polytechnic of Milano and how you started to get interested in organometallic chemistry

After my degree in Chemistry I finished my military service in December 1953. I was lucky enough to join the research group of Professor Natta at the Polytechnic Institute of Milan as a research associate. A series of fortunate circumstances led to this opportunity. The most important one is that several people who had received their degree in Chemistry from the University of Florence before me, had already joined the research team of Professor Natta, namely Piero Pino who had graduated in 1943 under the supervision of Professor Adolfo Quilico, Raffaele Ercoli, Giorgio Mazzanti, Franco Piacenti, Paolo Chini, Gino Caroti. All of these people later took up important positions in Industry or in the University. In January 1954 I began my research at the Polytechnic Institute and in March 1954 organometallic chemistry became the main interest. My first research topic in this field was the so-called stoichiometric hydroformylation reaction, which requires the use of relatively large quantities of octacarbonyldicobalt, not commercially available of course at that time, so we had to prepare this compound ourselves. This compound was converted to dodecacarbonyltetracobalt under the combined action of dihydrogen and olefins and this work was done under the supervision of Piero Pino. However, a further step was represented by our intention to enter the new area of organometallic chemistry, which was pioneered by Wilkinson and Fischer on cyclopentadienyl and arene complexes of transition metals. The laboratory in Milano was very well equiped for high-pressure work, but initially it was not adequate for work under an inert atmosphere and we soon realized that if we wanted to work with the new classes of compounds we were reading about in the literature we had to organize ourselves with a completely new conception of carrying out reactions and working up products. I remember that the first really difficult organometallic compound we decided to prepare was biscyclopentadienylchromium(II). I believe that $CrCp_2$ was prepared in Milano early in 1956 for two main reasons: to test our ability to handle nasty air-sensitive compounds and to repeat an experiment described a year earlier by E.O. Fischer and coworkers about the synthesis of hexacarbonylchromium by reacting $CrCp_2$ with carbon monoxide under high pressure. In 1957 we published a new synthesis of $Cr(CO)_6$ in the Journal of the American Chemical Society. This new method consisted of starting from an easily accessible compound of chromium in an usual oxidation state and reducing it in the presence of carbon monoxide and an electropositive metal, a type of reaction which had rarely been tried before. However, we also wanted to discover what happened to our reductive carbonylation system by using an already reduced compound of chromium. This led us to prepare chromium(II) acetate, which of course requires a controlled atmosphere for its synthesis. This presented us with the possibility of testing our experimental efficiency in preparing such an air-sensitive compound with experimental tools which were rather deficient for handling readily oxidized products. This was the beginning of our successful attempts to design new (for us) glassware and a new methodology for handling air-sensitive compounds. A good glassblower used to follow patiently and competently our instructions. Years later I discovered that just about the same type of glassware was being used in other laboratories in other countries, thus proving that there is usually one good solution to any given problem and therefore the same track is probably used by different people. Having large quantities of hexacarbonylchromium(0) at our disposal, we began to study its chemistry. It was soon realized that carbon monoxide substitution from $Cr(CO)_6$ yields the corresponding arene derivatives and we discovered, at the same time as Nicholls and Whiting in Great Britain, that both the arene ligand of chromium(0) and the cyclopentadienyl ligand of vanadium(I) in $CpV(CO)_4$ could be subjected to a Friedel–Crafts type of electrophilic substitution. This was the beginning of several studies on aromatic substitutions for metal-complexed arene ligands within our group and outside. We also studied the isotopic exchange between ^{14}CO and hexacarbonylchromium(0). We found that the reaction is first-order in metal concentration and independent of the concentration of carbon monoxide. The activation energy was established to be about 39 kcal mol^{-1}. In acquiring these results most important was the presence at the Polytechnic Institute of Milano of the late Gastone Paiaro—he died about a year ago—who had received his degree at the University of Padova under the supervision of Antonino Fava, an expert of reaction mechanisms, both organic and inorganic. Our studies in Milano happened to be very timely, since they almost coincided with the similar studies Basolo and Wojcicki were carrying out on the carbonyl substitution reactions: our paper on chromium was released to the journal on September 1960 and Basolo and Wojcicki had presented a paper at the 17th IUPAC Congress in Munich a year earlier on the mechanism of the substitution reactions on octacarbonyldicobalt(0) and tetracarbonylnickel(0), results which appeared some time later in the Journal of the American Chemical Society. I believe that this was the beginning of my first experience with the mechanism of organometallic reactions, which later on kept me busy for a long time. My first acquaintance with Professor Basolo was useful and encouraging, he was spending a sabbatical at the University of Rome at that time. As far as I recall, I first met Fred in Florence and then in Milano, on the occasion of two lectures he delivered in 1959 at these Universities.

R.P. Tell us about your personal relationship with Natta, Ercoli, Pino and other important figures of the group in Milano

The Polytechnic of Milano was an extraordinary place. Work on polymerization of olefins was going on and people were rushing new results almost every day, one after the next. There was a joke circulating that a fortuitous encounter on the main entrance of the Institute at the beginning of the working day always started with the usual question by Natta “What’s new?”. Some embarassment was noted if the same person was asked the same question in the late afternoon of the day before. I was not directly involved in the polymerization problem; basic knowledge on organometallic chemistry of transition elements was considered to be essential for the understanding of catalytic systems. Not only had Natta a tremendous intuition for the important research items, and of the capabilities of people carrying out the research, but he was able to transfer his enthusiasm for research to his affiliates. I used to see much more of Pino and Ercoli than of Natta. Natta was extremely busy in entertaining contacts with industry, namely Montecatini which sponsored our research. My activity at the Polytechnic Institute continued from 1954 to 1960; in these 6 years I mainly interacted with Raffaele Ercoli, especially after Pino had moved in November 1955 to the University of Pisa as Professor of Industrial Organic Chemistry. Incidentally, I was asked by Pino to move to Pisa with him, but at that time I remember deciding to stay in Milano: eventually I moved to the University of Pisa, but this happened 12 years later after a rather long detour through the States and Switzerland. Ercoli was really a first class scientist in terms of profoundness of his analysis of the problems; he was also a very interesting and an extremely intelligent person. He had suffered a lot during the war, but had not been bitterly hit by the events and had kept a very positive view on life. During that period I developed a close personal relationship with Paolo Chini, who had started his important and fruitful studies on metal carbonyl clusters of cobalt and on mixed metal clusters. I believe that much of the impetus for carrying out these studies, which led Paolo Chini to become an internationally well-established scientist, as a staff member of the Inorganic Chemistry Institute of the University of Milano, actually originated from the early findings on the so-called negative effect of carbon monoxide pressure on the rate of hydroformylation discovered by Natta and Ercoli and from the naturally consequent interest in the $Co_2(CO)_8/Co_4(CO)_{12}$ equilibrium.

R.P. What do you recall about the controversies of those years around the nature of hexacarbonylvanadium?

Since we had previously worked with the chromium system as we has seen before, it was an obvious extension to try the synthesis of some unknown carbonyl derivatives and the idea was to try vanadium. On the basis of the well-known EAN rule, it was to be expected that vanadium could give a dinuclear compound, as the atomic number of vanadium is odd. We set up the experiments and used high pressure and high temperature to reduce vanadium salts with the electropositive metals which we had already used for chromium. It was immediately clear from the decrease of carbon monoxide pressure and from the evolution of carbon monoxide from the crude solutions from the autoclave that carbonylation had occurred. Thus, vanadium(III) salts could be reduced in much the same way as it had been done before with chromium(III). The isolation of $V(CO)_6$ was far from being a straightforward operation; it was first necessary to realize that during the reductive carbonylation vanadium had in fact been reduced to the -I oxidation state, forming the much more stable haxacarbonylvanadate(-I). Acidification and extraction with diethylether led to the discovery of the neutral species $V(CO)_6$. This happened one afternoon during a steam-distillation under reduced pressure which was carried out by Angel Alberola, now Professor at the University of Valladolid, whereby black crystals appeared in the cold parts of the apparatus. Those black crystals were in fact of $V(CO)_6$ as we now know it. This experiment was carried out in the Autumn of 1958. Much was known about $Cr(CO)_6$, nothing was known about carbonyl derivatives on the left hand side of Group 6. Hexacarbonylvanadium(0) proved to be a very difficult compound to handle; it is still somewhat of a curiosity nowadays and some details of its properties have not yet been completely clarified. However, a few weeks after the initial appearance of the black crystals of this compound, it was clear that the compound had the unusual property of being paramagnetic for one unpaired electron per vanadium atom. So, we would say today, vanadium in hexacarbonylvanadium(0) is a low-spin system of d^5 electronic configuration. The convincing experimental evidence that the compound was mononuclear came from some X-ray diffractometric experiments carried out by Paolo Corradini, who is presently at the University of Naples, who could show that a single crystal of hexacarbonylvanadium, sealed in a Lindemann capillary under an inert atmosphere, had a diffraction pattern consistent with a mononuclear structure similar to that of hexacarbonylchromium, with the *Pnma* space group being very probable and an inversion center being present in the molecule, as expected for an octahedral structure. Almost exactly 20 years later in a 1979 paper published by Sheldrick, the

Pnma space group was confirmed for hexacarbonylvanadium. Moreover, the cell constants given by us in the original paper were confirmed to a higher degreee of accuracy, due to the better set of data collected of course. Our preliminary data for this paramagnetic metal carbonyl were presented by Giulio Natta at a meeting of the National Academy on 8th October 1959. Giulio Natta was a member of the National Academy, that is to say the Academia dei Lincei. On 21st March 1960 a paper was submitted by us to the Journal of the American Chemical Society, which appeared in print in the same year. However, an extraordinary thing happened, Pruett and Wyman working at the Union Carbide Chemical Company in South Charleston, West Virginia, had submitted a paper on 15th December 1959 to Chemistry and Industry, this appeared in the January issue of that journal in 1960. In this paper, hexacarbonylvanadium, obtained by a different route to ours, was reported to be dinuclear and diamagnetic, and therefore it was formulated as $V_2(CO)_{12}$. Our X-ray and magnetic susceptibility data could only be explained with a mononuclear formulation; thus, the controversy about the molecular composition of the new compound vanished within a few months and another paper submitted by us to Chemistry and Industry reinforced our original data and was published by the journal with an accompanying note by Dr Pruett who agreed on the mononuclear nature of the compound in the solid state. Many years later I met Dr Pruett when he moved to Exxon and we discussed with great pleasure, I would say, our scientific encounter. Hexacarbonylvanadium(0) has been the object of several subsequent papers by us at the University of Pisa, in collaboration with Guido Pampaloni, and its chemistry is now completely understood. However, some solid-state properties of this compound still deserve further investigation and we are planning to carry them out in the near future. Hexacarbonylvanadium was, at that time, a great surprise for the scientific community due to its unusual properties. Now we know that the dinuclear structure with a localized vanadium–vanadium bond is not stable simply because single metal–metal bonds are rather weak in the 3d sequence of elements, and therefore a vanadium–vanadium bond would not be strong enough to withstand the high steric crowding resulting from a binuclear structure. However, carbonyl derivatives of Group 5 did in fact keep another surprise for us. Many years after the original discovery of hexacarbonylvanadium we found out that niobium halides are equally well carbonylated with exactly the same reductive carbonylation process we had used years before for vanadium, the only difference being that the carbonylation process of niobium occurs under even milder conditions than that of vanadium. Our paper on the carbonylation of niobium was received by the journal on 30th August 1982 and appeared almost simultaneously with another paper by John Ellis of the University of Minnesota, on a similar reductive carbonylation of the pentachlorides of niobium(V) and tantalum(V) which was received by the journal Organometallics on 5th October 1982. This competition makes things even more interesting especially for the students involved in the project.

R.P. I would like you to recall what circumstances made it possible for you to spend a year as a Sloan Fellow with Al Cotton at MIT, and particularly what made you chose Al as a postdoctoral mentor.

The Institute of Industrial Chemistry of the Polytechnic of Milano had rapidly been recognized worldwide as a first class research center for transition metal compounds for their use as metal-based catalysts for olefin polymerization and as the object of fundamental studies on their properties. Scientists from all over the world visited the Institute and this was of course a very exciting thing for us. On one of those occasions I met Dr Irving Wender; on another occasion John Waugh from MIT visited us, I believe this happened shortly after Salvatore Castellano, a member of the Milano staff, had spent a year with John Waugh at MIT working on NMR in 1959. On that occasion, I told John Waugh that I would be interested in spending sabbatical leave in the USA and a few weeks later I received a letter from Al Cotton telling me that he could a see way to get a post-doctoral fellowship for me. This was a Sloan Foundation fellowship at MIT and of course I accepted this offer immediately. I remember around the 10th of July 1960 I left Genova to go to New York on a boat, I think it was the Vulcania, which in a couple of weeks crossed the Mediterranean and the Ocean and towards the end of July I arrived in New York. I stayed in Manhattan for a couple of days and then I moved by train from New York to Boston, where I met Al Cotton.

R.P. There you started your investigations on the carbonylation reaction of methylpentacarbonylmanganese(I). What led to the selection of this research project?

Al Cotton and his wife Dee invited me for dinner (I think this happened on the very first day of my arrival in Boston, probably on the 25th of July). After dinner, in the context of a discussion about several other things including the fact that Al discovered that I did not care much about operatic music, something that Al did not expect at all from an Italian, we started to talk about a possible project for my postdoctoral year. As many other people had done, I was struck by the paper released about a year earlier by the group working at the Ethyl Corporation in Detroit, namely Coffield and coworkers, on the carbon monoxide insertion in alkylpentacarbonyl derivatives of manganese(I). In view of my earlier experience with carbonylation reactions in Milano and with metal-assisted carbonylations in general, this looked like an appropriate research project to carry out. The thermodynamic parameters of the carbonylation reaction were measured. In the meantime Inorganic Chemistry had just started as volume 1 in 1962; the paper was submitted to this journal and appeared in print in the first issue of volume 1. In September 1961 I went back to Milano and I was able to measure additional thermodynamic parameters as a function of the nature of the manganese-bonded alkyl group. Later on, the carbonylation of pentacarbonyl-alkyl derivatives presented me with another opportunity of an interesting scientific encounter with Fred Basolo. Further studies on the mechanism of the carbonylation of alkylmanganese pentacarbonyl derivatives, however, had to wait until I went to Geneva and joined the research laboratories of American Cyanamid.

R.P. I recall you saying that you yourself blew the gas-volumetric burette that you used at MIT for the first CO insertion studies. This is not a very common apparatus.

I have seen it only in your lab. A professional glassblower who recently built one for me said to me that it had been a challenge! How did you become such a skilled glassblower?

The prototype of the burette was designed by Salvatore Castellano in collaboration with Ercoli at the Polytechnic of Milano; I must admit that the chemical engineering training of Salvatore Castellano made him the most appropriate person to design such an experimental apparatus. This turned out to be very useful over the years and is still used in our research even now, both as an analytical tool and as a method for measuring equilibrium and kinetic data. The Polytechnic of Milano had a glassblower but no such person existed, as far as I remember, at MIT. It was too complicated to have such equipment made outside and therefore I decided to try to set up the burette myself, which I did with some difficulties. The esthetical part of my gasburette was not excellent but certainly there were no holes in it and I could carry out my measurements without any problem.

R.P. Can you share with us other anecdotes from your experience at MIT?

The year I spent at MIT as a Sloan Foundation fellow has been very important for me. First of all, I met Al Cotton, I learned a lot from him in terms of the beauty of facing new problems and the importance of carrying out significant new experiments. It was also very interesting to be in a Sloan Foundation company; the school was headed at that time by Professor Buerger and the scholars were from different countries and different cultural origins. I remember we used to meet every month in the Club of the School at night and, after dinner, we were asked to give a speech on a subject of our choice, generally but not necessarily connected with our professional activity. Of course I was asked to give a talk about my research. This was the first occasion that I realized how difficult it is to talk to non-chemists about Chemistry. The level of understanding between the speaker and the audience can easily approach zero unless an enormous effort is made by the speaker. This is, of course, a very important general problem and unfortunately chemists have a confraternity-like way of expressing themselves to other scientists. This certainly does not help the reciprocal understanding and communication: sometimes it would be better to give up a little precision in favour of a more colloquial talking. An interesting thing about my stay at MIT was that I met Adriano Sacco there for the first time, he was coming from the University of Milano and not the Polytechnic. The two institutions are separated by about half a kilometer. My stay at MIT was postponed for about 2 months after the expiration of my Sloan fellowship and I spent some time doing exploratory research in several directions. One of the experiments I remember doing, it was on December 29th 1960, I checked the date on the MIT lab book which I still keep with me, was to react $Mo(CO)_6$ with acetylacetone at a temperature between 140 and 150°C. The idea I had was to intercept some low-valent carbonyl derivatives of molybdenum. Heating the two components yielded a red–brown solid, which I noted in the lab book to be tris(acetylacetonato)molybdenum(III). I did not in fact realize that this compound was unknown at that time. I did not check in the literature. Some weeks later, Al told me that during one of his visits to one of the external laboratories someone had expressed an interest in an acetylacetonato derivative of low-valent molybdenum and he asked me whether I could think of a synthesis for it. My answer was that I probably had the compound he wanted in a drawer in several gram quantities. In fact the compound later turned out to be what I expected.

R.P. Many young European readers will be interested in your perspective on how a postdoctoral experience in the USA has changed from that time to the present

My stay at MIT and in America in general has been very important. I met several interesting people, I became acquainted with different methods of carrying out experimental work, and therefore I chose the best part of what I could see. Going to a foreign laboratory is an experience I keep recommending to all my students. Visiting foreign research institutions is a valuable experience for everybody, across the Ocean(s), both ways of course.

R.P. What made you decide to move on to the Cyanamid European Research Institute in Geneva?

In 1961 I returned to Milano and continued my research on the carbonyl insertion and on other subjects I had left behind during my leave of absence in the USA. I collected some new thermodynamic data on the carbonyl insertion, which I presented at the ICCC meeting in Stockholm in June 1962. At that meeting I met Dr Erwin Weiss, who later became involved in the Cyanamid European Research Institute in Geneva and further on became Professor at the University of Hamburg. This acquaintance turned out to be of some importance for the later development of my career. During 1962 I was approached by American Cyanamid, probably under the suggestion of Erwin Weiss and finally I decided to move to Geneva. It was not an easy decision to make; my son Marco was seven at that time. I asked my wife to move to a foreign country and my son Marco had to discontinue his studies at the elementary school in Milano and to move to a completely new school where teaching was carried out in a different language. And so it was that in 1962 I accepted an offer to join CERI, the Cyanamid European Research Institute, located in Cologny on a hill overlooking the lake of Geneva. It is really difficult to imagine a better location for research than the one we had in that place. Settling down in Geneva was not very difficult. It was in fact quite easy. At the end of the same year, 1963, my son spoke French fluently and his marks in school were very good.

R.P. Tell us about the evolution of your career at the Cyanamid Institute

The Institute was founded in 1959 and I started working there in January 1963; I joined the group of Synthetic Inorganic Chemistry headed by Erwin Weiss. The research institute was organized in a unique and efficient manner. The Geneva location had an administrative director and six research groups, each headed by a scientist. The scientific director of the Institute was sitting in Stamford, Connecticut, at the American Cyanamid location. Organometallic chemistry was still a hot subject at that time and I was therefore free to carry out the research I really wanted to do. When Erwin Weiss left CERI to get a chair in Hamburg I was promoted to director of the research group. Some spontaneous turn-over occurred on that occasion; several people from the group went back to their Countries of origin, mainly Germany and Britain and I could recruit new people. In 1965 Carlo Floriani, now at the University of Lausanne, just graduated from the University of Milano, and Francois L'Eplattenier, with a Ph.D. degreee from the Eidgenössische Technische Hochschule of Zürich, joined the group. These were both very important additions to the group. As a head of one of the research groups, I had the duty to spend, once or twice a year, a couple of weeks in the research laboratories of American Cyanamid in Stamford, Connecticut, Princeton and Bound Brook. This was a very interesting opportunity to learn about the problems of chemical industry. In the last 2 years of its activity, the Geneva institute was more and more directed towards studies which could possibly lead to some industrial applications. This was a further stimulus for me; I was, since my time at the Polytechnic Institute, involved in problems associated with the chemical industry. Even nowadays a problem with practical potential aspects has an additional flavour for me. I also learned how stringent the conditions imposed by industry can be, in terms of cost and availability of materials, yields and simplicity of the process. A good solution, chemically speaking, to a problem can be shown not to withstand an economical examination of the costs. This is an important aspect of the problem that you must transfer to your students. Life and research in industry is more challenging than it is in a laboratory dedicated to pure research (Figs. 1 and 2).

R.P. In Geneva, you carried out the mechanistic studies on the methylpentacarbonylmanganese(I) carbonylation reactions that gave you the highest recognition

My research on the carbonylation of alkylpentacarbonyl derivatives of manganese in the meanwhile had progressed, mainly because I was able to get Klaus Noack, an excellent spectroscopist, interested in the problem. In 1968 we were able to show, mainly by IR spectroscopy, that the most likely mechanism of the reaction of CO with $MeMn(CO)_5$ was in fact what is now commonly known as the migratory insertion. Since then, this is the generally accepted mechanism for this important metal-assisted elementary step, forming a new carbon–carbon bond. The alternative mechanistic possibility of CO insertion, which for some specific cases has been proposed from time to time in the literature, turned out to be incorrect.

R.P. What do you recall of other research avenues that you have initiated during those years?

In the research laboratories of Geneva dioxygen complexes were studied with particular care, thanks to the competence and ability of Floriani and we could in fact identify the conditions under which the Schiff base complexes of cobalt(II) form the dioxygen complexes in solution. Again this was an occasion for overlapping with Fred Basolo and I remember at the S. Moritz ICCC meeting of 1966 I met Fred and we soon discovered that we were again interested in the same subject, although on different aspects of dioxygen forming metal complexes. Metal carbonyl chemistry was also going on with L'Eplattenier and, for that time, we studied the still largely unexplored chemistry of metal carbonyl derivatives of ruthenium and osmium.

R.P. What is your personal opinion on the relationship between fundamental and applied research between the academic and industrial worlds?

I would tend to believe that the main problem between fundamental research and possible applications is a transfer of knowledge between the researchers on one side and industry on the other. People who like to do fundamental research are as important as those carrying out applied research. The methodology is the same and the research in both fields must be carried out at the highest possible level. There is no difference as far as quality is concerned. Researchers in fundamental aspects of science will spontaneously put their competence at the disposal of industry, provided they know what is of interest for industry. The misunderstanding which may sometimes exist between the two worlds very often is a problem of information

Fig. 1. The leadership of the Cyanamid European Research Institute in Geneva (ca. 1967). From left: P. Baud (Administrative Director), E.A.C. Lucken (Instrumental Analysis), E. Moser (Solid State Physics), R.F. Hudson (Organic Chemistry), F. Calderazzo (Synthetic Inorganic Chemistry), W. Mehl (Electrochemistry), C.K. Jørgensen (Theoretical Inorganic Chemistry).

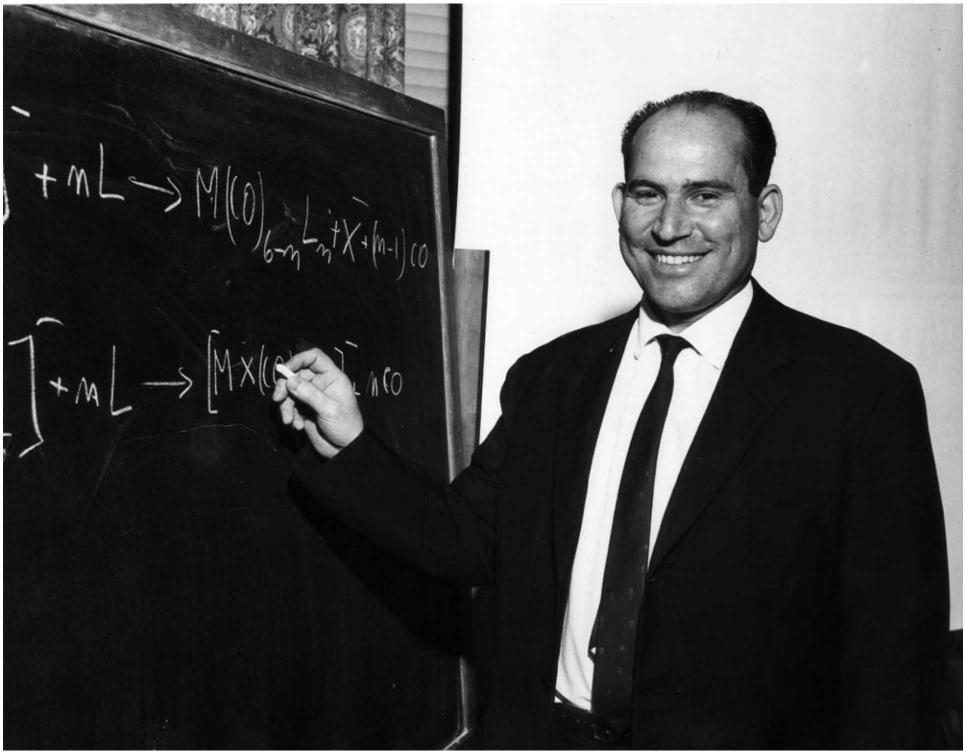

Fig. 2. Fausto Calderazzo photographed at the Stamford Cyanamid Laboratories on the occasion of a research report.

and communication only. The worst thing one can do is to divert a scientist from the problem the scientist is interested in. The compatibility of scientific interests and competence of the operators with the target is the secret of success. Shifting people from one methodology to the next or from one project to the next may be dangerous because it may result in producing scientists incapable of carrying out any reasonable research: although it may appear a longer procedure, it is better to spend some time and find the appropriate expertise for any given scientific or technological target. I remember discussing these points with the management at Cyanamid, especially with Dr Donald Salley, who at a certain time became vice-president of CERI.

R.P. What were the events leading to your return to Italy?

Sometime towards the end of 1967 I was contacted by Piero Pino, at that time on his way from the University of Pisa to the ETH in Zürich, about the possibility of me getting a professorship in Italy. At that time the promotion procedure—now it has changed—consisted of a national context whereby candidates should submit their curricula and copies of the publications to a committee to be read and judged.

There were two openings in two different Universities in 1967, and therefore I accepted the suggestion by Piero Pino and sent my documents in two separate envelopes. One of the envelopes never got to its destination because it was caught in a fire at the main railway station in Rome. The second arrived safely and so it happened that I got a professorship position: no envelope, no promotion, I guess. At this point one was eligible to be called by any Italian University having an opening, which later turned out to be Pisa. Once I knew how things were developing concerning my future, I sent a letter of resignation to my supervisors at American Cyanamid. I believe it was the end of May 1968, and I think it was exactly the 29th of May. The date can be easily checked by going through the political events of that interesting period. I wrote my resignation letter, as far as I recall, exactly on the same morning I went to the ETH Zürich for a seminar. I came home that same evening by train from Zürich to Geneva the day Charles de Gaulle was expected to give a speech towards the end of the 'French May'.

R.P. You mentioned that Piero Pino has played an important role at various stages of your career. Your interaction with him has in fact continued after your move to Pisa

As I said before, Pino was my first supervisor at the Polytechnic of Milan and he encouraged me on repeated occasions to engage myself in an academic career. Later, while I was in Pisa and he was in Zürich we interacted considerably with the Scuola Normale Superiore of Pisa to organize, together with other teachers of the University of Pisa, a Ph.D. curriculum in applied molecular sciences financed by the Italian chemical industry, mainly ENI. Pino was a person of wide scientific interests initially ranging from organic chemistry to polymer chemistry, to organometallic chemistry. I have sat with Pino in examination committees for the admission of undergraduate students to the Ph.D. curriculum connected with the Scuola Normale Superiore and I have always been very much impressed by his clear understanding of phenomena and his curiosity in getting to the core of the problems.

R.P. What have been the main difficulties you encountered after your move back from an industrial to an academic environment?

When I arrived at the University of Pisa at the end of 1968 some difficulties had to be overcome. Firstly, there was student unrest which caused some small problems; as far as my initial teaching activity was concerned I am proud to say that I have not lost one single hour of lecture time. Secondly, at that time there was still some money left for newcomers and the University of Pisa was kind enough to provide money in order to fix the furniture, laboratory benches and other items. On the other hand, the time of scientific expansion had already gone and the generous funding of the early sixties within Europe had already considerably dwindled. It would have been difficult to carry out the experimental work, or at least to initiate it at such an early date after our arrival in Pisa if it was not for the fact that American Cyanamid, while they decided to close the Institute in Geneva, at the same time agreed to donate most of the equipment of the Synthetic Inorganic

Chemistry Group to the University of Pisa. This in fact materialized in 1969 and, at the beginning of 1970, a little more than a year after our move to Pisa, we were able to begin our experimental activity. Teaching has always been an interesting part of my job; thus, I enjoy teaching very much even now. Our research activity has continuously been funded by chemical industry, particularly ENI, and I must say that we have to be grateful to industry, both American or European, specifically Italian, for supporting our research. I only hope that the return has been rewarding for them. Everything has always been done on a basis of reciprocal confidence and everything has worked out very well. I can quite convincingly state that there has been cross fertilization in these contacts with industry. Consequently, our students have been introduced to an important aspect of chemical research being somewhat related to practical problems of industrial interest. Research has therefore acquired for them a further flavour. Contacts with industry should be encouraged for the benefit of both partners. Almost 30 years have passed since I arrived in Pisa. I am therefore entitled to draw a conclusion about the longest section of my scientific career. I have to recognize that moving to Pisa was, professionally speaking, a wise decision. I found some very good students and excellent coworkers here, and numerous colleagues with whom it has been possible to overcome the usual difficulties of everyday life in the Department. I am therefore grateful to all of them for what they have allowed me to perform here.

R.P. In Pisa your interest in carbonyl chemistry has extended to the other side of the periodic table, in particular systems of Pt(II), Pd(II) and Au(I). What do you consider to be the major achievements of your research in that area?

At that time one of our initial problems was the combination of noble metals and carbon monoxide. It was somewhat of a mystery in inorganic chemistry the fact that certain neutral binary metal carbonyls do not exist. This was particularly difficult for us to understand since we had gone through the positive experience of synthesizing hexacarbonylvanadium one decade earlier. The area of the non-existing binary metal carbonyls appeared to be an interesting one. One such area obviously was at the end of the transition series, namely within the noble metals. Of particular interest was the contrast between the stability of tetracarbonylnickel and the unavailability of the corresponding derivatives of palladium(0) and platinum(0). Together with Daniela Belli Dell'Amico, whose thesis was on carbonyl derivatives of platinum, we initiated an extensive investigation into palladium and platinum carbonyls. As early as 1986 we came to the conclusion that both $Pt(CO)_4$ and $Pd(CO)_4$ are thermodynamically unstable species, in spite of the relatively low atomization energy (especially for palladium); the low stability was naturally assigned to the M–CO bond enthalpy being too small to compensate for the energy expenditure connected with the atomization of the metal. More than 10 years ago we proposed that these noble metals do not like to π-back bond. The M–CO bond is substantially weak, or at least not strong enough to let the fully carbonylated uncharged products survive under normal conditions of temperature and pressure. This is particularly true for palladium and silver. We also carried out considerable work on gold and we soon arrived at a quite convenient synthetic procedure for the halocarbonyl derivatives of gold(I). The chloro derivative can easily be prepared by treating tetrachloroauric acid with carbon monoxide using thionyl chloride as solvent. Dehydration by thionyl chloride and further reductive carbonylation of the intermediate anhydrous gold(III) chloride explains the formation of Au(CO)Cl. Work with these compounds became much easier than before for us and for other people interested in this field. Our work with gold offered us the possibility of getting acquainted with Joachim Strähle of the Universität Tübingen, who, being interested in gold chemistry, was attracted by our crystal structure of Au_4Cl_8. An initial letter after the publication of our crystal and molecular structure of the tetranuclear gold derivative initiated a long period of collaboration which is still going on with important scientific results and extremely good personal relationships. The major achievement in this area is to have pointed out that the conventional mechanism of σ and π synergic bonding probably should be revised within this area of the periodic table. Metal–CO bonds can be stable enough without a strong contribution from π-back donation; this is for example, particularly true for carbon monoxide bonded to gold(I), whereby a relatively strong bond is presumably not associated with any relevant back bonding. On the other hand, the formation of M–CO bonds is known even outside the transition metal area. This is a fascinating problem on which much discussion is still going on and we have contributed to modify some of the existing ideas on this subject.

R.P. What other important contributions from the work in Pisa would you single out?

Of course, another interesting area of research, still concerning metal carbonyl chemistry, is represented by organometallic derivatives of early transition elements. As stated above, much to our surprise, we found that reductive carbonylation of niobium to the corresponding hexacarbonylniobate(-I) is easier than the corresponding transformation with vanadium. Of course, our idea was to synthesize the neutral binary uncharged derivatives of niobium and tantalum, which are still unknown, not considering, of course, the derivatives obtained in an argon low-temperature matrix. Our research carried out at the University of Pisa has contributed to some extent to the area of organometallic derivatives of early transition elements, which has been expanded and clarified. However, one should not forget that similar chemical–physical properties can be found in different areas of the Periodic Table. For example, one of the last additions to this area is the identification of the doubly charged cation $[TiCp_2(CO)_2]^{2+}$, which has a wavenumber value of the carbonyl stretching vibration close to that of AuCl(CO). The collaboration with both Guido Pampaloni and Daniela Belli Dell' Amico has been essential for the development of the research area concerned with dialkylcarbamato complexes of transition and nontransition elements. This is a relatively new class of compounds, still under intensive exploration, which has given a lot of satisfaction in terms of isolation of new compounds, discovery of interesting properties and, in more recent times, transferring our past experience into a quite new field for us, namely solid-state chemistry or surface chemistry. We have in fact extensively used the solubility and reactivity properties of *N*,*N*-dialkylcarbamates for their implantation on the surface of inorganic matrices, mainly amorphous silica. Another aspect of chemistry which has considerably interested us is the area of complex formation with chemical elements. In addition to the dioxygen complexes initially isolated by Carlo Floriani, we have been able to characterize coordination compounds of cyclo-octasulfur and cyclo-heptaselenium, the latter studied by X-ray crystallography. In the successful outcome of this research, carried out by a particularly skillful and prepared young man by the name of Walter Baratta who is presently at the University of Udine, a fundamental role has been played by the studies carried out by my interviewer, Rinaldo Poli presently at the University of Dijon, on the binuclear solvento species of rhenium, which were initially used by him as substrates for the coordinative addition of dichalcogenides.

A fascinating aspect of inorganic chemistry is to attempt to systematize the thermodynamic properties of coordination compounds. Studying the effect of ligands and metals as they individually vary along vertical sequences of elements on displacement equilibria in solution, is the method we have chosen to throw some light on the multidecennial problem of periodical changes. The problem is quite clear: do the systematic changes in the properties of chemical elements as we know them in their disposition in the Periodic Tables reflect themselves somehow in the compounds they form? With some caution the answer is probably yes, and it would be very interesting to collect some more data to verify the statement. Along the sequence of chalcogenide ligands, as far as low oxidation states are concerned, the heavier chalcogens appear to be slightly favored in one of the systems we have studied. Systematizing coordination properties as a function of both the metal and the ligand in their group tendency and finding out about the coordination ability of chemical elements, where sometimes very weak interactions are involved, are both areas of intense research presently with strong implications in several fields, including reaction mechanisms in terms of the identification or indirect evidence of reaction intermediates.

R.P. How do you see the evolution of your chemical thought and where will you be going from here?

The main research effort has always been on the synthesis of classes of largely unexplored compounds and the study of their properties. Understanding the mechanism of chemical transformation is a fascinating field and, of course, we have contributed to this area by studying the mechanism of some metal-assisted reactions, including as I mentioned before the carbon monoxide insertion reaction. At a later stage, after moving to Pisa, we realized that maybe chemical experimental observations contain some order in their nature. However, I still believe today that inorganic chemistry is a field where research should be mainly oriented to the discovery of innovative classes of compounds. For example, we still do not know much about the area of 'weak interactions' which is coming under the scrutiny of several people because of the implications of this subject over several aspects of science. The aptitude of the chemist in the laboratory should be directed more and more to refining the synthetic procedures in order to isolate and possibly study spectroscopically and even crystallographically, preferably at low temperatures, compounds of low stability. Thus, an important area of research, in strict collaboration between synthetic chemists and crystallographers, is represented by the diffraction methods at low temperatures. Also, the area of phase transitions has not yet been explored at a sufficiently high degree of sophistication, I believe, and probably not at a molecular level of understanding.

R.P. What other acquaintances made during your career, besides those with coworkers and collaborators already mentioned, do you recall with particular pleasure?

During the years spent first at Geneva and later in Pisa I have very much enjoyed the personal contacts I have had with many people working in the field of inorganic chemistry. I certainly cannot forget to mention both Geoffrey Wilkinson and Ernst Otto Fischer. Especially with the former I have maintained, until it has been possible, extremely good personal relations based on reciprocal understanding about science policy and education. I am grateful to both of them for the time they have dedicated to me. I have also a very pleasant recollection of my first personal meeting with Professor Walter Hieber in Munich: he was very kind to invite me to his home during one of my visits at the Technische Hochschule, I believe around 1966. The cup of tea he offered me was probably the best one of my life!

R.P. How do you see the evolution, the current status, and the future directions of public Italian and European funding for chemical research?

Funding research is a problem of primary importance. It is the turning point towards going ahead or going back in Science. Chemistry is a science per se with its own dignity; collaboration with other branches of science is important and probably culturally diversified teams of people may be more successful than other less diversified teams, when dealing with scientific interdisciplinary projects. What I believe should be carefully avoided, at any given time, is to oblige people to become involved in areas far from their specific competence and interests: they will get interested only after a difficult procedure and they will produce little in terms of scientific acquisition. The problem for the entrepeneurs of research is to properly define the problem in their minds, then to find the correct people with the appropriate knowledge and skill promoting the acquisition of new skills when necessary. Asking people to change their field of activity drastically is frequently a shortcut to the difficult but more profitable way of finding out what people with the right competences already exist. If an effort to detect the appropriate competence is made by the funding agencies European science will produce more results than it presently does. To this end, it is important that people sitting on those funding agencies understand how important is to leave good scientists do their work with enthusiasm and efficiency. Economically attractive discoveries have come out from innovative experimental observations and from the correct interaction between the primary researchers who did the original observations and other people who have been able to understand the practical relevance of the new findings. There are plenty of examples of nice scientific work which has been exploited by people other than the original discoverers. In those cases, the scientists were not aware of the practical relevance of their work. On the other hand, we cannot ask scientists working in institutions financed with public or private money to do good science and at the same time to be so knowledgeable to even find the correct justification of their work in terms of utilizable results. I believe that we should primarily ask them to do good science. Someone else should be clever enough to identify and visualize the technical aspects of the scientific results. For the time being, I personally believe that funding of European research, obtained through the intermediacy of public money coming from the EC countries, has been extremely useful and sometimes essential for the survival of several research teams. However, the portion of money dedicated to fundamental research has to increase drastically in the future. Also, there has been too much red tape within the EC research business, too much concern for both practical problems and applied technologies with a low degree of innovation. In other words, it has been frequently forgotten that really profitable applications can only come from good innovative science. A scientific breakthrough will produce more money for EC countries than small technical improvements on well-established subjects.

R.P. You have served for several years as the Editor of Gazzetta Chimica Italiana before it merged with other journals in a new European publishing endeavour. What are the positive and negative recollections of those years?

I believe that Europe and European Chemical Societies, by and large and with the appropriate exceptions, have not carried out a satisfactory editorial policy in the last 20 years. As a result of that, few important chemical journals are now still run by the Chemical Societies. They are important journals but their number has decreased in the recent years. The remaining journals and some of the new ones are no longer under the full control of the Chemical Societies. I think this is not an appropriate move; this opinion is shared by a limited number of people in this continent and isolated voices do not make a big impact, I know that. However, I am glad to see that the major chemical journals worldwide, namely those published in USA, are run according to a scheme which is not far from the one whereby a substantially complete control of the scientific chemical literature is still in the hands of the domestic chemical society. Commercial publishers have undoubtedly done a wonderful job for science both in Europe and in USA; however, we cannot ask them to substitute the Chemical Societies in their institutional role having to do with the diffusion of science. Within Europe, I believe there is still room for a general agreement within the Chemical Societies aimed at establishing new chemistry journals, or the equivalent computerized scientific sources of information in the different areas of chemistry. European chemistry is well advanced and progressing all the time; however, it is unfortunate that the last step of research, represented by the vehicles of diffusion of the results, is not organized in such a way as to create real competition within the scientific community.

R.P. Have you been involved in many other public service activities? How do you see the impact of your efforts in those areas?

No, I did not do much of this type of activity. Once I remember being asked to give a seminar in a social club in Pisa and discussing problems connected with the deterioration of our environment. The basic problem is of course how to produce energy, as I discussed on that day, in a cleaner way than it is done today, or we used to do at that time. Much to my surprise I noted that the local newspaper had a quite long and complete report on that talk of mine. I have to say that my experience was definitely positive. The readers of that newspaper may have profited and my consideration of newpaper operators has considerably increased. However, I personally believe that chemists should be much more careful than they are now with respect to transferring the beauty of their science onto the public opinion. In order to do that, the best scientists should be put on stage in an attempt to transfer the fascinating field of chemistry to young people. As I stated above, there is a problem of language here, which is particularly serious for chemistry.

R.P. You have been recently honored with the Sacconi Medal. Please share with us your feelings for being the first to be honored with a price named after your professional 'father'

This event happened quite recently, last Summer, and it was really a big honour for me. As I mentioned earlier, Sacconi was my first mentor and I learned a lot from him about interest in research, the sequence of events which must occur in a chemical laboratory in order to get recognizable scientific results, which different types of competence are required when one goes from the synthesis of a new material to the publication of the new results. I am very grateful to him for what I learned and to the national scientific community for the recognition I have received (Fig. 3).

R.P. What message would you want to leave with current and future generations of students who are considering a career in chemistry?

I have constantly considered that telling freshmen and high-school students that chemistry is going to solve the problems of our everyday life, although this may be true in an overwhelming number of cases, it is not the most appropriate approach to attract young men and women towards science and chemistry in particular. Also, at the age of 18 not many people are particularly careful about their future life and the economical aspects of it; young people should be more interested in understanding how and why things happen. Thus, the approach to science should be more phenomenological than it is now in most of our high

Fig. 3. Fausto Calderazzo receives the first Luigi Sacconi medal, July 1998. From left: Mrs Maria Sacconi, Professor Antonio Tiripicchio, Professor Ivano Bertini.

schools and universities. Teachers should more carefully try to generate the interest of their students in '*De rerum natura'*. The introduction of computers, frequently considered as 'black boxes', in science and ordinary life makes this requirement even more urgent, not less urgent. Understanding why things happen is the secret to getting young people interested in science. I believe every teacher has done the following experiment: during a lecture attention by the audience is promptly obtained when a well-known phenomenon coming from personal observation is explained in detail. The experiment can be repeated over the years at different degrees of sophistication. Young people should realize that chemistry is an interesting branch of science; how atoms combine to make molecules and extended aggregates, how the thermodynamics govern the combination of atoms and how the thermodynamic laws depend on microscopic properties is something that still requires further investigation. The scientific acquisitions within the domain of microscopic entities are as important as those obtained with the observation of the universe.