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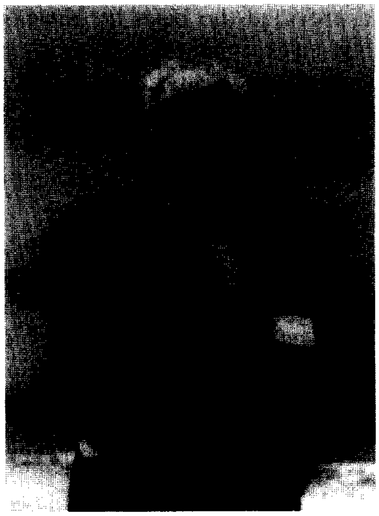
Preface



Fausto Calderazzo

Fausto Calderazzo was born in Parma on 8th March 1930 and studied in Florence, where he graduated in chemistry in 1952. It was at the time when Italy was in the process of recovering from the aftermath of World War 2, and the chemical community was committed to reaching a high standard. In these circumstances the fact that Calderazzo enrolled as a Research Associate in the Institute of Industrial Chemistry of the Polytechnic of Milano was particularly fortunate. At that time the reactions of carbon monoxide were the subject of intensive study because of its use in important industrial processes, and Giulio Natta, Director of the Institute, concentrated a fairly large part of the research activity on carbon monoxide chemistry. The presence of Professor Raffaele Ercoli in this group also ensured a high scientific standard, both in research and in the training of younger people. This association led Fausto Calderazzo to achieve an important success right from the start, namely the synthesis of chromium hexacarbonyl through reduction of chromium salts [1] and, a little later, that of vanadium hexacarbonyl [2]. These discoveries determined the subsequent direction of Calderazzo's researches. His novel view was that preparative methods could be profitably used to extend the knowledge of metal–carbon bonds in complexes of the same metal in different environments (neutral, cationic and anionic complexes of vanadium [2]) and in a set of related complexes containing different metals. This was the beginning of a journey that has continued up to the present, and has involved a series of fascinating excursions throughout the Periodic Table.

Calderazzo's inclination to concentrate on fundamental aspects is also reflected in the reactivity studies he undertook when, after six years as a Research Associate at the Polytechnic of Milano, he spent one year (1960–61) with Professor F.A. Cotton at MIT as Sloan Fellow. The insertion of carbon monoxide into alkylmanganese pentacarbonyls had just been discovered, and the mechanism of the Fischer–Tropsch and related carbon–carbon bond-forming reactions awaited elucidation. Calderazzo felt that a thorough study of the reactivity of the carbonyl group towards internal and external nucleophilic reagents and towards oxidation and reduction was needed. This approach has led him to important discoveries, as we shall show below. The choice of very simple and direct methods to solve problems is a constant feature of Calderazzo's work. It is clearly evident in the research that most especially reflects his creativity, namely the investigation of the mechanism of fundamental chemical reactions. Devising the experiments that will give unequivocal answers to intriguing problems is by no means a simple task. In collaboration with Professor Cotton, Fausto Calderazzo studied the kinetics and the equilibria of carbonylation and decarbonylation of alkylmanganese pentacarbonyl [3], a central research topic for advancing understanding of the mechanism of insertion reactions.

The experience he had gained could be fully exploited when Calderazzo returned to Italy and after a further year

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at the Polytechnic became a Research Associate (1963–65) and later (1965–68) Director of the Synthetic Inorganic Chemistry Group at the Cyanamid European Institute in Geneva. This was at the happy time when basic research was promoted by several big companies, and Calderazzo had the opportunity to develop some important ideas. First of all he was able to answer in a superb way the key question in the mechanism of the carbon monoxide insertion reaction, namely whether this was true insertion of carbon monoxide into the metal–carbon bond or migration of the metal-bonded group on to the carbonyl group. He utilised the thirteen CO bands of methylmanganese pentacarbonyl in the IR spectrum to monitor what turned out to be a migration of the methyl to the carbonyl group [4]. He was also able to discover new reactions and mechanistic pathways, such as nucleophilic attack on coordinated carbon monoxide [5], and the reduction of nitro-derivatives by the latter [6]. Once again the experiments were impressively simple, and provided the basis for developments that still continue throughout the world because of the interest in devising environmentally friendly processes for preparing carbamates and isocyanates. In this fertile period he also carried out his studies of metal complexes derived from Schiff's bases, and their conversion into organometallic species containing metal–carbon bonds [7]. This was the beginning of his rewarding researches on problems relevant to biochemistry, such as the ability of cobalt, nickel and copper complexes of Schiff's bases to complex with lithium, sodium and ammonium cations [8], and the chemistry of uranium(IV) [9].

In 1968 Calderazzo was appointed to the Chair of General and Inorganic Chemistry in the University of Pisa. There he was faced with the formidable tasks of reorganising an academic institution shaken by student troubles and of carrying out scientific research efficiently in the face of the increasing difficulties created by demagogy and bureaucracy in the Italian universities. In Pisa, his research continued to develop very fruitfully along the main lines described above (methods of preparing complexes, studies of the variation of properties across the Periodic Table, and investigation of the mechanism of insertion and nucleophilic attack) with a series of innovative ideas. Furthermore the study of halocarbonyl derivatives of late transition metals (gold(I), palladium(II), platinum(II)) led Calderazzo and his coworkers to postulate that there is a negligible π-contribution to the M–CO bond in these systems; this is a subject of much interest because of its implications for the reactivity of coordinated carbon monoxide [10]. In the limited space available only some of his achievements can be mentioned, such as the use of cyclopentadienyl derivatives of vanadium as models for the assessment of reversible coordinative addition of carbon monoxide [11], the preparation and characterization of carbonyl halides of transition metals [12], the carbonylation of gold chloride [13], the preparation of metal carbonyls in thionyl chloride as solvent [10], the preparation of new dialkylcarbamato complexes [14] and phthalocyaninato complexes [15], the variation in the stabilities of chalcogenide low-valent metal complexes [16], the stabilisation of niobium(0) and tantalum(0) in mixed metal clusters containing silver atoms [17], the preparation of complexes of manganese and rhenium containing new ligands such as P_2Ph_4 [18], and the preparation of arene complexes of metals [19]. Special mention must be made of his recent contributions to carbon dioxide chemistry through studies of alkylcarbamato metal complexes as precursors both to inorganic systems and to organic molecules through reaction with nucleophiles and electrophiles [20,21].

What is amazing on going through Calderazzo's publications is the range of elements he has been able to utilise as well as the variety of ligands; because of this approach he has greatly increased knowledge of the changes in the properties of complexes as the central metal is varied along groups and series. Among the more recent advances particular mention should be made of the use of the tetraphenylborate anion as a 12-electron donor ligand [22] and the coordination of elemental selenium to rhenium(I) [23]. A very recent achievement involved the formation of a zirconium-coordinated ketenylidene group by metal-assisted deoxygenation of a carbonyl group and C–C coupling with a second carbonyl group [24]. This is an important result in so far that coupling of two carbon monoxide units can be viewed as a molecular model for reductive cleavage of carbon monoxide on metal surfaces. It also is characteristic of Calderazzo's approach in that it combines preparative novelty with the mechanistic implications of a model.

Calderazzo has now published about 220 papers. The school he created in Pisa is one of the most productive, and several of his former students, whose names appear in the references, have gone on to chairs in academic institutions or are carrying out successful independent research. In spite of Calderazzo's rather demanding manner and authoritative personality, they were allowed free expression of their scientific creativity. At present the number of students under his guidance is increasing, and this is another consequence of Calderazzo's insistence on teaching the fundamental concepts of general and inorganic chemistry in a very simple and basic way.

Fausto Calderazzo has received many awards and distinctions in recognition of his scientific achievements. He was awarded the Miolati medal in Inorganic Chemistry in 1988 and recently received the medal of the Organometallic Chemistry Group of the Italian Chemical Society. He has been a member of the Istituto Lombardo di Scienze e Lettere since 1986, an honorary member of the Belgian Société Royale de Chimie since 1987 and of the Società Chimica Italiana since 1991, a Corresponding Member of the Accademia Nazionale dei Lincei since 1989, a member of the Editorial Board of the *Journal of Organometallic Chemistry* (1981–) and that of *Organometallics* (1986–88), an Advisory Regional Editor for *Journal of the Chemical Society, Dalton Transactions*, Editor of *Gazzetta Chimica Italiana* since 1985, a Foreign Associate of *Inorganic Syntheses* since 1982, and is a member of the International Advisory Committee of the International Conference on Organometallic Chemistry and that of the International Symposium on Homogeneous Catalysis. He has also made several invited lecture tours abroad, in England, Germany, France, Switzerland and the USA. Needless to say he has also given a number of plenary lectures at major conferences around the world.

We turn now to the human aspects of Fausto Calderazzo, which have also played a major role in his scientific achievements. To describe his strong and captivating personality would require more than the few lines available, but one feature stands out, namely his unshakable confidence in the ability of an individual to change things and to initiate a process that will then develop by its own logic. Most of us have had the experience of being crushed by so many problems that there seems no way of overcoming them. Fausto's invariable approach is to say: "Let's begin to do what we believe to be appropriate at present, then things will develop on their own." This is indeed the key to the success of human action, provided that one has the courage to do the right thing, irrespective of any obstacle. This is exactly the way Fausto behaves and teaches others to behave. He does not spare himself in doing what has to be done and his committment is total.

Fausto's friends and the many others who hold him in high esteem join now in honouring him on the occasion of his 65th birthday and wishing him much future happiness and continuing success in his scientific activities.

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