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Palladium-catalyzed carbonylative synthesis of carboxylic acid anhydrides from Alkenes

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Propositions (Stellingen)

Accompanying this thesis

Palladium-Catalyzed Carbonylative Synthesis of Carboxylic Acid Anhydrides

1. It is not *a priori* impossible to perform a reaction with a computed ΔG of $+5.0 \text{ kcal.mol}^{-1}$. (*This thesis, Chapter 2*)
2. Hydrocarbonylation reactions with poor nucleophiles require catalytic systems with electron-poor palladium centers. (*This thesis, Chapter 2, 3, 4*)
3. Symmetric acid anhydrides can be prepared from alkenes without the availability of the corresponding acid. (*This thesis, Chapter 3*)
4. The need for different carbonylative conditions to synthesize amides, esters, thioesters and ketones from alkenes can be avoided. (*This thesis, Chapter 2, 3*)
5. It is unlikely that in hydroaminocarbonylation reactions of alkenes with amine hydrochloride salts proceed *via* direct nucleophilic attack of the amine on the acyl-palladium species. (*Angew. Chem.* **2016**, *128*, 13742–13746 ; *Chem. Sci.* **2018**, *9*, 380–386)
6. Reports concerning catalytic reactions involving alkenes should not neglect regioselectivity. (*Eur. J. Org. Chem.* **2022**, e202201018)
7. Okada *et al.* overlook potential attack of formate on the acyl-rhodium intermediate as the most likely mechanistic step for the formation of carboxylic acid. (*Organometallics* **2022**, *41*, 1640–1648)
8. CO releasing agents such as benzene-1,3,5-triyl triformate, 9-methylfluorene-9-carbonyl chloride or metal carbonyl compounds are not sustainable alternatives for CO gas. (*Chem. Rec.* **2022**, *22*, e202100220, *Chem. Commun.* **2021**, *57*, 1955-1958, *Tetrahedron Lett.* **2014**, *55*, 3482–3485, *Acc. Chem. Res.* **2016**, *49*, 594–605)

9. A sustainable solution to a problem is usually preceded by a number of unsustainable approaches or trials.
10. The electron-richness or electron-poorness of a ligand should always be assessed relative to a standard reference.
11. Mass balance is one of the most important results to be included in publications related to catalysis.
12. Introducing novel reaction concepts without in-depth analysis of the outcome is unacceptable.

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Leiden, December 2023