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

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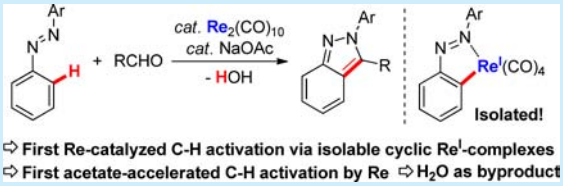
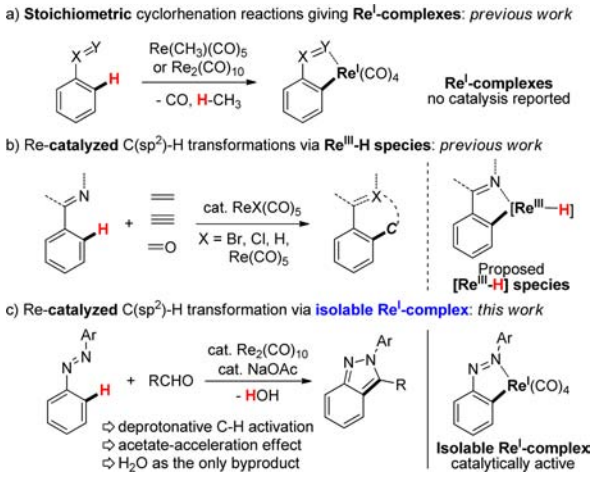
Supporting Information

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(sp^2)−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 cyclorhenation reactions and the Re-catalyzed C(sp^2)−H functionalization reactions from a mechanistic point of view.

Scheme 1. Re-Mediated and -Catalyzed C(sp^2)−H Bond Transformations



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 H_2O 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(sp^2)−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 $Re_2(CO)_{10}$ (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 $Re_2(CO)_{10}$ as the catalyst (entry 1). Then, we intended to examine a series of bases as catalytic promoters for this

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

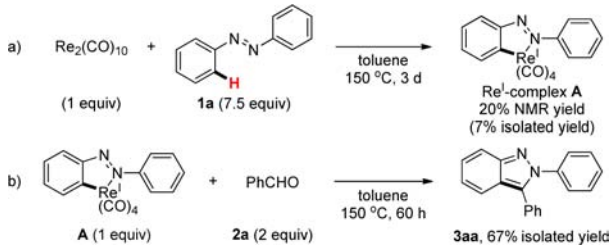
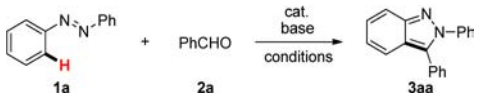


Table 1. Screening of Reaction Parameters[a]



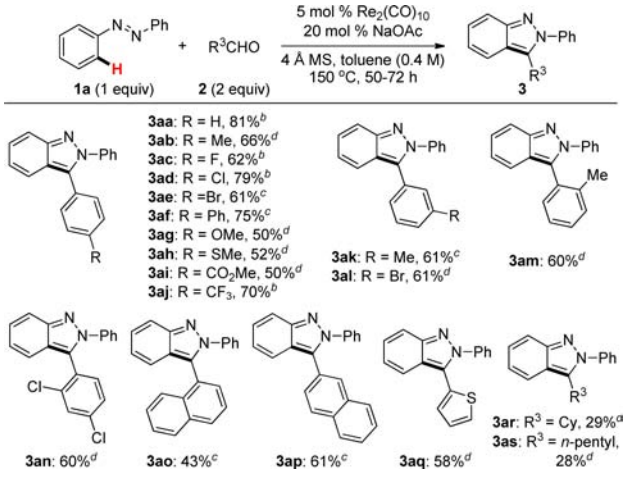
entry	cat. (mol %)	base (20 mol %)	solvent	yield (%)[b]
1	$Re_2(CO)_{10}$ (5)	–[c]	toluene	5
2	$Re_2(CO)_{10}$ (5)	DBU	toluene	0
3	$Re_2(CO)_{10}$ (5)	$PhNH_2$	toluene	25
4	$Re_2(CO)_{10}$ (5)	Cy_2NH	toluene	41
5	$Re_2(CO)_{10}$ (5)	KO^{t}Bu	toluene	27
6	$Re_2(CO)_{10}$ (5)	Na_2CO_3	toluene	48
7	$Re_2(CO)_{10}$ (5)	NaOAc	toluene	59
8[d]	$Re_2(CO)_{10}$ (5)	NaOAc	toluene	66
9[d]	$Re_2(CO)_{10}$ (5)	NaOAc	DMF	0
10[d]	$Re_2(CO)_{10}$ (5)	NaOAc	DCE	26
11[d]	$Re_2(CO)_{10}$ (5)	NaOAc	1,4-dioxane	60
12[e]	$Re_2(CO)_{10}$ (5)	NaOAc	toluene	73
13[e]	$Re(CO)_5Br$ (5)	NaOAc	toluene	23
14[e]	$Mn_2(CO)_{10}$ (5)	NaOAc	toluene	0
15[e]	$Fe_3(CO)_9$ (5)	NaOAc	toluene	0
16[e]	$Pd(OAc)_2$ (5)	NaOAc	toluene	0
17[e]	$Cu(OAc)_2$ (5)	NaOAc	toluene	0
18[e,f]	**$Re_2(CO)_{10}$ (5)**	**NaOAc**	**toluene**	**85 (81)[g]**
19[e,f]	$Re_2(CO)_{10}$ (2.5)	NaOAc	toluene	56

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), cat. (5 mol %), base (20 mol %), solvent (0.1 M), 150 °C, 50 h. [b]Determined by ^{1}H NMR. [c]No base. [d]0.2 M. [e]0.4 M. [f]4 Å MS (100% cat. weight). [g]Isolated yield on 0.5 mmol scale.

reaction. To our delight, Cy_2NH 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 H_2O scavenger (entry 18). Of note, the use of 2.5 mol % of $Re_2(CO)_{10}$ 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, CO_2Me, and CF_3 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]

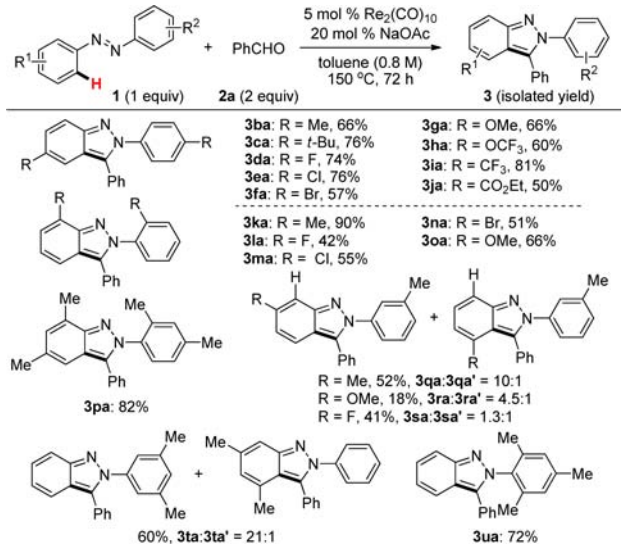


[a]Isolated yields of product **3** are shown. [b]50 h. [c]60 h. [d]72 h.

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

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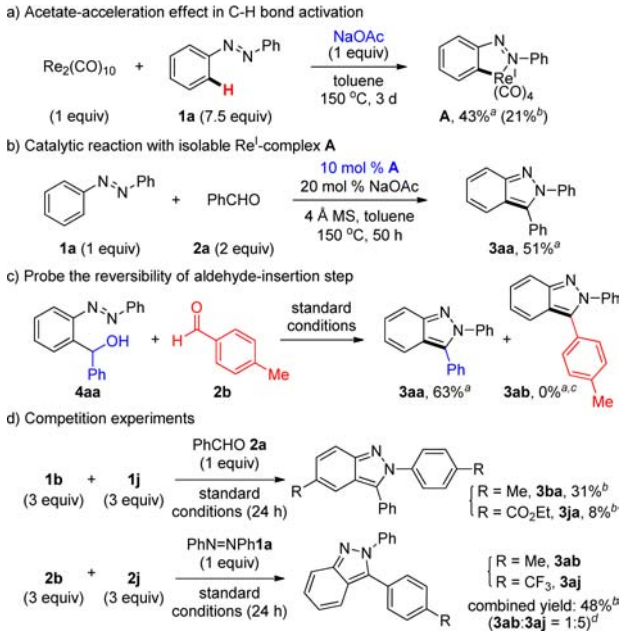
in the C−H activation step (**3ra**−**sa**). In addition, the increased bulkiness of *N*-substituent of *2H*-indazole (**3ua**) had no apparent effect on the reaction yield.

To validate the acetate-acceleration effect in the C−H activation step, the stoichiometric reaction of $Re_2(CO)_{10}$ with **1a** in the presence of NaOAc was carried out. Gratifyingly, Re^I-complex **A** was obtained in clearly improved yield (Scheme 5a 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).

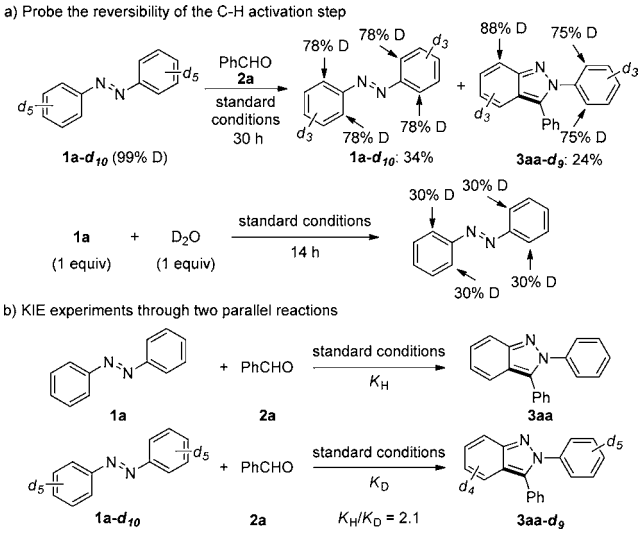
Scheme 5. Mechanistic Experiments



[a]^{1}H NMR yield. [b]Isolated yield. [c]Determined by GC-MS. [d]Determined by ^{1}H NMR

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 D_2O 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]

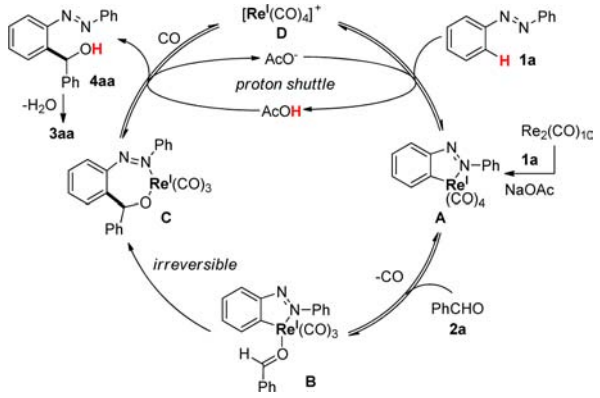
Scheme 6. Deuterium-Labeling Experiments



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 H_2O 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

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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.

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