Rise of the Zinc Age in Homogeneous Catalysis?

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ABSTRACT: During the past years a number of interesting zinc catalyzed reactions have been reported, spanning a range from reduction to oxidation, (de)polymerization, synthesis of amines, or cyclopropanation reactions. This Perspective will focus on a selection of recent achievements applying catalytic amounts of zinc in organic transformations and raise the question if zinc can be a future option or tool for organic synthesis.

1. INTRODUCTION

The development of sustainable, efficient, and selective procedures to access organic compounds with higher values is one of the fundamental research goals in modern chemistry. Among all of the methodologies considered thus far, catalysis offers an efficient and economical approach to achieve this goal.[1] In particular, transition metal catalysts modified by ligands are one of most successful examples of practical catalysis. Clearly, most of the applied metals (e.g., Pd, Rh, Ru, Ir) displayed difficulties by their low abundance, high price or toxicity.[2] For instance the current prices are for palladium 1703 € per mol, iridium 5280 € per mol, rhodium 3602 € per mol, and for ruthenium 281 € per mol. In contrast, the current price for one mol of zinc is 0.07 €.[3] Moreover, the adjustment of process technology to more environmentally benign alternatives has been initiated.[4−8] Hence, today's research is focusing on the replacement by cheaper and low toxicity metals or to invent new protocols with such metals. Here the use of zinc can be of great interest, because of its abundance (0.0076% in the earth crust), biological relevance (essential trace element: daily dose for humans 12−15 mg), and distinct abilities. Surprisingly, in comparison to other metals the interest in zinc as catalyst core was underdeveloped. More recently, the situation changed, and the potential of zinc has been demonstrated in several applications.[9,10] On the basis of that, this Perspective will focus on a selection of recent achievements applying catalytic amounts of zinc in organic transformations and raise the question if zinc can be a future option or tool for organic synthesis.

2. REPRESENTATIVE APPLICATIONS OF ZINC CATALYIS IN ORGANIC SYNTHESIS

The reduction of functional groups is one of the key transformations in organic chemistry. During the past decades, countless methodologies have been established based on transition metal-cat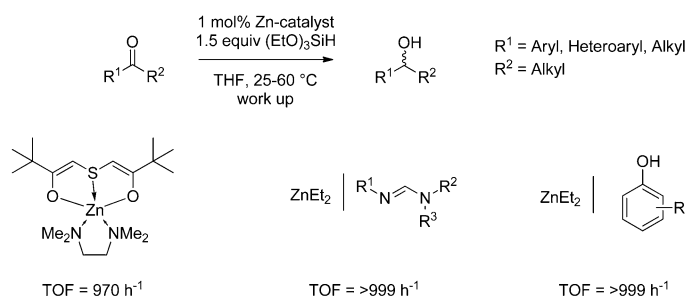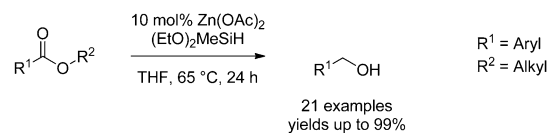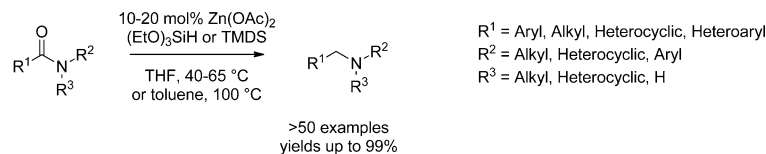alysis. In comparison zinc-catalysis versions were not well explored. Pioneering work in the field was reported by the groups of Noyori[11] and Mimoun[12,13] for the reduction of aldehydes and ketones applying silanes as reducing reagents. Later on, several research groups enhanced this method for increased functional group tolerance, in situ deprotection of the silyl ether, and the application of PMHS (polymethylhydrosiloxane) as inexpensive hydride source or incorporation of chirality.[14−29] In more detail, for transferring chirality to the substrate zinc complexes modified by ligands based on the chiral motifs 1,2-diaminocyclohexane or 1,2-diphenylethylenediamine have been found to be superior. For instance highest enantioselectivity of 91% enantiomeric excess (*ee*) for the reduction of the benchmark substrate acetophenone was observed for the in situ system composed of $ZnEt_2$ and ligand **1** (Scheme 1a).[28] A slight increase to 93% *ee* was realized for the utilization of boranes as hydride source.[30,31] Noteworthy, state of the art enantioselectivities for zinc catalysis are to some extent lower than those obtained by well established Rh, Ru catalysts, but having a backwardness of several decades. Unfortunately, a one-to-one transfer of the ligand concepts of other metals gained unsatisfactory results; hence, tailor-made concepts for zinc catalysis are required to significantly improve the reaction outcome. Moreover, some zinc catalysts display some drawbacks: the use of high catalyst loadings and long reaction times reduces the efficiency of the methods. Hence, the development of improved methods is highly desired. Recently, the groups of Driess and Enthaler reported on the achiral reduction of carbonyl functionalities exhibiting excellent catalyst activity applying zinc systems containing tridentate O,S,O-ligands comprising hard (O) and soft (S) donor atoms (Scheme 1b).[32] Remarkably,

Scheme 1. Zinc Catalyzed Hydrosilylation of Carbonyl Compounds

a) Asymmetric Hydrosilylation (*Carpentier et al.*, Ref. 28)

R^1 = Aryl, Heteroaryl
R^2 = Alkyl

yields up to 99%
ee up to 91%

1 (Ar = o-MeOC$_6$H$_4$)
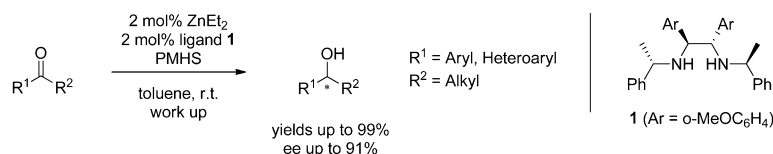
b) Achiral Hydrosilylation (*Enthaler, Driess et al.*, Ref. 32-34)

R^1 = Aryl, Heteroaryl, Alkyl
R^2 = Alkyl

TOF = 970 h^{-1} TOF = >999 h^{-1} TOF = >999 h^{-1}

c) Reduction of Esters (*Beller et al.*, Ref. 38)

R^1 = Aryl
R^2 = Alkyl

21 examples
yields up to 99%

d) Reduction of Amides (*Beller et al.*, Ref. 39-41)

R^1 = Aryl, Alkyl, Heterocyclic, Heteroaryl
R^2 = Alkyl, Heterocyclic, Aryl
R^3 = Alkyl, Heterocyclic, H

>50 examples
yields up to 99%

highest catalytic activity was reported with a turnover frequency of 970 h^{-1}. Further advancement was realized by diethyl zinc as the precatalyst, which can be easily modified by commercially available phenol ligands or formamidine ligands, which allows the efficient reduction of various aryl and alkyl ketones with excellent turnover frequencies up to 1000 h^{-1} and a broad functional group tolerance.[33,34] Future studies should be directed to the marriage of highly active systems with enantioselective versions. For a better understanding of the zinc catalyzed reductions and for a higher level of improvement a deeper understanding of the underlying reaction mechanism can be a useful tool. During the course of studies in hydrosilylation of carbonyl compounds contrary types of reaction mechanisms have been proposed.[14−33] On the one hand zinc can act as a Lewis acid by activation of the carbonyl function and on the other hand via a Zinc-hydride intermediate. More recently, the group of Kwit carried out an experimental and theoretical study to shed light on the discussion of this controversy and found that the Zn-hydride pathway appears energetically most favorable for the investigated zinc-diamine-diol system.[35] Besides, stoichiometric amounts of organometallic zinc reagents have been extensively used in addition reactions for the conversion of carbonyl compounds.[36,37] The high potential of zinc catalysts and silanes has been once more demonstrated in the conversion of

carboxylic acid derivatives. For instance the group of Beller demonstrated that the straightforward and inexpensive zinc(II) acetate and hydrosilanes can convert esters to alcohols in excellent yields and chemoselectivities (Scheme 1c).[38] Interestingly, a high functional group tolerance was observed under mild reaction conditions, which makes the protocol probably attractive for organic synthesis. Besides the reduction of ketones and esters the synthesis of amines by reduction methodologies is one of the targets for catalysis, because of their key role in bulk and fine chemicals, and pharmaceutical synthesis. A quite similar zinc system can provide amines by the reduction of amides (Scheme 1d).[39−41] In the presence of catalytic amounts of zinc(II) acetate, tertiary amides were easily reduced by using monosilanes as reductant, whereas for the reduction of secondary amides, zinc triflate and disilanes were successfully applied. Noteworthy, a broad scope and functional group tolerance was shown for this methodology. Preliminary mechanistic investigations revealed the activation of the hydrosilane by the zinc catalyst rather than the activation of the amide functionality, and zinc hydride species are proposed as intermediates. Moreover, the reduction of prochiral imines allows an access to chiral amines, which are of interest in natural product synthesis and useful pharmaceutical targets. Different zinc catalyzed approaches have been reported mainly based on

Scheme 2. Zinc Catalyzed Synthesis of Amines

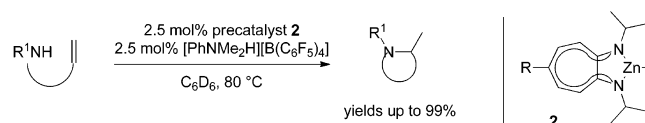a) Asymmetric Hydrosilylation (*Yun et al.*, Ref. 44-45)

8 examples
yields up to 86%
ee up to 98%
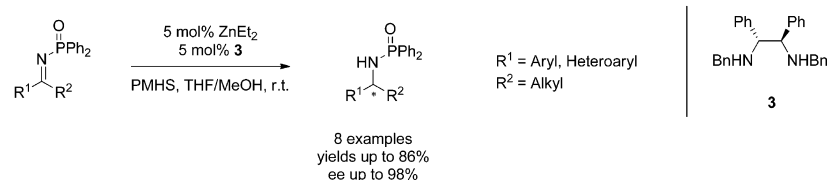
b) Reductive Amination (*Enthaler*, Ref. 46)

30 examples
yields up to 99%
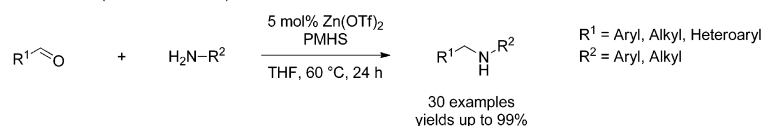
c) Hydroamination-Hydrogenation (*Beller et al.*, Ref. 47-48)

13 examples
yields up to 88%

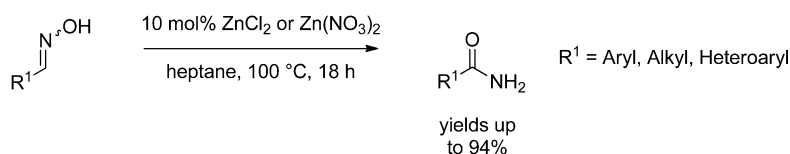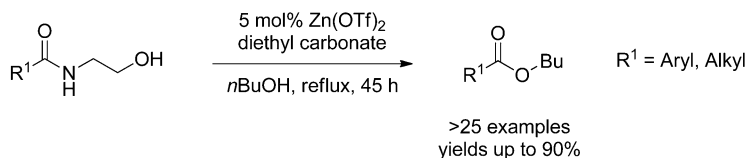d) Hydroamination (*Blechert, Roesky et al.*, Ref. 50-54)

yields up to 99%

hydrosilylation protocols.[21,42,43] An outstanding system has been introduced by Yun and co-workers applying in situ generated zinc catalysts modified by chiral diamine ligands (Scheme 2a).[44,45] Excellent enantioselecitivities up to 98% were realized for the hydrosilylation of *N*-diphenylphosphinylimines. The embedding of the $[Ph_2P=O]$ unit probably allows for a bidentate coordination fashion of the substrate and increases the stability of potential intermediates and in consequences increases the transfer of the chiral information, while unfunctionalized side chains resulted in lower enantioselectivity. Noteworthy, the $[Ph_2P=O]$ functionality can be easily removed after the catalysis to provide the primary chiral amine.

Moreover, one current aspect is to realize environmental benign and efficient chemistry by the replacement of step-by-step construction of molecular bonds by performing several steps in one-pot. In this regard, the reduction of in situ formed imines offers a straightforward access to higher functionalized amines. In more detail, this one-pot reductive amination protocol is based on two synthetic steps. For instance the group of Enthaler reported on the application of simple zinc salts as precatalysts in the reductive amination of aldehydes (Scheme 2b).[46] First the imine is synthesized by condensation of a carbonyl compound and a primary amine, and in the second step the reduction is carried out applying hydrosilanes as reductants. Excellent yields and functional group tolerance were observed for the system zinc(II) triflate and PMHS as reductant. A different one-pot approach to access amines has been recently accounted by Beller and co-workers (Scheme 2c).[47,48] In the first part, the zinc

catalyzed hydroamination of terminal alkynes with primary amines is performed resulting in the formation of imines. Noteworthy, the hydroamination is highly selective as reported for other zinc based systems as reviewed recently.[49] In the final step the zinc catalyst reduces the in situ formed imines to secondary amines applying molecular hydrogen as reductant. Interestingly, the activation of molecular hydrogen by zinc complexes is quite unusual. The group of Beller proposed a ligand (substrate) assisted activation of hydrogen. On the basis of that protocol, various products have been obtained in good to excellent yields. Moreover, among others the groups of Roesky and Blechert[50−54] reported on an access to functionalized amines by zinc catalyzed hydroamination of alkenes (Scheme 2d).[55−59] As excellent catalyst $ZnMe_2$ modified by aminotroponimines **2** was applied in the intramolecular hydroamination of nonactivated alkenes and different factors influencing the reaction outcome have been studied. A variety of products can be easily formed under mild reaction conditions, which could be of interest for total synthesis applications.

On the other hand, carboxylic acid derivatives are of interest as precursors for numerous organic transformations. Enthaler and Inoue have been examining the potential of catalytic amounts of zinc salts in the dehydration of a variety of amides with *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA) as the dehydration reagent to produce the corresponding nitriles (Scheme 3a).[60,61] With the straightforward and commercially available zinc(II) triflate as the precatalyst and MSTFA, an excellent system has been established to afford nitriles in excellent yields and chemoselectivities. Noteworthy, the method can tolerate functional

Scheme 3. Zinc Catalyzed Synthesis or Conversion of Carboxylic Acid Derivatives

a) Dehydration of Amides (*Enthaler et al.*, Ref. 60)

16 examples
yields up to 99%
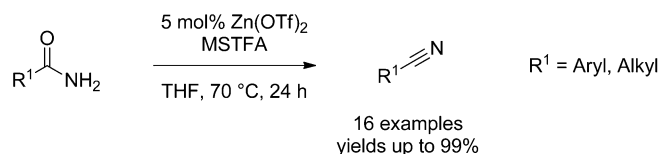
b) Dehydration of Amides (*Lalitha et al.*, Ref. 62)

16 examples
yields up to 95%
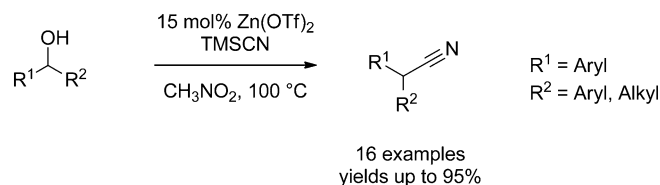
c) Oximes to Amides (*Williams et al.*, Ref. 63)

yields up
to 94%

d) Amide Cleavage (*Mashima et al.*, Ref. 64)
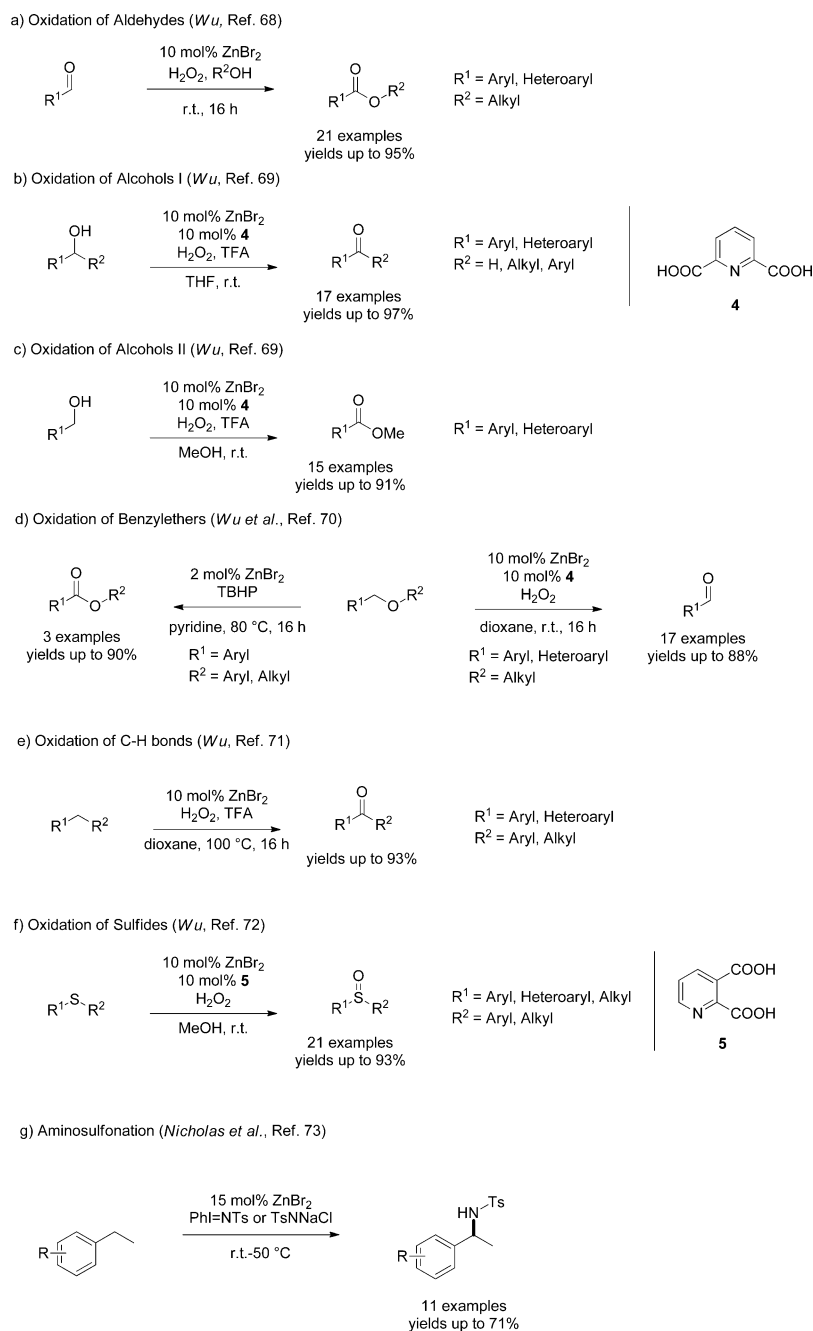

>25 examples
yields up to 90%

groups, which can be easily reduced by other methods applying hydrosilanes. A different approach has been presented by Lalitha and Theerthagiri applying catalytic amounts of zinc(II) triflate to convert secondary benzylic alcohols with trimethylsilyl cyanide (TMSCN) to α-aryl nitriles (Scheme 3b).[62] Good to excellent yields were obtained at 100 °C with the protocol tolerating various functional groups. Moreover, the group of Williams converted oximes to the corresponding primary amides in the presence of zinc salts (Scheme 3c).[63] Remarkably, depending on the reaction conditions the reaction outcome can be shifted to the formation of the corresponding nitrile, for instance simple acetonitrile can be applied as water scavenger to switch the selectivity. Furthermore, Mashima and co-workers developed a protocol for the transformation of secondary carboxamides to organic esters in the presence of simple zinc(II) triflate under neutral conditions (Scheme 3d).[64] Importantly, the substituent at the nitrogen unit should contain a β-hydroxy function. Remarkably, the potential of the protocol has been demonstrated in the cleavage of peptide bonds.

The catalytic oxidation of functional groups has received significant attention in industry and academia as a methodology to create bulk chemicals, fine chemicals, agrochemicals, and pharmaceuticals. In this regard, the cheap, abundant, and

biological relevant zinc was the recent subject of homogeneous catalyzed oxidation reactions.[65−67]

Recently, the groups of Cao, Gree, and Sekar investigated the oxidation of secondary alcohols to the corresponding ketones in excellent yields. Interestingly, the Zn(II)−DABCO system presented by Sekar was an efficient catalyst in the presence of molecular oxygen and after modification with chiral ligands an oxidative kinetic resolution of benzoins was feasible.[65−67] Recently, the group of Wu has extensively studied the potential of zinc(II) bromide as precatalyst in oxidation chemistry (Scheme 4). With 10 mol % ZnBr$_2$ the oxidative esterification of various aldehydes was carried out in excellent yields in the presence of an alcohol as solvent, which was embedded in the final product (Scheme 4a).[68] Noteworthy, as green oxidant hydrogen peroxide has been applied under mild reaction conditions, since only water is formed as unproblematic side product. The scope of the system was enlarged to benzyl acohols as starting material to produce various esters by addition of ligand 4 (Scheme 4c).[69] The reaction outcome can be easily changed to the formation of the corresponding aldehyde or ketone by exchanging the solvent from the alcohol to tetrahydrofuran (THF) (Scheme 4b).[69] Moreover, an oxidative cleavage of benzyl ethers has been developed applying the same system (Scheme 4d).[70] As main products the corresponding aldehydes were obtained in good

Scheme 4. Application of Zinc Catalysts in Oxidation Chemistry

a) Oxidation of Aldehydes (*Wu*, Ref. 68)

21 examples
yields up to 95%

R^1 = Aryl, Heteroaryl
R^2 = Alkyl

b) Oxidation of Alcohols I (*Wu*, Ref. 69)

17 examples
yields up to 97%

R^1 = Aryl, Heteroaryl
R^2 = H, Alkyl, Aryl

4

c) Oxidation of Alcohols II (*Wu*, Ref. 69)

15 examples
yields up to 91%

R^1 = Aryl, Heteroaryl

d) Oxidation of Benzylethers (*Wu et al.*, Ref. 70)

3 examples
yields up to 90%

pyridine, 80 °C, 16 h
R^1 = Aryl
R^2 = Aryl, Alkyl

17 examples
yields up to 88%

R^1 = Aryl, Heteroaryl
R^2 = Alkyl

e) Oxidation of C-H bonds (*Wu*, Ref. 71)

yields up to 93%

R^1 = Aryl, Heteroaryl
R^2 = Aryl, Alkyl

f) Oxidation of Sulfides (*Wu*, Ref. 72)

21 examples
yields up to 93%

R^1 = Aryl, Heteroaryl, Alkyl
R^2 = Aryl, Alkyl

5

g) Aminosulfonation (*Nicholas et al.*, Ref. 73)


11 examples
yields up to 71%

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yields under mild conditions. A change of the oxidant to *tert*-butyl hydroperoxide and applying pyridine as solvent resulted in the direct oxidation of benzyl ethers to produce the corresponding esters (Scheme 4d). Furthermore, zinc(II) bromide was capable to oxidize CH bonds, for example, benzylic C−H bonds were easily converted to the corresponding ketones (Scheme 4e).[71] Besides, the zinc systems were able to oxidize organic sulfides to the corresponding sulfoxides in excellent yields (Scheme 4f).[72] The recent examples impressively show the potential and simplicity of zinc catalysis in oxidation chemistry. However, even if various successful catalytic zinc systems have been established the reaction mechanism is still unknown and should be one focus for future investigations. Further on enantioselective versions are quite rare and can open a new field for zinc catalysis. Interestingly, zinc catalysis has been

furthermore successfully applied in the aminosulfonation of hydrocarbons to produce tosyl protected amines in good yields.[73] Especially, benzylic and allylic C−H bonds were selectively converted to the corresponding secondary amines.

Along with applications in reduction and oxidation chemistry zinc catalysis has been extensively studied in the conversion of carbon dioxide an abundant and nontoxic C1 source to produce products with higher value. Especially, the formation of cyclic carbonates and polycarbonates by the reaction of epoxides and carbon dioxide has received much attention over the last decades (Scheme 5).[74,75] For instance poly(propylene carbonate) (PPC) has many potential applications especially in industry; hence cheap and straightforward methods are required for large scale applications. Indeed, numerous zinc based catalysts for the copolymerization of carbon dioxide and epoxides have been

Scheme 5. Zinc Catalysis for the Conversion of CO_2: Copolymerization of Carbon Dioxide

Coates et al. Ref. 92   *Williams et al.* Ref. 82
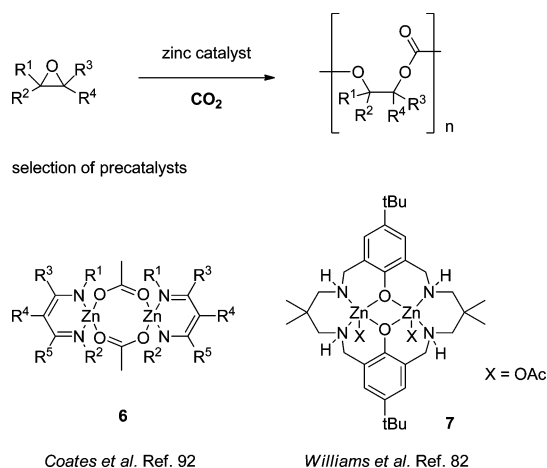
reported dating back to the initial work of Inoue and co-workers applying a mixture of diethyl zinc and water as the precatalyst.[76] In the 1970s, the protocol was advanced by Kuran and co-workers by the assumption of a dinuclear based process, which was later on proven by various research groups.[77−82] However, several issues have been addressed, which lowers the impact of the copolymerization. For example, as side reactions the backbiting reaction, to form the thermodynamically stable cyclic carbonate, and the consecutive insertion, to form ether bonds in the polymer, occur.[83] To overcome this limitation various homogeneous zinc based catalysts have been introduced.[84−91] In this regard, Coates and co-workers reported on one of the most active zinc catalyst containing the β-diketiminato ligand motif, which is easily tunable by variation of the substitution pattern.[92−97] Moreover, numerous zinc system are now available to perform the copolymerization reactions.[70,98−101] For the optimization and advancement of these catalysts, a deeper understanding of the mechanistic background of the reaction is worthwhile to realize additional large scale applications in the future.[74]
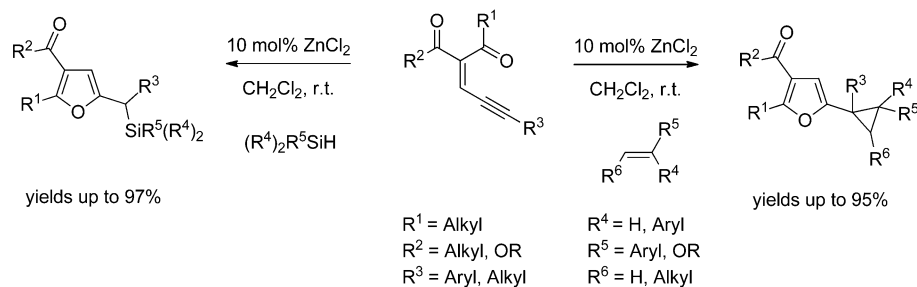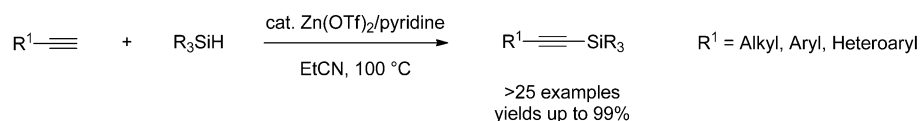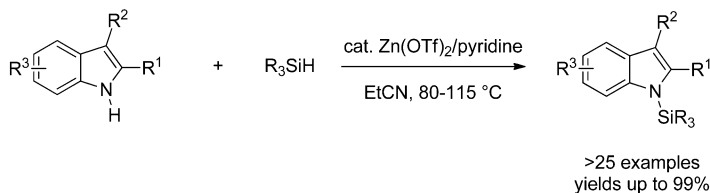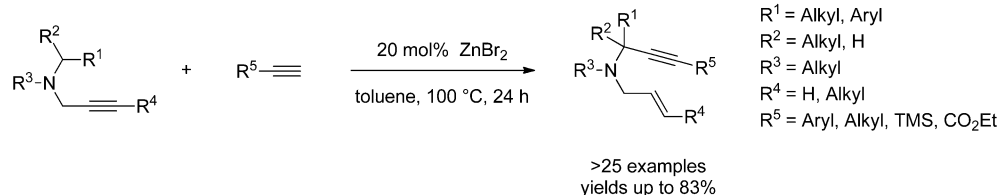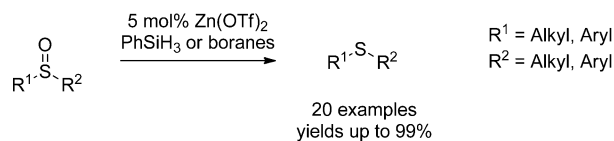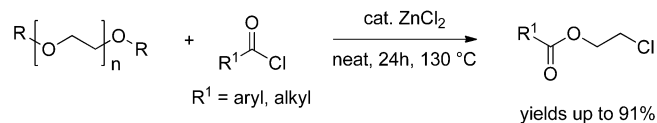
A recent example of an interesting impact of zinc catalysis on organic chemistry has been accounted by Vicente, López, and co-workers (Scheme 6a).[102] The use of zinc carbenoids in cyclopropanation reactions was reported in 1958 by Simmons and Smith, and based on that, countless protocols using this methodology have been established.[103,104] Importantly, all methods are based upon the use of stoichiometric amounts of zinc reagents. The situation changed quite recently by the catalytic generation of zinc-carbenes and embedding this protocol in the synthesis of complex molecules. For instance zinc(II) carbenes are generated from carbonyl-ene-yne compounds, and the reactivity was studied in addition reaction in the presence of olefins and hydrosilanes, resulting in the formation of interesting structural motifs. The group of Tsuchimoto reported on a highly selective functionalization of terminal alkynes (Scheme 6b).[105] A catalytic mixture of zinc(II) triflate and pyridine generated a system, which is capable to perform a dehydrogenative silylation under mild reaction conditions. The excellent abilities of the system have been demonstrated for a variety of substrates to produce alkynylsilanes, which are interesting building blocks for follow-up chemistry, for example, coupling or reduction chemistry. Moreover, the same mixture of zinc(II) triflate and pyridine was able to catalyze the

dehydrogenative *N*-silylation of indoles with hydrosilanes (Scheme 6c).[106] Interestingly, commonly a two step protocol is necessary to obtained silylated *N*-heterocycles. A broad scope of substituted *N*-heterocycles (e.g., indoles, pyrrols) was converted in good to excellent yields under mild conditions. With respect to the reaction mechanism a zinc hydride species is assumed as active species formed by the reaction of the hydrosilane with the zinc(II) triflate. The catalytic amounts of pyridine were proposed as a proton shuttle to produce finally molecular hydrogen. The methodology presented by Tsuchimoto and co-workers can be an interesting option to prepare such compounds under mild conditions and realizing more sustainable chemistry. Besides the formation of C−Si, N−Si bonds via dehydrogenative reactions the group of Nakamura demonstrated the potential of simple zinc(II) bromide as the precatalyst for the formation of C−C bonds via cross-dehydrogenative coupling (Scheme 6d).[107] Propargylic amines were reacted with terminal alkynes to yield *N*-tethered 1, 6-enynes and creating a C(sp)-C(sp³) bond adjacent to the nitrogen atom. Noteworthy, the hydrogen is embedded in the propargylic amine to access a C−C double bond. Numerous products were accessible by this method allowing a broad functional group tolerance. Moreover, the zinc catalyzed reduction of a variety of sulfoxides with silanes or boranes as reductant to the corresponding sulfide has been examined by the group of Enthaler. With the straightforward and commercially available zinc(II) triflate as the precatalyst, excellent yields and chemoselectivities for a broad variety of substrates were realized (Scheme 6e).[108−110] More recently, Enthaler and co-workers have set up for the first time a capable protocol for the depolymerization of polyethers with acid chlorides in the presence of catalytic amounts of abundant and cheap zinc salts to yield chloroesters as defined products (Scheme 6f).[111,112] Remarkably, the chloroesters were obtained at comparable mild reaction conditions and can be useful synthons in polymerization chemistry to prepare new polymers. Overall a recycling of polymers is feasible. Furthermore, the formation of ether bonds was performed by zinc catalysis. Aromatic alcohols and organic halides were converted in a Williamson ether type synthesis in the presence of catalytic amounts of zinc powder under microwave conditions in good yields.[113] Noteworthy, no additional base was necessary to realize a variety of ethers.

3. SUMMARY AND FUTURE OUTLOOK

In this Perspective we have briefly summarized the applicability of easy accessible zinc complexes/salts in catalysis spanning a range from reduction to oxidation chemistry to carbon dioxide functionalization. Indeed, initial studies have demonstrated the potential of zinc in organic synthesis, and interesting results have been observed. Interestingly, a positive aspect for various methodologies is the application of simple zinc salts avoiding any type of additional ligands, which allows a straightforward removal of the catalyst and reduces the costs of the system. In contrast, for chiral transformations novel and tailor-made zinc catalysts are highly desired to improve the current systems. Unfortunately, a simple method transfer, the application of the same ligands or the same reaction conditions, from well-established catalysts based on, for example, Rh, Ir, Ru, Pd, to zinc, is not possible or displayed difficulties. Moreover, generality, long-term activity, and stability will remain as a key challenges for future research. In addition, a deeper understanding of the reaction mechanism could be crucial to reach the next level of sophistication. In summary, the realized methodologies and the

Scheme 6. Application of Zinc Catalysis

a) Catalytic Generation of Zinc-Carbenes (*Vicente, López et al.*, Ref. 102)

10 mol% ZnCl₂
CH₂Cl₂, r.t.
(R⁴)₂R⁵SiH

yields up to 97%

10 mol% ZnCl₂
CH₂Cl₂, r.t.

yields up to 95%

R¹ = Alkyl
R² = Alkyl, OR
R³ = Aryl, Alkyl

R⁴ = H, Aryl
R⁵ = Aryl, OR
R⁶ = H, Alkyl

b) Dehydrogenative Silylation (*Tsuchimoto et al.*, Ref. 105)

R^1—≡   + R_3SiH $\xrightarrow[\text{EtCN, 100 °C}]{\text{cat. Zn(OTf)}_2/\text{pyridine}}$ R^1—≡—SiR_3

R¹ = Alkyl, Aryl, Heteroaryl

>25 examples
yields up to 99%

c) Dehydrogenative N-Silylation (*Tsuchimoto et al.*, Ref. 106)

+ R_3SiH $\xrightarrow[\text{EtCN, 80-115 °C}]{\text{cat. Zn(OTf)}_2/\text{pyridine}}$

>25 examples
yields up to 99%

d) Cross-Dehydrogenative Coupling (*Nakamura et al.*, Ref. 107)

+ R^5—≡ $\xrightarrow[\text{toluene, 100 °C, 24 h}]{\text{20 mol% ZnBr}_2}$

R¹ = Alkyl, Aryl
R² = Alkyl, H
R³ = Alkyl
R⁴ = H, Alkyl
R⁵ = Aryl, Alkyl, TMS, CO₂Et

>25 examples
yields up to 83%

e) Deoxygenation of Sulfoxide (*Enthaler et al.*, Ref.108-110)

$\xrightarrow[]{\substack{\text{5 mol% Zn(OTf)}_2 \\ \text{PhSiH}_3 \text{ or boranes}}}$

R¹ = Alkyl, Aryl
R² = Alkyl, Aryl

20 examples
yields up to 99%

f) Depolymerization (*Enthaler et al.*, Ref.111-112)

+ $\xrightarrow[\text{neat, 24h, 130 °C}]{\text{cat. ZnCl}_2}$

R¹ = aryl, alkyl

yields up to 91%

growing interest in zinc catalysis potentially presage a future position in the organic chemistry repertoire.

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Notes

The authors declare no competing financial interest.

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