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Switching between borrowing hydrogen and acceptorless dehydrogenative coupling by base transition-metal catalysts

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ABSTRACT

Taking the advantages of sustainability and economy, the borrowing hydrogen (BH) and acceptorless dehydrogenative coupling (ADC) methodologies based on earth-abundant transition-metal catalysts have recently attracted enormous interest in both academia and industry. Novel strategies to achieve switchable synthesis of the BH and ADC products by precise control of the reaction parameters and the catalytic systems are desirable and will significantly promote the field. In this mini-review, we summarized the published work on the switchable synthesis of amine/imine, alcohol/ketone, nitrile/acrylonitrile, and alkane/alkene through BH and ADC pathways, respectively. Specifically, we discussed the origin of the product-switching.

1. Introduction

The construction of C–C and C–N bonds belongs to one of the essential transformations in organic synthesis of products of high values [1]. One preeminent synthetic strategy is borrowing hydrogen (BH), which takes advantage of transfer hydrogenation to avoid the use of hydrogen gas and provide an attractive environmentally benign and atom- and process-efficient process, with water as the sole byproduct [2–15]. Alcohols, which are readily available, less toxic, and obtainable from biomass feedstock can be directly utilized to replace the toxic and mutagenic alkylating agents such as alkyl halides and alkyl sulfonates in the conventional synthetic methods [16].

The early examples of BH can be dated back to the early 1980s [17,18], and the term "borrowing hydrogen" was first defined by Whittlesey, Williams, and coworkers in 2004 [19]. Since the discovery of the BH methodology, the development of reactive catalysts based on precious transition-metals, e.g., Ir, Ru, Rh, Pd, etc. Have been the focus [12–15]. It is only around early 2010s that with the increasing concerns on the sustainability and economy, more research efforts have been shifted towards the earth-abundant and less expensive base metal analogs using Fe, Co, Mn, and Ni, etc. [20]. Some base metals are less toxic. For example, as the first and third most abundant transition-metal in the Earth's crust, respectively, Fe and Mn impose minimal environmental and toxicological impacts.

The BH falls into the category of cascade reaction, in which a consecutive series of reactions lead to the final products [21]. In the general BH process, alcohols are first dehydrogenated with the catalyst taking two hydrogens forming [MH_2] (Scheme 1). The in-situ formed reactive carbonyl intermediates, e.g., aldehydes and ketones, undergo condensations with nucleophiles to generate the unsaturated intermediates such as imines or alkenes, with the elimination of water. In the last step, the catalyst returns the "borrowed" hydrogens and reduces the unsaturated intermediates, affording the desired saturated products (Scheme 1, in red). In an alternative pathway, the hydrogen gas can be released from the "hydrogenated" catalyst, thus the reaction stops at the level of the unsaturated compounds. This process is recognized as the acceptorless dehydrogenative coupling (ADC) as no external hydrogen acceptors are employed (Scheme 1, in blue) [2–15,22,23]. BH and ADC have recently attracted increasing interest in both academia and industry due to the high sustainability and cost efficiency of these methods.

Recently, several excellent reviews have appeared on the general BH and ADC methodologies using homogeneous base transition-metal catalysts [2–11]. It is still a challenge to efficiently tune the selectivity, e.g., the ADC products are often identified as the major side products in the synthesis of the BH products and *vice versa* [2–15]. In this mini-review, we will focus on a new and unique direction by surveying the novel synthetic methods that can

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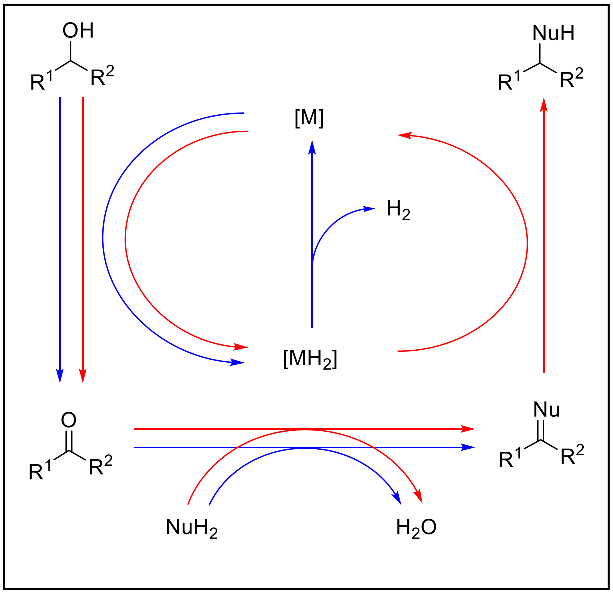


Scheme 1. General pathways of the BH (in red) and the ADC (in blue) mediated by transition-metal catalysts [M]. Nu represents nucleophile.

be applied to achieve switchable synthesis of the BH and ADC products. Although still scarce in the literature, these protocols exhibit the appealing control of the outcomes of the reactions by precisely adjusting the catalytic parameters, which is imperative from both practical and mechanistic points of view.

Herein, we will summarize the state-of-the-art switchable synthesis of a large variety of valuable products, such as amine/imine, alcohol/ketone, nitrile/acrylonitrile, and alkane/alkene, through the BH and ADC processes, respectively, mediated by homogeneous base transition-metal catalysts. We will focus on the design principles of the multifunctional catalytic systems for the product-switching. The current challenges and opportunities will be highlighted. Lastly, future development directions of this chemistry will be discussed.

BH/ADC switching by precious metal catalysis is not the focus of this mini-review. Such examples are surprisingly rare, and we will briefly mention them here. Interesting reviews on the general precious metal catalyzed BH and ADC reactions are available [12–15]. Representative heterogeneous and transition-metal-free cases will also be briefly discussed.

2. Switching between BH and ADC by base transition-metal catalysts

2.1. Switchable amine/imine formation

2.1.1. Alcohol amine couplings

The formation of amines and imines through the BH and ADC processes by base transition-metal catalysts has been extensively studied and reviewed [2–11]. However, synthetic strategies on switchable amine/imine generation are still underdeveloped.

Hanson and coworkers reported the first Co catalyzed ADC reaction with primary amines to form imines in 2013 (Scheme 2, A) [24]. Three years later, Zheng, Zhang, and coworkers employed the same Co catalyst **1** for the alternative amine generation through BH (Scheme 2, A) [25]. Interestingly, the presence of molecular sieves was found to be critical for the selective amine formation. However, the mechanism is still unclear thus far. Interestingly, it was showed by others that the addition of molecular sieves can also promote the imine formation [26,27]. The seemingly contradictory results may suggest that the method by utilizing molecular sieves for the amine/imine switching depends on the specific transition-metal catalysts in use. In addition, a large reaction vessel (100 ml) was used in both cases to facilitate the alcohol dehydrogenation [24,25].

Kirchner and coworkers described an interesting example that the amine/imine switching depends on the choice of transition-metals, in which the isoelectronic PNP Fe^{II} **2** and Mn^{I} **3** pincer complexes lead to the amine and imine formations, respectively (Scheme 2, B) [28]. Notably, these transformations proceed without base but require the presence of excess molecular sieves or Lewis acids to achieve the desired yields in both amine and imine formations. Closed system was proven more feasible than the open system as the latter led to the product mixture. The observed amine/imine selectivity might stem from the higher hydrogenation ability of **3** on imine under the same reaction conditions. It is worth mentioning that if the N—H linker on the ligand arm is substituted by the N—Me one, the resulting complexes became inactive in both cases.

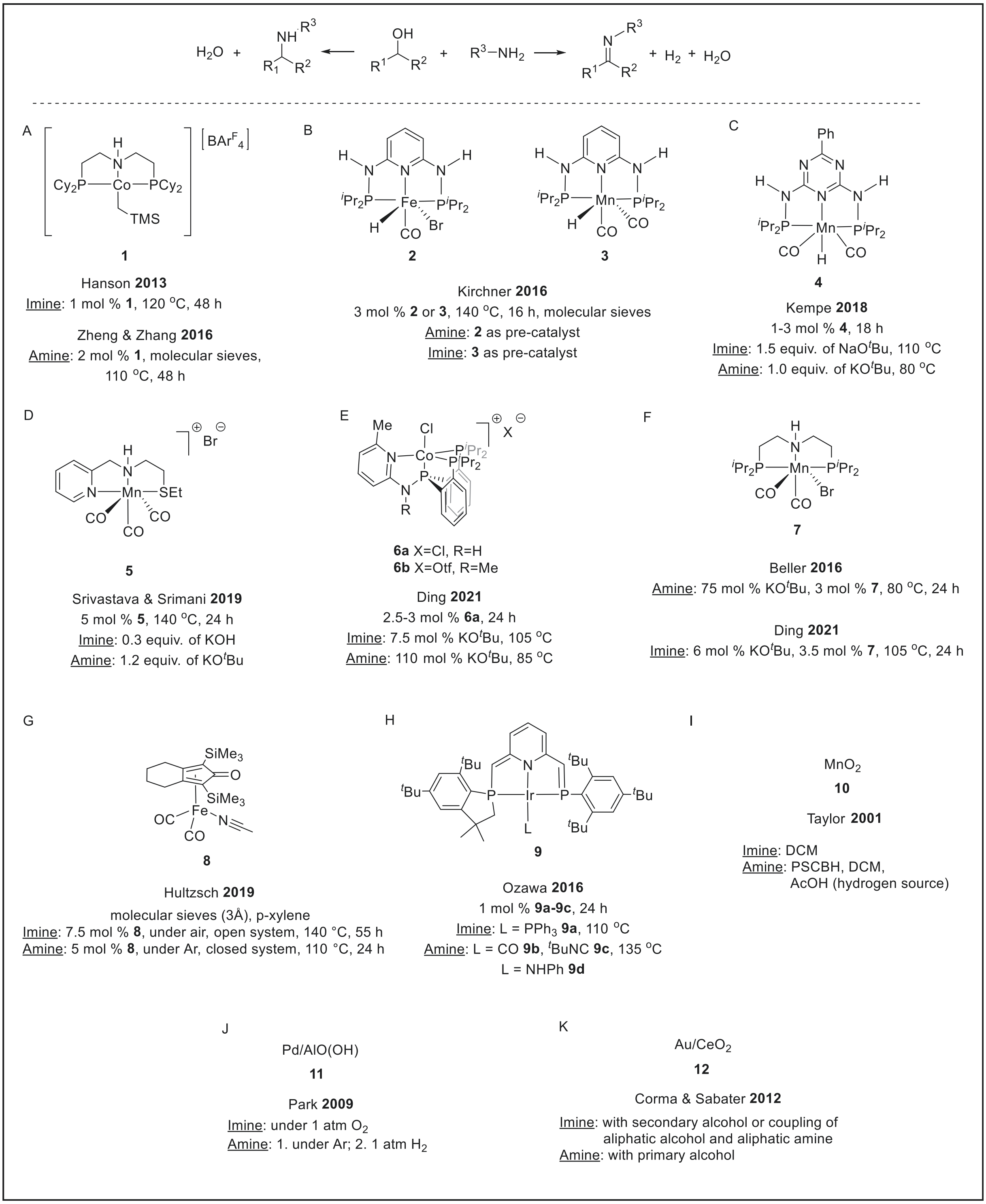
Kempe and coworkers elaborated that the switching from amine to imine can be realized by changing the base types from KO^tBu (1 equiv.) to NaO^tBu (1.5 equiv.) based on an PNP Mn pincer complex **4** (Scheme 2, C) [29]. Interestingly, it was found that the potassium or sodium manganate hydride formed by the reactions of the Mn hydride and KO^tBu or NaO^tBu is the active catalyst. Mechanistic study showed that the potassium manganate hydride is 40 times faster in the imine hydrogenation than the Sodium analogue, which sheds light on the origin of the selectivity. Closed system was used for the amine generation, and open system was chosen for the imine formation. This base-switchable method does not extend to the Co and Ir analogs supported by the same ligand [29].

Srivastava, Srimani, and coworkers later reported a similar strategy for the amine/imine switching by changing the base types mediated by a phosphine-free NNS Mn pincer complex **5** (Scheme 2, D) [30]. Notably, in contrast to the Kemp's system, 30 mol % KOH was employed for the imine formation. 1.2 Equiv. Of KO^tBu was utilized for the amine synthesis.

Very recently, our group reported on the switchable amine/imine synthesis by simply adjusting the base loadings using a Co catalyst **6a** (Scheme 2, E) [31]. We found that excess KO^tBu (1.1 equiv.) leads to amine formation, whereas catalytic amount of KO^tBu (7.5 mol %) results in imine formation. Mechanistic study showed that the distinct imine hydrogenation abilities at different base loadings may account for the amine/imine selectivity, where the imine hydrogenation is dramatically suppressed at low KO^tBu loadings. Closed and open systems were used for the formations of amine and imine, respectively. Interestingly, if the N—H linker on the ligand is replaced by the N—Me moiety **6b**, the product-switching is lost, whereas a poor imine yield was resulted, although amine was still efficiently formed.

In 2016, Beller and coworkers introduced the first Mn-catalyzed amine formation via BH (Scheme 2, F) [32]. A high KO^tBu loading (0.75 equiv.) was required. In a complementary study, we found that if the KO^tBu loading was reduced to 6 mol %, imines could be selectively formed in good yield using an open system [31]. These results indicate that our protocol of adjusting the base loadings is also amenable for Beller's Mn catalytic system **7**, although further optimization of the reaction conditions is still required.

Hultzsch and coworkers reported that the amine/imine switching can be realized simply by adjusting the reaction setups based on a nitrile ligated Knölker's complex **8** (Scheme 2, G) [33]. Amines are afforded in a closed system under argon, but imines turn out to be the major products in an open system in air. The selectivity shift is likely because under air, the Fe hydride species is



Scheme 2. Summary of the switchable amine/imine formations from alcohol amine couplings.

aerobically quenched other than hydrogenates the imine under the inert conditions. It is noteworthy that a higher temperature (140 °C) and a longer reaction time (55 h) are used in the imine forming reaction.

Ozawa and coworkers reported on an amine/imine switching case by altering the monodentate co-ligands based on an Ir complex **9** (Scheme 2, H) [34]. Although heterogeneous catalysis is not the focus of this review, this study provides great insights on how the choices of co-ligands affect the selectivity. It was shown that π-acceptor co-ligands such as CO and ᵗBuNC afford amines, while phosphine co-ligands like PPh_3 switch the products to imines. Closed and open systems were used for amine and imine synthesis, respectively. Mechanistic study revealed that the elimination of amine from a presumed intermediate Ir(NHPh) (PPEP) **9d** is dramatically promoted by the CO co-ligand compared to that using PPh_3, which likely contributes to the amine/imine switching.

Closed system was used for the amine formation and open system was applied for the synthesis of imine.

Heterogeneous catalysts such as MnO_2 **10** [35], Pd/AlO(OH) **11** [36], and Au/CeO_2 **12** [37], have been applied to the switchable formations of amines and imines as shown in Scheme 2.

2.1.2. Alcohol nitroarene couplings

Switchable access to amines and imines can also be achieved from reductive couplings of nitroarenes with alcohols (Scheme 3). In contrast to the alcohol amine couplings, excess alcohol reactants or external hydrogen source like glycerol are normally required in these reactions, generating the carbonyl compound wastes. Heterogeneous catalysts, such as CoOx@NC-800 **13** [38], Co—N—C/CNT@AC **14** [39], $RuCl_3$ **15** [40], and Ag-MCP-1 **16** [41], have been reported to mediate the amine/imine switching. Heterogeneous catalysis is beyond the scope of this review. The product control strategies are briefly summarized in Scheme 3.

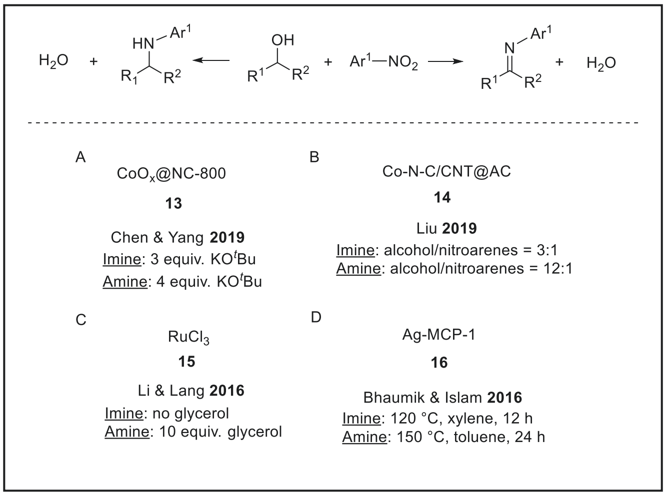
2.2. Switchable alcohol/ketone formation

2.2.1. Primary and secondary alcohols couplings

Homogeneous base-transition metal catalyzed couplings of primary and secondary alcohols have seen a rapid development recently [42–48]. However, the cases on the product-switching are rare.

Li, Lang, and coworkers established the first nickel catalyzed switchable alcohol/ketone formation by precisely controlling the reaction conditions (Scheme 4, A) [49]. It was observed that ketones are the major products at 100 °C using an open system, on the contrary, at 120 °C with a closed system, alcohols are selectively formed. The authors proposed that a higher temperature and closed system leads to higher H_2 pressure, thus the ketones can be further hydrogenated to the alcohols. Although not emphasized in the article, the base loadings could also play a role. Notably, 0.5 equiv. Of KOH was used for the ketone formation, whereas 1.5 equiv. Of KOH was utilized for the alcohol generation.

Interestingly, it was further shown that at an even lower temperature of 70 °C with an open system, the addition of ^{t}BuOH cosolvent shifts the selectivity to the α,β-unsaturated ketones [49]. The authors surmised that the low hydrogenation ability of the catalyst towards the C=C and C=O bonds, which may result from the low temperatures and the interactions between ^{t}BuOH and the active Ni catalyst, prohibits the reduction of the α,β-unsaturated ketones. A clear mechanistic understanding of the role of ^{t}BuOH is still elusive.



Scheme 3. Summary of the switchable amine/imine formations from alcohol nitroarene couplings.

Our group recently disclosed the first Co catalyzed alcohol/ketone switching synthesis by the rational control of the base loadings (Scheme 4, B) [50,51]. We found that excess (110 mol %) or catalytic amount (7.5 mol %) of KO^{t}Bu results in the formations of alcohols or ketones, respectively, which is analogous to our reported amine/imine case [31]. The different hydrogenation ability of the catalyst at different base loadings is proposed to be responsible for the product switching. Closed and open systems were utilized for the alcohol and ketone formations, respectively. It is worth mentioning that only 0.7 mol % catalyst is sufficient for the alcohol formation. Preliminary mechanistic study revealed that the transfer hydrogenations of α,β-unsaturated ketones and alkylated ketones using 1-phenylethanol as the hydrogen source can be efficiently mediated by base alone via the Meerwein-Ponndorf-Verley (MPV) process [52–54]. Thus, these reactions may not follow the BH pathway, as in the BH process it is the metal hydride species that is involved in the hydrogen transfer [2–15]. Comprehensive mechanistic exploration is still required. Interestingly, in the presence of excess base, the Co complex even hindered the ketone transfer hydrogenation, probably because the active Co species has proven to be an alcohol dehydrogenation catalyst [55], converting the alcohol products back to the ketones. Notably, using the Co complex with an N—Me linker **6b** led to the desired alcohol/ketone switching as well.

2.2.2. Primary alcohol and ketone couplings

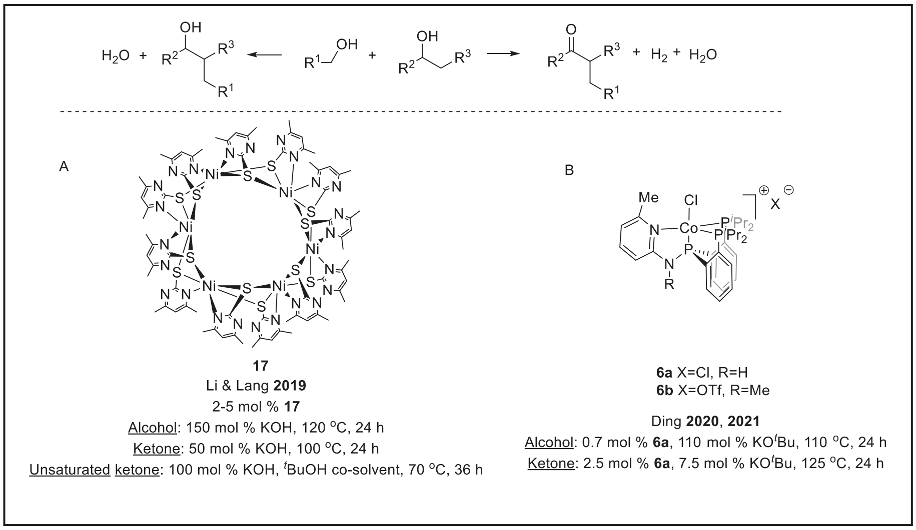
Ketones and α,β-unsaturated ketones can be selectively formed by the couplings of ketone and primary alcohol (Scheme 5). Mishra and coworkers demonstrated that the hydrotalcite supported copper catalyst (Cu-HT) led to a ketone/α,β-unsaturated ketone ratio of 60%:40% [56]. Interestingly, when Cu-HT was calcined to the Cu-containing metal oxides of MgO and Al_2O_3 (Cu-AHT), the resulting catalyst led to excellent selectivity toward the α,β-unsaturated ketone with an α,β-unsaturated ketone/ketone ratio of 95%:5% (Scheme 5, A). A case based on Pd/AlO(OH) is also known (Scheme 5, B) [57].

Switchable formations of alcohols and ketones can also be achieved by the couplings of ketone and primary alcohol (Scheme 6). To the best of our knowledge, there is only one example based on a transition-metal-free system. Xu and coworkers reported that under nitrogen atmosphere and an alcohol/ketone ratio of 3:1, alcohols are selectively formed. However, if the reaction is under air and an alcohol/ketone ratio of 1.2:1, ketones become the major products [58]. It is proposed that under air, it is likely that alcohols are oxidized into ketones under basic conditions. The reduced loading of the alcohol substrates, which also serve as the hydrogen source, shall contribute to the selective formations of ketones as well.

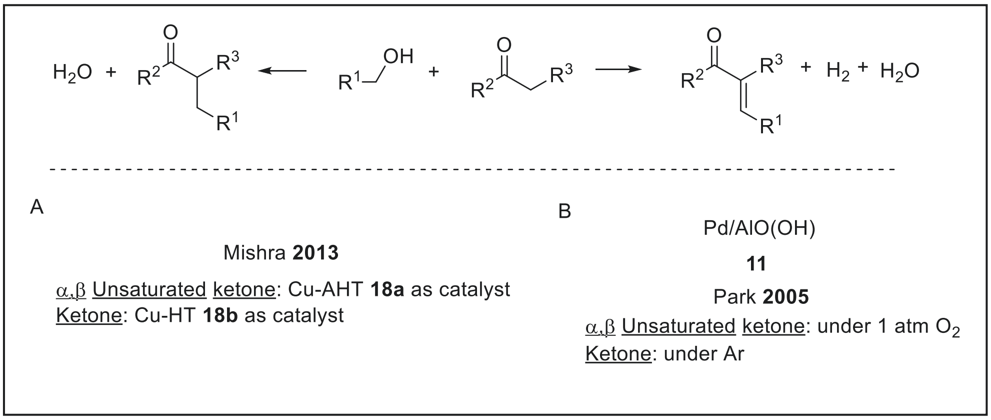
2.3. Switchable nitrile/acrylonitrile formation by primary alcohol nitrile couplings

Reports on the base transition-metal catalyzed α-alkylation and α-olefination of nitriles with alcohols are still limited in the literature [59–66].

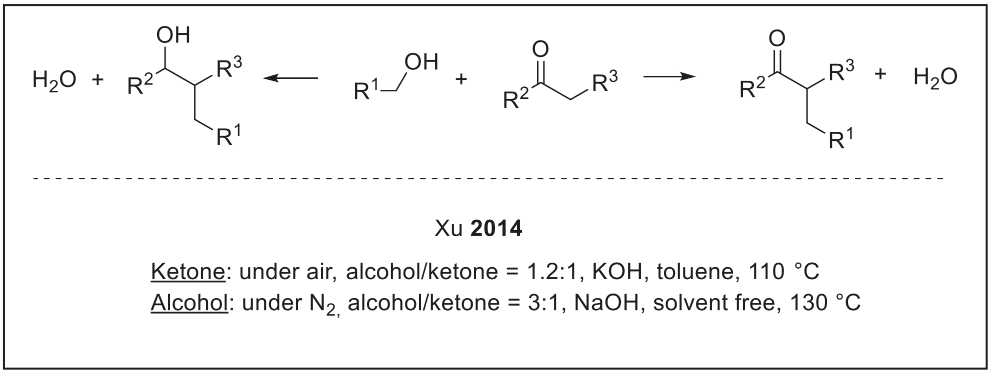
Very recently, our group reported the first base transition-metal Co catalyzed switchable nitrile/acrylonitrile synthesis by simply adjusting the base loadings (Scheme 7) [67,68]. Analogous to our reported cases on the switchable amine/imine and alcohol/ketone formation, 20 mol % KOH and 3.5 mol % $KHBEt_3$ leads to the nitrile formation, while acrylonitriles are selectively formed in the presence of 3 mol % NaO^{t}Bu. It is noteworthy that a short reaction time of 6 h is sufficient for the acrylonitrile formations. A sealed small



Scheme 4. Summary of the switchable alcohol/ketone formations from primary and secondary alcohols.

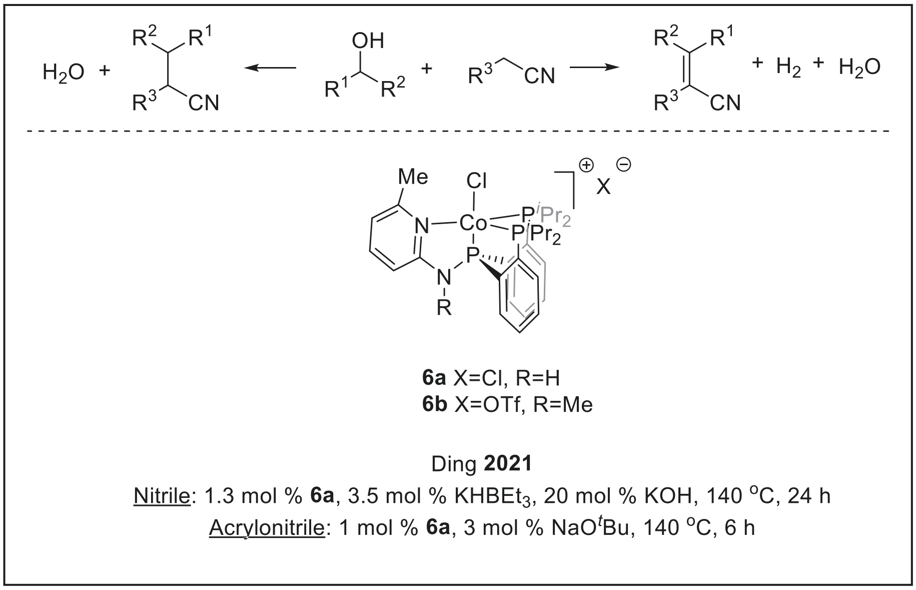


Scheme 5. Summary of the switchable α,β-unsaturated ketone/ketone formations from primary alcohol ketone couplings.



Scheme 6. Summary of the switchable ketone/alcohol formations from primary alcohol ketone couplings.

reaction vessel was used for the nitrile formation. The same reaction vessel with an argon balloon on top was set up for the acrylonitrile generation. Preliminary mechanistic study revealed that the lack of hydrogenation ability of the active Co catalyst towards acrylonitriles at low base loadings is crucial for the product-switching from nitriles to acrylonitriles. Notably, in the selective nitrile formation, the hydrogenation of the acrylonitrile intermediates likely follows the base mediated MPV-type pathway, which deserves further investigations. Interestingly, the Co complex bearing the N—Me linker **6b** also promoted the product-switching.



6a X=Cl, R=H
6b X=OTf, R=Me

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Nitrile: 1.3 mol % **6a**, 3.5 mol % $KHBEt_3$, 20 mol % KOH, 140 °C, 24 h
Acrylonitrile: 1 mol % **6a**, 3 mol % NaO^{t}Bu, 140 °C, 6 h

Scheme 7. Summary of the switchable nitrile/acrylonitrile formations from primary alcohol nitrile couplings.

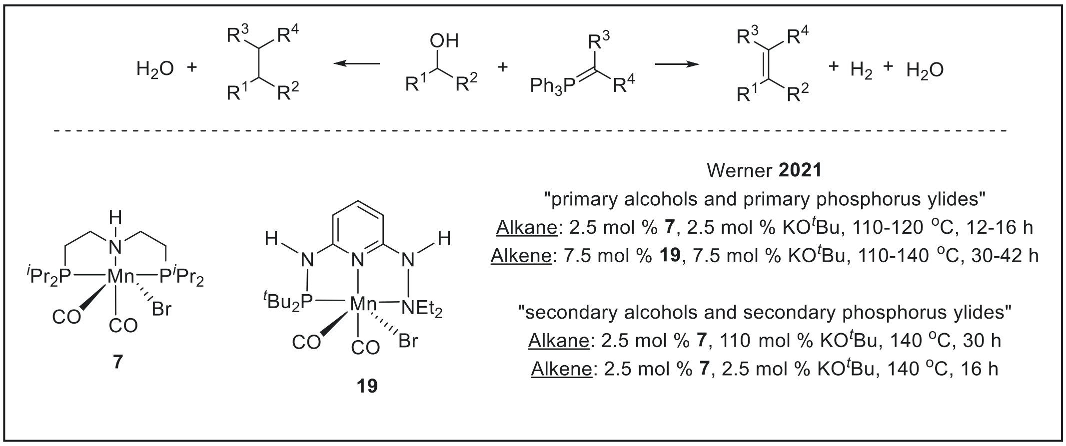
2.4. Switchable alkane/alkene formation by alcohol phosphorus ylide couplings

Reports on the base transition-metal catalyzed couplings of alcohols and phosphorus ylides are extremely rare. Alonos, Yus, and coworkers disclosed a heterogeneous Ni nanoparticle catalyzed formation of alkenes via ADC [69].

Werner and coworkers very recently described the first homogeneous base transition-metal Mn catalyzed switchable alkane/alkene formations by couplings of primary alcohols and primary phosphorus ylides (Scheme 8) [70]. Interestingly, it was found that the PNP-Mn complex **7** is more suitable for generation of the BH products, while a PNN-Mn complex **19** leads to the ADC products, albeit higher catalyst and base loadings with longer reaction time are required in the latter case. The ylides are limited to the ones stabilized by the electron withdrawing groups such as ester, amide, ketone, etc. Closed system was used in both transformations. Mechanistic studies showed that **19** exhibited much poorer hydrogenation ability towards alkenes than **7**, suggesting the critical role of the ligand structure on the selectivity. Moreover, the product-switching can be achieved with secondary alcohols and secondary ylides mediated by **7**. Excess base (1.1 equiv.) was employed for the alkane formations, and catalytic amount of base (2.5 mol %) was utilized for the alkene generations.

3. Summary and outlook

The development of novel BH and ADC methodologies using base transition-metal catalysts has become a highly active research area due to the significant advantages in terms of sustainability [2–11]. Studies on the methodology to achieve switchable synthesis of the BH and ADC products will further enrich this chemistry, potentially opening a new direction of research endeavor. Currently, this field is still underdeveloped. As described in this mini-review, the state-of-the-art strategies involve the rational control of the significant factors such as additives [24,25], metal types [28], base types [29,30,58,67,68], base loadings [30–32,38,49–51,67,68,70], ligands [34,70], solvents [49], temperatures [29,31–34,41,49–51,58], hydrogen sources for the BH products [35,39,40,58], and experiment set-ups [24,25,28–36,40,49–51,57,58,67,68]. These methods are summarized in Table 1. It is noted that in-depth mechanistic understanding



Werner **2021**
"primary alcohols and primary phosphorus ylides"
Alkane: 2.5 mol % **7**, 2.5 mol % KO^{t}Bu, 110-120 °C, 12-16 h
Alkene: 7.5 mol % **19**, 7.5 mol % KO^{t}Bu, 110-140 °C, 30-42 h

"secondary alcohols and secondary phosphorus ylides"
Alkane: 2.5 mol % **7**, 110 mol % KO^{t}Bu, 140 °C, 30 h
Alkene: 2.5 mol % **7**, 2.5 mol % KO^{t}Bu, 140 °C, 16 h

Scheme 8. Summary of the switchable alkane/alkene formations from alcohol phosphorus ylide couplings.

Table 1
Summary of strategies for the switching of ADC and BH products.

Reactions	ADC Products	ADC Strategies	BH Products	BH Strategies
Alcohol Amine Couplings	Imine	PNP-Mn [28]; lower base loadings [30–32]; NaO^{t}Bu [29] or KOH [30]; higher temperature [29,31,33]; PPh$_3$ co-ligand [34]; under air [33], under O$_2$ [36]; open system [29,31,33,34]	Amine	Molecular sieves [25]; PNP-Fe [28]; higher base loadings [30–32]; KO^{t}Bu [29,30]; lower temperature [29,32,34]; CO or ^{t}BuNC co-ligand [34]; under Ar [33,36]; extra hydrogen source required, e.g., AcOH [35] and H$_2$ [36]; closed system [29,31–34]
Alcohol Nitroarene Couplings	Imine	Lower base loadings [38]; lower alcohol/nitroarene ratio [39]; lower temperature [41]	Amine	Higher base loadings [38]; higher alcohol/nitroarene ratio [39]; higher temperature [41]; extra hydrogen source required, e.g., glycerol [40]
Primary and Secondary Alcohols Couplings	Ketone α,β-Unsaturated Ketone	Lower base loadings [49,50]; higher temperature [50] ^{t}BuOH co-solvent, lower temperature [49]	Alcohol	Higher base loadings [49,51]; higher temperature [49]; lower temperature [51]
Primary Alcohol and Ketone Couplings	α,β-Unsaturated Ketone	Cu-AHT [56]; under O$_2$ [57]	Ketone	Cu-HT [56]; under Ar [57]
	Ketone	Under air, lower alcohol/ketone ratio, KOH, lower temperature [58]	Alcohol	Under N$_2$, higher alcohol/ketone ratio, NaOH, higher temperature [58]
Primary Alcohol Nitrile Couplings	Acrylonitrile	Lower base loadings [68]	Nitrile	Higher base loadings [67]
Alcohol Phosphorus Ylide Couplings	Alkene	With primary alcohol: PNN-Mn [70]; With secondary alcohol: PNP-Mn, lower base loadings [70]	Alkane	With primary alcohol: PNP-Mn [70]; With secondary alcohol: PNP-Mn, higher base loadings [70]

on the product-switching is still lacking in most cases. For example, molecular sieves and temperature could lead to completely opposite results, depending on the catalytic systems in use. Moreover, harsh reaction conditions such as high temperatures and high base loadings are still mandatory in many of these reported cases. In addition, there is no report on the switchable constructions of the saturated and unsaturated heterocycles. Future studies in these directions could be fruitful.

We expect that this mini-review will provide readers insights into precise control over the chemical processes for switchable synthesis of valuable products by designing novel multifunctional catalytic systems based on earth-abundant transition-metals, leading to fascinating new findings.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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