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# Quasi-Nature Catalysis: Developing C–C Bond Formations Catalyzed by Late Transition Metals in Air and Water

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## ABSTRACT

This Account outlines the recent efforts of developing catalysis under the ambient conditions of air and water for synthetic purposes from the author's laboratory. The discussions are focused on catalytic reactions (mostly C–C bond formations) other than oxidations via late transition metals. It includes the following aspects: (1) copper-catalyzed C–C bond formations; (2) palladium-catalyzed C–C bond formations; (3) rhodium-catalyzed C–C bond formations; (4) ruthenium-catalyzed olefin isomerizations and C–H activations. The mechanism, limitations, and synthetic applications of these reactions are also discussed.

## Introduction

The use of late transition metals for catalyzing reactions is of growing importance in modern organic chemistry.<sup>1</sup> These catalyses are widely used in the synthesis of pharmaceuticals, fine chemicals, petrochemicals, agricultural chemicals, polymers, and plastics. Among the various catalytic reactions, the formations of C–C, C–O, C–N, and C–H bonds are particularly important in synthesis. Conventionally, organometallic chemistry and transition-metal catalysis are carried out under an inert gas atmosphere and the exclusion of moisture has been essential.<sup>2</sup>

On the other hand, the catalytic actions of transition metals under ambient conditions of air and water have played a key role in various enzymatic reactions including biocatalysis, biodegradation, photosynthesis, nitrogen fixation, digestions, and the evolution of bioorganisms.<sup>3</sup> All these “natural” catalytic reactions occur under aqueous conditions in an air atmosphere, which is in sharp contrast to most transition-metal-catalyzed reactions commonly used in the laboratory. Although many transition-metal-catalyzed oxidations such as the renown Wacker oxidation process<sup>4</sup> are carried out in air and water, this account concerns mostly catalytic reactions involving a carbon–metal (C–M) bond that leads to the formation of carbon–carbon bond in air and water.

In a recent Account, Roesky and co-workers elegantly discussed the reactivity of C–M bonds involving main group metals toward water by examining the bonding characteristics of s-block and p-block organometallic compounds.<sup>5</sup> For p-block organometallic compounds, the increased covalent nature of C–M bonds dramatically decreased their sensitivity toward water. On the other hand, the reactivity of C–M bonds of d-block organometallic compounds was much more complicated as well as synthetically more versatile than those of both the s-block and p-block organometallic compounds due to the participation of d-orbitals in bonding. There is no doubt that many more interesting catalytic reactions can be discovered by the exclusion of competing hydrolysis and oxidation due to the presence of air and water. However, the ambient feature offers convenience in chemical synthesis involving small-scale combinatorial synthesis, large-scale manufacturing, and catalyst recycling. Such advantages have been well demonstrated by the recent large volume of work with water-soluble catalysts,<sup>6,7</sup> such as catalytic hydrogenation,<sup>8</sup> hydroformylation (e.g., the well-known Rhone-Poulenc process),<sup>9</sup> palladium-catalyzed carbon–carbon bond formation reactions,<sup>10</sup> and ruthenium-catalyzed metathesis reactions.<sup>11</sup> This Account describes the development of synthetically useful catalytic coupling reactions under the ambient conditions of both air and water, which comes down to the competitive reactivity of C–M bonds toward water (hydrolysis), air (oxidation), and organic substrates (often an electrophile to generate the desired product) (Figure 1). Through a delicate balance of these reactivities, this Account demonstrates that various air- and water-sensitive catalytic reactions can in fact be carried out in air and water.

## Background

Since Wolinsky et al.<sup>12</sup> made the observation in 1977 that the allylation reaction of carbonyl compounds with allyl bromide mediated by zinc could be carried out in 95% ethanol and *tert*-butyl alcohol, a growing interest in metal-mediated Barbier–Grignard type carbonyl addition in water has been seen.<sup>13</sup> One particularly interesting characteristic of such reactions is that they can also be carried out in air. Chan<sup>14</sup> and Whitesides<sup>15</sup> have elegantly demonstrated the potentials of such reactions with synthetic applications in carbohydrate chemistry. However, most of the successes have been limited to the use of organic halides involving an activated C–X bond (such as allyl halides). This is primarily due to the fact that a highly reactive metal is required to break a nonactivated carbon–halogen bond and, with a highly reactive metal, various competing side reactions (such as the reduction of water, the reduction of starting materials, and the hydrolysis of the organometallic intermediate, even if it is successfully generated) will prevail. On the other hand, the chemistry of d-block transition metals is much more complex and rich in diversity. The methods for forming C–M bonds

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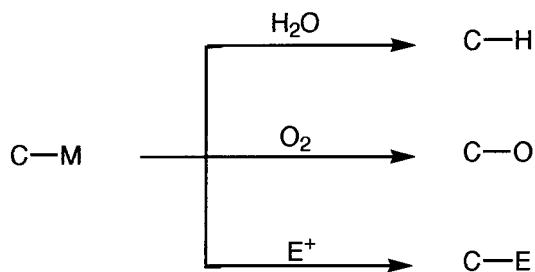
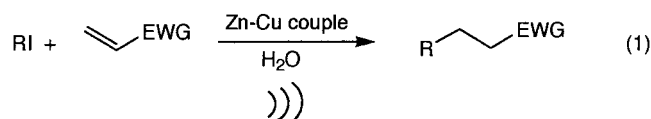


FIGURE 1.

involving d-block metals (late transition metals in particular) are both rich and facile. In addition, the C–M bonds related to these metals can be tuned readily to balance their stability toward air and water and their reactivity toward organic substrates. This Account illustrates the efforts to extend the aqueous Barbier–Grignard-type reaction to nonactivated organic halides via late-transition-metal catalysis in air and water.

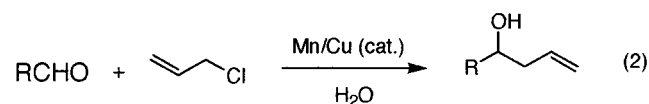
### Copper-Catalyzed C–C Bond Formations in Air and Water

An early effort was made to activate a nonactivated C–X bond by using a copper catalyst together with a metal mediator (such as tin or zinc), to mediate a coupling between an aldehyde and a simple alkyl halide in air and water. The efforts were, by and large, unsuccessful. Chan demonstrated that alkyl halides tend to undergo copper-catalyzed Wurtz-type coupling and dehalogenation in water.<sup>16</sup> However, Luche found that when a zinc–copper couple was used, alkyl halides reacted with conjugated carbonyl compounds and nitriles to give 1,4-addition products in good yields under sonication conditions in aqueous media (eq 1).<sup>17</sup> A moderate diastereoselectivity



was observed in these reactions where a mixture of diastereomers could be generated.<sup>18</sup> The difference between carbonyl addition and conjugated addition could be due to the increased reactivity of the transient alkyl-copper species toward the conjugated carbon.

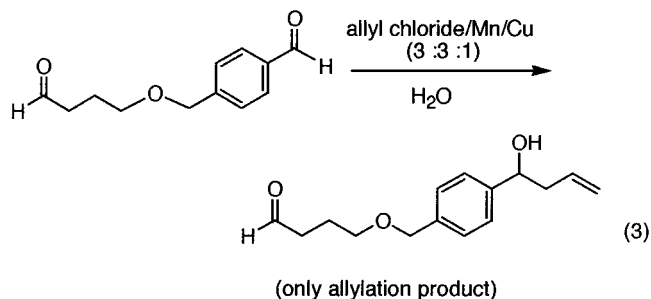
A more recent study by Li and Chan<sup>19</sup> showed the combination of manganese and copper to be a highly *regioselective* mediator for the allylation of aryl aldehydes in water alone (eq 2). No reaction was observed with either



manganese or copper alone as the mediator and only a catalytic amount of copper was required for the reaction. The use of Cu(0), Cu(I), and Cu(II) as the copper source were all effective. Under such reaction conditions, better yields of allylation products were obtained with allyl chloride than with allyl bromide and iodide. This was

attributed to the formation of Wurtz-type coupling product with the bromide and iodide.

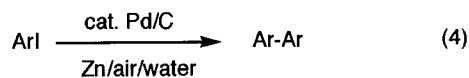
An exclusive selectivity was also observed when both aliphatic and aromatic aldehyde functionalities were present in the same molecule (eq 3). In the presence of



acetic acid or ammonium chloride, manganese was found to effect pinacol-coupling reactions in water.<sup>20</sup> The reaction proceeded also selectively with aryl aldehydes.

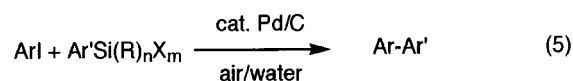
### Palladium-Catalyzed C–C Bond Formation in Air and Water

The utilization of a palladium catalyst is due to an effort in effecting coupling between carbonyls and organic halides involving a  $\text{sp}^2$ -carbon–halogen bond. Through the Heck reaction, Suzuki reaction, Sonigashira reaction, and Stille reaction, palladium is known to be particularly effective in activating  $\text{sp}^2$ -carbon–halogen bonds even in aqueous media.<sup>21</sup> Thus, efforts were made to couple aryl and vinyl halides with carbonyl compounds in water by using a catalytic amount of palladium and a stoichiometric amount of another metal. When iodobenzene was reacted with benzaldehyde and zinc together with a catalytic amount of palladium on charcoal in air and water, the desired carbonyl addition product was not generated, instead a Ullmann-type phenyl–phenyl coupling product was obtained (eq 4).<sup>22</sup> The presence of crown ethers<sup>23</sup> or



poly(ethylene glycol)s<sup>24</sup> were found to be beneficial for obtaining the Ullmann-type product.

A simple synthesis of unsymmetrical biaryls through palladium-catalyzed coupling of arylsilanes with aryl halides was also developed in air and water.<sup>25</sup> The reaction of methylphenyldichlorosilane with a variety of aryl halides was examined under the Pd/C catalyzed conditions to generate the unsymmetrical biaryls (eq 5). This



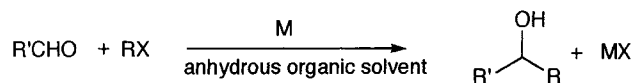
provided a convenient alternative to the use of hypervalent silicon reagents reported by Hiyama<sup>26</sup> and DeShong<sup>27</sup> and highly activated silicon reagents developed by Denmark for related cross couplings.<sup>28</sup>



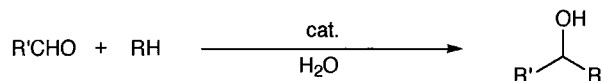


Scheme 1

## I. Classical Grignard-type reaction



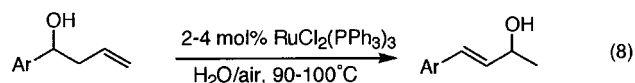
## II. Grignard-type reaction via C-H Activation in aqueous media



## Ruthenium-Catalyzed C–H Activation in Air and Water

The use of ruthenium is mostly related to searching for cleaner C–C bond formation in air and water via C–H activations. Despite the tremendous usefulness of the Grignard reaction and its related modifications in synthesis, the standard practice for carrying out such reactions involving the reactions of carbonyl compounds with organic halides mediated by a stoichiometric amount of metals is less than satisfactory (Scheme 1, route I). Such a practice would generate both a stoichiometric amount of halide waste and a stoichiometric amount of metal waste. It also requires multistep synthesis of the halides, which further generates a fair volume of waste due to reactions and separations. On the other hand, an alternative Grignard-type reaction between carbonyl compounds and a hydrocarbon via catalytic C–H activation<sup>31</sup> in water by using a water-soluble catalyst (Scheme 1, route II), if successful, would provide a cleaner solution for a Grignard-type reaction and organic synthesis. Furthermore, the reaction would provide a theoretical 100% atom efficiency.<sup>32</sup>

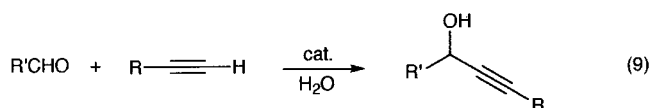
The first investigation was on the activation of the allylic C–H bond by using ruthenium catalysts in water. The initial intention was to overcome the difficulties encountered in coupling reactions between carbonyl compounds and organic halides involving a  $\text{sp}^2$ -carbon–halogen bond by an alternative approach involving a simple isomerization of the readily accessible homoallyl alcohols to the more difficult allyl alcohol.  $\text{RuCl}_2(\text{PPh}_3)_3$  was chosen since the complex is compatible with water and air. Through the catalysis of  $\text{RuCl}_2(\text{PPh}_3)_3$ , the functional groups of homoallylic alcohols are repositioned to give allylic alcohols with controlled regioselectivity (eq 8).<sup>33</sup> The selectivity in product formation was found to be



affected by the reaction temperature and the amount of the catalyst being used. A higher reaction temperature and the use of a smaller amount of the catalyst are preferable for the formation of allylic alcohols. The reaction process was postulated as a tandem olefin migration–allylic rearrangement. Under the same reaction conditions, the functional groups of allylic alcohols undergo allylic rear-

rangements. With a water-soluble ruthenium catalyst, a living catalytic system is possible in which the catalyst has been recycled many times.<sup>34</sup>

The second investigation is on the addition of alkynyl-metal reagents to aldehydes, a fundamental reaction in synthesis.<sup>35</sup> Most methods employ a stoichiometric amount of organometallic reagents such as organolithium or organomagnesium for forming alkynylmetal reagents from alkynes<sup>36</sup> or alkynyl halides<sup>37</sup> in anhydrous organic solvent. Because aldehydes also react with organometallic reagents readily, the preparation of alkynyllithium and organomagnesium reagents must be carried out as a separate step. These new studies show an effective addition reaction of phenylacetylene to aldehydes in aqueous solution via C–H activation where various aldehydes reacted with phenylacetylene catalyzed by a bimetallic Ru–In catalytic system to give Grignard-type nucleophilic addition products in water—with one to catalyze the overall reaction and the other to activate the carbonyl (eq 9).<sup>38</sup> This



appears to serve the dual purpose of being able to perform aqueous Barbier–Grignard-type reactions involving a  $\text{sp}$  C and achieving such reactions via a C–H activation in water.

## Tentative Explanation of Air and Water Stability

During the study, a subtle phenomenon was observed: catalytic reactions are less air sensitive in water than in organic solvent. The insensitivity and stability of C–M bonds related to late transition metals toward water can be explained by the hard–soft and acid–base principle, in which water molecules (hard) interfere very little with the late transition metals (soft).<sup>39</sup> However, the exact nature of the apparent increased stability toward air in water in these catalytic reactions is not very clear.

## Conclusion and Outlook

We have shown in this account that catalysis via late transition metals cannot only be carried out in water but can also take place under an atmosphere of air. The open-air feature offers convenience in chemical synthesis involving small-scale combinatorial synthesis, large-scale manufacturing, and catalyst recycling. In the area of environmental science and technology, transition-metal-catalyzed reactions in air and water offer convenient ways to use catalytic remediation of large areas of polluted water in open fields as well as reduce the consumption of potential polluting organic solvents in chemical manufacturing. Such reactions could also shed some light on the mechanism of biological and evolutionary processes in nature.<sup>40</sup> We hope that this Account will generate interest in the field.

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