Second coordination sphere effects in [FeFe]-Hydrogenase mimics

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Acknowledgments
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After about four years, another chapter of my life is now coming to an end. However, this cannot be done without first spending few words of appreciation for those who contributed either directly or indirectly to my work and thesis.

Firstly, I would like to express my gratitude to my supervisor Joost for giving me the opportunity to join the HomKat group and the chance to further explore the fascinating hydrogenase topic under a different perspective than what I was used to. I really appreciated the complete freedom I could experience, being able to explore my own ideas and routes. Thanks for your useful insights and discussions to reconstruct many scientific puzzles.

I am very grateful to my copromotor Jarl. Without you this book would have been very different! Thanks for solving my crystal structures, for your inputs, remarks and attention to the smallest details. In particular, thank you for being extremely patient and always available to help and listen. Among the things I learned from you there is a key lesson: each and every day deserves a new colorful shirt!

Special thanks to Remko for being my second copromotor, but also for being a daily companion always ready to enter an interesting and endless discussion about electrochemistry, devices and so on. I do miss those times when you also were around in the lab. Good luck and all the best for the near future!

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I would now like to express my sincere gratitude to the rest of the committee members Lies Bouwman, Marc Koper, Jan van Maarseveen and Sander Woutersen for making time to read this manuscript and accepting to be part of this important day.

Very special thanks to Tom Rauchfuss for accepting to join the committee and for travelling about 6,000 km to be here. But most importantly thank you for initiating me to the hydrogenase topic and to the academic research in general. I am very grateful for your enthusiasm and motivation without which I probably would have never started a PhD. Looking forward to welcome you in Amsterdam. I really miss our conversations in front of delicious food. This time, I'll bring you to the Dutch version of the Black Dog in Urbana, I am sure you will like it!

A big thanks to my paranymphs Simon and Tessel. Thank you for taking up this difficult task; I am sure you will do just great, looking forward to it. And Tessel... good luck dealing with the Australian! I’m sure you will have a lot of fun, but you will also need a lot of patience.
Next, I want to thank the technicians as their hidden role is essential for research and keeping the labs in good order. Lidy, thank you very much for sharing with me your experience, expertise and most often random, weird and extremely rare pieces of glassware. Thanks for doing your best at keeping all the supplies under control so that the lab could run smoothly. Erik, thanks for solving countless issues, in particular, for every time I brought an issue to your attention and you always solved it in no time. Jan Meine and Ed thanks for keeping the NMR and mass equipment in good order and for getting around my NMR questions and my urgent mass samples. I really appreciated your contribution. Thanks also to Fatna and Taasje.

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Simon, since the very first moment you stepped into our office (and lab) you have been talking about sardines... Lots of bla bla bla but nothing happened yet. So disappointing! I cannot move on to my next chapter without having a taste of this delicious dish of yours. Aside from this, thanks for sharing all the knowledge you have accumulated over the years and thanks a lot for all your valuable TIPS (both the one from Fluorochem and your actual synthetic tips and support during demanding experiments).

René, you were the most helpful person in the entire lab when I joined the group. You always had a good answer to my questions (although 80% of the time your answer was: ask Erik). I am very happy we have shared a lot of nice chemistry, conferences and cooking experiences. Nevertheless, you were also the first person ever giving me a psychological trauma; I now know white asparagus are the real deal and that one must discard not less than 80% of their volume as that part is skin! Anyhow, is it asparagus season, isn’t it?
Tessel, E1.41 is known for being the smelliest lab of the entire UVA, nevertheless only few know that you actually hold the record for the smelliest compound ever made! I always enjoyed helping you out whenever I could but that day... not so much! Besides this, I remember as it was yesterday (maybe because it actually was yesterday) when I asked you to be my paronymph and you happily and gladly accepted the task. The smile on your face was really flattering. Also, thanks for translating my summary; I feel I owe you a full Sunday of fun at some point!

Pauline, was very nice having you in the lab as your smile and laugh were contagious. Bid, I always have been very jealous of your green and blue air-stable compounds! Joeri, someday I will get you a real birthday present. Good luck with your two-thousand projects. Bradja, you are a machine; so many reactions and columns every day. Was very nice having you in the lab. David, thanks a lot for your endless effort to model my cages, I really appreciate that. I am very positive we can become good friends, I look forward to that but dude, you should talk way slower if you want me to understand you! Vivek, you are not technically part of E1.41 as you don’t need a lab for your simulations, but at least in my mind you are. Thanks for helping me out with the DFT calculations and bearing with my super basic questions. Thanks for sharing your cooking; it’s amazing and I do think that you should be doing that more often. Fengshou, welcome to our lab!

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job finishing your PhD, you should teach me how you managed to be extremely calm during your defense, or was that your twin brother? **Monalisa**, good luck with starting your own company, it's a brilliant idea. The younger HomKat generation. **Raoul**, so that you know... I will keep borrowing your soxhlet apparatus and eventually I will steal it. **Arnout**, I like how you are passionate about things, **Valentinos, Charles, Kaj, Pim** cannot wait for your defense, I have so much material for your paronymphs! **Tijmen** and **Marianne**, nice you joined our office. **Tiddo**, looking forward to your inputs and suggestions. **Bin** and **Shaotao**, thanks for your enthusiasm and for sharing some of your chemicals with me.

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Riccardo
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About the author
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Riccardo was born on the 18th of January 1987 in Como, Italy. Since the high school formation, he has always been interested in food chemistry, cooking science and fishkeeping. Such interests brought him to the chemistry field. After a high school training with a chemist specialization, Riccardo started his academic education at the University of Milano Bicocca at the chemistry department. During the bachelor he participated in the “Erasmus” exchange program and completed a six-month internship at the Royal Institute of Technology (KTH) in Stockholm, Sweden. Under the supervision of Prof. Lars Kloo he investigated the preparation of homo-poly-cationic naked clusters of group 15 elements in unconventional reaction media. During the master period, Riccardo obtained a Cariplo scholarship to perform a ten-month internship at the University of Illinois Urbana-Champaign (UIUC) under the daily supervision of Prof. Thomas B. Rauchfuss. Throughout this period he maturated a strong interest in renewable energies, in particular aimed at transferring the knowledge he gained regarding hydrogenase enzymes to sustainable hydrogen producing devices. In 2012 he graduated from the University of Milano Bicocca under the supervision of Prof. Luca De Gioia and Prof. Thomas B. Rauchfuss, with a thesis on synthesis and characterization of bio-inspired models of the [Fe-Fe]-hydrogenase active site. In the same year, he joined the homogeneous catalysis group (HomKat) lead by Prof. Joost N.H. Reek, at the University of Amsterdam (UVA). His four-year PhD project focused on understanding second coordination sphere effects in synthetic mimics of the [Fe-Fe]-hydrogenase active site. After his PhD, Riccardo will continue to explore his leading interests that have been accompanying him throughout his scientific formation.
List of publications


“New Tetracobalt Cluster Compounds for Electrocatalytic Proton Reduction: Syntheses, Structures, and Reactivity”


“Contrasting Protonation Behavior of Diphosphido vs Dithiolato Diiron(I) Carbonyl Complexes”


“Terminal vs. Bridging Hydrides of Diiron Dithiolates: Protonation of Fe$_2$(dithiolate)(CO)$_2$(PMe$_3$)$_4$”


“Reaction of Aryl Diazonium Salts and Diiron(I) Dithiolato Carbonyls: Evidence for Radical Intermediates”


“Dichloromethane as solvent for the synthesis of polycationic clusters at room temperature; a link to standard organometallic chemistry”
“W e must not forget that when radium was discovered no one knew that it would prove useful in hospitals. The work was one of pure science. And this is a proof that scientific work must not be considered from the point of view of the direct usefulness of it. It must be done for itself, for the beauty of science, and then there is always the chance that a scientific discovery may become, like the radium, a benefit for humanity.”

Marie Curie