1. Does the paper address relevant scientific questions within the scope of MR?

   The authors worked on HET-PHIP which is related to the field of NMR and hyperpolarization and fits the scope of MR.

2. Does the paper present novel concepts, ideas, tools, or data? All submitted papers are assumed to report on new observations and/or new theory; there is no need to draw attention to the novelty in title, abstract, or conclusions.

   On the one hand they tested a novel type of bimetallic heterogenous catalyst based on Pd-Ag or Pd-In. On the other hand, the work is embedded in a series of Pd type catalysts these authors used for the same reaction several times. The novelty compared to their former works should be highlighted more in detail.

3. Are substantial conclusions reached?

   The authors achieved further progress in the field of PHIP employing heterogenous catalyst systems. It is shown that a second metal such as Ag or In acts on the selectivity of the Pd catalyst and let achieve it more selectivity towards pairwise hydrogen transfer which is required to produce PHIP.

4. Are the results sufficient to support the interpretations and conclusions?

   In part they are sufficient but a deeper characterization of the system would be helpful. Did the authors obtain molecular bimetallic complexes or did they obtain metallic Pd nanoparticles that are doped with In or Ag to reach the selectivity? When talking about selectivity, what are the byproducts of this reaction?

   Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists with reasonable effort? Detailed technical and graphical explanations and documentation of limited file size can be provided as supporting information. Access to raw data, processed spectra, and other experimental data must be provided by depositing in a publicly accessible repository or archive as far as practically feasible, and the DOI provided in the article. Hardware developments need to be documented by photos or equivalent drawings (blueprints with precise dimensions if possible). New software must be accompanied by user instructions. New software should be open source and access to it provided through a software repository if possible.

   In part the experiments could be reproduced but I miss more details for the catalyst preparation. Especially amounts of precursors etc. used in the synthesis are missing. Furthermore, details on the catalytic tests are not provided. How did they perform the PHIP experiments? Such details should be provided either in the experimental section or in the ESI.

5. Are numerical data accompanied by error estimates with a description of the methods used to obtain these estimates?

   Can the authors provide errors of their calculated enhancement factors?

6. Do the authors give proper credit to related work and clearly indicate their own new/original contribution?

   In part. The authors should consider additional citations on HET-PHIP in the introduction

   [1] U. Obenaus, S. Lang, R. Himmelmann, M. Hunger, J. Phys. Chem. C 2017, 121, 9953-9962.

   [2] T. Gutmann, T. Ratajczyk, Y. Xu, H. Breitzke, A. Gruenberg, S. Dillenberger, U. Bommerich, T. Trantzschel, J. Bernarding, G. Buntkowsky, Solid State Nuclear Magnetic Resonance 2010, 38, 90-96.

   [3] A. M. Balu, S. B. Duckett, R. Luque, Dalton Transactions 2009, 5074-5076.

   Although these works do not name the technique HET-PHIP they show PHIP with heterogenous catalysts.

   In the introduction the authors talked about DNP, but do not specify. When they talk about DNP in general also citations of recent reviews should be included.

   [1] A. G. M. Rankin, J. Trebosc, F. Pourpoint, J. P. Amoureux, O. Lafon, Solid State Nuclear Magnetic Resonance 2019, 101, 116-143.

   [2] A. S. L. Thankamony, J. J. Wittmann, M. Kaushik, B. Corzilius, Progress in Nuclear Magnetic Resonance Spectroscopy 2017, 102, 120-195.

   [3] U. Akbey, W. T. Franks, A. Linden, M. Orwick-Rydmark, S. Lange, H. Oschkinat, in Hyperpolarization Methods in NMR Spectroscopy, Vol. 338 (Ed.: L. T. Kuhn), 2013, pp. 181-228.

   Line 66-67 “So far, however, most heterogeneous catalysts demonstrated a limited efficiency in the pairwise hydrogen addition, or in some cases the low yields of the desired product, or both (Kovtunov et al., 2013, 2016, 2020a)”

   Here also the works of Duckett and of Buntkowsky and co-workers should be considered.

7. Does the title clearly reflect the contents of the paper?

   Yes

8. Does the abstract provide a concise and complete summary?

   Yes

9. Is the overall presentation well-structured and clear?

   Yes

10. Is the language fluent and precise?

Yes, but few typos have to be corrected:

Line 199: should be “experimental”

Line 204: should be “hyperpolarized”

11. Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated?

In principle table 2 and table 3 can be combined in one table.

12. Are the number and quality of references appropriate?

In part. See comment 6

13. Is the amount and quality of the supporting information and supplementary material appropriate?

There is no ESI available