

Professor Marcial Moreno-Mañas

A Tribute



Prof. M. Moreno-Mañas (MMM) was born in Barcelona (Spain) on September 30, 1941. I met him for the first time in 1973 as a student of Chemistry (“Licenciatura”) at the Universitat Autònoma de Barcelona. He had just joined this young University (as Associate Professor) along with a group of talented and very active organic chemists headed by Prof. Josep Castells. His courageous and indomitable character impressed me from the very beginning, and my association with him has continued since then – as a Ph. D. student, as a senior member of his Research Group, and later as fellow chemist, colleague, admirer and friend. I feel highly privileged to contribute this article to an issue of ARKIVOC dedicated to him.

MMM was educated through his B. Sc. Degree at the University of Barcelona, and carried out his Ph.D. at the same University under the supervision of Prof. Josep Pascual Vila. At that time, research was not easy in Spain due to the lack of tradition and very poor funding. However, MMM, and others of his generation, decided to change things. First, it was necessary to get the best background in chemistry; second, to establish stable research groups, demonstrating that with some economic assistance, chemistry at the highest level could be done. Nowadays, the historic perspective shows that they succeeded since chemistry in Catalonia, and in general in Spain is thriving. Many competitive groups exist, and it is fair to recognize the effort of people like MMM that made this possible. In 1968, MMM joined the group of Prof. Alan R. Katritzky at the University of East Anglia (Norwich, England) as a post-doctoral associate for two years (he returned there for another stay in 1974). In this environment, MMM became familiar with the basic principles of physical organic chemistry, heterocyclic chemistry, and conformational analysis, fields that he never has abandoned in spite of the changes in his main research interests over the years. In the group of Prof. Katritzky, he worked mainly on the conformational analysis of saturated heterocycles. After returning to Barcelona, he was appointed Associate Professor at the Universitat Autònoma de Barcelona (UAB). This University had been created in 1968, and

therefore there were many things to do there just to keep it running; however, on the positive side, the faculty members were devoid of the old habits that were holding the traditional Spanish Universities at a very low pace in research. The Department of Organic Chemistry of the UAB quickly became one of the leaders in organic chemistry research in the country, contributing tremendously to the prestige of the UAB as a research oriented University. MMM was its Director from 1978 to 1986 when it was integrated in the Department of Chemistry. Since 1983 MMM has been a Full Professor of Organic Chemistry at the UAB.

Upon his arrival at the UAB, MMM commenced to build his research group, and decided to focus his research on the use of transition metals in organic synthesis. In this sense he was a real pioneer since very few organic chemistry groups were involved in organometallic chemistry at that time in the country. In 1975 his first article on the subject appeared ("Alkylations in Neutral Media. Reactions of Nickel (II) bis-2,4-Pentanedionato with Alkyl Halides" *Tetrahedron Letters* **1975**, 1727). The field of the alkylation of polycarbonyl compounds in neutral media through the use of nickel, cobalt, and copper complexes achieved a rapid development in the group giving rise to an important number of research articles. The subject has been reviewed several times, and over the years all of its aspects have been tackled (synthesis, reactivity, mechanisms, catalysis, asymmetric induction, related reactions such as Michael additions, etc.).

A specific commentary must be made about the work of MMM on palladium catalyzed reactions. This field has been central in the research activity of MMM over the years, his group having significantly contributed to its extraordinary development. Especially remarkable are his studies on the regioselectivity of the allylation using ambident nucleophiles, the mechanistic studies on the regioselectivity of nucleophilic attacks on π -allylpalladium complexes, and the development of methods to achieve the allylic C-alkylation of highly acidic substrates.

In spite of his interest on organometallic chemistry, MMM has never forgotten his origins, and therefore, heterocyclic chemistry and conformational analysis have been very much evident in his research at the UAB. Work on the chemistry of pyrones derived from dehydroacetic acid and from triacetic acid lactone occupied an important period of his life, and in many cases, they were used to test the methods derived from the studies on transition metals. A review published in 1992 summarizes the more important results in this field. He also paid attention to the metallations, especially lithiations, of heterocyclic compounds such as imidazoles and thiazoles. Since 1998 he has been an Honorary Fellow of the Florida Center for Heterocyclic Compounds, at the University of Florida, USA. On the conformational analysis side, MMM, in collaboration with C. Jaime and H. Hernandez-Fuentes, introduced a very useful mixed approach: theoretical calculations plus validation through dipole moment determinations.

One of the big interests of MMM over the years has been in the area of medicinal chemistry. In this sense, his group has always been in close collaboration with the local pharmaceutical industry. From this work (published in several patents), it is noteworthy to emphasize his interest in antifungal agents since it has led to the development of products that are currently in the market. He has been, and currently is, a consultant for several industrial companies.

One example of the broad scientific interests of MMM, and his generosity, is his work on nucleophilic aromatic photosubstitution and on photoaffinity labeling. At this point I must recognize the enormous influence of MMM on my scientific career, not only as my Ph.D.thesis

supervisor, but also as the person who started what lately has become my main research interest, the photochemistry and the electron transfer chemistry of electron deficient aromatic compounds. It began by the suggestion of a biologist colleague of using the nucleophilic aromatic photosubstitution reaction as a tool in the photoaffinity labeling technique. At that time it was thought that this photoreaction (the Havinga reaction) was well known, and therefore, it was a good candidate for the development of new approaches to photoaffinity labeling. We had no previous training on photochemistry, but the determination of MMM made things possible. Several biologically active compounds were modified in order to test the idea, but more importantly, it was found that electron transfer had a great influence in the outcome of the Havinga photoreaction. A new, very fruitful, and in principle unexpected, research area was opened from that point, and MMM deserves the credit. More remarkable, when, after years of collaboration, I got my own independent research group, MMM completely abandoned his research in photochemistry and electron transfer in order that my group could fully develop the matter.

In order to conclude this concise, not comprehensive (MMM has published more than 200 research articles and reviews) survey of the research activity of MMM, it is noteworthy to document some of his current interests. These include recovery of catalysts, synthesis of unnatural amino acids and amino alcohols, enantio- and diastereoselective reactions, etc. Very recently, his group has commenced studies in the field of materials science and nanoparticles and aerogels are now common words. I am sure he will be successful here, as he has succeeded in all the other fields he has researched. MMM is an example of a problem solving scientist, without being afraid of what he will have to learn to achieve his goal (organometallics, heterocyclic chemistry, conformational analysis, medicinal chemistry, photochemistry, supramolecular chemistry, new materials, etc.). Once he said to me: "Jordi, I have a problem, I have solved that particular scientific problem so I must look for another one".

His sabbatical leave in Toulouse (France) with J. P. Majoral, several invited professorships in French universities, and his participation in several COST programs of the European Union have strengthened the scientific ties between different European countries (especially France) and Spain. He has lectured extensively in Spain, France, USA, Belgium, Hungary, Italy, Denmark, Sweden, and Cuba.

The research career of MMM does not end with his scientific contributions. From his group, many high-level chemistry professionals have evolved, including university professors and high level industry executives. His personal influence on a whole generation of organic chemists in Spain cannot be ignored, and this includes his responsibility as co-author and co-editor of the report "Tendencias Actuales en Química" (1986), a sort of Spanish "Pimentel report" with an enormous influence on the orientation of the lines of research in chemistry in Spain since then.

On the home front, MMM has two daughters, but neither of them have followed their father's career, as they have preferred humanities. This is not strange since MMM surprises with his erudition, and he is very fond of philosophy and history (not the least being sports). It is always a pleasure to have a relaxed, non-chemical, conversation with him in front of a glass of one of those very old smoked whiskies he always keeps in his office. His opinions can be often controversial, but they are always well founded, forcing people to think.

Selected Publications of Marcial Moreno-Mañas

1. Preparation of Nitrogen-Containing 20-Membered Tetraolefinic Macrocycles: (*E,E,E,E*)-1,6,11,16-Tetra(arylsulfonyl)-1,6,11,16-tetraazacycloicosa-3,8,13,18-tetraenes. Belén Blanco, Silvia Cerezo, Marcial Moreno-Mañas, Roser Pleixats, Jan Spengler. *Tetrahedron Lett.* **2001**, 42, 9001.
2. Fluorous Phase Soluble Palladium Nanoparticles as Recoverable Catalysts for Suzuki Cross-Coupling and Heck Reactions. Marcial Moreno-Mañas, Roser Pleixats, Silvia Villarroya. *Organometallics* **2001**, 20, 4524.
3. Metal Complexes of 15-Membered Triolefinic Macrocycles. (*E,E,Z*)-1,6,11-Tris[(2,4,6-triisopropylphenyl)sulfonyl]-1,6,11-triazacyclopentadeca-3,8,13-triene and its Palladium(0), Platinum(0), and silver(I) Complexes. Jordi Cortès, Marcial Moreno-Mañas, Roser Pleixats. *Tetrahedron Lett.* **2001**, 42, 4337.
4. The First Transition Metal Complexes of 15-Membered Triolefinic Macrocycles: (*E,E,E*)-1,6,11-Tris(arenesulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-triene Complexes of Palladium(0), Platinum(0), and Silver(I). Silvia Cerezo, Jordi Cortès, Elena Lago, Elies Molins, Marcial Moreno-Mañas, Teodor Parella, Roser Pleixats, Javier Torrejón, Adelina Vallribera. *Eur. J. of Inorg. Chem.* **2001**, 1999.
5. Preparation of Nitrogen-Containing 15-Membered Triolefinic Macrocycles. (*E,E,E*)-1,6,11-Tris(arylsulfonyl)-1,6,11-triazacyclopentadeca-3,8,13-trienes. Silvia Cerezo, Jordi Cortès, David Galvan, Elena Lago, Caroline Marchi, Elies Molins, Marcial Moreno-Mañas, Roser Pleixats, Javier Torrejón, Adelina Vallribera. *Eur. J. of Inorg. Chem.* **2001**, 329.
6. Oxidative Addition of Allylic Carbonates to Palladium(0) Complexes: Reversibility and Isomerization. Christian Amatore, Sophie Gamez, Anny Jutand, Gilbert Meyer, Marcial Moreno-Mañas, Lurdes Morral, Roser Pleixats. *Chemistry, European Journal* **2000**, 6, 3372.
7. Conjugate Addition to Diethyl Azodicarboxylate under Organic-Perfluorinated Biphasic Homogeneous Catalysis by Nickel(II) Species. Miriam Meseguer, Marcial Moreno-Mañas, Adelina Vallribera. *Tetrahedron Lett.* **2000**, 41, 4093.
8. Copper(I) Oxide Mediated Perfluoroalkylation of Anilines. Marcial Moreno-Mañas, Roser Pleixats, Silvia Villarroya. *Synlett* **1999**, 1996.
9. Density Functional Study on the Regioselectivity of Nucleophilic Attack in 1,3-Disubstituted (Diphosphino)(η^3 -allyl)palladium Cations. Vicenç Branchadell, Marcial Moreno-Mañas, Francesca Pajuelo, Roser Pleixats. *Organometallics* **1999**, 18, 4934.
10. Electrospray Ionization Mass Spectrometry (ESI-MS) Detection of Intermediates in the Palladium-Catalyzed Oxidative Self-Coupling of Areneboronic Acids. María A. Aramendía, Fernando Lafont, Marcial Moreno-Mañas, Roser Pleixats, Anna Roglans. *J. of Org. Chem.* **1999**, 64, 3592.
11. Palladium(0)-Catalyzed Allylation of Highly Acidic and non Nucleophilic Anilines. The Origin of Stereochemical Scrambling when Using Mixed Carbonates. Marcial Moreno-Mañas, Lurdes Morral, Roser Pleixats. *J. of Org. Chem.* **1998**, 63, 6160
12. Stereospecific Preparation of (*E*) and (*Z*)-3,3-Diarylacrylonitriles by Heck Reaction. Marcial Moreno-Mañas, Roser Pleixats, Anna Roglans. *Synlett* **1997**, 1157.

13. Preparation and NMR Spectroscopy of (1,2-Bis(diphenylphosphino)ethane)(η^3 -1,3-diarylallyl)-palladium Tetrafluoroborates. Correlation of Chemical Shifts with Hammett Substituent Constants and with the Regioselectivity of Nucleophilic Attack. Marcial Moreno-Mañas, Francesca Pajuelo, Teodor Parella, Roser Pleixats. *Organometallics* **1997**, *16*, 205.
14. Stereospecific Preparation of Ethyl (*E*) and (*Z*)-3-Aryl-3-phenylpropenoates by Heck Reaction. Marcial Moreno-Mañas, Montserrat Pérez, Roser Pleixats. *Tetrahedron Lett.* **1996**, *37*, 7449.
15. Palladium(0)-Catalyzed Allylation of Ambident Nucleophilic Aromatic Heterocycles. Marcial Moreno-Mañas, Roser Pleixats. *Advances in Heterocyclic Chemistry* **1996**, *66*, 73.
16. Cobalt-Mediated Alkylation of (4*R*) and (4*S*)-3-Acetoacetyl-4-benzyloxazolidin-2-ones. Preparation of Enantiopure Diphenylmethyl-, 9-Fluorenyl- and (1-Adamantyl)glycines. Nicanor Gálvez, Marcial Moreno-Mañas, Adelina Vallribera, Elies Molins, Araceli Cabrero. *Tetrahedron Lett.* **1996**, *37*, 6197.
17. Palladium-Catalyzed Suzuki-Type Self-Coupling of Arylboronic Acids. A Mechanistic Study. Marcial Moreno-Mañas, Montserrat Pérez, Roser Pleixats. *J. of Org. Chem.* **1996**, *61*, 2346.
18. (1-(Dimethylamino)-2-(diphenylphosphino)ethane)(η^3 -1-arylallyl)palladium Tetrafluoroborates. Preparation, Isomeric Equilibria and Correlations of NMR Chemical Shifts with Hammett Substituent Constants. Ramón Malet, Marcial Moreno-Mañas, Teodor Parella, Roser Pleixats. *J. of Org. Chem.* **1996**, *61*, 758.
19. Transformations of β -Dicarbonyl Compounds by Reactions of Their Transition Metal Complexes with Carbon and Oxygen Electrophiles. Marcial Moreno-Mañas, Jordi Marquet, Adelina Vallribera. *Tetrahedron* **1996**, *52*, 3377. (*Tetrahedron Report* 391).
20. (1,2-Bis(diphenylphosphino)ethane)(η^3 -1-arylallyl)palladiumtetrafluoroborates. Distribution of the Positive Charge Density by Correlation of NMR Chemical Shifts with Hammett Substituent Constants. Ramón Malet, Marcial Moreno-Mañas, Teodor Parella, Roser Pleixats. *Organometallics* **1995**, *14*, 2463.
21. Preparation of 1,3-Diarylpropenes by Phosphine-Free Palladium(0)-Catalyzed Suzuki-Type Coupling of Allyl Bromides with Arylboronic Acids. Marcial Moreno-Mañas, Francisca Pajuelo, Roser Pleixats. *J. of Org. Chem.* **1995**, *60*, 2396.
22. Expedient Preparation of η^3 -Allylpalladium Tetrafluoroborates Using 2,4,6-Triphenylpyridine Neutral Leaving Group. Ramón Malet, Marcial Moreno-Mañas, Roser Pleixats. *Organometallics* **1994**, *13*, 397.
23. A Radical-Organometallic Glycine Synthone. Preparation of Homochiral Heterocyclic α -Amino Acids. María E. Lloris, Marcial Moreno-Mañas. *Tetrahedron Letters* **1993**, *34*, 7119.
24. Mechanistic Studies on the Alkylation of Pentane-2,4-dione through its Co(II) Complex. Adelina Vallribera, Jorge Marquet, Marcial Moreno-Mañas, Eduard Cayón. *Tetrahedron* **1993**, *49*, 6437.
25. Palladium-Catalyzed Allylation of Pyrimidine-2,4-diones (Uracils) and of 6-Membered Heterocyclic Ambident Sulfur Nucleophiles. Marcial Moreno-Mañas, Roser Pleixats, Mercè Villarroya. *Tetrahedron* **1993**, *49*, 1457.

26. The Search for Biochemical Photoprobes. III. The Photoreactions of 4-Nitroveratrole and 2-Fluoro-4-nitroanisole with Bovine Pancreatic Ribonuclease A and with Model Nucleophiles. Jorge Marquet, Lourdes Rafecas, Albert Cantos, Marcial Moreno-Mañás, Maria Cervera, Francisco Casado, M. Victòria Nogués, Claudi M. Cuchillo. *Tetrahedron* **1993**, *49*, 1297.
27. 1H-Imidazole Derivative Compounds and Pharmaceutical Compositions Containing the Same. Rafael Foguet, Marcial Moreno, Manuel Raga, Rosa M. Cuberes, José M. Castelló, José A. Ortiz. *US Patent* 5,135,943, 1992.
28. Dehydroacetic Acid, Triacetic Acid Lactone and Related Pyrones. Marcial Moreno-Mañás, Roser Pleixats. *Adv. in Heter. Chem.* **1992**, *53*, 1.
29. Alkylations of α -Methyl Substituted β -Diketones through their Cu(II) Complexes. Preparation of Sterically Congested β -Diketones. M.E. Lloris, J. Marquet, M. Moreno-Mañás. *Tetrahedron Lett.* **1990**, *31*, 7489.
30. C-Allylation of *L*-Ascorbic Acid under Palladium(0) Catalysis. Marcial Moreno-Mañás, Roser Pleixats, Mercè Villarroya. *J. of Org. Chem.* **1990**, *55*, 4925.
31. On the Regioselectivity of 4-Nitroanisole Photosubstitution with Primary Amines. A Mechanistic and Theoretical Study. Albert Cantos, Jorge Marquet, Marcial Moreno-Mañás, Angels González-Lafont, José Ma Lluch, Juan Bertrán. *J. of Org. Chem.* **1990**, *55*, 3303.
32. Electronic Effects on the Regioselectivity of Nucleophilic Attacks on π -Allylpalladium Complexes. Marcial Moreno-Mañás, Jordi Ribas. *Tetrahedron Lett.* **1989**, *30*, 3109.
33. Copper Protection in the Palladium Catalyzed Regioselective Allylation of a Model Polyketide: Methyl 3,5-Dioxohexanoate. Jorge Marquet, Marcial Moreno-Mañás, María Prat. *Tetrahedron Letters* **1989**, *30*, 3105.
34. Palladium Catalyzed C-Alkylations of the Highly Acidic and Enolic Triacetic Acid Lactone. Mechanism and Stereochemistry. Marcial Moreno-Mañás, Jordi Ribas, Albert Virgili. *J. of Org. Chem.* **1988**, *53*, 5328.
35. Tandem [2,3]Sigmatropic Rearrangement of Sulphonium Ylides and Bromine Allylic Rearrangement on a 4-Methoxy-2-pyrone Derivative. Pedro de March, Marcial Moreno-Mañás, José L. Roca. *J. of Org. Chem.* **1988**, *53*, 5149.
36. Cobalt(II) Chloride Bistriphenylphosphine Catalyzed Alkylations of β -Dicarbonyl Compounds. A. González, J. Marquet, M. Moreno-Mañás. *Tetrahedron Lett.* **1988**, *29*, 1469.
37. On the Regioselectivity of the Nucleophilic Aromatic Photosubstitutions of 4-Nitroveratrole. A Threefold Mechanistic Pathway. Albert Cantos, Jorge Marquet, Marcial Moreno-Mañás, Assumpta Castelló. *Tetrahedron* **1988**, *44*, 2607.
38. Molecular Mechanics and Dipole Moments as a Useful Combination in Conformational Analysis of Open-Chain Compounds. Application to α -Adamantyl- β -diketones. Marcial Moreno-Mañás, Asensio González, Carlos Jaime, Jorge Marquet, Irmina Hernández-Fuentes, Catalina Salom, Juana Bellanato. *J. of the Chem. Soc., Chem. Commun.* **1987**, 1706.
39. On the Regioselectivity of the Nucleophilic Aromatic Photosubstitution. The Photoreaction of 4-Nitroveratrole with *n*-Hexylamine. Albert Cantos, Jorge Marquet, Marcial Moreno-Mañás. *Tetrahedron Lett.* **1987**, *28*, 4191.

40. Copper Complex Protection in the Regioselective Alkylation of Methyl 3,5-Dioxohexanoate. Preparation of 3-Alkyl Derivatives of 4-Hydroxy-6-methyl-2-pyrone. Jordi Cervelló, Jorge Marquet, Marcial Moreno-Mañás. *Tetrahedron Letters* **1987**, 28, 3715.
41. Cobalt Mediated Regioselective Alkylation of Methyl 3,5-Dioxohexanoate. Preparation of 5-Alkyl Derivatives of 4-Hydroxy-6-methyl-2-pyrone. Jordi Cervelló, Jorge Marquet, Marcial Moreno-Mañás *J. of the Chem. Soc., Chem. Commun.* **1987**, 644.
42. 4-Nitropyrocatechol Ethers as Possible Photoaffinity Labels. Photochemical Reactions of 4-Nitropyrocatechol Ethers of Biologically Active Compounds. A. Castelló, J. Cervelló, J. Marquet, M. Moreno-Mañás, X. Sirera. *Tetrahedron* **1986**, 42, 4073.
43. Alkylation of β -diketones through their Co(II), Co(III) and Zn(II) Complexes. 1-Bromoadamantane as Alkylating Agent. A. González, F. Güell, J. Marquet, M. Moreno-Mañás. *Tetrahedron Lett.* **1985**, 26, 3735.
44. A Very Simple Synthesis of Natural Saturated δ -Substituted δ -Lactones. The Pheromone of *Vespa orientalis*. Bacardit, R.; Moreno-Mañás, M. *Chem. Lett.* **1982**, 5.
45. Double Bond Formation by One Pot Palladium Induced Reactions between Aldehydes, Allylic Alcohols and Triphenylphosphine. Moreno-Mañás, M.; Trius, A. *Tetrahedron Lett.* **1981**, 22, 3109.
46. Hydrogenations of Triacetic acid Lactone. A New Synthesis of the Carpenter Bee (*Xylocopa hirsutissima*) Sex Pheromone. Bacardit, R.; Moreno-Mañás, M. *Tetrahedron Lett.* **1980**, 21, 551.
47. Reactions of Bis(pentane-2,4-dionato)cobalt(II) with Alkyl Halides. Marquet, J.; Moreno-Mañás, M. *Synthesis* **1979**, 348.
48. Alkylations in Neutral Media. Reactions of Nickel(II) bis-2,4-Pentanedionato with Alkyl Halides. Boya, M.; Moreno-Mañás, M.; Prior, M. *Tetrahedron Lett.* **1975**, 1727.

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