

Evaluation report on a doctoral thesis

Author: **Mr Alexandros Paparakis**

Title: **Lewis acids and Frustrated Lewis pair catalysts for reduction and reductive coupling reactions of carbon dioxide**

The main theme of the submitted thesis is the use of frustrated Lewis pairs as catalysts for molecular hydrogen reductions that also utilize carbon dioxide. As such, it amalgamates environmental aspects of catalysis with a recent modern trend in fundamental inorganic chemistry. Research on such a topic is very important and timely.

The thesis consists of Introduction (16 pages), statement of Aims (2 pages), Summary of the results including Conclusions (24 pages), References (113 items), and is supplemented by four Appendices (three published papers each including Supporting Information (SI) and one unpublished text, in fact only SI of it, likely being prepared for publication soon) making a total of 275 pages. There is no Experimental part in the main body of the thesis, but experimental details are amply described in the SI parts of the papers. Mr Paparakis is the first author in three papers and the corresponding author in none. It should also be mentioned that unpublished results do not deal with catalysis by FLPs and appear to have been added simply to make the volume thicker.

The aims of the thesis are quite narrowly defined. The author mentioned that he was motivated by the lack of efficient water tolerant main group catalysts using predominantly molecular hydrogen. He has developed new R_3SnX Lewis acids that selectively hydrogenate CO_2 with concomitant coupling to amines, with water as the only byproduct. The catalysts have also been used in the synthesis of azoles from ortho-substituted anilines, CO_2 and H_2 . Here a new concept of "transfer formylating agent" was introduced when it was found that polyethyleneimine was predominantly formylated but later transferred the formyl group to anilines. To further extend the scope of tin-based LAs for FLPs several Schiff base complexes of tin were successfully tested in this role in imine hydrogenations. In my opinion, the aims of the thesis as stated in the relevant part of the text, have been achieved.

The author claims that the results represent a major advance in water tolerant FLP hydrogenations of CO_2 . The catalytic activities of the systems developed by the PhD student are rather moderate which is perhaps to be expected and tolerated in a new hot branch of research. However, while a comparison of catalytic activity with much more reactive transition metal-based catalysts is reported (their disadvantages are also mentioned), a comparison with known FLPs from the literature is missing. Is it really true that there are no known FLPs in the literature for the reported transformations?

The three papers mentioned have all been published in good/high quality international impacted journals and I am not in the least tempted to play the game of finding errors in documents that have gone through conscientious peer review. With a dissertation such as this, one is immediately confronted with the question of authorship. To answer this, the reader must consider whether the text of the dissertation is the story of the subject of the publications, retold in the author's own words. I am afraid that the submitted thesis does not quite fulfil this task.

Following the Introduction part dealing with the concept of catalysis by FLPs, the thesis is in its part Summary of the results divided into chapters according to publications. However, due to this the beginnings of the chapters always contain introductory information that duplicates in many instances

what has been the content of the Introduction. Many of the Schemes and Figures in the text of the thesis are taken over from the literature with errors, even from the author's own attached publications, which shows his carelessness. For example Tables 2.1 and 2.2 have no footnotes although upper right indexes appear there. In Fig. 8, taken from Ref. 22, there is a wrong structure "CH₂BR₂"; in Fig. 9 (ref. 43) instead of Me substituent nonsensically Mes substituent is shown; in Fig. 10 negative charge is wrongly put on oxygen; Fig. 12 is unclear, probably compiled from ref. 44; charges are missing in the right part of Fig. 22; reference X (Fig. 2) is not listed under references; Fig. 20 shows formylated products not parent amines; Fig. 4: starting materials are in fact above products; Fig. 11: structure of tris(pentafluorophenyl)boroxine is wrong; Fig. 15: structure of the cobalt complex has not been corrected; Fig. 16: symbol R for dialkyl/diarylphosphinyl groups is quite inappropriate; the formula of the ylide on page 8., l. 2 from the bottom is wrong.

As a non-native speaker myself, I will be very charitable about the language of the thesis. Nevertheless, in the sentence on p. 19, l. 6 from the bottom, a verb is missing. In the sentence on p. 9, l. 9 from the bottom "although" and "but" appear simultaneously, making the sentence unclear; on p. 9, line 2 from the bottom there is a noun + verb disagreement; "donor" not "donator" is a well established term in chemistry (p. 10, l. 1). "Higher" is better than "larger" when writing about activity (Abstract, l. 7), and instead "one of the only examples" one should better use "one of the rare examples" or "one of the only a few examples". There are still some typographical errors which I will not list, but no more than usual. The List of abbreviations is not in alphabetical order and contains some very common abbreviations, e.g. MS or GC. The format of the list of references was not always the same and the author did not bother to correct lower indexes in formulas, presumably after export from a citation software.

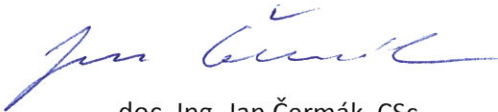
Finally, if you ask me whether Mr Paparakis is capable of being a useful member of a team producing very good quality research, my answer is yes, undoubtedly. However, if you ask me whether he can quite independently embark on a new topic my answer would be: "I am not sure". I look forward to hearing his defence.

I would like the candidate to answer several questions:

- i) On p. 12, l. 3 from the bottom the author writes that most of the syntheses where CO₂ is the C1 source require reduction of CO₂. Are there syntheses that do not require reduction?
- ii) Temperature 180 °C, long reaction times leading to TONs < 400 with TOFs only in one case as high as about 17. In your opinion is this a characteristic feature of an atom-economy and energy-saving process? Transition metal based catalysts are a lot more reactive. Would it not be better to start from them and inhibit their activity in a controlled way (the well-known concept of catalyst poisoning)? A decrease in activity is usually associated with an increase in selectivity and perhaps in tolerance.
- iii) Do you agree with the statement (p. 9, l. 5 from the bottom), allegedly taken from the literature (ref. 12), that "transition metals can act as both the Lewis base and as the Lewis acid leading to the homolytic splitting of dihydrogen"?

In conclusion I declare that the submitted thesis fulfils the aims and conditions required for this type of academic work and I recommend it for acceptance in the procedure leading to the award of the title of Doctor of Philosophy.

Horoměřice, 5th September 2024



doc. Ing. Jan Čermák, CSc.