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# Pentamethylcyclopentadienyl Ir(III) metallacycles: recent developments in catalysis

VINCENT RYSAK,<sup>1,2</sup> YANN CORRE,<sup>1,2</sup>

FRANCINE AGBOSSOU-NIEDERCORN<sup>\*,1,2</sup> CHRISTOPHE MICHON<sup>\*,1,2</sup>

<sup>1</sup> Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, F-59000 Lille, France.

<sup>3</sup> ENSCL, CCM-MOCAH (Chimie-C7) BP 90108 59652 Villeneuve d'Ascq Cedex, France

(\*) corresponding authors: [Francine.Agbossou@ensc-lille.fr](mailto:Francine.Agbossou@ensc-lille.fr), [Christophe.Michon@ensc-lille.fr](mailto:Christophe.Michon@ensc-lille.fr)

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**KEYWORDS:** homogeneous catalysis, iridium, hydrosilylation, hydrodefluorination, energy storage

**ABSTRACT:** Iridium (III) metallacycles have been applied successfully in organic transformations and in processes relevant to energy and environmental sciences. The ongoing interest for these complexes and their corresponding catalysts has led to new developments taking a strong advantage of the properties imparted by the chelate carboligand. Recent publications in this field are highlighted in order to underline the usefulness of such catalysts in oxygen and hydrogen production as well as for hydrodefluorination and hydrosilylation reactions for the synthesis of bulk and fine chemicals.

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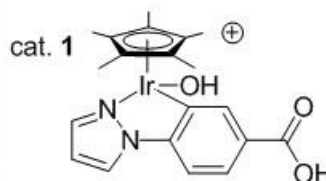
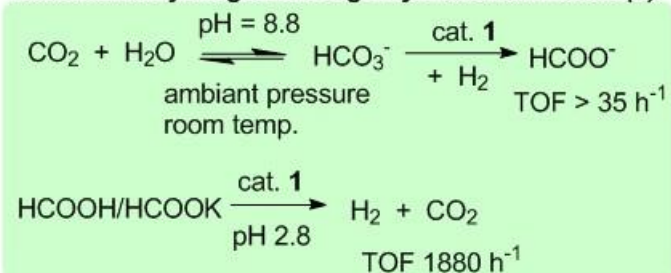
## INTRODUCTION

Over the past decade, transition-metal-catalysed C-H activation has allowed various ortho-selective C-C and C-X bond-forming reactions through in situ generation of metallacycle intermediates (1). Although C-H activation and its applications have been quite developed for ruthenium and rhodium, they have been far less studied for iridium, which has nevertheless attracted a rising interest in the past years (1). Since the 1960's, the cyclometallation reaction has provided an easy access to original organometallic compounds bearing a metal-carbon  $\sigma$  bond as part of one chelate carboligand (2). The C-H (or C-C) bond activation required by the cyclometallation process is assisted intramolecularly by coordination of a directing donor atom (for example N, P, O or C). As a result, complexes bearing such ligands are displaying increased stability with exclusive reactivity. Recently, half-sandwich (i.e. pentamethylcyclopentadienyl, Cp\*) iridium (III) metallacycles have demonstrated a great potential in homogeneous catalysis and displayed significant activities for a range of organic reactions. In two recent reviews, the applications of Cp\* iridium(III) metallacycles in homogeneous catalysis for fine chemical synthesis have been summarised (3). The organic transformations developed up to recently were centred on hydrogenation, dehydrogenation, amine alkylation, oxidation and hydrofunctionalisation reactions as well as dynamic kinetic resolution (DKR). Herein, we would like to highlight recent works involving Cp\* iridium(III) metallacycles in challenging organic reactions and in processes relevant to energy and environmental sciences.

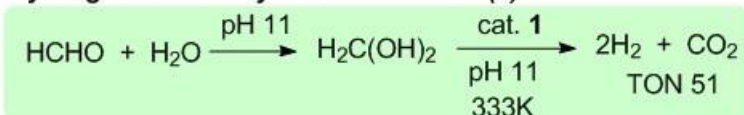
## RESULTS AND DISCUSSION

Within the research field of storage of transient energy for fuel cell applications, the development of efficient catalytic systems able to store and release hydrogen gas has led to explore Cp\* iridium(III) metallacycles which, by comparison to ruthenium and rhodium counterparts, have been far less considered (3, 4). Fukuzumi et al., who applied cyclometallated iridium catalysts to the production of hydrogen peroxide (5) and oxidation of formic acid (6), explored further the potential of the designed catalysts in the storage of hydrogen in formic acid (7) or its release from formic acid (7) and paraformaldehyde (8) within reversible processes. Thus, Fukuzumi et al. applied a water soluble phenylpyrazolyl based aqua Cp\* iridium(III) metallacycle **1** in the two above mentioned transformations devoted to the production of hydrogen (Scheme 1). The complex was shown to allow a reversible storage of hydrogen through hydrogenation of CO<sub>2</sub> (bicarbonate under the basic aqueous experimental conditions) under controlled pH or through hydrogen evolution from formic acid/potassium formate (Scheme 1). The control of the pH was central for the highest activities of the catalyst in carrying out both transformations. Later, the same catalyst was applied to the decomposition of paraformaldehyde into H<sub>2</sub> and CO<sub>2</sub> allowing the release of two equivalents of hydrogen (Scheme 1). Thus, paraformaldehyde was a convenient solid H<sub>2</sub> carrier with a higher energy density than formic acid.

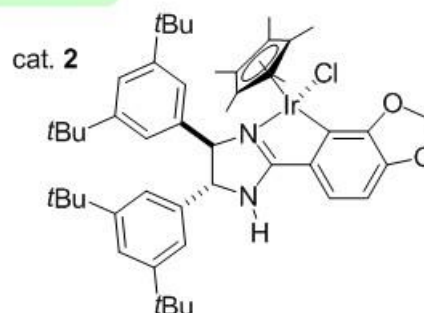
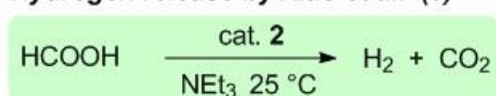
### Reversible hydrogen storage by Fukuzumi et al. (7)



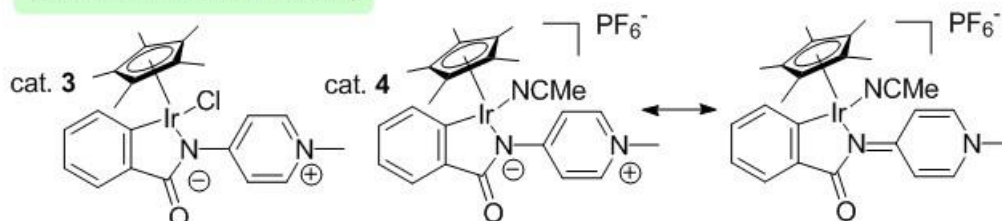
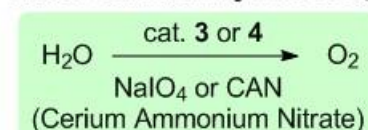
### Hydrogen release by Fukuzumi et al. (8)



### Hydrogen release by Xiao et al. (9)



### Water oxidation by Albrecht, Bernhard et al. (10)

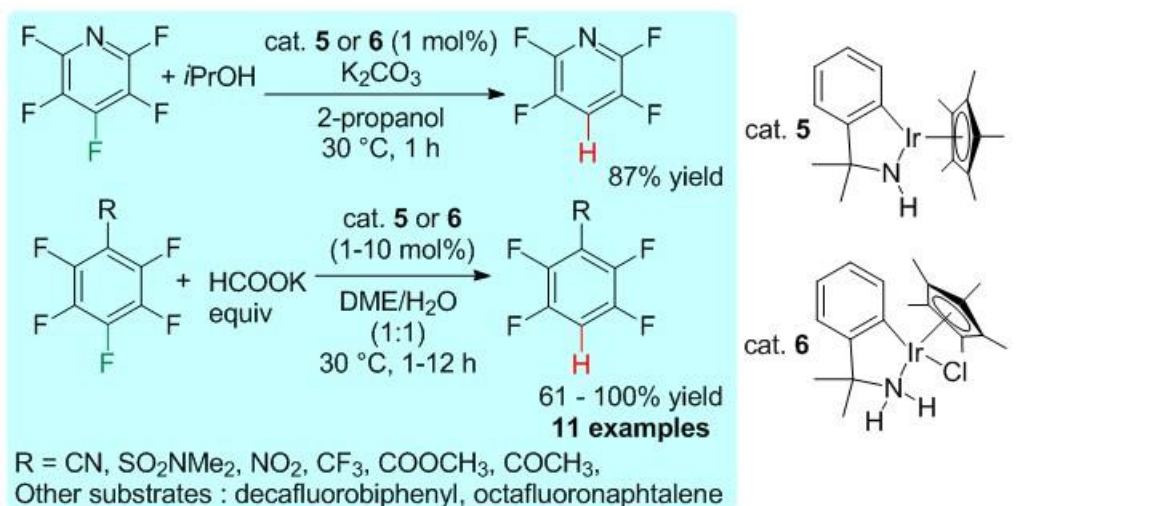


**Scheme 1.** Applications of Cp\* iridium(III) metallacycles in water oxidation and hydrogen release or storage (7-10).

At the mean-time, Xiao et al. developed bifunctional Cp\* iridium(III) metallacycle catalyst **2** for the **dehydrogenation of formic acid** (azeotrope with NEt<sub>3</sub>) into H<sub>2</sub> and CO<sub>2</sub> (Scheme 1) (9). Optimisation of the catalyst resulted in the discovery of a highly effective and robust catalytic system which was selective without formation of CO and was operating rapidly in mild conditions, with TOFs up to 147 000 h<sup>-1</sup>. The reported reaction mechanism proceeded first through the concomitant release of CO<sub>2</sub> and formation of an iridium hydride. By relying on long-range metal-ligand cooperation, the subsequent protonation of the iridium hydride species produced H<sub>2</sub> via a formic acid assisted proton hopping from the distal gamma-NH functionality to the proximal nitrogen.

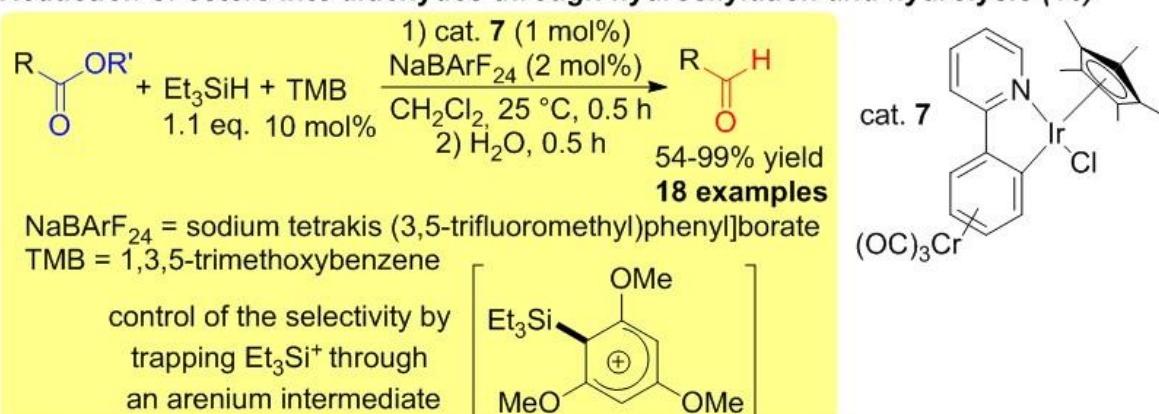
Recently, Albrecht, Bernhard et al. developed donor-flexible nitrogen based Cp\* iridium (III) metallacycles **3** and **4** for the catalytic oxidation of water, a challenge towards the development of artificial photosynthetic processes (10). The variable bonding properties of the pyridylideneamide chelating ligand and its dynamic trend were decisive for the stabilisation of high and low iridium oxidation states, allowing the elementary steps of the water oxidation catalytic cycle to proceed. Two iridium complexes were efficient for the oxidation of water using either CAN (cerium ammonium nitrate) or NaIO<sub>4</sub> as sacrificial oxidants. By comparison to previously evaluated C,N-chelated iridium complexes (10 min<sup>-1</sup>), higher TOF (28 to 112 min<sup>-1</sup>) were obtained (10). In addition, the chloro-iridium catalyst was kept active over 28 days while running in the presence of 406510 equivalents of CAN without any CO<sub>2</sub> detected.

Due to the growing demand for partially fluorinated organic compounds, the catalytic hydrodefluorination has recently attracted a great interest. In this context, the hydrogen transfer approach has appeared as a promising perspective provided its efficiency is increased. Indeed, transformations using sacrificial agents could not avoid the production of side products (case of hydrosilanes and aluminium hydrides) and the use of pressurised hydrogen resulted in reactions with modest activities. Hence, Kayaki et al. applied a transfer hydrogenation catalyst using 2-propanol or potassium formate as hydrogen donor. The catalytic system relied on metal-ligand cooperation in protic amine Cp\* iridium (III) metallacycles **5** and **6** (11). Perfluoroarenes could efficiently be hydrodefluorinated under mild conditions (Scheme 2). The strong σ-donating nature of the C-N-chelate ligand was essential for the easy hydride transfer step of the catalytic cycle.

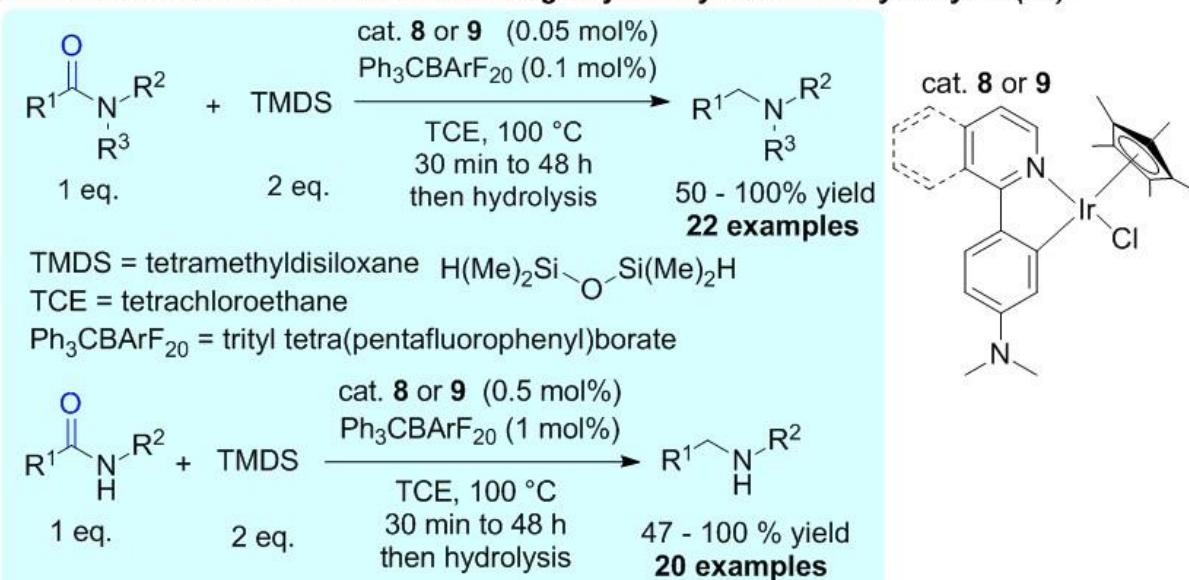


**Scheme 2.** Catalytic hydrodefluorination of perfluoroarenes by Kayaki et al. (11).

### Reduction of esters into aldehydes through hydrosilylation and hydrolysis (16)



### Reduction of amides into amines through hydrosilylation and hydrolysis (18)



**Scheme 3.** Reduction of carboxylic acid derivatives through combined hydrosilylation and hydrolysis by Michon et al (16, 18).

Following the first application of Cp\* iridium(III) metallacycle catalysts in a tandem hydroamination-hydrosilylation of terminal alkynes by Djukic et al. (13), a joint collaborative work between Djukic's laboratory and our research group allowed to report the efficient hydrosilylation of a series of aldimines and ketimines catalysed by Cp\* iridium(III) metallacycles bearing a 2-phenylpyridine chelate ligand (12). We subsequently performed the regioselective hydrosilylation of terminal alkynes furnishing the (*Z*)-alkenylsilanes in high yields (14). In order to pinpoint the potential of such catalysts in the reduction of more difficult

substrates such as carboxylic acid derivatives, further investigations were pursued. We focused first on the reduction of carboxylic esters into aldehydes as this transformation has been scarcely reported (15) compared to the more straightforward reduction of esters into alcohols (Scheme 3). The use of Cp\* iridium(III) metallacycle catalyst **7** in combination with a catalytic amount of 1,3,5-trimethoxybenzene led to a unique reactivity with triethylsilane as the aldehydes could be obtained selectively at room temperature in high yields after a further catalytic hydrolysis (16). These unprecedented catalytic reductions which provide selectively aldehydes from esters were studied by DFT calculations. It appeared the 1,3,5-trimethoxybenzene (TMB) additive was critical in trapping elusive cationic silylium species through an arenium species and therefore in controlling the selectivity of the reaction.

Amides are other challenging substrates to reduce when the preparation of more functionalised amines is required in pharmacy and fine chemistry. Although the combined use of hydrogen and homogeneous catalysts has allowed active and selective hydrogenation reactions (17a), the use of hydrosilanes as reductants of carboxylic acid derivatives can be quite relevant provided that inexpensive and abundant hydrosilanes are used (17b). Indeed, we have shown selected Cp\* iridium(III) metallacycle **8** catalysed the chemoselective reduction of tertiary and secondary amides in a very efficient way (Scheme 3). With TONs up to 10000 h<sup>-1</sup>, the reactions were fast at low catalyst loadings using inexpensive tetramethyldisiloxane and proceeded in high yields after hydrolysis (18). A fine ligand tuning could improve the catalyst performance by changing the chelating 2-phenylpyridine ligand for a 1-phenyl isoquinoline one while keeping the NMe<sub>2</sub> donating substituent on the phenyl group. Indeed, the resulting iridium metallacycle catalyst **9** allowed the straightforward reduction of sterically hindered tertiary and secondary amides. Regarding the reaction mechanism, a transient iminium intermediate has been observed for the first time by mass spectrometry and the activations of the catalyst and the silane reagent have been rationalised by DFT calculations, a cohesive hydrido-iridium(III)→silylium donor–acceptor complex being formed at first (19).

## CONCLUSIONS

This article has concisely summarised the recent efforts devoted to apply Cp\* iridium(III) metallacycles in catalysis. These organometallic complexes were successfully implemented in two main areas related to energy storage (H<sub>2</sub> and O<sub>2</sub>) and fine chemistry (hydrodefluorination and hydrosilylation). The contribution of the chelate carboligand in assisting the catalytic event is generally crucial to stabilise catalytic intermediates and to impart original reactivity to the catalyst. Indeed, the ligand can take part directly to the catalytic process within bifunctional catalytic systems. Before any application in industry, modifications of these active but precious Cp\* iridium(III) metallacycle catalysts will be needed in order to develop valuable recycling methods and processes.

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