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Conference paper

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Organometallic catalysis for applications in radical chemistry and asymmetric synthesis[1]

Abstract: Two organometallic catalysis studies are presented. The first one deals with the development of a new catalytic agent based on the mixture of a hydride and an iron salt to trigger efficient radical cyclization processes. In a second line of research, we have shown that the use of chiral anions can outperform chiral ligands in a carbocyclization reaction and a [2 + 2 + 2] cycloaddition.

Keywords: carbocyclizations; chirality; electrochemistry; homogeneous catalysis; hydrides; ion pairs; iron; OMCOS-17; radicals.

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Introduction

Homogeneous catalysis has been at the center of our concern for more than two decades. More recently, two emerging themes have particularly drawn our attention. The first one consists in the development of a more sustainable radical synthesis which does not rely on the use of toxic stannane mediating agents, instead relying on organometallic catalysis [1]. For that purpose, we have shown that the simple mixture of a cheap hydride with an iron(II) salt catalyzes radical cyclization processes of iodo- and bromo-precursors. Mechanistic investigations have been pursued, and cyclic voltammetry has provided valuable insight to determine a catalytic species. The second activity is based on the electrophilic activation of alkynes to promote asymmetric cyclization transformations [2]. It has focused on the utilization of a chiral anion in lieu of a chiral ligand in an iridium(I)-catalyzed carbocyclization process, as well as in a rhodium(I)-catalyzed [2 + 2 + 2] cycloaddition between a diyne and an isocyanate. Results relating to this research are given below.

Results and discussion

Iron hydride-mediated reductive radical cyclization of organic halides

Free radical carbon–carbon bond-forming reactions are powerful and versatile tools for modern synthetic chemistry [3]. Worldwide it has become increasingly important to make advances in ecological and sustainable chemistry, and for free radical chemistry in particular it is necessary to develop alternatives to traditional radical mediators, namely, trialkyltin hydrides or their precursors [4]. Transition-metal complexes based on titanium [5], zirconium [6], gallium [7b], and indium [7a–d] are particularly suitable owing to their ability to generate a variety of reactive metal hydride species (Scheme 1).

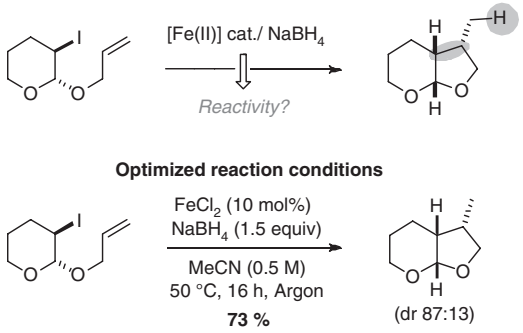
$TiCp_2Cl_2/NaBH_4$ Schwartz | Cp_2ZrCl_2/Red-Al Oshima | $GaCl_3$/Red-Al Oshima | $InCl_3/NaBH_4$ Baba

Scheme 1 Metal hydride systems as new mediators of radical reactions.

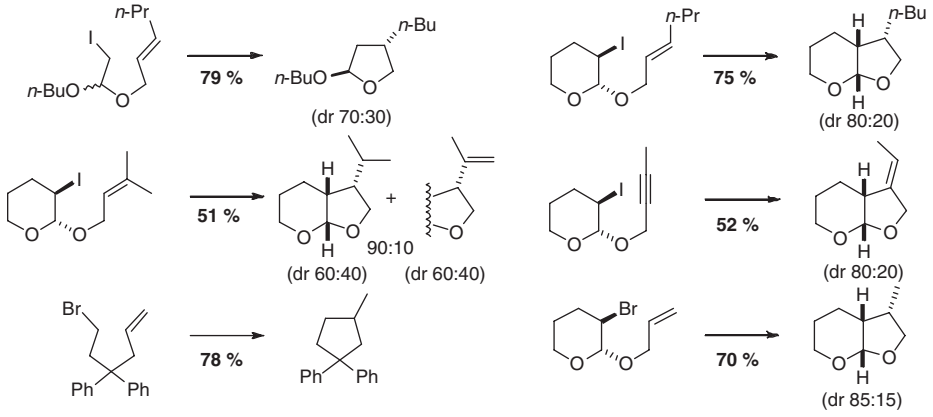
In this regard, we have been interested in exploring the reactivity of iron hydride in radical reactions and subsequently developing efficient methodologies mediated by environmentally benign iron complexes. Firstly, we tested the reactivity of the iron(II)/$NaBH_4$ system for the reduction of halides [8]. After optimization of the reaction conditions, the model iodoalkene when treated with 10 mol% of iron dichloride, 1.5 equiv of $NaBH_4$ in acetonitrile at 50 °C for 16 h gave the cyclized product in 73 % yield with 87:13 diastereoselectivity ratio (Scheme 2).

With this proof of concept we examined the scope of the reaction as shown in Scheme 3, with primary and secondary iodoalkenes giving rise to the corresponding cyclic adducts in good-to-moderate yields. Cyclization of the iodoalkyne leads to the 5-*exo*-dig product in 52 % yield. Also, the reduction of primary and secondary bromides proved efficient, and both primary and secondary bromoalkenes furnished the corresponding cyclic compounds in 78 and 70 % yield, respectively.

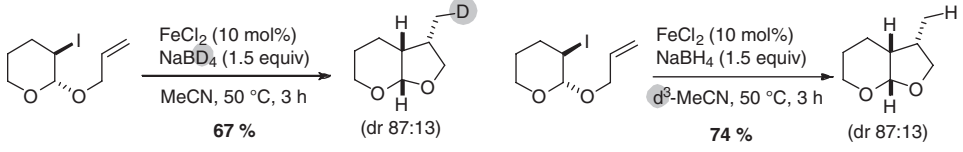
To determine the nature of the H-donor species, we ran deuterium labeling experiments as shown in Scheme 4. In the presence of $NaBD_4$, we observed complete deuterium incorporation into the cyclization



Scheme 2 Reductive cyclization by catalytic iron dichloride in the presence of $NaBH_4$.



Scheme 3 Scope of the reaction (reaction conditions: $FeCl_2$ (10 mol%), MeCN (0.5 M), NaBH4 (1.5 equiv), 50 °C, 16 h).



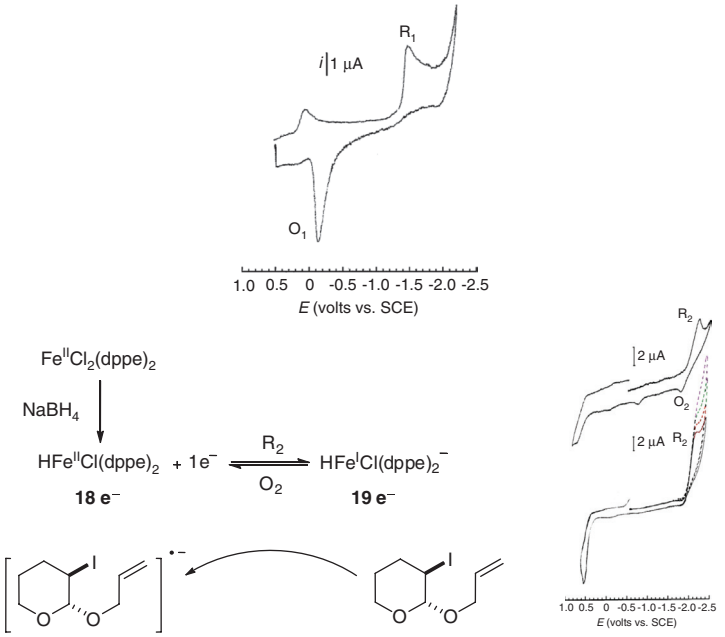
Scheme 4 Deuterium-labeling experiments.

product. In contrast, no deuterated product was detected when the reaction was carried out in deuterated acetonitrile. This suggests that the hydrogen atom incorporated in the product is donated by the borohydride [7] or an *in situ* generated hydrido iron species.

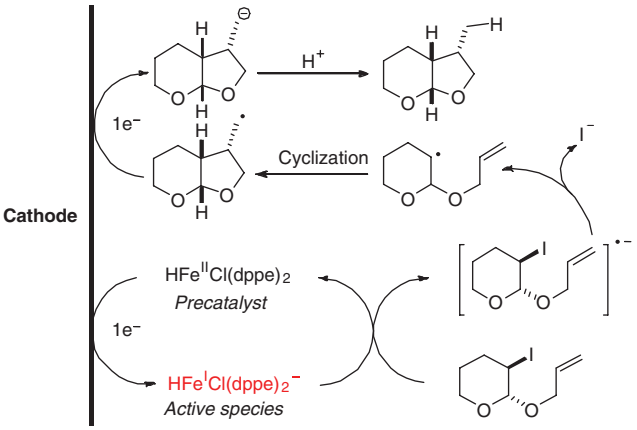
Next, we set out to determine the nature of the active catalytic species and prove the radical pathway of this process. But the major hurdle to overcome was identifying the iron complex(es) generated in situ because they are difficult to isolate and NMR spectra of the reaction mixture are not revealing due to the presence of paramagnetic species. For these reasons, we turned to electrochemical investigations, using cyclic voltammetry (CV) techniques. The voltammogram of the complex [$FeCl_2(dppe)_2$] with sodium borohydride showed the disappearance of the reduction peak at R_1 (arising from the dppe complex alone) and the appearance of a new reduction peak at R_2 (Scheme 5). This suggests the formation of a new iron complex, which could be either the monohydrido [$HFeCl(dppe)_2$] or dihydrido [$H_2Fe(dppe)_2$] complex. Both of these complexes were synthesized independently and analyzed by CV. Interestingly, the CV of the dihydrido complex [$H_2Fe(dppe)_2$] did not show any reduction or oxidation peak and no reductive cyclization occurred with this complex. In contrast, the monohydrido complex [$HFeCl(dppe)_2$] exhibited the same reduction peak at R_2 as when the dppe complex was reacted with sodium borohydride, and this peak is partly reversible at a higher scan rate (Scheme 5). This suggests that the hydrido iron(II) complex is reduced at R_2 to the partly stable anionic iron(I) complex which is oxidized at O_2.

We conclude that the monohydride complex is a precatalyst for the reductive cyclization and that this transformation is monoelectronic. In the presence of substrate RI and the hydrido iron species [$HFeCl(dppe)_2$], an increase of the reduction peak at R_2 is observed and the oxidation peak disappears (Scheme 5). Thus the electrogenerated complex exhibits catalytic activity in the presence of the substrate. Therefore, we propose that the in situ generated [$HFe(I)Cl(dppe)_2$]$^-$ species transfers one electron to the substrate to generate the radical anion and regenerate the hydrido iron(II) in a catalytic cycle.

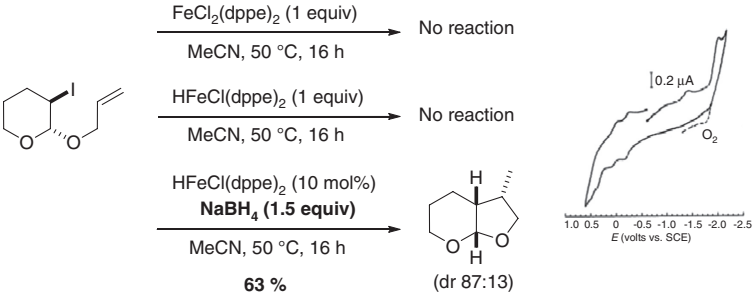
To validate this hypothesis we performed a preparative electrolysis experiment. After the passage of two electrons per mole of substrate at a fixed potential (–2 V), we obtained the cyclization product in 50 % yield. We propose the following mechanism where [$HFe(II)Cl(dppe)_2$] is reduced at the cathode to [$HFe(I)Cl(dppe)_2$]$^-$ as shown in Scheme 6. The catalyst is then able to transfer one electron to the substrate generating the radical anion and regenerating the hydrido iron(II) precatalyst. The intermediate radical cyclizes, and then is reduced at the electrode to the carbanion that is protonated by the reaction medium.



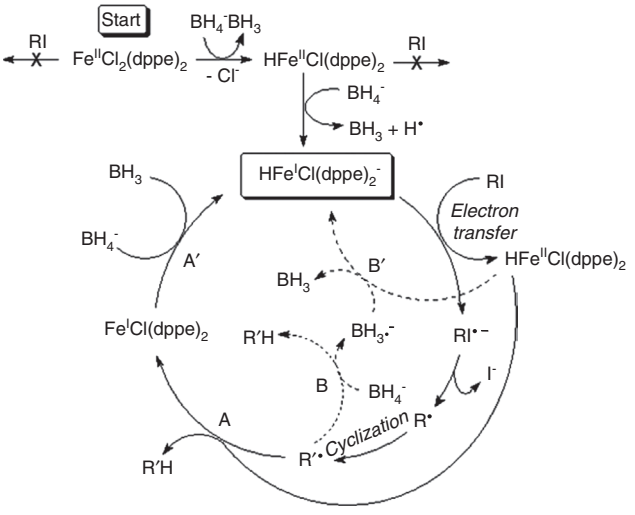
Scheme 5 Evidence of an active hydrido iron(I) catalyst [$HFe(I)Cl(dppe)_2$]$^-$ by CV.



Scheme 6 Preparative electrolysis experiment.



Scheme 7 Experiments to determine the role of $NaBH_4$ in the cyclization reaction.



Scheme 8 Proposed mechanism.

Finally, we wished to determine the role of $NaBH_4$ in the formation of the active iron species and conducted a series of control experiments (Scheme 7). No reaction occurred when 1 equiv of iron dichloride or monohydrido complex was used in the absence of $NaBH_4$. However, 10 mol% of the hydrido complex $[HFeCl(dppe)_2]$ in the presence of $NaBH_4$ furnished the cyclized product in 63 % yield. The CV of the hydrido complex showed an increase of the oxidation peak at O_2 in the presence of $NaBH_4$ providing confirmation that $NaBH_4$ reduced the hydrido iron(II) complex $[HFeCl(dppe)_2]$ in a one-electron process.

In summary, the reaction of sodium borohydride with iron dichloride generates in situ the hydrido complex [HFe(II)Cl(dppe)$_2$]. Further reduction occurs in the presence of $NaBH_4$ to give the catalytically active species [HFe(I)Cl(dppe)$_2$]$^-$. This transfers one electron to the substrate, leading to the radical anion and regenerating the iron(I) complex. The radical anion gives rise to the carbon radical, which is then able to cyclize. The radical (R$^\bullet$) is reduced to RH by one of two pathways: by abstracting an hydrogen from [HFe(II)Cl(dppe)$_2$], which itself will regenerate the active iron(I) species by action of BH_4^-; or by reacting with BH_4^- directly to generate a boryl radical, which itself will regenerate the active iron(I) species by action of BH_4^-. Also, the boryl radical can transfer one electron directly to the iodo compound and propagate the chain reaction (Scheme 8). Studies are still underway in order to determine the finer details of this reaction mechanism.

Chiral counterion strategy for enantioselective C–C bond formation

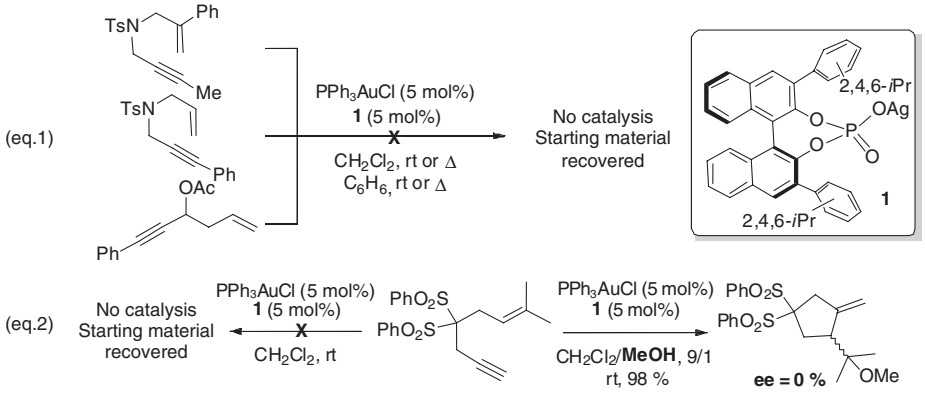
Another challenge in organic synthesis, and particularly in organometallic catalysis, is the control of the absolute configuration of newly created centers. A classical approach with a strong track record relies on the introduction of the chiral information in the inner-sphere ligand of the metallic species. A major drawback of this strategy is that L-ligands often influence the steric and electronic properties of the metallic center, forcing the chemist to compromise between enantioinduction and activity.

In contrast to L-ligands, the outer-sphere counterions were envisioned to have less impact on the cationic metallic center. Moreover, introducing the chiral information on the labile counterion of the metallic species would allow, if adequately selected, to bring the chiral information closer to the reactive center, thus improving the enantioinduction [10]. Indeed, asymmetric counterion directed strategy has been revolutionizing the organometallic catalysis landscape for the past 10 years [11]. We thus investigated its potential in enantioselective carbocyclizations of polyunsaturated substrates, building several carbon–carbon bonds in a single-step process.

Enantioselective [Ir]-catalyzed 1,6-enyne cycloisomerization

Among carbocyclizations, cycloisomerizations are of particular interest due to their high dependence on the properties of the catalyst. Moreover, when we started our study, only a few asymmetric versions had been reported that proved highly substrate-dependent [12]. We thus selected gold-catalyzed cycloisomerizations as model reactions to develop a chiral counterion approach to enantioselective carbocylization reactions.

However, when the gold precatalyst was treated by silver phosphate **1**, although the gold-phosphate ion pair was effectively formed [13], no catalysis was observed in cycloisomerization reactions, even at elevated temperature (Scheme 9, eq. 1). We hypothesized that the lack of reactivity could be due to the strong Au–O bond existing between the gold atom and the phosphate counterion [14]. Indeed, we observed it could be



Scheme 9 Cycloisomerization attempts in the presence of a gold-phosphate ion pair.

restored by using methanol as a co-solvent (Scheme 9, eq. 2). However, the product formed was a racemate, probably due to the full dissociation of the ion pair in this polar solvent [15].

We therefore chose to explore a steric dissociation, exploiting the repulsion between the counterion and the ligands of a square planar metallic species of type **A** to achieve reactivity (Scheme 10, eq. 1). We selected Vaska's type iridium(I) complexes, which had previously been used by Shibata et al. in a chiral ligand-based asymmetric cycloisomerization of *N*-tethered 1,6-enynes **B** (ee up to 78 %) [16]. Introduction of the chiral counterion occurred by simple treatment of Vaska's complex [IrCl(CO)(PPh_3)$_2$] with the corresponding silver salt **1**. Indeed, under optimized conditions, *N*-tethered 1,6-enyne **2** led to bicyclo[4.1.0]hept-2-ene **3** in 80 % yield and 81 % ee when treated by [IrCl(CO)(PPh_3)$_2$] (10 mol%) and Ag(*S*)TRIP **1** (12 mol%) as the unique source of chirality (toluene, 90 °C) (Scheme 10, eq. 2) [17].

We then investigated the scope and limitations of this transformation (Scheme 11). The reaction conditions are compatible with a wide range of *N*-protected 1,6-enynes of type **B**, bearing a tosyl-, nosyl- or even carbamate protecting group at the nitrogen atom. The desired bicycles **C** were isolated in good to excellent ee (72–93 % ee). Substitution of the aryl at R^1 with either an electron-donating or -withdrawing group increased the enantiomeric excess to 86 and 89 % ee, respectively. This aryl substituent can be efficiently replaced by a methyl substituent without loss of selectivity (86 % ee) but with a slight loss of the isolated yield. On the other hand, in the absence of substitution at the R_1 position, both selectivity and yields dropped. We then changed from *N*- to *O*-substituted tethers, and the opposite reactivity pattern was observed: a high 88 % ee was obtained in the absence of substitution at the R_1 position. Finally, introduction of a carbonated bridge led to a different reactivity as no desired bicycle **C** was observed (Scheme 11).

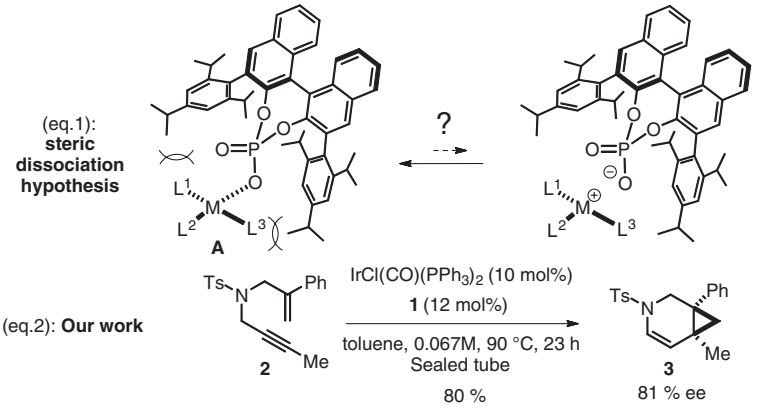
Overall, the use of a hindered phosphate chiral counterion provided bicyclo[4.1.0]hept-2-ene of type **C** with improved enantiomeric excesses compared with chiral diphosphines iridium(I) catalysis.

In order to extend the chiral counterion strategy to another key carbocyclization reaction, we turned to asymmetric rhodium-catalyzed [2 + 2 + 2] cycloaddition reaction.

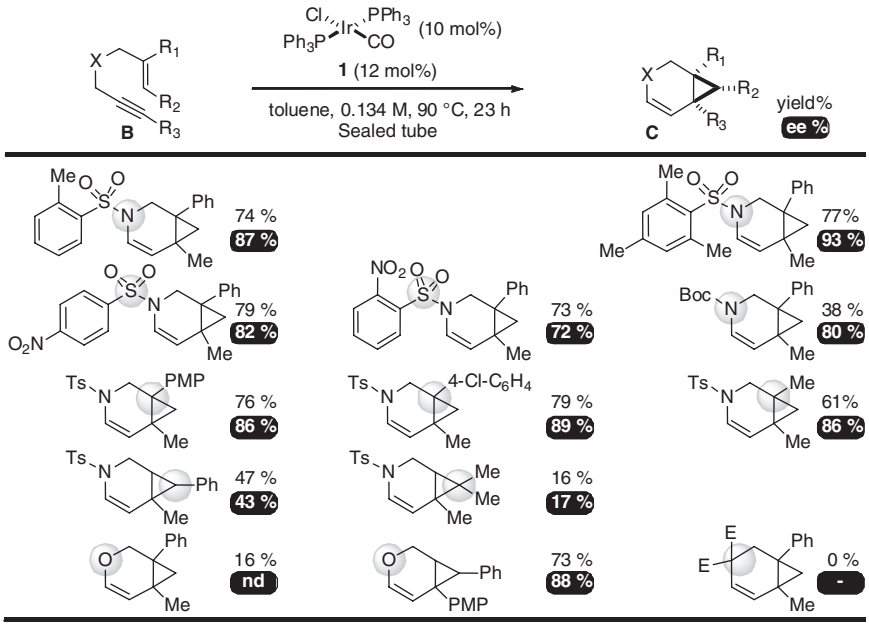
Atroposelective [Rh]-catalyzed [2 + 2 + 2] cycloaddition

In light of the [2 + 2 + 2]-literature [18], a diyne/isocyanate system was selected to evaluate the influence of the chiral counterion in cycloaddition reactions. Indeed, Tanaka et al. [19] reported the formation of the corresponding pyridones in modest to good enantiomeric excess, in the presence of [Rh(cod)$_2$][BF_4] as the rhodium source and (*R*)-BINAP as the chiral ligand (up to 68 % ee) thus providing a benchmark to compare the counterion effect to (Table 1, entry 1). Moreover, the use of cationic rhodium in this reaction already paves the way for the introduction of a chiral counterion.

After screening the different reaction parameters, we found that treatment of diyne **4** and isocyanate **5** by 2.5 mol% [Rh(cod)Cl]$_2$ as the rhodium source, 5 mol% 1,4-bis(diphenylphosphino)butane (dppb) as the



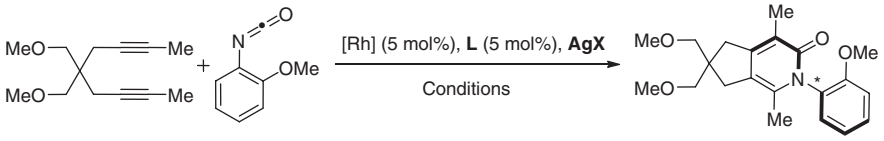
Scheme 10 Choice of a square planar iridium complex as the catalyst and optimized reaction conditions.



Boc = *tert*-butoxycarbonyle; E = CO_2Me, Ts = 4-Me-C_6H_4; PMP = 4-MeO-C_6H_4

Scheme 11 Scope and limitations.

Table 1 Optimized reaction conditions.

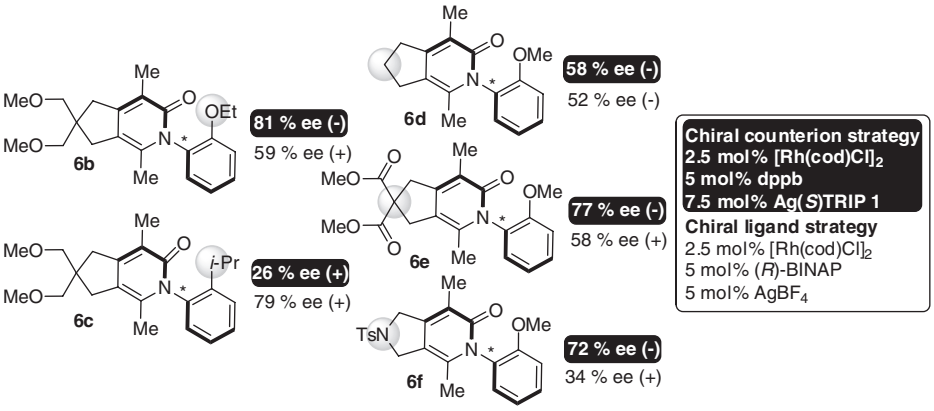


	Strategy	[Rh]	L	AgX (mol%)	Conditions	Yield	ee
1	Chiral ligand [17]	$[Rh(cod)_2][BF_4]$	(*R*)-BINAP		CH_2Cl_2, rt	72 %	68 % (+)
2	Chiral ligand [18]	$[Rh(cod)Cl]_2$	(*R*)-BINAP	$AgBF_4$ (5)	CH_2Cl_2, rt	84 %	67 % (+)
3	Chiral counterion [18]	$[Rh(cod)Cl]_2$	dppb	**1** (7.5)	DCE, 80 °C	77 %	71 % (–)

achiral ligand, and a slight excess of Ag(*S*)TRIP **1** as the chiral silver salt (dichloroethane, 80 °C) led to the desired pyridone **6a** in 71 % ee (Table 1, entry 3) [20].

The scope and limitation of the title reaction were explored, both in the chiral ligand and chiral counterion conditions (Scheme 12). Introduction of an ethoxy substituent on the aryl isocyanate led to an interesting increase in selectivity, and the pyridone **6b** was isolated in 81 % ee. It is noteworthy that these conditions outperformed the use of the (*R*)-BINAP chiral ligand, which only furnished a selectivity of 59 % ee. In contrast, whereas an apolar hindered *iso*-propyl substituent was perfectly suitable for the chiral ligand approach (79 % ee), the chiral counterion strategy afforded the corresponding pyridone **6c** in nearly racemic fashion (26 % ee). We also screened the diyne tether. A simple propanyl tether led to a drop of the selectivity and provided pyridone **6d** in 58 % ee, underlying the positive *gem*-dialkyl effect. Introduction of a *gem*-diester or a protected amine increased the selectivity compared with the chiral ligand strategy, and pyridones **6e** and **6f** were obtained in 77 and 72 % ee, respectively (Scheme 12).

In conclusion, we reported the first axial (counterion) to axial (pyridone) chirality transfer in the presence of a rhodium-phosphate ion pair. Of particular interest, the chiral anion strategy proved complementary to the chiral ligand one. This work emphasizes the importance of the chiral counterion as a suitable alternative to chiral ligand to induce enantioselectivity in organometallic transformations, and particularly carbocyclization processes.



Scheme 12 Scope and limitations: comparison of the two strategies.

Conclusion

These two stories are a reflection of the exceptional vivacity of the organometallic catalysis field. In a very few years, new opportunities for synthesis have emerged. Radical processes based on cheap hydrides and metallic salts such as the $FeCl_2$–$NaBH_4$ blend are now available. It is also clear that the chiral anion strategy should always be considered when dealing with asymmetric organometallic catalysis studies as an alternative or a complement to chiral ligands.

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