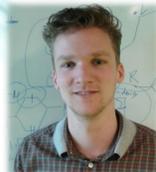
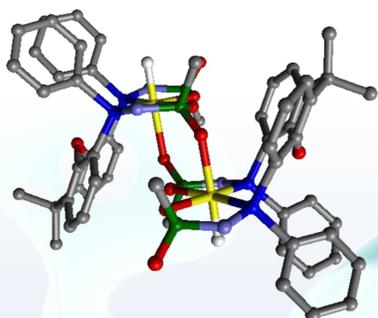


A Cooperative Complex for the Dehydrogenation of HCOOH

Sander Oldenhof, Bas de Bruin, Jarl Ivar van der Vlugt, Joost Reek*
 van 't Hoff Institute for Molecular Sciences, University of Amsterdam
 s.oldenhof@uva.nl



Solid state structure

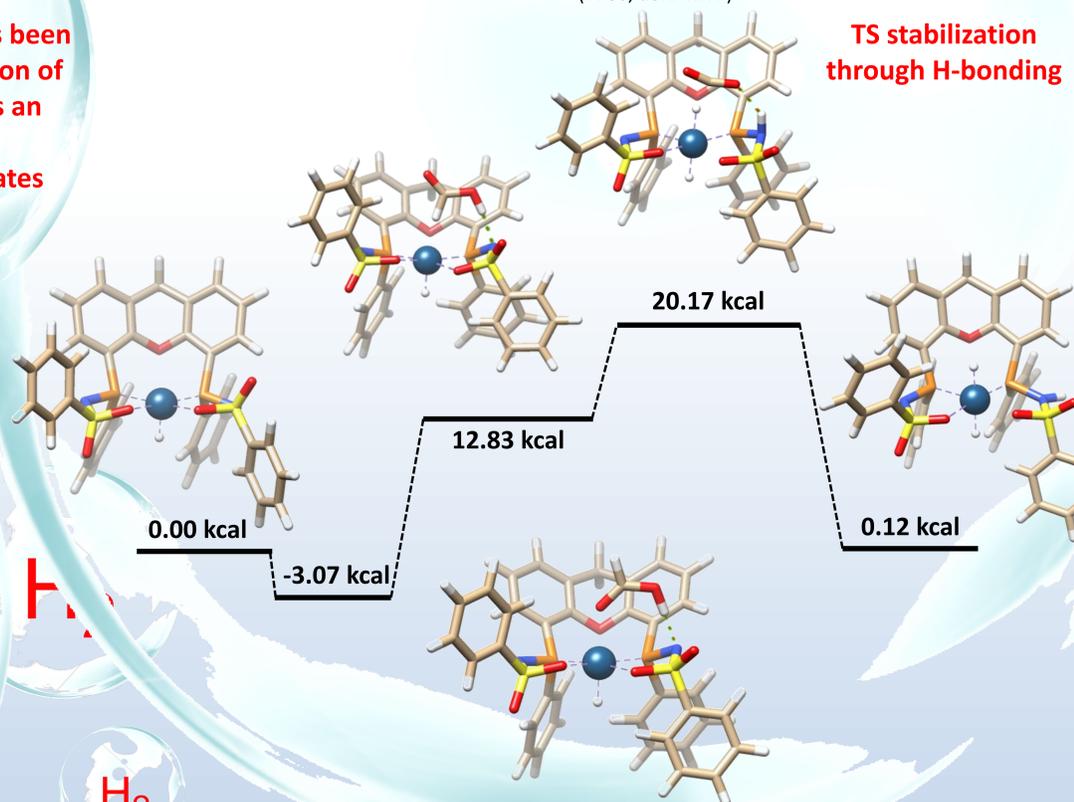


To conclude:

A selective and stable catalyst has been developed for the dehydrogenation of HCOOH. The ligand functions as an internal base and stabilizes intermediates and transition states through H-bonding.

DFT calculations

(BP86, def2-TZVP)

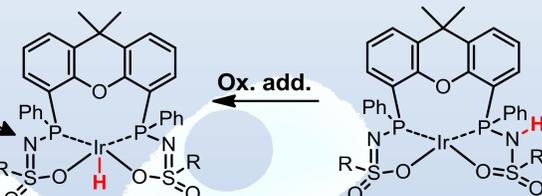


TS stabilization through H-bonding

Complexation

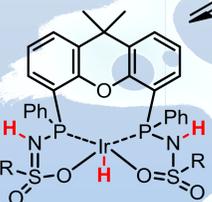


Bronsted basic site



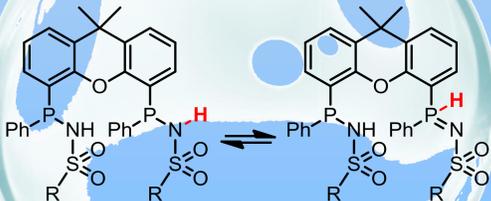
Ox. add.

Protonation



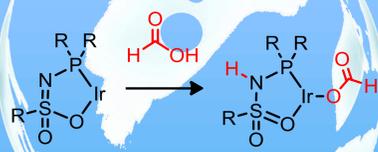
Inactive

The ligand



Prototropic behaviour

The concept

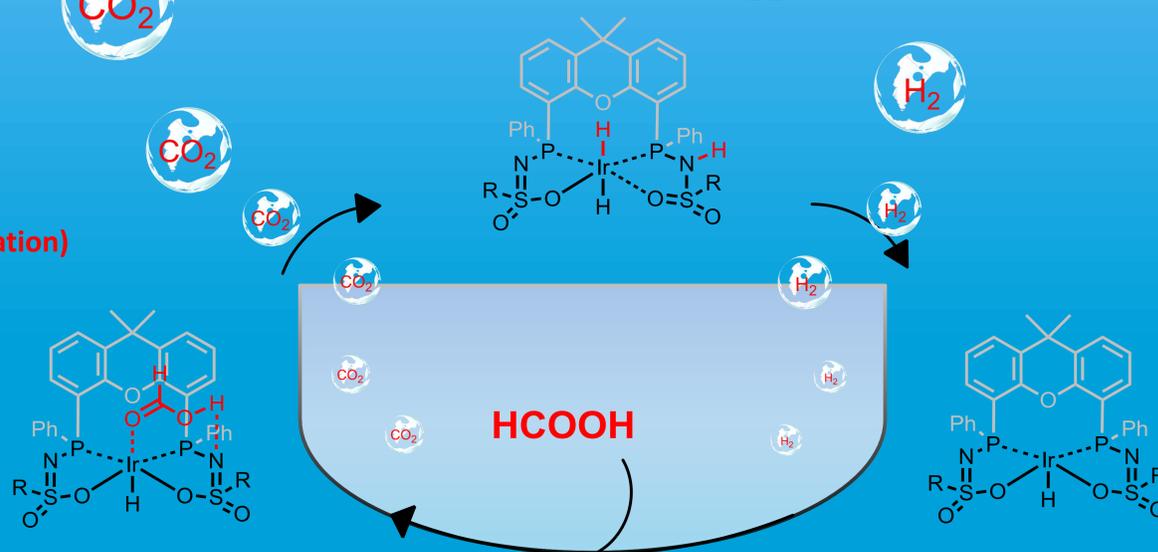


The aim

The base-free release of H₂ by using a bifunctional iridium-bisMETAMORPhos complex

The challenges

- Base-free
- No solvents
- Catalyst stability
- High selectivity (no CO formation)



Catalytic activity

Entry ^[a]	Solvent	TOF (h ⁻¹) ^[b]
1	Toluene	1050
2 ^[c]	Toluene	3092
3 ^[d]	Toluene	1074
4	THF	632
5	Dioxane	605
6	Dioxane/FA (1:1)	951
7 ^[c]	Dioxane/FA (1:1)	3271

[a] Catalyst 5' (5 · 10⁻³ mmol), HCOOH (5 mmol), 65 °C, solvent (1 mL). [b] TOFs were determined between 12-35% conversion. [c] Dehydrogenation was performed at 85 °C. [d] Activity after exposure to air for one week.

Energy content of formic acid compared to H₂

	MJ/L
H ₂	0.01
H ₂ (liquid)	8.49
H ₂ (690 bar)	4.50
HCOOH	6.53

Hydrogen holds the potential to be one of the major energy carriers for the future, however, a hydrogen-based economy requires technology that allows efficient and safe storage and release of H₂. In this light, the reversible attachment of hydrogen to CO₂ to form formic acid (HCOOH) provides an interesting H₂ storage-release system.^[1] The dehydrogenation is typically performed with an HCOOH/base mixture, which drastically decreases the hydrogen content (from 4.4 to 2.3 wt% for a typical HCOOH/NEt₃, 5:2 mixture). Ideally this reaction is performed base-free to retain the maximum H₂ content. We anticipated that a metal complex bearing an internal base^[2] as part of the ligand might act as a cooperative catalyst for HCOOH dehydrogenation, a strategy that so far has not been exploited for this transformation. Here we present an iridium-bisMETAMORPhos complex wherein the ligand functions as a internal base in the dehydrogenation of HCOOH.

[1] (a) M. Beller et al., *Angew. Chem. Int. Ed.* 47, 2008, 3962. (b) G. Laurenczy et al., *Angew. Chem. Int. Ed.* 47, 2008, 3966. (c) M. Beller, G. Laurenczy et al., *Science*. 333, 2011, 1733. (d) J. N. H. Reek et al., *Chem. Eur. J.* 19, 2013, 11507. (e) D. Milstein et al., *Chem. Eur. J.* 19, 2013, 8068 [2] J. N. H. Reek et al., *J. Am. Chem. Soc.* 131, 2009, 6683.