

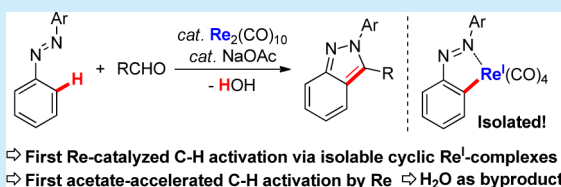
Rhenium-Catalyzed [4 + 1] Annulation of Azobenzenes and Aldehydes via Isolable Cyclic Rhenium(I) Complexes

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S Supporting Information

ABSTRACT: The first Re-catalyzed [4 + 1] annulation of azobenzenes with aldehydes was developed to furnish 2*H*-indazoles via isolable and characterized cyclic Re^I-complexes. For the first time, the acetate-acceleration effect is showcased in Re-catalyzed C–H activation reactions. Remarkably, mechanistic studies revealed an irreversible aldehyde-insertion step, which is in sharp contrast to those of previous Rh- and Co-systems.

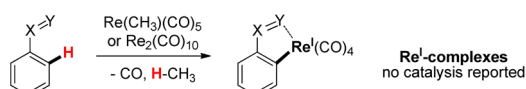
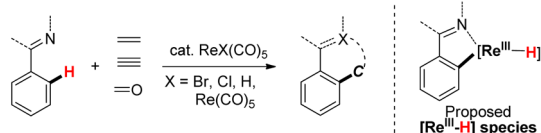
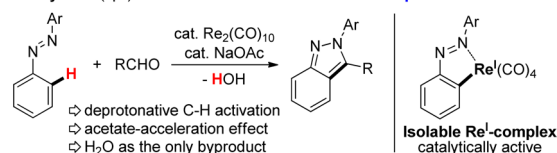


Over the past three decades, transition-metal-catalyzed inert C–H bond activation has received extensive attention due to its intrinsic atom- and step-economic characteristics, which avoids the required prefunctionalization of substrates for traditional organic synthesis.¹ In comparison with widely used late transition metals such as Pd, Rh, Ir, Ru, and so on, the activation of inert C–H bonds promoted by rhenium, an early transition metal, has been considerably less studied despite their unique properties and promising reactivities.^{2–4} Since 1970, Bruce, Stone, Kaesz, and others had reported a few stoichiometric cyclorhenation reactions of arenes (Scheme 1a).⁵ Although thus-formed cyclic Re^I-complexes could be isolated and structurally characterized, there has been no report on the catalytic C–H transformations involving these isolable cyclic Re^I-complexes until now. Since 2005, Kuninobu and Takai et al. have disclosed a series of Re-catalyzed C(sp²)–H functionalization reactions, which were

proposed to occur through [Re^{III}–H] species, originating from the oxidative addition of C–H bonds to the Re^I-catalyst (Scheme 1b).⁴ However, this type of [Re^{III}–H] species has never been isolated and/or structurally characterized so far. Thus, a gap still remains between the stoichiometric cyclo-rhenation reactions and the Re-catalyzed C(sp²)–H functionalization reactions from a mechanistic point of view.

Herein, we describe the stoichiometric reaction of an isolable cyclic Re^I-complex of azobenzene with benzaldehyde to give 2*H*-indazole. Then, with the essential aid of a catalytic amount of sodium acetate, the Re-catalyzed [4 + 1] annulation of azobenzenes with aldehydes to furnish 2*H*-indazoles with H₂O as the only byproduct was successfully developed (Scheme 1c).⁶ Importantly, the isolable cyclic Re^I-complex demonstrated comparable catalytic reactivity in this protocol, which bridged the mechanistic gap between stoichiometric cyclorhenation reactions and Re-catalyzed C(sp²)–H functionalization reactions. This reaction also represents the first example of Re-catalyzed C–H transformations of azobenzenes.⁷ Notably, the acetate-acceleration effect disclosed herein is unprecedented for Re-catalyzed C–H activation reactions.⁸

Initially, we tried to synthesize Re^I-complex **A** from azobenzene **1a** and commercially available Re₂(CO)₁₀ (Scheme 2a).^{5b} It turned out that the reaction was rather sluggish and gave the expected Re^I-complex **A** in 20% NMR yield and 7% isolated yield after sublimation. Then, the stoichiometric reaction of Re^I-complex **A** with benzaldehyde **2a** was examined and the aldehyde-insertion/cyclization product, 2*H*-indazole **3aa**, was obtained in 67% isolated yield (Scheme 2b). Encouraged by these results, we further explored the catalytic version of this two-step reaction (Table 1).⁹ It occurred to us that only a very small amount of **3aa** was observed with 5 mol % of Re₂(CO)₁₀ as the catalyst (entry 1). Then, we intended to examine a series of bases as catalytic promoters for this

Scheme 1. Re-Mediated and -Catalyzed C(sp²)–H Bond Transformationsa) Stoichiometric cyclorhenation reactions giving Re^I-complexes: previous workb) Re-catalyzed C(sp²)–H transformations via Re^{III}–H species: previous workc) Re-catalyzed C(sp²)–H transformation via isolable Re^I-complex: this work

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Scheme 2. Synthesis of Re^I-Complex A and Its Stoichiometric Reaction with Benzaldehyde

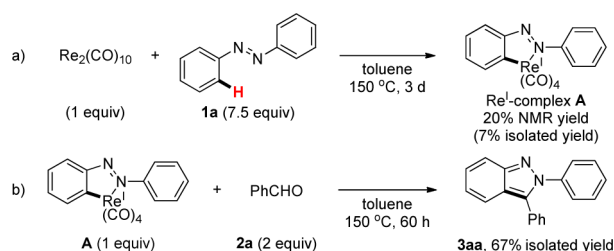


Table 1. Screening of Reaction Parameters^a

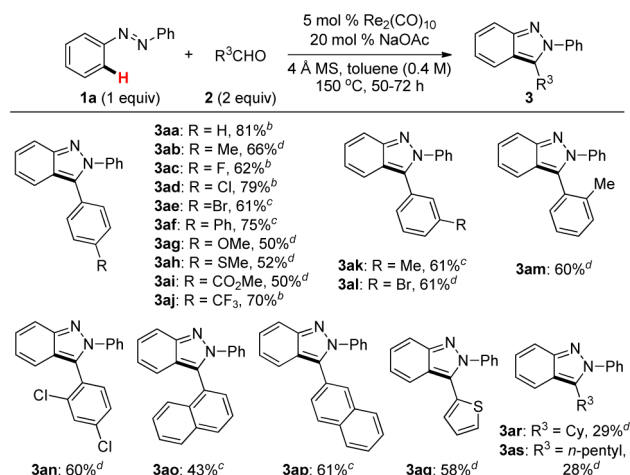
entry	cat. (mol %)	base (20 mol %)	solvent	yield (%) ^b
1	$\text{Re}_2(\text{CO})_{10}$ (5)	— ^c	toluene	5
2	$\text{Re}_2(\text{CO})_{10}$ (5)	DBU	toluene	0
3	$\text{Re}_2(\text{CO})_{10}$ (5)	PhNH ₂	toluene	25
4	$\text{Re}_2(\text{CO})_{10}$ (5)	Cy ₂ NH	toluene	41
5	$\text{Re}_2(\text{CO})_{10}$ (5)	KO ^t Bu	toluene	27
6	$\text{Re}_2(\text{CO})_{10}$ (5)	Na ₂ CO ₃	toluene	48
7	$\text{Re}_2(\text{CO})_{10}$ (5)	NaOAc	toluene	59
8 ^d	$\text{Re}_2(\text{CO})_{10}$ (5)	NaOAc	toluene	66
9 ^d	$\text{Re}_2(\text{CO})_{10}$ (5)	NaOAc	DMF	0
10 ^d	$\text{Re}_2(\text{CO})_{10}$ (5)	NaOAc	DCE	26
11 ^d	$\text{Re}_2(\text{CO})_{10}$ (5)	NaOAc	1,4-dioxane	60
12 ^e	$\text{Re}_2(\text{CO})_{10}$ (5)	NaOAc	toluene	73
13 ^e	$\text{Re}(\text{CO})_5\text{Br}$ (5)	NaOAc	toluene	23
14 ^e	$\text{Mn}_2(\text{CO})_{10}$ (5)	NaOAc	toluene	0
15 ^e	$\text{Fe}_3(\text{CO})_9$ (5)	NaOAc	toluene	0
16 ^e	$\text{Pd}(\text{OAc})_2$ (5)	NaOAc	toluene	0
17 ^e	$\text{Cu}(\text{OAc})_2$ (5)	NaOAc	toluene	0
18 ^{e,f}	$\text{Re}_2(\text{CO})_{10}$ (5)	NaOAc	toluene	85 (81) ^g
19 ^{e,f}	$\text{Re}_2(\text{CO})_{10}$ (2.5)	NaOAc	toluene	56

^aReaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), cat. (5 mol %), base (20 mol %), solvent (0.1 M), 150 °C, 50 h. ^bDetermined by ¹H NMR. ^cNo base. ^d0.2 M. ^e0.4 M. ^f4 Å MS (100% cat. weight). ^gIsolated yield on 0.5 mmol scale.

reaction. To our delight, Cy₂NH enabled the product formation dramatically and gave the best result among the amines tested (entries 2–4).⁹ Surprisingly, the cheap inorganic base, NaOAc, showed even better performance (entries 5–7). Toluene proved to be the best choice of solvent (entries 8–11). Other rhenium-, manganese-, and iron-carbonyls as well as Pd- and Cu-catalysts displayed only inferior reactivity, if any at all (entries 12–17). Finally, **3aa** was obtained in 81% isolated yield with addition of molecular sieves as a H₂O scavenger (entry 18). Of note, the use of 2.5 mol % of $\text{Re}_2(\text{CO})_{10}$ resulted in decreased yield of **3aa** (entry 19).

With the optimized conditions in hand, we first investigated the scope of aldehydes (Scheme 3). Both electron-donating and -withdrawing groups on aromatic aldehydes were well tolerated affording the expected products in good yields (**3aa–j**). Importantly, varied functional groups such as F, Cl, Br, MeS, CO₂Me, and CF₃ were all compatible to the reaction conditions, which allowed for further synthetic elaborations thereby broadening the diversity of the products. *Meta*- and *ortho*-substituents on the benzene moiety showed no obvious influence on the reaction outcome (**3ak–n**). Naphthaldehydes

Scheme 3. Scope of Aldehydes^a

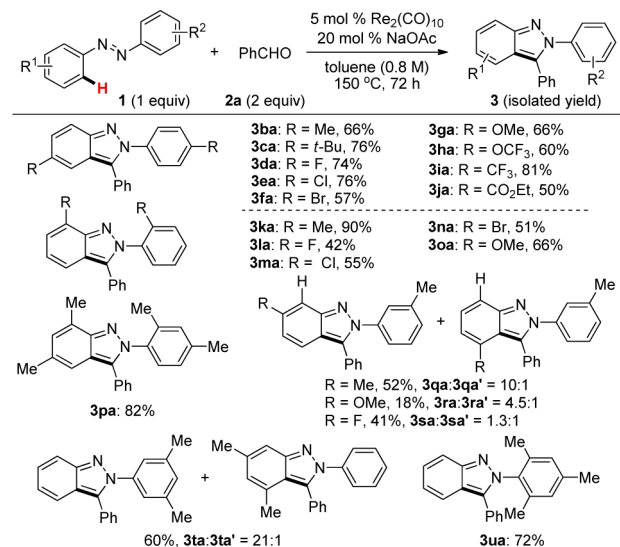


^aIsolated yields of product **3** are shown. ^b50 h. ^c60 h. ^d72 h.

were also suitable substrates giving the corresponding products (**3ao–p**) in synthetically useful yields. Thiophene-2-carbaldehyde reacted smoothly with **1a** giving product **3aq**. Aliphatic aldehydes showed lower reactivity (**3ar–s**) than aromatic aldehydes, which echoed the results of Rh- and Co-systems.⁶

Next, we examined the scope of azobenzenes (Scheme 4). Under the slightly modified conditions, a wide range of *para*-

Scheme 4. Scope of Azobenzenes



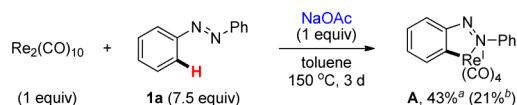
substituted azobenzenes was well compatible in this reaction (**3ba–ja**), again tolerating various functional groups. Notably, different substituents could be regiospecifically placed at the 7-position of 2*H*-indazoles (**3ka–oa**) by using *ortho*-substituted substrates, which are often problematic for Re-catalyzed C–H bond transformations.^{4a,b,d,e,n} Disubstituted azobenzene furnished also the expected product (**3pa**) in good yield. High regioselectivity was observed when *meta*-methyl or unsymmetrical azobenzenes were applied in the reaction favoring the formation of sterically more accessible C–H bond functionalized products (**3qa**, **3ta**). The selectivity decreased when *meta*-methoxy and -fluoro azobenzenes were used presumably due to the secondary coordination effect of MeO and F groups

in the C–H activation step (**3a**–**sa**). In addition, the increased bulkiness of *N*-substituent of *2H*-indazole (**3aa**) had no apparent effect on the reaction yield.

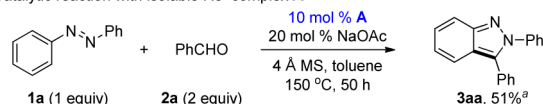
To validate the acetate-acceleration effect in the C–H activation step, the stoichiometric reaction of $\text{Re}_2(\text{CO})_{10}$ with **1a** in the presence of NaOAc was carried out. Gratifyingly, Re^{I} -complex **A** was obtained in clearly improved yield (Scheme 5a)

Scheme 5. Mechanistic Experiments

a) Acetate-acceleration effect in C–H bond activation



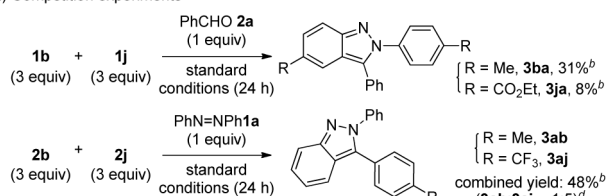
b) Catalytic reaction with isolable Re^{I} -complex **A**



c) Probe the reversibility of aldehyde-insertion step



d) Competition experiments



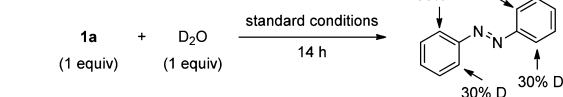
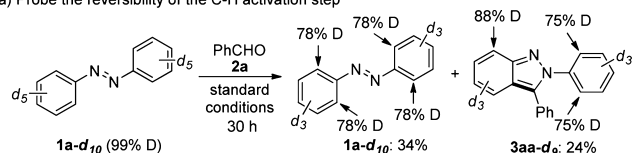
^a¹H NMR yield. ^b Isolated yield. ^c Determined by GC-MS. ^d Determined by ¹H NMR

vs Scheme 2a). Importantly, Re^{I} -complex **A** did catalyze the [4 + 1] annulation of **1a** and **2a** giving *2H*-indazole **3aa** in comparable yield (Scheme 5b), which supported its involvement in the catalytic reaction. Furthermore, in order to check the reversibility of the aldehyde-insertion step, the reaction of alcohol **4aa** with 4-methylbenzaldehyde **2b** was examined (Scheme 5c). It turned out that no crossover product **3ab** was detected with **3aa** as the sole product. This result was in sharp contrast to previous Rh- and Co-promoted aldehyde-insertion steps, which are reversible and thermodynamically unfavored.^{10,11} In addition, the competition experiments with substrates bearing varied electronic properties were conducted and the formation of products derived from electron-rich azobenzene **1b** and electron-deficient benzaldehyde **2j** was favored (Scheme 5d).

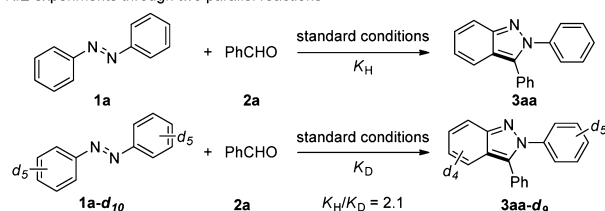
To further probe the reversibility of the C–H activation step, fully deuterated azobenzene **1a-d**₁₀ was subjected to the reaction conditions and deuterium loss was observed at the *ortho* positions of both substrate **1a-d**₁₀ and product **3aa-d**₉ (Scheme 6a). This result indicated that a reversible deprotonative C–H bond activation step might exist in the reaction. To confirm this hypothesis, azobenzene **1a** was treated with D₂O under the similar reaction conditions. As expected, partial D-incorporation was detected at the *ortho* positions of **1a**. Moreover, kinetic isotope effect (KIE) experiments were conducted through two parallel reactions and the KIE value was determined to be 2.1 (Scheme 6b),⁹

Scheme 6. Deuterium-Labeling Experiments

a) Probe the reversibility of the C–H activation step



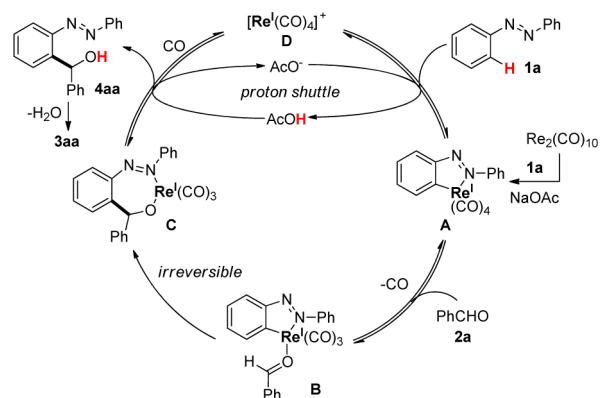
b) KIE experiments through two parallel reactions



which suggested that the C–H activation step might be involved in the rate-determining step.

A plausible reaction mechanism is proposed in Scheme 7 based on the above experiments. The reaction starts with

Scheme 7. A Plausible Reaction Mechanism



cyclorhenation of azobenzene **1a** to give the cyclic Re^{I} -complex **A**. Replacement of one CO ligand by aldehyde **2a** provides intermediate **B**. An irreversible aldehyde insertion to the Re –C_{aryl} bond of **B** forms the seven-membered rhenacycle **C**. Protonation of **C** liberates alcohol **4aa** and leads to the rhenium species **D**, which promotes reversible acetate-accelerated C–H activation of **1a** to regenerate Re^{I} -complex **A**. In total, acetate acts as a catalytic proton shuttle in the reaction. In the end, an intramolecular nucleophilic substitution reaction of **4aa** followed by rearomatization affords the final product **3aa**.⁶

In summary, a Re -catalyzed [4 + 1] annulation of azobenzenes with aldehydes has been achieved to provide a streamline access to *2H*-indazole with H₂O as the only byproduct. It represents the first example demonstrating that isolable and characterized cyclic Re^{I} -complexes are involved in Re -catalyzed C–H transformations even though they were synthesized by cyclorhenation reactions as early as in 1970.^{5b} Mechanistically, the C–H activation step was proven to be a reversible redox-neutral deprotonation process, which provides an alternative pathway to the generally proposed mechanism through oxidative addition of C–H bonds to the Re^{I} -catalyst

giving [Re^{III}–H] species.⁴ Also, the observed acetate-acceleration effect in this protocol is unprecedented for Re-catalyzed C–H activation reactions. Further mechanistic studies revealed an irreversible aldehyde-insertion step, which is in sharp contrast to those of Rh- and Co-systems. Collectively, these results are believed to find more synthetic applications in diverse Re-catalyzed C–H functionalization reactions.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental details, characterization data, and NMR spectra for all new compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b00938.

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Notes

The authors declare no competing financial interest.

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- (11) For Rh-catalyzed reversible aldehyde insertion to C–H bonds, see: (a) Chen, K.; Li, H.; Lei, Z.-Q.; Li, Y.; Ye, W.-H.; Zhang, L.-S.; Sun, J.; Shi, Z.-J. *Angew. Chem., Int. Ed.* **2012**, *51*, 9851. (b) Zhang, X.-S.; Li, Y.; Li, H.; Chen, K.; Lei, Z.-Q.; Shi, Z.-J. *Chem.—Eur. J.* **2012**, *18*, 16214. (c) Li, H.; Li, Y.; Zhang, X.-S.; Chen, K.; Wang, X.; Shi, Z.-J. *J. Am. Chem. Soc.* **2011**, *133*, 15244. For Co-catalyzed reversible aldehyde insertion to C–H bonds, see ref 6b.