



Preface



Fausto Calderazzo

When Barry Lever asked me to be the Guest Editor of a special issue of Coordination Chemistry Reviews dedicated to Fausto Calderazzo on the occasion of his 80th birthday, I had to contact a number of scientists. I remember that I was in difficulty, because the limited number of invitations was really low in comparison with all the people who are still in close contact with Fausto Calderazzo. My final choice was for 25 well-known scientists and, just three days after Barry's request, I had received sufficient approvals to go on with the edition of the special volume.

The result of this effort is an issue of Coordination Chemistry Reviews covering several aspects of inorganic chemistry: as shown in Table 1. Contributions span from classical coordination chemistry (halide-bridged polymers, complexes of substituted adamantane, zwitterionic ligands containing the thioamidyl-phosphonium functionality), organometallic chemistry (synthesis, reactivity and applications of late transition metal carbonyls, metal arenes, bridging vinylalkylenes, tris(hydroxymethyl)phosphine- and ansa-metallocene derivatives), to bioinorganics (study of copper binding sites in proteins and classification based on their structural features), material chemistry (design, synthesis and photophysical properties of luminescent species based on lanthanide complexes), and supramolecular chemistry (extended networks based on halogen bonds). Some of the papers deal with catalysis (transition metal catalyzed arylation reactions, olefin polymerization, iridium-based asymmetric reduction of ketones, rhodium-catalyzed hydroformylation, ketone oxidation, enantioselective catalysis based on carbohydrates), a research topic which attracted Fausto Calderazzo greatly since the "Swiss" period that he spent at the Cyanamid European Institute in Geneva. As an indication of the long-standing interactions between Fausto and industrial research, Masi, Ricci and coworkers (Polimeri Europa and CNR, Milan) have produced a review on the metal-catalyzed polymerization of 1,3-dienes.

This special issue of Coordination Chemistry Reviews, embracing almost all the fields of chemistry which have been the subject of Fausto's research, wishes to be a birthday's present to Fausto Calderazzo from former students, colleagues and friends.

In the following, a short summary of the scientific career of Fausto Calderazzo is presented. An interview of Fausto, by Rinaldo

Poli, has already appeared in this Journal [1], and clearly describes the origin of Fausto's curiosity in science which probably has been the driving force of a journey involving a series of fascinating excursions through the Periodic Table and affording important contributions to the advancement of inorganic and organometallic chemistry.

Fausto Calderazzo was born in Parma in 1930 and graduated in chemistry at the University of Firenze (supervisor: Professor Luigi Sacconi) in 1952. His subsequent enrolment as Research Associate at the *Istituto di Chimica Industriale* of the *Politecnico* (Milan) and the collaboration with Giulio Natta and Raffaele Ercoli led Fausto to the preparation of vanadium hexacarbonyl, $V(CO)_6$ [2]. This new compound, the only example of a paramagnetic binary metal carbonyl, was defined as "*solido cristallino di colore verde-nero e di odore caratteristico, ingrato, simile a quello del cobalto ottacarbonile*" [3].

Fausto's inclination to concentrate on fundamental aspects is reflected in the studies he carried out when, after six years at the *Politecnico* of Milan, he spent about one year with Frank Albert Cotton at the Massachusetts Institute of Technology. The insertion of carbon monoxide into alkylmanganese pentacarbonyls had just been discovered and, in collaboration with Cotton, Fausto studied the kinetics and the equilibria of carbonylation and decarbonylation of $MnR(CO)_5$, a central research topic for advancing understanding of the mechanism of insertion reactions.

Back to Italy, after one year at the *Politecnico*, Calderazzo became Research Associate and then Director of the Synthetic Inorganic Chemistry Group at the Cyanamid European Institute in Geneva. There, he was able to answer the key question of the mechanism of the carbon monoxide insertion reaction, namely whether this was a true insertion reaction of CO into the M–C bond or a migration of metal-bonded groups onto the carbonyl group. He also discovered new reactions and mechanistic pathways such as nucleophilic attacks on coordinated carbon monoxide and the reduction of nitro derivatives by CO in the presence of ruthenium. In this fertile period, he also carried out studies on metal complexes derived from Schiff's bases and their conversion into organometallic species containing metal–carbon bonds.

In 1968, Calderazzo was appointed to the Chair of *Chimica Generale ed Inorganica* at the University of Pisa, where his research continued with the study of halocarbonyl derivatives of palladium(II), platinum(II) and gold(I), leading to the noteworthy conclusion that there is a negligible π -contribution to the M–CO bond in these systems. The isolation and the characterization of the so-called "non-classical" carbonyls, which occurred ca. 20 years after Fausto's proposition, confirmed his ideas.

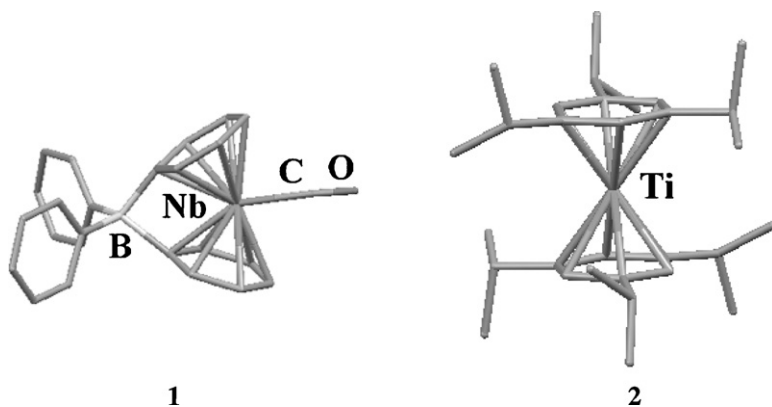
Considering Fausto's achievements during in his career, special mention must be made of his contributions to carbon dioxide chemistry through studies of *N,N*-dialkylcarbamato metal complexes as precursors to inorganic and organic systems (reactions

Table 1

List of authors and titles of the contributions.

| Authors | Title of the contribution |
|--|---|
| D. Belli Dell'Amico, L. Labella, F. Marchetti, S. Samaritani (Pisa, Italy) | Halo-carbonyl complexes of palladium, platinum and gold |
| R. Bertani, P. Sgarbossa, A. Venzo, F. Leij, M. Amati, G. Resnati, T. Pilati, P. Metrangolo, G. Terraneo (Padova, Italy) | Halogen bonding in metal–organic–supramolecular networks |
| I. Bertini, G. Cavallaro, K.S. McGreevy (Firenze, Italy) | Cellular copper management—a draft user's guide |
| C. Bianchini, G. Giambastiani, L. Luconi, A. Meli (Firenze, Italy) | Olefin oligomerization, homopolymerization and copolymerization by late transition metals supported by (imino)pyridine ligands |
| D. Cauzzi, M. Delferro, C. Graiff, R. Pattacini, G. Predieri, A. Tiripicchio (Parma, Italy) | Coordination properties of the multifunctional S,N,S zwitterionic ligand EtNHC(S)Ph ₂ P=NPh ₂ C(S)NEt |
| G.P. Chiusoli, M. Catellani, M. Costa, E. Motti, N. Della Ca', G. Maestri (Parma, Italy) | Catalytic C–C coupling through C–H arylation of arenes or heteroarenes |
| U. Englert (Aachen, Germany) | Halide-bridged polymers of divalent metals with donor ligands—structures and properties |
| B.R. James, F. Lorenzini (Vancouver, Canada) | Developments in the chemistry of tris(hydroxymethyl)phosphine |
| A. Raith, P. Altmann, W.A. Herrmann, F.E. Kühn (Munich, Germany) | η^5, η^1 -Coordinated cyclopentadienyl transition metal complexes featuring σ -metal–carbon ansa bridges |
| R. Lazzaroni, R. Settambolo, G. Alagona, C. Ghio (Pisa, Italy) | Investigation of alkyl metal intermediates formation in the rhodium-catalyzed hydroformylation: experimental and theoretical approaches |
| R.A. Michelin, P. Sgarbossa, A. Scarso, G. Strukul (Padova, Italy) | The Baeyer–Villiger oxidation of ketones: a paradigm for the role of soft Lewis acidity in homogeneous catalysis |
| G. Pampaloni (Pisa, Italy) | Aromatic hydrocarbons as ligands. Recent advances with the synthesis, the reactivity and the applications of bis(η^6 -arene) complexes |
| J.B. Bernárdez, S. Bolaño, L. Gonsalvi, M. Peruzzini (Firenze, Italy) | Coordination chemistry of 1,3,5-triaza-7-phosphaadamantane (PTA) and derivatives. Part II. The quest for tailored ligands, complexes and related applications |
| R. Malacea, R. Poli, E. Manoury (Toulouse, France) | Asymmetric hydrosilylation, transfer hydrogenation and hydrogenation of ketones catalyzed by iridium complexes |
| E.A. Quadrelli, J.-M. Basset (Villeurbanne, France) | On silsesquioxanes' accuracy as molecular models for silica-grafted complexes in heterogeneous catalysis |
| A.M. Raspolli Galletti, G. Pampaloni (Pisa, Italy) | Niobium complexes as catalytic precursors for the polymerization of olefins |
| G. Ricci A. Sommazzi, F. Masi, M. Ricci, A. Boglia, G. Leone (Milan, Italy) | Well-defined transition metal complexes with phosphorus and nitrogen ligands for 1,3-dienes polymerization |
| V. Benessere, R. Del Litto, A. De Roma, F. Ruffo (Napoli, Italy) | Carbohydrates as building blocks of privileged ligands |
| L. Armelao, S. Quici, F. Barigelletti, G. Accorsi, G. Bottaro, M. Cavazzini, E. Tondello (Padova, Italy) | Design of luminescent lanthanide complexes: from molecules to highly efficient photo-emitting materials |
| L. Busetto, P.M. Maitlis V. Zanotti (Bologna, Italy, Sheffield, UK) | Vinylalkylidene transition metal complexes |

with nucleophiles, electrophiles and with silica surfaces) and to the preparation of “rare” organometallic compounds such as the niobium(I) derivative containing the tetraarylborate anion behaving as a 12-electron donor ligand, **1**, and the first well-defined titanium(I) derivatives, Ti(η^6 -1,3,5-triisopropylbenzene)₂[BAr₄], **2**.



What is amazing on going through Fausto's publications is the range of elements as well as the variety of ligands he has tested, Fig. 1. Because of this approach, he has largely increased knowledge of the changes in the properties of complexes as the central metal is varied along Periods and Groups.

[illegible]

A black and white photograph showing two men in suits shaking hands across a table. The man on the left is handing a large, textured, cone-shaped object to the man on the right. There are glasses and a bottle on the table.

Fausto Calderazzo has received numerous awards (the Miolati Medal in Inorganic Chemistry, the medal of the Organometallic Chemistry Group of the Italian Chemical Society and the Sacconi Award) and distinctions. In recognition of his scientific career, he was elected as a member of the Accademia dei Lincei in 1999, [Fig. 2](#), and in 2006 was appointed *Professore Emerito* of the University of Pisa.

Fausto Calderazzo retired in 2005 but he is still present at the Department and, free from didactic and bureaucratic duties, he carries out and enjoys his own laboratory experiments, being firmly convinced that chemistry is an important branch of science and that laboratory experiments are the fundamentals of the research. Let me report a phrase taken from the cited interview [1]: *“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.”*

Finally, I wish to express my warmest thanks to all the authors for their contributions and especially to the Journal Editor, Barry Lever, for allowing a special issue of CCR honouring Fausto Calderazzo to be issued.

References

- [1] R. Poli, *Coord. Chem. Rev.* 188 (1999) 1.
- [2] G. Natta, R. Ercoli, F. Calderazzo, A. Alberola, P. Corradini, G. Allegra, *Rend. Accad. Nazl. Lincei, Cl. Sci. Mat. Fis. Nat.* 27 (1959) 107.
- [3] Crystalline, black-green solid of characteristic, nasty, smell similar to that of cobalt octacarbonyl.

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