Ústav fyzikální chemie J. Heyrovského AV ČR, v. v. i.
Dolejškova 2155/3, 182 23 Praha 8
VAT #: CZ61388955
Michal Horáček, Ph.D.
+420 26605 3965, michal.horacek@jh-inst.cas.cz

Review

Review of the thesis by Alexandros Paparakis entitled "Lewis acids and Frustrated Lewis pair catalysts for reduction and reductive coupling reactions of carbon dioxide".

The submitted thesis is written in the following format: introduction, aim and summary of the main results of the thesis, conclusion and bibliography in a total length of 60 pages without appendices. The appendices, which are an essential and integral part of the thesis, are comprehensive and present three published results, with one appendix dedicated to unpublished results. The thesis is written in English.

The summary of results is based on three publications in prestigous impact journals in the field of inorganic and coordination chemistry, including catalysis (Catalysis Science & Technology, ChemCatChem and Chemical Communications). Alexandros Paparakis is first author on two of them. The role of the reviewer is "simplified" in such an organised and presented thesis to evaluate the work as a whole, since the experimental results, their evaluation and conclusions have already been peer-reviewed in individual editorial processes prior to the publication of the individual articles.

Alexandros Paparakis' thesis deals with Lewis acids based on tin compounds and their use in catalytic hydrogenation. In particular, these are reductive condensation reactions of carbon dioxide with amines in the presence of hydrogen. The thesis is divided into four main units (according to the attached published and unpublished results). The first two units are linked by the ability of the synthesised tin compounds to form frustrated Lewis pairs, mainly due to the steric difficulty of the substituents limiting the formation of Lewis adducts. Prepared FLPs are able to activate molecular hydrogen and act as catalysts for hydrogenation reactions. The knowledge gained from the N-formylation of amines, in which carbon dioxide is reduced and bound to the amine, was used in a second study on the synthesis of azoles from ortho-substituted anilines. In the third part of the work, Schiff base stabilised tin complexes based on salen were prepared. The catalytic reactions of the hydrogenation of imines with hydrogen were tested. The last part is devoted to unpublished results of the reductive condensation reaction of carbon dioxide with amines in the presence of hydrogen donating organic molecules, catalysed by indium triflate complexes.

I consider the thesis as a whole to be a successful work, in my opinion the submitter has managed to put together a comprehensive study. I would like to point out a number of formal deficiencies in the submitted thesis, probably caused by typing errors or copying of figures, tables and text from

Ústav fyzikální chemie J. Heyrovského AV ČR, v. v. i.
Dolejškova 2155/3, 182 23 Praha 8
VAT #: CZ61388955
Michal Horáček, Ph.D.
+420 26605 3965, michal.horacek@jh-inst.cas.cz

manuscripts of published articles. For example: indexes in the tables, errors in the formulas in the introduction, etc. In my opinion, the summary of results is written concisely and focuses on the description of the main results. To understand the context and to get a more detailed explanation, it was easier for me to get the necessary information from the original articles. I would like to mention here that the attached copy of the article in Catal. Sci. Technology is of poor quality and practically unreadable.

In conclusion, I find that the thesis submitted by Alexandros Paparakis complies with the requirements of a doctoral thesis and I recommend it for defence.

As an opponent of the work presented, I would like to put forward the following questions and suggestions for discussion:

1. In result 4.1 you state that one of the best precatalysts is a compound containing three cyclohexane (Cy) and one triflate (OTf-) substituent. Can you please comment on the role of these substituents as well as the choice of the type of Lewis base used to form the FLPs and possibly the stability and reactivity of the tin hydride complex?
2. When studying catalytic N-formylation and substrate selection, you found that aromatic and benzylic amines were unreactive. Can you comment on what you think is the reason for this observation?
3. Could you please comment on the stability and potential toxicity of the tin compounds prepared in the thesis? Why do you think that tetravalent tin compounds are a better alternative for the formation of FLPs against transition metal complexes?
4. Using the results for FLPs from section 4.1 for the synthesis of benzimidazoles and other azoles from ortho-substituted anilines is an elegant synthetic method. Is this method limited in the choice of substrates suitable for this reaction? Aren't the higher temperature required for the reaction and the high hydrogen pressure limiting factors for its use in the pharmaceutical industry?

In Prague on 11 September 2024

Mgr. Michal Horáček, Ph.D.