

## Shafir Research Group



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### Abstract

The Shafir group was created in 2013 and has since begun research on metal-catalyzed processes and on the coupling reactions involving hypervalent iodine reagents. The group's work on metal catalysis combines ligand development with the studies of the reaction mechanism. Thus, during 2013 the group has pursued intermediates involved in the Cr- and Ti-catalyzed selective conversion of ethylene to 1-hexene and 1-octene. The process is mechanistically distinct from the classical

Ziegler-Natta oligomerization, and the group is working on the detection of the putative fleeting metallacyclic and electron-deficient low-valent intermediates. The group has begun work on other industrially relevant processes, including ethanol upgrade and related H<sub>2</sub>-borrowing approaches. The group is also active in the development of new oxidative processes involving iodine(III) reagents. As an example, a new strategy for the  $\alpha$ -arylation of ketones has been developed in which the simple  $\text{PhI}(\text{O}_2\text{CCF}_3)_2$  is employed as an Ar-transfer agent.

## Catalysis

Having completed in 2013 the setup of a new laboratory at ICIQ, the Shafir group has pursued research covering two interconnecting research areas, namely the metal-catalyzed transformations and in the discovery of new oxidative processes based on hypervalent iodine reagents.

Thus, the group has been studying the selective conversion of ethylene to 1-hexene and 1-octene catalysed by certain Cr and Ti complexes. The process is mechanistically distinct from the classical Ziegler-Natta oligomerization, and allows for the generation of a specific  $\alpha$ -olefin, rather than an olefin distribution. In order to improve our understanding of the reaction mechanism, we are focusing on generating and detecting (NMR, other techniques) the putative fleeting metallacyclic and electron-deficient low-valent intermediates (Figure 1). In addition to shedding light on the mechanism, we are interested in the creation of catalysts with improved selectivity profiles. An important question remains as to whether the selective (or even semi-selective) formation of olefins larger than 1-octene is possible using this approach.

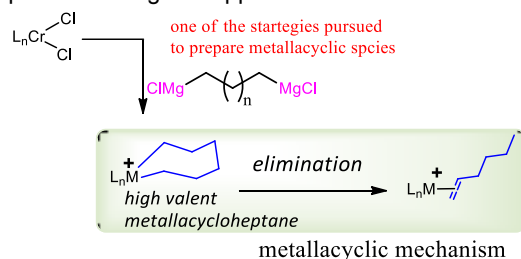


Figure 1. A salt metathesis approach to the hypothetical metallacyclic ethylene trimerization intermediate

Towards the goal of rapidly generating diverse catalyst structure, a modular approach to the synthesis of chelating aminosphosphine ligands has been developed. Thus, several of these PNP and PNNP ligands have been prepared through an optimized condensation procedure, which yields essentially pure ligands solution after a simple filtration (Figure 2). The *structure-activity* relationship studies for such ligands in chromium-catalyzed ethylene oligomerization are currently underway.

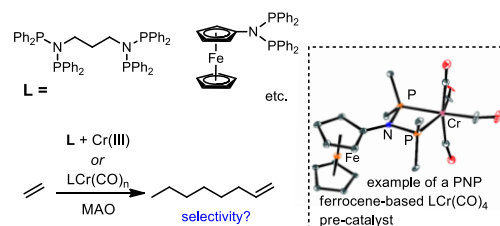


Figure 2. Chromium-catalyzed ethylene oligomerization.

Synergistically, the performance of this ligand set has also shown promise in several methodologies based on  $H_2$  auto-transfer. Thus, we are focused on the application of PNP ligands to the ethanol upgrade, *i.e.* the dimerizative “upgrade” of ethanol to 1-butanol (Figure 3).

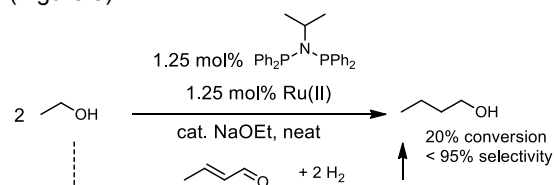


Figure 3. Ru-catalyzed ethanol-to-butanol conversion.

## Hypervalent Iodine

The group is also active in the research of new oxidative processes involving iodine(III) reagents. Thus, it has been reported (Kita group, later our group) that metal-free Ar-Ar coupling is promoted by  $PhI(O_2CCF_3)_2$  in the presence of  $BF_3 \cdot Et_2O$ . Intrigued by this process, we are investigating the interaction between iodine(III) reagents and Lewis acid. For the first time, the hypothetical  $PhI(O_2CMe)_2 \cdot LA$  complex has been characterized by NMR and by DFT calculation (with the group of Lledós and Ujaque). Relevant to CH functionalization, the activation of mesitylene using this activated complex takes place in <5 sec to give a diaryliodonium salt.

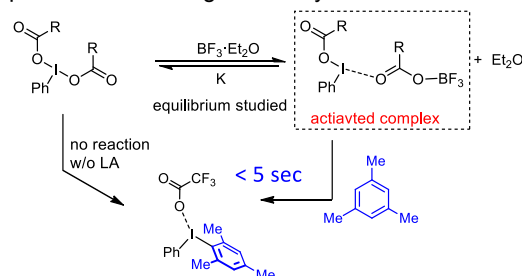


Figure 4. Synthetic and mechanistic aspects of implications of organoiodane activation.

As an example of new transformations, we are working on a new strategy for the  $\alpha$ -arylation of ketones in which the simple  $\text{PhI}(\text{O}_2\text{CCF}_3)_2$  is employed as an Ar-transfer agent (Figure 5).

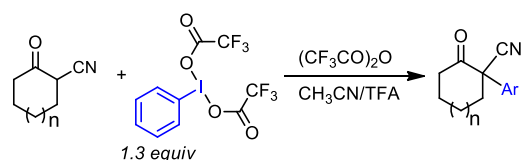


Figure 5. A new approach to metal-free  $\alpha$ -arylation of ketones using  $\text{ArI}(\text{O}_2\text{CCF}_3)_2$ .

We are currently working on establishing the scope of this transformation. We are also developing an attractive one-pot approach to ketone  $\alpha$ -arylation consisting in simply mixing the ketone with an iodoarene in the presence of a suitable oxidant for the *in situ* generation of the active iodine(III) species.