Organometallic Chemistry and Homogeneous Catalysis: Advances and Prospects

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The discovery of ferrocene in the early 1950s, and the elucidation of its structure, in which two parallel cyclopentadienyl rings coordinate an iron(II) to form an unique cylindrical molecule, not only brought a new life into coordination chemistry, but also provided the impetus for establishing organometallic chemistry as a specific and independent chemistry discipline.

Ferrocene immediately received an enormous amount of attention and soon became an iconic molecule – a symbol of organometallic chemistry that combines its inherent beauty with unique properties. Investigations aimed at understanding the physicochemical properties and reactivity of the new molecule were performed extensively during the early days and resulted in vast set of data that serves nowadays as a solid foundation for applications of ferrocene and its derivatives in various fields. As a prominent structural motif, the ferrocene moiety has spread into nearly all chemical fields and some neighboring disciplines. The most prominent areas are represented by the design of ligands for coordination chemistry and catalysis, studies and applications of electron-transfer processes and redox reagents, and rapidly developing fields of bioorganometallic chemistry and the related pharmaceutical research. Apart from reflecting the current research in the field of ferrocene derivatives, our own results clearly indicate that ferrocene chemistry is far from exhausted.

1. Dehydrogenation of alkanes and alcohols by iridium pincer complexes

Selective homogeneous dehydrogenation of alkanes is one of the most significant tasks of organic chemistry and catalysis. Presently the most active and robust homogeneous catalysts for alkane dehydrogenation are iridium pincer complexes [1]. Kaska, Jensen *et al.* [2], as well as Goldman *et al.* [3] showed that iridium bis(phosphine) pincer complexes **1** are effective catalysts for alkane dehydrogenation. Later, Brookhart *et al.* [4] established that iridium bis(phosphinite) pincer complexes **2** are approximately an order of magnitude more active than their bis(phosphine) counterparts. Developed in our group [5] iridium bis(phosphine) pincer complexes **3** and **4** with a metallocene backbone show excellent catalytic activity for cyclooctane dehydrogenation, exceeding even that shown by **2a**. For example, turnover numbers (TONs) of 3300, 2571, and 1843 were obtained for **3**, **4**, and **2a**, respectively at 180°C, for 8h [5].
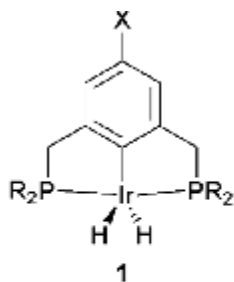
R = *t*Bu, X = H (**1a**), OMe (**1b**),
COOMe (**1c**), NMe$_2$ (**1d**)
R = iPr, X = H (**1e**), OMe (**1f**)
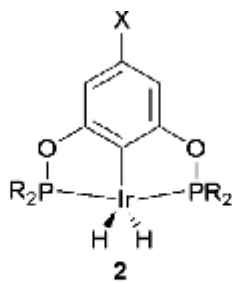
R = *t*Bu, X = OMe (**2a**), Me (**2b**), H (**2c**)
F (**2d**), C$_6$F$_5$ (**2e**), 3,5-(CF$_3$)$_2$C$_6$H$_3$ (**2f**)
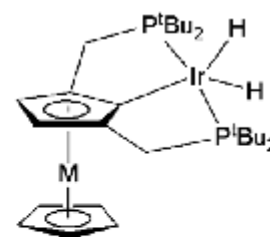
M = Fe, **3**
M = Ru, **4**

Given the favorable results obtained thus far, and the ability to exploit the bound CpM unit to tune electronic and steric propertics of the princer, our metallocene-based catalysts would seem to hold considerable promise.

Apparently, catalytic activity of iridium pincer complexes should be affected by both a steric factor (the accessibility of catalytic center for a substrate), and an electronic factor, i.e. the relative electron density at the iridium atom. The steric accessibility of the iridium atom is determined by the bulkiness of organyl groups of the phosphorous donor atoms (*t*-Bu are common groups) and by the value of the P-Ir-P angle in pincer complexes [5]. While the difference in geometry between pincer complexes is well-defined, evaluation of the electronic factor appeared to be more complex.

We have prepared a series of new *p*-flourophenylpalladium complexes with four different pincer ligands. The measurement of ^{19}F NMR parameters and Pd^{II}/Pd^{IV} oxidation potentials allowed us to make conclusions on the electronic properties of the appropriate ligands [6], which correlate well with previously reported data based on vCO stretching frequencies of Ir-CO complexes with the same pincer ligands. The data obtained support our conclusion that the higher catalytic activity of complexes **2**, **3** and **4** in alkane dehydrogenation *versus* that of complex **1** have mainly steric reason. Thus, compounds **2** and **3** have smaller P-Ir-P angle than **1** (for the respective Ir-CO adducts, the P-C-P angles are 157.55, 157.93 and 164.51°, respectively), which provides a higher accessibility of the Ir atom for a substrate, while there are clear similarity in the electronic properties of the pincer ligands in complexes **1** and **3,4** [6].

Hydrogen is potentially an ideal energy carrier, as it is nonpolluting and has a high energy density by weight. Significant efforts are devoted to the development of catalysts able to dehydrogenate some hydrogen-rich liquids such as alkanes, formic acid, nitrogen heterocycles and alcohols. We have studied dehydrogenation of alcohols by bis(phosphinite) benzene based and bis(phosphine) ruthenocene based iridium pincer complexes [7].
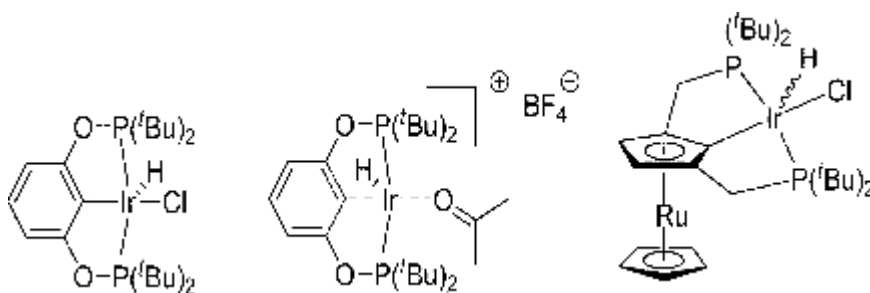
Dehydrogenation of secondary alcohols proceeds in a catalytic mode with TON up to 3420 (85% conversion) for acceptorless dehydrogenation of 1-phenylethanol. Primary alcohols are readily decarbonylated even at room temperature to give Ir-CO adducts. The mechanism of this transformation was studied in detail, especially for EtOH; new intermediates were isolated and characterized.

Performance of the most active catalyst, cationic bis(phosphinite) iridium pincer complex, is comparable to those of the most active current catalytic systems concerning conversion and TON. At the same time, the advantage of the studied catalysis is that it proceeds under solvent-free conditions.

2. Reactions of electron-deficient alkynes and alkenes with *N*-heterocyles and amines

Such *N*-heterocycles as indoles, pyrroles and imidazoles are a type of nitrogen containing molecules occurring in numerous natural and biologically active compounds with a wide range of pharmaceutical properties. Amines are ubiquitous in nature. Due to prevalence of amines in therapeutics, as well as in the production of dyes, solvents, agrochemicals, and fine chemicals, the formation of carbon-nitrogen bonds is of tremendous unportance. Hydroamination, the net addition

of amino group and hydrogen atom across a carbon-carbon multiple bond, represents a direct approach to access amines from alkene and alkyne precursors.

On the other hand, it is well known that ferrocene is a considerable pharmacophore. We hope that introduction of ferrocenyl group into the biologically active molecules will reveal the enhanced biological activity. We have developed a simple, efficient catalyst-free addition of indoles and pyrroles to ferrocenylnitroethylene Fc-CH=CH-NO$_2$ (Fc=ferrocenyl), with formation of 3-(2-nitro-1-ferrocenyl)-indole and 2-(2-nitro-1-ferrocenyl)-pyrrole. Because of the presence of the nitro group, these products can be readily transformed into a variety of functionalities.

As part of our current studies on the reactions of ferrocenyl-containing electron-deficient alkynes and alkenes [8,9] with *N*-heterocycles and amines, we found that alkyne Fc-C≡C-CN reacts with 1-methylimidazole to give corresponding C(2)-vinylated derivative-3-(1-methyl-imidazole-2-yl)-3-ferrocenyl-2-propenenitrile.

Acetylenic nitrile Fc-C≡C-CN smoothly adds amines-diethylamine, morpholine, pyrrolidine and others, with formation of the corresponding enaminonitriles.

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