Transition metal compounds with S/N-functionalized NHC ligands: structures, redox properties and electrocatalytic activity

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Propositions (Stellingen)

Accompanying the thesis

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1. The fact that research related to the electrochemical and electrocatalytic properties of metal-NHC complexes has been largely neglected is unwarranted. *This thesis, Chapter 7.*

2. The nickel compounds of imidazole-based NHC ligands show better activity in electrocatalytic proton reduction than nickel compounds of benzimidazole-based NHC ligands.
   This thesis, Chapters 3 and 5.

3. When a compound shows irreversible redox properties, cumulative charge consumption for a solution containing the compound and protons could aid in determining its catalytic activity.
   This thesis, Chapters 2 and 4.

4. The presence of free pendant pyridine groups can improve the catalytic activity of compounds for proton reduction.
   This thesis, Chapters 4 and 6.

5. In the proposed mechanism for electrocatalytic proton reduction by a cobalt compound of a carbene-pyridyl ligand the potential role of the pyridyl group as proton relay is ignored.
   M. van der Meer, *et al. Angew. Chem. Int. Ed.* **2015**, *54*, 13792-13795.

6. When reporting overpotentials for an electrocatalytic reaction, the specific conditions should always be described in detail.
   S.E. Smith, *et al. Angew. Chem. Int. Ed.* **2012**, *51*, 3152-3155; J.G. Kleingardner, *et al. J. Am. Chem. Soc.* **2014**, *136*, 4-7.

7. The general methods to calculate TOF and rate constants for an electrocatalytic reaction cannot be used for compounds showing irreversible redox properties. This seems to be ignored by some researchers.
K. Hou, *et al. Chem. Commun.* **2014**, *50*, 6630-6632; S. Ding, *J. Am. Chem. Soc.* **2016**, *138*, 12920-12927; B.R. Garrett, *Inorg. Chem.* **2016**, *55*, 3960-3966.

8. It is unfortunate that in reports of new types of electrocatalysts for proton reduction most attention is given to overpotentials and turnover frequencies, whereas the mechanisms are largely ignored. This makes the development of new catalysts a shot in the dark.
P. Tong, *et al. Dalton Trans.* **2016**, *45*, 18559-18565; R. Tatematsu, *et al. Angew. Chem. Int. Ed.* **2016**, *55*, 5247-5250; P. Zhang, *et al. Angew. Chem. Int. Ed.* **2014**, *53*, 13803-13807.

9. In experimental design, keeping the total number of variables as low as possible is essential to seek causation and to make a comparison.

10. Every beginning is difficult, especially in scientific research.

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