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Pioneers and Influencers in Organometallic Chemistry: Professor David Carrillo Contreras, an Inspiring Contributor to Chemistry in Chile.

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The "Pioneers and Influencers" project at Organometallics is designed to spotlight the careers and contributions of individuals who have made noteworthy contributions to this field of chemistry, but whose accomplishments may not be so well known. Dr. David Carrillo Contreras, Emeritus Professor at Pontificia Universidad Católica de Valparaíso (PUCV), in Chile, is one of these "unsung heroes" in the organometallics community whose work and commitment have played a pivotal role in advancing the field, by inspiring and training generations of chemists.

Professor Carrillo, hailing from the resource-constrained environment of South America, may not have had a career that resonates as loudly as some researchers in the field, but his journey has been marked by unwavering dedication and substantial achievements. For example, he has forged meaningful and fruitful chemical collaborations between Chile and France, earning him the honor of being recognized in 2013 by the French government with the title of "*Chevalier of the Palmes Académiques*" for his significant contributions to education. We wish to share his story, as we believe it will inspire many others.

Born in 1939 in the coastal city of Talcahuano in southern Chile, David was marked by an insatiable curiosity and a drive to understand the world at a molecular level. He obtained his bachelor's in Philosophy and Education (1964) at PUCV. Following his initial academic pursuits, he secured a prestigious scholarship for his Ph.D. studies (1968) at Universidad Complutense in Madrid, Spain. During this period, he immersed himself in groundbreaking research, focusing on the intricate process of separating stable isotopes of nitrogen through ion chromatography.¹ Then, he returned to PUCV as a young professor, and started a family with Elsa Marín Figueroa, raising four daughters: Araceli, Gisela, Maria Soledad, and Marcela.

In 1980, David and his family relocated to Paris, France, where he secured a postdoctoral position sponsored by the French Embassy in Chile at Université Pierre et Marie Curie (Paris VI), under the guidance of Prof. Yves Jeannin working in close collaboration with Dr. Pierre Gouzerh. This experience provided David with an invaluable opportunity to further his research skills and expand his academic horizons. Upon concluding his postdoctoral studies in 1981, David made the decision to return to PUCV. His aim was clear: to fortify his position within the academic community and take on a multitude of academic responsibilities that would contribute to the enrichment of the educational environment in Chile. During his career at PUCV he assumed significant roles, such as Director of the Chemistry Institute, overseeing pivotal areas of research and graduate studies. His leadership extended to becoming Dean of the Science Faculty, and he eventually ascended to the position of Academic Vice President. Each of these roles demonstrated his commitment to the advancement of academic excellence and his ability to drive positive change within the educational community (Figure 1).



Figure 1. Prof. Carrillo in a PUCV laboratory circa 2013, smiling and gesturing toward the bench, suggesting ideas and helping solve students' or colleagues' daily chemical challenges. Moreover, he consistently provides insightful commentary on Chile's sociopolitical landscape, offering a clear and thoughtful vision of areas that needed enhancement for the prosperity of future generations.

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Throughout his career, David has maintained a number of long-term fruitful collaborations with French researchers and institutions. In the 1990s, he coordinated several formalized bilateral research projects, and since 2009 participated in the International Associated Laboratories and International Research Project that involve chemists from Université de Rennes and several Chilean universities, including PUCV. Through such cooperation structures, David has strongly encouraged his students to carry out extended internships in France or enhance their thesis under joint supervision (cotutelle program). Altogether, he has mentored countless students, shaping the current and next generation of industrial and academic chemists and biochemists in Chile and beyond.

After an intense and successful career with his many roles at PUCV serving as a foundation, Prof. Carrillo was invested as professor emeritus in 2011. Beyond his academic achievements, David's life has been enriched by his family weaving a tapestry of memories filled with both academic milestones and cherished family moments.

Advancements in Molybdenum and Iron Organometallic Chemistry: Exploring Disulfide Ligands and Hydrazine Derivatives.

Studying disulfide bonds as ligands offers intriguing insights, particularly in their role in biological redox processes. Prof. Carrillo's work underscores the significance of coordinated sulfur in biological systems and illuminates the redox equilibrium between organic disulfides (RS-SR') and mercaptides (RS-) in aqueous solutions, intricately influenced by metal-ion complexation.^{2,3} He brought this phase of his research to a culmination by authoring a review on organodisulfide complexes.⁴ David's contributions to the field were not only evident in his publications but also in his interactions with other eminent scholars. Indeed, in July 1995, with David as Visiting Professor and F. Albert Cotton of Texas A&M University as a Doctor honoris causa recipient, met coincidentally at the Université de Rennes. Their encounter led to an astonishing, and meaningful, scientific dialogue in French, a language fluently spoken by both of them. They mainly discussed the bioinorganic and coordination chemistry of the aforementioned disulfide complexes, and Cotton promised to introduce elements of David's review into the next edition (6th) of his renowned textbook.⁵

In the initial stages of his career, David quickly realized the indispensable value of international collaborations for the progression of his research, especially when it came to utilizing crucial characterization techniques such as single crystal X-ray diffraction, ¹H and ¹³C-NMR, elemental analysis, and high-resolution mass spectrometry. Considering the challenges of establishing a chemistry research group in Chile, especially in light of the severe economic downturn in 1982, David proactively sought to enhance his collaborative network. He reached out to distinguished colleagues, including the late <u>Professor Alan H. Cowley at the University of Texas, Austin.</u>⁶ Professor Cowley had a notable history and connection with Chile and France, and expressed admiration for David's efforts and professional path. Their joint efforts culminated in a published article,⁷ marking a significant milestone in David's research journey.

This piece elaborated on the synthesis and characterization of binuclear *cis*-dioxomolybdenum(VI) cation complexes. The team conducted X-ray analyses on two specific complexes, $[MoO_2(o-OC_6H_4-NN=CSNHN=CHC_6H_4OH-o)Me_2SO]$ and $[(MoO_2)_2(o-OC_6H_4CH=NN=CONN=CHC_6H_4O-o)(Me_2SO)_2]$

 $0.5Me_2SO$ (Figure 2), providing a deeper insight into the structural intricacies. This comprehensive study enriched the existing knowledge of *cis*-dioxomolybdenum(VI) complexes, showcasing the complexity and versatility of these organodinitrogen molybdenum compounds in coordination chemistry.⁸



Figure 2. ORTEP view of $[(MOO_2)_2(o-OC_6H_4CH=NN=CONN=CHC_6H_4O-o)(Me_2SO)_2]$ 0.5Me₂SO. Thermal displacement ellipsoid plotted at the 50% probability level.

In the mid-1990s, David's research focused on the synthesis and characterization of a series of cationic organometallic complexes featuring a *cis*-[Mo(NNRR')₂]^{2+,9,10} The metal-organodinitrogen ligand bonding was investigated by theoretical methods within the framework of the fertile collaboration that David initiated, in the late 1990s, with Dr. Samia Kahlal, and Professor Jean-Yves Saillard (Université de Rennes). They provided a theoretical foundation for this specific "Mo-NN" subject, 11,12 and later on, for many of the novel experimental observations from David's research fields such as organometallic hydrazones¹³ and transitionmetal complexes of unsymmetrically substituted Schiff base ligands (see below).14 Through this extended study on organodinitrogen-molybdenum species, David and co-workers have not only bridged a significant gap in the field of organometallic chemistry but also laid a solid foundation for the research on compounds with the *cis*-[Mo(NNRPh)₂]²⁺ unit.

Synthesis and Characterization of Hydrazine and Hydrazone-Based Organometallic Complexes for Nonlinear Optical Applications

David's other key collaboration is with Dr. Jean-René Hamon (who is a co-author of this Pioneers and Influencers article) at the Université de Rennes. They published their first peer-reviewed article together in 1997 and have jointly published 66 scientific articles to date. David likes to describe this long-term collaboration as "having been catalyzed" by Professor Didier Astruc (Université de Bordeaux) he had met first in Santiago de Chile (1985) and then in Bordeaux (1989). David and Jean-René's research work involved the investigation of cationic hydrazine- and hydrazone- based organometallic complexes, and Schiff base coordination compounds for Second-Order Nonlinear Optics (NLO-2) applications.¹⁵ On the other hand, David and his colleague from

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PUCV, Dr. Carolina Manzur (who is also a co-author of this Pioneers and Influencers article), have developed a multifaceted partnership characterized by professional rigor and a profound personal bond. Together, they have collaboratively expanded their research in the field, notably advancing it through innovative condensation reactions, successfully synthesizing three high-yield organometallic π -conjugated push-pull chromophores between cyclopentadienyl iron(II)-complexed p-tolylhydrazines and variously substituted archetypal pyranylideneacetaldehydes.¹⁶ The organometallic systems prepared in this work emerged as strongly polarized D- π -A systems, displaying solvatochromic properties, low-lying intramolecular charge-transfer bands in their electronic absorption spectra, and amplified NLO-2 properties (Hyperpolarizability β). Theoretical computations have been essential for an in-depth exploration of the electronic structures of the complexes, as well as the electronic transitions that contribute to the NLO-2 response.

Advancing Nonlinear Optical Applications: Synthesis and Characterization of Dissymmetrical Schiff base Organometallic Complexes with Enhanced NLO-2 Properties.

David's and Carolina's research team synthesized a series of complexes supported with Schiff base ligands,¹⁷ aiming to uncover compounds with desirable properties for NLO-2 response.^{14,18–27}



Scheme 1. Synthetic pathway for organometallic half unit ONN ligands and its N_2O_2 dissymmetric Schiff base complexes in the presence of the appropriate salicylaldehyde derivative and metal(II) ion cores.

One of the main iterations was the synthesis, spectroscopic, and structural characterization, as well as the linear and NLO-2 properties of a series of robust neutral binuclear and ionic trinuclear organometallic complexes. These D- π -A conjugated complexes are based on neutral M[ONNO]-type dissymmetrical Salophen and Salen complexes,²⁸ which incorporate a push-pull system based on ferrocenyl, donor, the salicylaldehyde ring of the acyclic tetradentate Schiff base core being π -coordinated to mixed sandwich acceptor [Cp*Ru(n⁶-salicylidene)]⁺[PF₆]⁻ (Scheme 1).¹⁴ Notably, the trinuclear complex of Ni(II) displayed a hyperpolarizability (β = 250 x 10⁻³⁰ esu) value 1.6 times greater than that of the mononuclear precursor metalloligand.

Additionally, the ability to tune these responses by altering the nuclearity (number of metal cores) of the complexes offers a versatile approach to designing materials with tailored NLO-2 properties. Moreover, David's group and its collaborators also moved to NLO -2 materials by incorporating the Schiff bases complexes into macromolecular matrices, ^{29,30} forming main-chain and side-chain polymers, showing values up to β = 970 × 10⁻³⁰ esu for a Pd(II) containing side-chain polymer.³¹

Conclusion and Legacy

We have highlighted the outstanding contributions and rich legacy of Emeritus Professor David Carrillo Contreras. Despite facing numerous challenges in a resource-constrained environment, he has persevered to make indelible marks in the field of organometallic/inorganic chemistry in Chile, particularly in the realm of diffusion, teaching, and research of coordination chemistry, bioinorganic chemistry, and macromolecule chemistry. His work has not only advanced our understanding of complex chemical processes but has also nurtured a generation of Chilean chemists, fostering academic excellence and innovation. Professor Carrillo's story is one of unwavering commitment, resilience, and profound impact, serving as a beacon of inspiration for future chemists and academics. Professor Carrillo's legacy is set to endure for many years, particularly through the successful students he has mentored in the Franco-Chilean research group. This group, a testament to his influence, continues to make significant contributions in the field. We are all honored and proud to be identified with such an eminent scientist, mentor, and great friend, and we wish him many more great accomplishments. A final aspect of David's personality is his humanism, and he will remain for us "Le Petit Prince", of whom he likes to talk about very often, which is also his favorite eponymous book by Antoine de Saint Exupéry, "Saint Ex" as he always likes to say with a mischievous smile.

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