Synthetic Methods

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Iridium-Catalyzed Oxidant-Free Dehydrogenative C–H Bond Functionalization: Selective Preparation of N-Arylpiperidines through Tandem Hydrogen Transfers**

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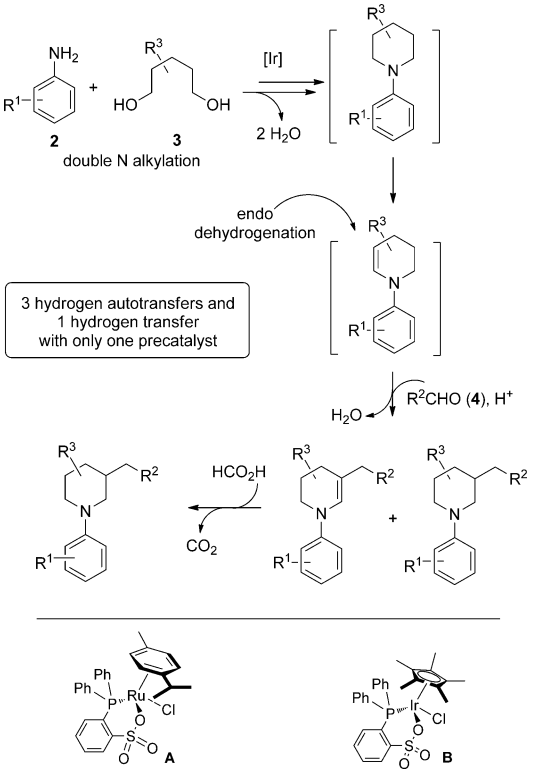
In addition to creating efficient and selective methodologies, the rise of green chemistry has led organic chemists and chemical industry to take into account the impact of these processes on the environment. Among the different eco-friendly approaches, homogeneous metal-catalyzed hydrogen autotransfers aimed at developing benign and atom-efficient protocols for the construction of carbon–heteroatom or carbon–carbon bonds have attracted considerable interest.[1–3] In these reactions, the transient formation of unsaturated carbonyl or imine intermediates, arising from the dehydrogenation of alcohols or amines acting as alkylating reagents, has been successfully used for the preparation of α-alkylated carbonyl derivatives[4] and amines[5,6] accompanied by the formation of either water or valuable ammonia[7] as the only side product. Owing to the potential of these transformations, recent developments have focused on the preparation of well-defined ruthenium and iridium complexes to allow more selective and milder reaction conditions,[8] water soluble or reusable catalysts, and continuous flow approaches.[9] In addition, the appealing amination from ammonia to afford alkylated amines has been reported by several groups.[10] However, to date no tandem methodologies based on hydrogen autotransfer involving three different partners have been reported.[11]

Recently, we achieved the unprecedented oxidant-free dehydrogenation of cyclic N-benzyl and N-alkylamines using a ruthenium(II)–arene catalyst (**A**; Scheme 1) featuring a phosphinesulfonate chelate.[12–14] This reactivity involves hydrogen autotransfers and was successfully applied to the preparation of various functionalized cyclic amines, thus taking advantage of the ability of the in situ generated ruthenium hydride species, resulting from the dehydrogenation of amines, to reduce the iminium intermediates formed upon condensation with aldehydes. Herein, we report on the preparation and catalytic application in hydrogen-transfer reactions of a new iridium catalyst which promotes dehydrogenative oxidation of alcohols into aldehydes or ketones, and of cyclic amines into enamines, and also reduces unsaturated intermediates. In particular, an efficient atom-economical and ecofriendly tandem[15] procedure involving multiple hydrogen-transfer processes was developed from three easily accessible components, namely the anilines **2**, diols **3**, and aldehydes **4** to produce C3-functionalized N-arylpiperidines (Scheme 1).[16]



Scheme 1. Key steps of the tandem hydrogen-transfer processes.

Thus, aniline (**2a**) was first reacted with pentan-1,5-diol (**3a**) without any bases, in the presence of a catalyst at 150 °C

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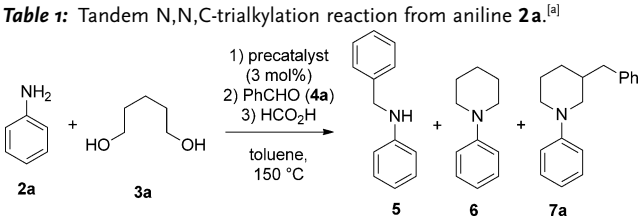
Table 1: Tandem N,N,C-trialkylation reaction from aniline **2a**.[a]



2a 3a 5 6 7a

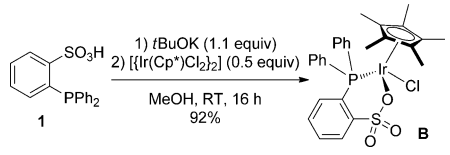
Entry	Catalyst	Conc. [M][b]	2a/3a/4a[c]	5/6/7a	Yield 7a [%][d]
1	[{Ru(*p*-cymene)Cl_2}$_2$]	0.6	1.1:1:1.2	1:0:0	n.d.
2	**A**	0.6	1.1:1:1.2	7:83:10	5
3	[{Ir(Cp*)Cl_2}$_2$]	0.6	1.1:1:1.2	82:13:5	1
4	**B**	0.9	1.1:1:1	3:45:52	42
5	**B**	0.4	1.1:1:1	4:33:63	50
6	**B**	0.6	1:1:1.2	1:22:77	50
7	**B**	0.4	1.2:1.1:1	3:27:70	58
8[e]	**B**	0.4	1:1:1.1	2:10:88	70(55)

[a] All reactions were carried in toluene. Step 1 was run for 16 h, step 2 for 19 h, and step 3 for 2 h under inert an atmosphere using a thermostated oil bath (150 °C). [b] Molar concentration of the limiting substrate; see column 4. [c] Ratio of the products. [d] Yield of **7a** determined by GC analysis using tetradecane as an internal standard. Value in parentheses is the yield of the isolated product. [e] 1 mol% of CSA was added in step 2. n.d. = not determined.

for 16 hours, and after cooling benzaldehyde (**4a**) was added and the reaction was heated for an additional 19 hours at 150 °C (Table 1). Based on our previous results obtained with ruthenium catalysts for C3 functionalization of cyclic amines with aldehydes, formic acid was added as a reducing agent at the last stage (step 3; 150 °C for 2 h) of the procedure to ensure complete reduction of the unsaturated intermediates. The expected formation of 3-benzyl-*N*-phenylpiperidine (**7a**) was observed, but *N*-benzylaniline (**5**) and *N*-phenylpiperidine (**6**) were also detected. The {ruthenium(II)(*p*-cymene)} dimer did not afford the C-alkylated piperidine **7a** but the presence of **5**, arising from N-alkylation of **2a** by **4a**, was observed as the main product (entry 1). Surprisingly, our previously reported ruthenium(II) catalyst **A**, which exhibited a high efficiency for N or C alkylation of *N*-benzylpiperidine, showed very low activity for the tandem protocol, thus affording less than 50% conversion of the diol **3a** and leading mainly to the piperidine derivative **6** and only 5% of **7a** (entry 2). We then investigated the reactivity of the new iridium(III) complex featuring the chelating phosphane sulfonate. The complex **B** was obtained in good yield upon treatment of the deprotonated diphenylphosphinobenzene sulfonic acid **1** with the cyclopentadienyl dichloride iridium-(III) dimer (Scheme 2). The solid-state structure of **B** revealed a piano-stool geometry around the iridium center and a six-membered ring arising from the chelation of the phosphinesulfonate ligand with an Ir–O bond of 2.140 Å.[17] The catalyst **B** was successfully involved in the tandem process under the reaction conditions used for **A**, thus affording the trialkylated amine **7a** as the major product (entries 4–7). This result demonstrated that **B** was active for the base-free N,N-dialkylation of **2a** with **3a** to give **6**, and that catalytic activity was maintained for the oxidant-free direct dehydrogenation of **6**, thus leading to a reactive nucleophilic enamine. It is noteworthy that [{$IrCl_2$Cp*}$_2$] was totally inactive toward C alkylation but led to **5** as a major compound (entry 3). With **B**, increasing the concentration resulted in lower conversion and higher relative amount of **6**, and the best result was obtained at 0.4 M (entries 4 and 5). A slight excess of **4a** ensured better selectivity for **7a** (entry 6). Finally, the presence of 1 mol% of camphorsulfonic acid (CSA) as a Brønsted acid was required to reach complete conversion and optimized reaction conditions, which afforded a 70% yield of compound **7a** as determined by GC analysis (entry 8). The tedious separation of the piperidines **7a** and **6** by column chromatography using silica gel led to the isolation of pure **7a** in 55% yield.

The overall transformation corresponds to three dehydrogenation and three hydrogenation steps, thus six formal catalytic hydrogen-transfer processes, and also two condensations of the intermediate aldehyde with aniline and one condensation reaction between an enamine and an aldehyde. If we assume that the organic reactions proceed quantitatively, each individual catalytic step presents an excellent yield (> 90%). These results show that only one organometallic precatalyst is sufficient for the overall transformation. Moreover, the reaction allows the first oxidant-free direct *endo* dehydrogenation of the cyclic saturated **6**, and does not require more-reactive substrates (i.e. containing activated benzylic positions as in N-benzyl amines or tetrahydroisoquinolines), for dehydrogenation[14] and thus highlights the improved activity of this new iridium precatalyst **B**.

To clarify the difference of reactivity between the ruthenium catalyst **A** and the iridium catalyst **B**, their efficiencies in the first step were evaluated. Thus, **2a** was reacted with **3a** in the presence of 3 mol% of catalyst **A** at 150 °C for 16 hours. A 50% conversion of **2a** into the monoalkylated amine **8** as the major product was observed (Scheme 3). Addition of **4a**, which also acts as hydrogen acceptor, to this mixture enhanced only the cyclization rate



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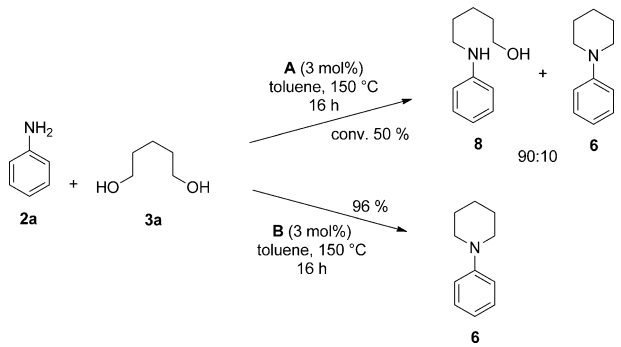
Scheme 2. Preparation of the catalyst **B**.

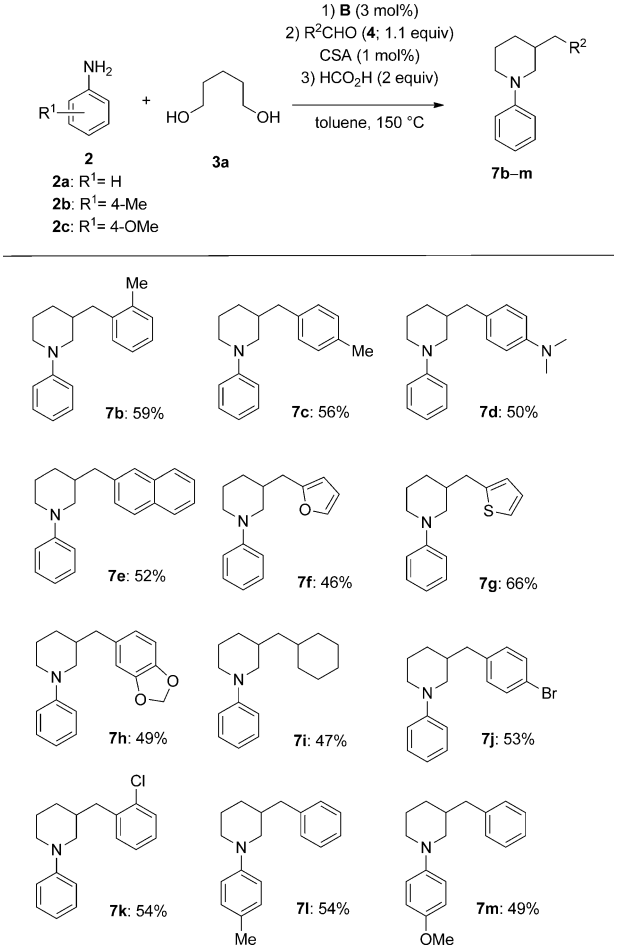


2a 3a

Scheme 3. Monoalkylation of **2a** using the catalyst **A** versus dialkylation with the catalyst **B**.

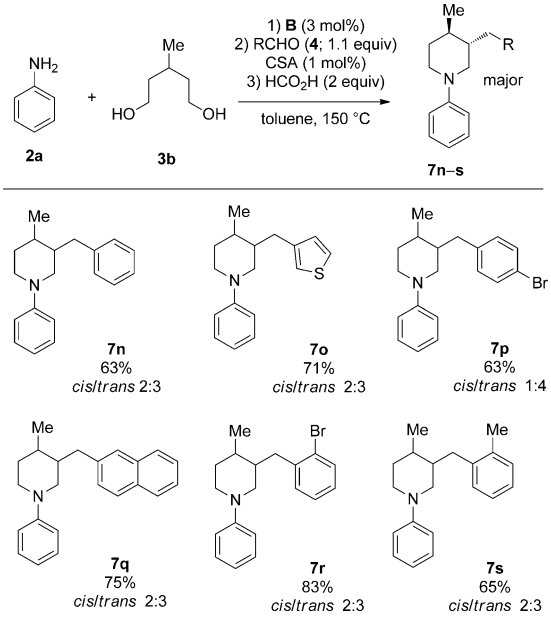
for the formation of **6**. In contrast, the reaction with **B** was more efficient and quantitative formation of **6** was obtained within 16 hours. These results clearly demonstrate that **A** is an efficient catalyst for mono N alkylation of aniline with diols, and explains why the formation of **7a** could not take place efficiently with this catalyst precursor.

With our optimized reaction conditions in hand (Table 1, entry 8), we next investigated the scope of this tandem transformation (Scheme 4). The reactions proceeded smoothly from a variety of aromatic aldehydes (**4b–e**), thus affording the N,N,C-trialkylated products **7b–e** in yields of up

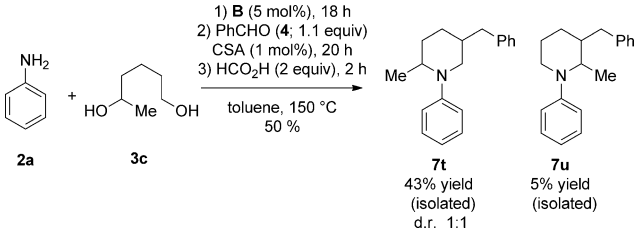


Scheme 4. Scope of the direct, tandem trialkylation. The yield is that for the isolated product **7** (3 steps) after purification by column chromatography. All reactions were carried in toluene with **2**/**3a**/**4**/**B**/HCO_2H in a 1:1:1.1:0.03:2 molar ratio. Step 1 was run for 16 h, step 2 for 20 h, and step 3 for 2 h under inert an atmosphere using a thermostated oil bath (150 °C).

to 59% after purification by column chromatography. Interestingly, the dimethylamino group of **7d** remained intact and no dealkylation/alkylation[7b] processes occurred under our reaction conditions, thus leading to **7d** in 50% yield upon purification. The more challenging heteroaromatic aldehydes were compatible with the experimental conditions and the best yield, 66%, was obtained for compound **7g** having a 2-thiophene carboxaldehyde. The acetal moiety did not undergo dehydrogenation or hydrolysis and reaction with piperonal led to 49% of **7h**. As previously observed with the ruthenium catalytic systems we used for C3 alkylation of cyclic amines, no dehalogenation occurred with halogenated aromatic aldehydes and the alkylated anilines **7j** and **7k** were obtained in 53 and 54% yield, respectively. The electron-rich anilines **2b**,**c**, substituted by a methyl or a methoxy group, afforded the products **7l**,**m** in 54 and 49% yield, respectively. Finally, the aliphatic formylcyclohexane **4i** was also reactive and gave **7i** in 47% yield. The tandem process can also be applied to substituted pentan-1,5-diols (Schemes 5 and 6).



Scheme 5. 3,5-disubstituted piperidines made by the tandem N,N,C3-alkylation reactions. The yield is that for the product **7** (3 steps) isolated by column chromatography. All reactions were carried in toluene with **2**/**3b**/**4**/**B**/HCO_2H in a 1:1:1.1:0.03:2 molar ratio. Step 1 was run for 16 h, step 2 for 20 h, and step 3 for 2 h under inert an atmosphere using a thermostated oil bath (150 °C).

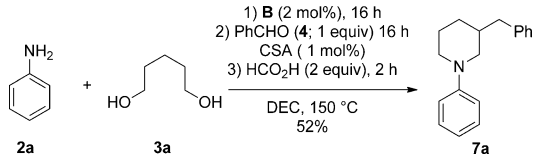


Scheme 6. Regioselective formation of 2,5-disubstituted piperidine **7t**

The treatment of **3b** with **2a** and subsequent reaction with various aldehydes afforded a better yield as compared to those obtained from **3a** (Scheme 5). The formation of two diastereoisomers resulting from the reduction of the enamine/iminium intermediates by the iridium hydride species was observed. Diastereoselectivities of up to 3:2 were obtained even in refluxing toluene when less-hindered, unsubstituted benzaldehyde and thiophene carboxaldehyde were used, thus

leading to **7n**,**o** in 63 and 71% yield, respectively, upon isolation. We expected formation of the *cis* isomer as the major product arising from the *anti* approach of the iridium hydride species to the enamine intermediate, but interestingly 2D NOESY studies highlighted the formation primarily of the *trans* isomers, which seems to indicate prior protonation of the enamine intermediate and subsequent reduction of the resulting iminium species. Similar diastereoselectivities were obtained with naphthaldehyde (see **7q**) and *o*-methylbenzaldehyde (see **7s**), whereas *p*-bromobenzaldehyde (see **7p**) led to the formation of the *trans* isomer in a *trans*/*cis* ratio of up to 4:1. Attempts to improve diastereoselectivities by lowering the temperature led to lower conversions for the C-alkylation step. To investigate the regioselectivity issues, we also extended the tandem process to hexan-1,5-diol (**3c**), which contains one secondary and one primary alcohol, and could lead to up to three regioisomers depending on the nature of the iminium/enamine equilibria (Scheme 6). The reaction of **2a** with **3c** afforded the expected *N*-phenyl-2-methylpiperidine, which readily reacted with benzaldehyde to regioselectively generate disubstituted piperidines. Complete NMR analyses revealed the almost exclusive formation of the distal piperidine **7t**, resulting from the formation of the less hindered enamine, with a diastereoisomeric ratio of 1:1. The proximal piperidine **7u** was also observed in a low 5% yield upon isolation.

The selective multicomponent transformation of the anilines **2**, diols **3**, aldehydes **4**, and formic acid into the products **7** produces only water and CO_2 as by-products. Although toluene proved to be a suitable solvent, the green impact of this transformation could be improved by using the more ecofriendly diethyl carbonate (DEC)[18] as a solvent. Under the same reaction conditions **7a** was isolated in 52% yield from the tandem process using **2a**, **3a**, and **4a** (Scheme 7).



Scheme 7. Diethyl carbonate: an ecofriendly alternative to toluene.

In summary, we have described the preparation of a new iridium complex **B** featuring a phosphanesulfonate chelate. This complex provides an efficient catalyst for the direct *endo* dehydrogenation of piperidine, allowing the first tandem protocol for the three-component preparation of diverse N-arylpiperidine derivatives, thus demonstrating the potential of tandem hydrogen transfers for the synthesis of elaborated azaheterocycles from easily accessible diols, primary amines, and aldehydes. Excellent regioselectivities and promising diastereoselectivities were obtained from substituted diols. In addition, we have demonstrated that the use of the environmentally benign diethyl carbonate was suitable for the transformation.

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