Catalytic Dehydrative Transformations Mediated by Moisture-Tolerant Zirconocene Triflate

Cristiana Margarita
Davide Di Francesco
Helena Lundberg*

Department of Chemistry, KTH Royal Institute of Technology,
Teknikringen 30, 10044 Stockholm, Sweden
hellundb@kth.se

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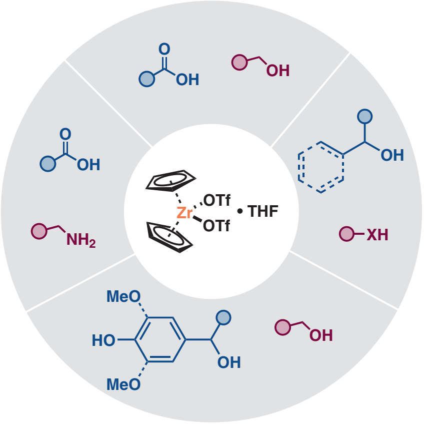

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Abstract Zirconocene triflate is a powerful moisture-tolerant catalyst for activation of C–O bonds in carboxylic acids and alcohols in the absence of water scavenging techniques. Herein, an overview of the use of this robust metal complex for direct amidation, esterification, and etherification is presented, along with a discussion on mechanistic aspects of the transformations and the catalyst class.

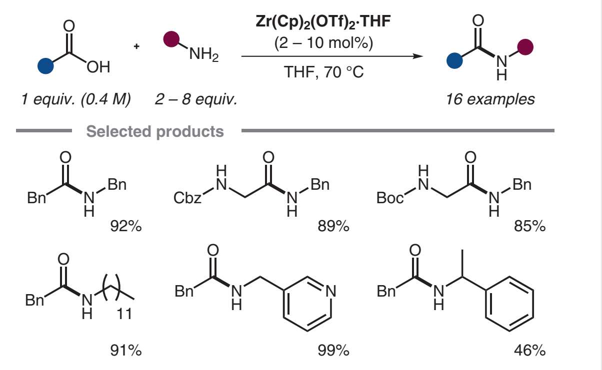
Key words Lewis acids, homogeneous catalysis, water-tolerant, kinetic analysis, zirconium, amides, esters, ethers

Lewis acidic reagents and catalysts are highly versatile in synthetic chemistry as they promote a wide range of organic reactions. Classic Lewis acids include halides of aluminum, boron, titanium and tin. These compounds have found use since a long time as mediator of Diels–Alder reactions, Friedel–Crafts acylations and alkylations, aldol condensations, and allylation of aldehydes, among many other transformations.[1] Despite their utility, these metal salts are commonly associated with hydrolytic instability, causing their deactivation. For example, hydrolysis of $TiCl_4$ results in HCl and TiO_2, a metal complex associated with considerably lower Lewis acidity.[2] Consequently, it has often been necessary to employ stoichiometric amounts of the Lewis acid, thus producing the corresponding amount of waste, and/or strictly anhydrous and inert conditions that result in less practical synthetic procedures. In addition, hydrolytically unstable Lewis acids are challenging to recover and reuse, which is a drawback from a sustainability perspective. In order to overcome these limitations, extensive research has been directed to the development of water-tolerant Lewis acidic metal complexes. In this context, seminal contributions were made by Kobayashi and co-workers in 1991 through their systematic assessment of the reactivities, properties and applications of rare-earth metal trifluoromethylsulfonate (triflate) complexes.[3] Due to their high activity and easy recovery, these water-tolerant Lewis acidic complexes have since been employed as catalysts for a great number of various bond-forming reactions. Early examples include the use of $Sc(OTf)_3$ and $Yb(OTf)_3$ to catalyze Mukaiyama aldol condensations in H_2O:THF mixtures, enabling the use of commercial aqueous aldehyde solutions,[4,5] as well as catalysis with water as sole reaction medium.[6–10] In addition, triflate and longer-chain perfluoroalkylsulfonate complexes of, for example, Bi and Ga have been found to be water-tolerant.[11–16] As a common feature, it has been suggested that the metal triflate complexes are activated by water, which induces a dissociation of the counterions from the central Lewis acidic metal ion, thereby allowing for Lewis bases to coordinate.[17]

Triflate complexes based on group IV metals are considerably less explored compared to their counterparts of lower valency. In this catalyst class, hafnium triflate ($Hf(OTf)_4$) has received the most attention due to its hydrolytic stability, strong Lewis acidity, and ability to catalyze a variety of transformations, including macrolactonizations and Friedel–Crafts reactions of hemiacetals.[18–20] The first use of metallocene triflate complexes as catalysts was reported in 1992 when Bosnich and co-workers employed $Ti(Cp)_2(OTf)_2$ and $Zr(Cp)_2(OTf)_2$·THF to mediate Diels–Alder reactions and aldol condensations,[21–23] soon followed by other transformations such as Sakurai reactions and cycloadditions.[24–27] Compared to their halide counterparts, these titanocene and zirconocene bis(triflate) complexes and their hydrates were reported to display improved stability in air and to be active catalysts even in the absence of anhydrous reaction conditions. In addition, metallocenes of group IV elements were developed in which longer perfluoroalkylsulfonate chains replaced the triflate ligands to enhance the Lewis acidity of the complex and further improve their hydrolytic stability.[13] By X-ray analysis, it was determined that the hydrate form of zirconocene perfluorooctanesulfonate was structurally similar to that of the corresponding triflate complex.[28] Three water molecules were found to coordinate to the metal center while the fluorinated counterions were found to pack around the cation, thereby creating hydrophobic domains.[29] These water-tolerant perfluorooctanesulfonate catalysts were determined to have a Lewis acidity similar to that of $Sc(OTf)_3$,[30] and demonstrated a similar ability to catalyze transformations such aldol reactions, acylations, amidations, glycosylations, and esterifications.[14,29–36] In addition, these perfluoroalkylsulfonate complexes could be recycled up to five times in Mannich reactions, allylations and aldol reactions,[30] similar to rare-earth metal triflate complexes. However, despite the efficiency of the reported protocols, the use of long-chain perfluorinated sulfonates raises concerns due to toxicity and bioaccumulative properties,[37,38] and these substances have been classified under REACH with restricted use as result.[39] In contrast, the use of the C1 counterpart – triflate – is not regulated and a wide variety of metal triflate complexes are commercially available for use in catalytic transformations.

Amidation

The use of Lewis acids as catalysts for direct amidation is usually related to boron- and transition-metal-containing compounds.[40–45] Group IV metal complexes are well represented in the latter category,[46–50] and their hydrolytic instability typically requires the use of water scavenging techniques such as azeotropic distillation to prevent deactivation of the metal catalyst by the water formed in the dehydrative reaction. For protocols carried out at temperatures below ca. 100 °C, molecular sieves are commonly employed as a dehydration technique. We were intrigued by the moisture-tolerant nature of the underexplored class of group IV metal triflate complexes and set out to assess their catalytic ability in direct amidation of carboxylic acids and amines in the absence of water-scavenging techniques.[51] As a result, zirconocene triflate and hafnium triflate were both identified as active catalysts for the transformation in the absence of drying agents, in stark contrast to the corresponding chloride and alkoxide complexes of group IV metals. With excess amine, the use of 2 mol% of the $Zr(Cp)_2(OTf)_2{\cdot}THF$ catalyst resulted in excellent yield of the model reaction between phenylacetic acid and benzylamine after 48 hours (Scheme 1). Benzylic and aliphatic amines furnished amide products in high yields, whereas the poor nucleophilicity of anilines rendered them unsuitable as coupling partners.[50,52]



Scheme 1 Zirconium-catalyzed direct amidation

Furthermore, secondary benzylic amines resulted in lower yields compared to their primary counterparts. This observation was interpreted as the result of steric hindrance, in line with observations previously made for group IV metal chloride catalysts under anhydrous conditions.[47,50] Under the applied catalytic conditions, amines were found to outcompete alcohols as nucleophiles, as evident from a competition experiment carried out in the presence of phenylacetic acid, benzylamine, and benzyl alcohol, that furnished the benchmark amide in 56% yield and 0% of the corresponding ester. Notably, the catalyst was not inhibited by alcohol, in contrast to what has been observed for corresponding metal chloride complexes.[47,50]

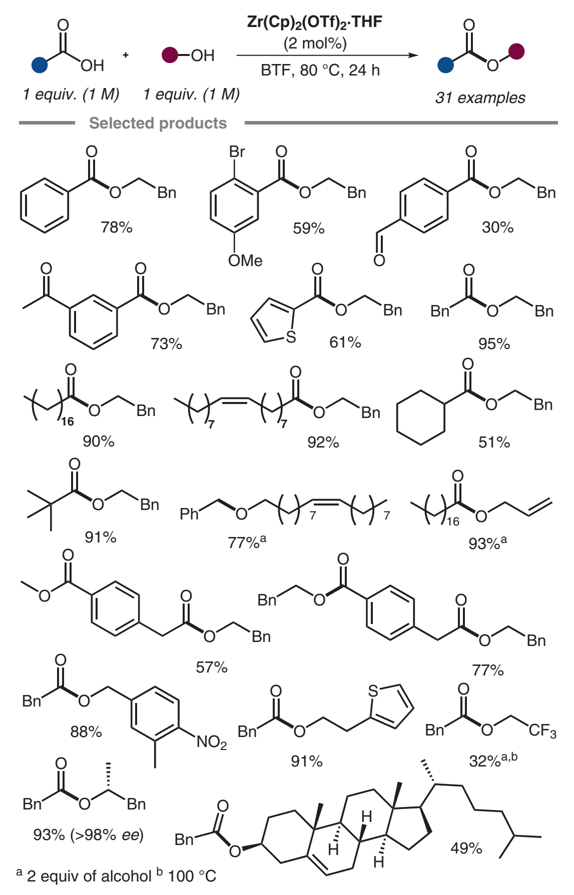
Esterification

In addition to amidation, esterification is another fundamental dehydrative transformation in which carboxylic acids and alcohols are condensed with water as by-product. While the classic Fischer esterification utilizes protic Brønsted acid catalysts, Lewis acids can also catalyze the reaction.[53,54] Using $Zr(Cp)_2(OTf)_2{\cdot}THF$ as catalyst, we sought to develop a robust esterification protocol without water scavenging and streamline the optimization through the use of modern kinetic analysis.[55] For this reason, reaction-progress kinetic analysis (RPKA) and variable-time normalization analysis (VTNA) were implemented in the early method development phase,[56–59] in order to obtain relevant mechanistic information and tune the reaction conditions accordingly. The zirconocene triflate catalyst was assessed in the model reaction using benzoic acid and 2-phenylethanol in an equimolar ratio (0.5 M), which proceeded reliably in aromatic solvents to form the ester product in ca. 70% yield after 24 hours at 80 °C. A study of the rate dependencies on reactant concentrations indicated a close to zero-order in both carboxylic acid and alcohol, suggesting that the concentration of these reactants could be increased without affecting the reaction outcome negatively. In contrast, the order in catalyst was positive and suggested that an increase in the global concentration of the reaction mixture would prove beneficial for the reaction rate. Further kinetic assessments revealed that catalyst inhibition or decomposition was not taking place with the formed water over the course of the reaction. In addition, up to 50 equivalents of water to catalyst could be added to the reaction mixture without negatively affecting the reaction rate, whereas the addition of molecular sieves reduced the activity of the zirconocene catalyst. These observations stand in stark contrast to what is observed in classic dehydrative reactions where water removal is beneficial for the yield.

The optimized conditions with 1 M reactant concentrations were successfully applied for esterification of various carboxylic acids and alcohols (Scheme 2). The catalytic system was found to preferentially promote esterification over transesterification, which enabled the formation of an unsymmetrical ester. Gratifyingly, the robust zirconocene complex could be recovered and reused in four consecutive cycles with negligible loss of activity. Aromatic alcohols did not undergo esterification using the reported system, likely due to their poor nucleophilicity under non-basic conditions. In addition, basic heterocycles were found to inhibit the reaction, likely via coordination to the metal catalyst. This behaviour stands in contrast to that of rare earth metal triflates, which did not suffer from deactivation by pyridines.[3]

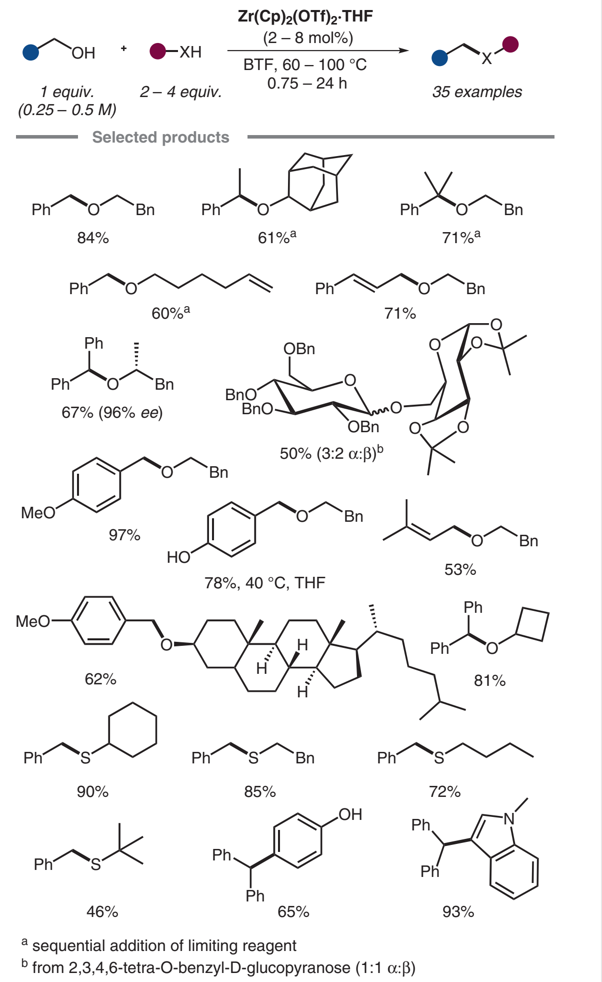
Direct Substitution of Alcohols

Direct substitution of alcohols is highly desirable from a sustainability perspective as it circumvents stoichiometric pre-functionalization of the hydroxyl group and generates water as by-product.[60] Different catalytic strategies have been used to accomplish this, including Lewis acid catalysis.[61–67] With our interest in group IV metal triflates, we set out to assess their activity towards C-OH activation in π-activated alcohols for subsequent nucleophilic substitution in the absence of drying agents.[68] The formation of unsymmetrical ethers was targeted, using benzyl alcohol and 2-phenylethanol as benchmark substrates. A common obstacle for direct substitution of alcohols is the formation of symmetrical ether side-products. To minimize this issue, we again used RPKA and VTNA[56–59] in the early method development stage to facilitate the optimization. Initial screenings revealed that the use of benzotrifluoride as solvent at 100 °C produced the highest yields of the desired unsymmetrical ether. It was found that both the unsymmetrical ether product and the symmetrical side-product formation had a close to first-order rate dependence on catalyst concentration, while the average order in the reactant alcohols differed for product and the side-product. Hence, we concluded that the formation of side-product could be suppressed by keeping the concentration of the electrophilic alcohol low and the concentration of the nucleophile high throughout the reaction. Such a setup was achieved by either changing the reactant stoichiometry at the onset of the reaction from 1:2 to 1:4, or by keeping the original 1:2 ratio but adding the electrophilic alcohol slowly in portions over 4 h. Both approaches resulted in improved selectivity for the unsymmetrical ether, which resulted in a yield increase from 70 to 84% after 24 h. The substrate scope of the direct alcohol substitution was evaluated, and a range of ethers were formed in good to excellent yields (Scheme 3). The use of substituted primary, secondary, tertiary benzylic, and allylic alcohols were well tolerated, including sterically hindered substrates and protected carbohydrates. Electrophilic alcohols bearing electron-donating groups, or a higher degree of benzylic substitution were found to react at lower temperatures and shorter reaction times, an observation compatible with a postulated carbocationic intermediate forming upon C–O activation. Similar to the observations made for the catalytic esterification protocol,[55] basic nitrogen-containing heterocycles were observed to inhibit the catalysis. In addition to O-nucleophiles, the methodology could be successfully extended to the use of thiols and aromatic compounds as S- and C-nucleophiles to furnish thioethers and Friedel–Crafts products in good to high yields and great selectivity (Scheme 3).



a 2 equiv of alcohol b 100 °C

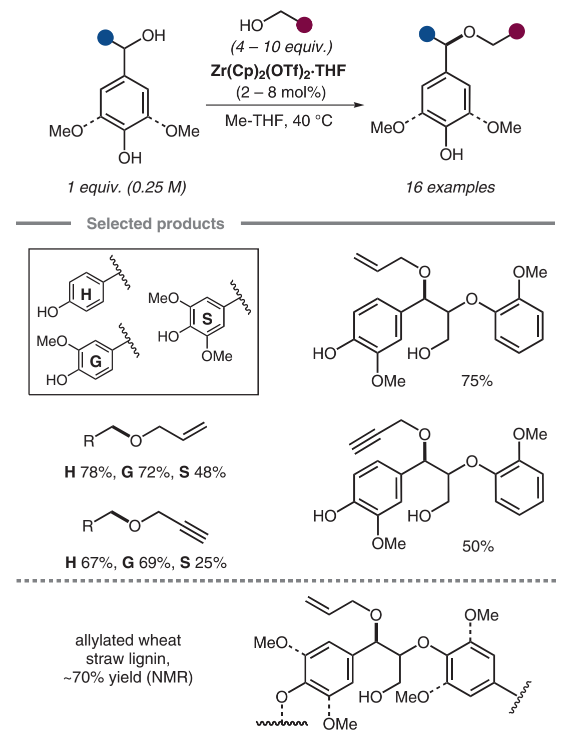
Scheme 2 Zirconium-catalyzed direct esterification



Scheme 3 Zirconium-catalyzed direct substitution of alcohols: dehydrative formation of ethers, thioethers and Friedel–Crafts products

Selective Etherification of Lignin Model Compounds and Lignin from Milled Wheat Straw

Lignin is an underutilized renewable component in land-living plants with high abundance in side-streams from, for example, pulping and processing of agricultural products. Lignin has great potential as feedstock for fuels, chemicals, and materials to replace fossil-based analogues, but its heterogeneity, hygroscopic character and high content of hydroxyl groups hampers its direct use. For this reason, catalytic valorization methods of lignin are of high interest. An established method to alter the properties of lignin is to functionalize its free hydroxyl groups (aromatic, aliphatic and benzylic) by etherification, with the dual goal of reducing the polarity and adding useful chemical functionalities to the oligomeric chain. For example, technical lignins have been successfully reported as precursors for thermoset applications after an allylation step using allyl chloride, mainly producing phenolic ethers.[69–72] With the high selectivity for benzylic alcohols observed in our catalytic etherification protocol, we were curious to see whether this strategy could be used for allylation of lignin using allyl alcohol as benign allylating agent with orthogonal selectivity compared to that of established protocols. Indeed, zirconocene triflate successfully catalyzed selective etherification of benzylic alcohols for a series of lignin model compounds using allyl alcohol as well as other functionalized alcohols as coupling partners (Scheme 4).[73] The use of 4-hydroxybenzyl alcohol (**H**) and vanillyl alcohol (**G**) resulted in good yields of both allyl and propargyl ethers, while the use of syringyl alcohol (**S**) resulted in lower yields. Furthermore, the **G-G** β-O-4 model, containing an aromatic, an aliphatic and a benzylic alcohol, formed the corresponding allyl and propargyl ethers in good yields with full selectivity for the benzylic position. Notably, the catalyst was not inhibited despite the rich opportunities for chelation by the aliphatic and benzylic hydroxyl groups. Kinetic analysis using vanillyl alcohol and the **G-G** β-O-4 model indicated similar rate dependencies on reaction component concentrations in both cases. Similar to our initial etherification protocol, it was found that a low concentration of the electrophile granted improved yields.[68] Using the mild reaction conditions, lignin derived from wheat straw via ball milling (milled straw lignin) was successfully allylated at the benzylic position without observable degradation of the polyphenolic chain.



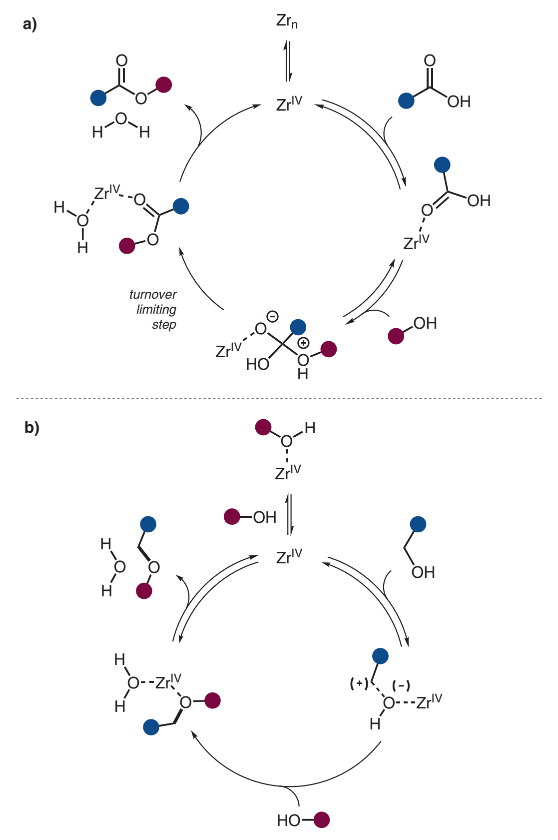
Scheme 4 Zirconium-catalyzed selective etherification of lignin model compounds and lignin from wheat straw

Mechanistic Considerations

The kinetic information obtained for the esterification indicated a close to first-order rate dependence in [Zr] and close to zero orders in [carboxylic acid] and [2-phenylethanol], suggesting that the turnover-determining step is found late in the catalytic cycle.[55] Due to the absence of product inhibition, it was thus proposed that the slowest step of the catalytic cycle is the collapse of the tetrahedral intermediate (Scheme 5a). The order in catalyst concentration was estimated to be 0.75, suggesting that the zirconium was divided between catalytically active species and inactive forms of higher order. Such catalyst behavior and rate-limiting step has previously been determined for amidation catalyzed by $ZrCl_4$.[74] For this reason, the mechanism for the zirconocene triflate-catalyzed esterification in Scheme 5 can be assumed to be similar for the analogous amidation.

The kinetic information obtained for the etherification indicated a close to first-order rate dependence in [Zr] and a positive order in electrophilic alcohol concentration, suggesting that activation of the C–OH bond is the rate-limiting step. The observation of faster reaction rates for electron-rich benzylic alcohols and slower rates for electron-poor analogues suggested the formation of a carbocationic intermediate. This hypothesis was further supported by the observed racemization in ethers formed from enantiopure (*S*)-1-phenylethanol as starting material. Negative orders in [nucleophile] for both product and side-product formation indicated that catalytically inactive off-cycle species form upon coordination of the nucleophilic alcohol to zirconium, thereby decreasing the concentration of active catalyst. A tentative mechanism for etherification is given in Scheme 5b.

While the structure of the catalytically active zirconium triflate species is not yet known, experimental observations provide indirect clues. In neither the esterification nor the etherification protocol was the zirconocene triflate catalyst observed to undergo inhibition by the products or the formed water, whereas its activity was decreased in the presence of molecular sieves. These observations suggest that a certain amount of water may be important for the catalytic activity of the Zr complex. Such behavior has previously been observed for rare earth metal triflate catalysts such as $Yb(OTf)_3$.[6] It has previously been shown that zirconocene complexes with fluorinated sulfonate ligands can form dimers in the presence of water.[15] Thus, the inhibiting effect resulting from molecular sieves may suggest that multinuclear complexes and/or aqua complexes are the catalytically active species in transformations mediated by zirconocene triflate as well as for similar systems. Water-tolerant rare-earth metal perchlorate and triflate complexes have previously been attributed common characteristics, including a high exchange rate constant for inner-sphere water ligands in their hydrated form.[17] From a catalytic point of view, the fast exchange of a water (or solvent) molecule for a substrate at the metal center would enable efficient activation of the substrate for subsequent attack by a nucleophile. Such a mechanism has also been proposed for perfluoroalkyl/arylsulfonate dimeric aqua complexes of group IV metals for Friedel–Crafts acylation of alkyl–aryl ethers, the Mukaiyama aldol reaction, and the allylation of aldehydes,[15,16] as well as for Mukaiyama aldol reactions catalyzed by titanocene and zirconocene triflate.[23] Nevertheless, detailed understanding of the nature of the catalytically active species is still missing and, specifically, insights that explain the protective role that the fluorinated sulfonate ligands play in hydrolytic decomposition of the group IV metal center that rapidly occurs for halide and alkoxide complexes.



Scheme 5 Zirconium-catalyzed esterification and etherification: proposed catalytic cycles

Conclusions

Zirconocene triflate is a powerful moisture-tolerant catalyst for activation of C–O bonds in carboxylic acids and alcohols in the absence of water scavenging techniques. This robust complex efficiently catalyzes direct amidation, esterification, and etherification, and can be recycled and reused without loss of activity. Future work to elucidate the nature of the catalytically active species and the protection against hydrolysis that the triflate ligands infer will reveal valuable mechanistic insights and accelerate the development of new catalytic protocols using this robust Lewis acidic complex.

Conflict of Interest

The authors declare no conflict of interest.

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