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LETTER

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Sequential Catalysis for the Production of Sterically Hindered Amines: Ru(II)-Catalyzed C−H Bond Activation and Hydrosilylation of Imines

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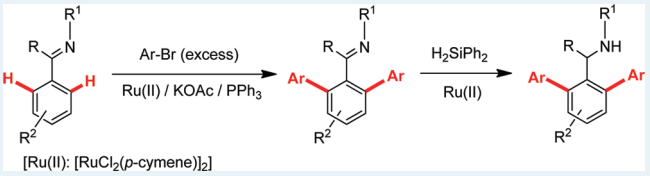
Supporting Information

ABSTRACT: Sequential ruthenium(II) catalyzed reactions for the production of secondary amines from simple imines are reported. They involve Ru(II)-acetate based catalytic systems for C−H Bond activation/diarylation of simple imines with aryl bromides followed by $[RuCl_2(arene)]_2$ hydrosilylation of diarylated imines. The direct diarylation of aldimines can be profitably produced by Ru(II) catalytic systems in the presence of both acetate and PPh_3 ligands. By contrast, PPh_3 additive disfavors diarylation of ketimines that is achieved with $[Ru(OAc)_2(p\text{-cymene})]$ alone. The catalytic hydrosilylation of the resulting imines was simply performed with H_2SiPh_2 in the presence of $[RuCl_2(arene)]_2$ catalyst at room temperature leading to overall yield of 70−86% of secondary amines

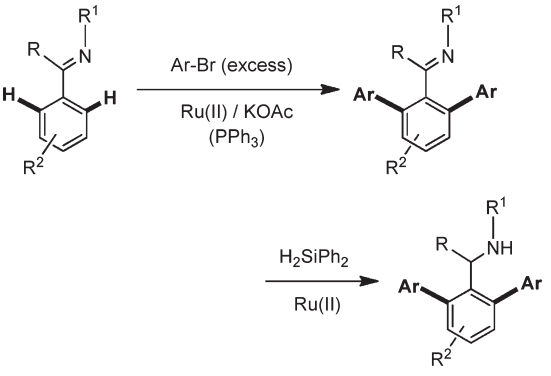


KEYWORDS: C−H bond activation, arylation, hydrosilylation, ruthenium(II) catalysts, imines, amine synthesis

An important challenge in molecule synthesis deals with sequential or tandem catalytic processes allowing to generate value-added, structurally complex molecules from inexpensive, readily available reagents with atom economy.[1,2] Significant examples of cascade or sequential reactions have been developed with Ru catalysts[3,4] such as alkene metathesis/hydrogenation,[5−8] dimerization of alkynes/cyclization or hydroarylation.[9,10] On another hand, the development of synthetic strategies toward amines is attracting interest because of their omnipresence in natural products, pharmaceutical and medicinal compounds, as well as useful component in ligand synthesis. Impressive progress in amine synthesis have been made via transition metal catalyzed C−N bond formation, in particular in the field of Pd catalyzed Buchwald−Hartwig[11,12] and Cu catalyzed Ullman reactions.[13,14] Another classical simple access to moderate size amines involves the reductive amination of carbonyl derivatives with primary amines via sequential condensation/catalytic reduction.[15−18]

During the past decade, selective C−H bond activation and functionalization promoted by metal catalysts have brought a revolution in C−C bond formation reactions.[19−25] An approach has been developed using arylketones and imines especially with Ru(0) and Rh(I) catalysts in the Murai[26−29] and Jun[30,31] reactions that usually allow the direct insertion of unsaturated molecules into C−H bonds, whereas, the direct arylation of arylketones using Ru(0) catalysts was only possible with arylboronates as coupling agents.[27−29] By contrast, the direct (hetero)arylation of arenes functionalized by a nitrogen containing directing group (pyridine, oxazoline, pyrazole, ...) has been performed using Ru(II) catalysts.[32−41] The C−H activation/functionalization of imines appears more difficult to perform, but several examples have been recently reported,[42−48] including the pioneering report of Oi and Inoue with Ru(II)/2PPh_3 catalyst system to obtain mostly monoarylated ketimines.[45] Ackermann has just reported the monoalkylation of aryl ketimines and obtained the corresponding amines using $ZnCl_2/NaBH_3(CN)$ system as stoichiometric reducing reagents.[48]

Here, we report sequential Ru(II)-catalyzed reactions to reach sterically hindered amines via C−H diarylation of arylimines followed by hydrosilylation of the resulting imines. (eq 1) These successive processes show several innovations in both C−H bond activation/diarylation using Ru(II)-acetate catalyst and in subsequent catalytic hydrosilylation simply with $[RuCl_2(p\text{-cymene})]_2$ catalyst.



(1)

The positive influence of the acetate ligand on Ru(II) catalyst has first been demonstrated on attempts to perform direct diarylation of aldimine **1a** with phenyl bromide **2a** (eq 2, Table 1).

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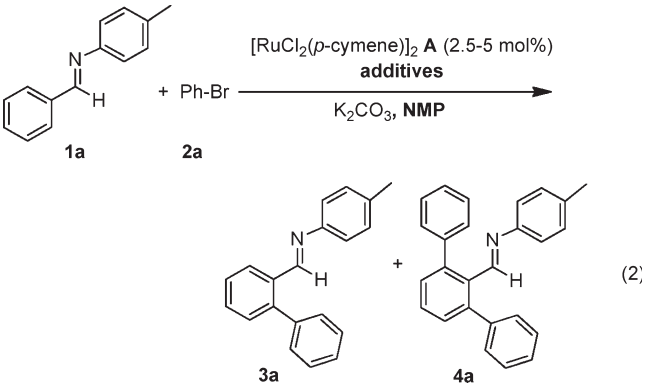
Table 1. Influence of Additives on the Direct Arylation of Aldimine 1a with Ru(II)/KOAc Catalytic System[a]

entry	Ru **A** (mol %)	additives (mol %)	time (h)	temp (°C)	conv.(%)[b]	mono/di **3a**/**4a**
1	5[c]		48	120	45	14:86
2	5[c]	KOAc(20)	48	120	85	15:85
3	5[c]	KOAc (20)	48	160	100	0:100
4	5[e]	PPh_3 (10)[d]	20	120	99	1:99
5	2.5[e]	KOAc (10)	20	100	34	5:95
6	2.5[e]	KOAc (5), PPh_3 (5)	20	100	100	1:99
7	2.5[e]	KOAc (10), PPh_3 (5)	20	100	100	0:100
8	2.5[e]	KOAc (5), PPh_3 (10)	20	100	91	5:95

[a] Imine (0.5 mmol), PhBr (1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ **A** (2.5 or 5 mol %), additives, NMP (2 mL), 10 μL of tetradecane as internal standard. [b] Conversion of imine determined by GC. [c] 2.5 equiv of PhBr, 3 equiv K_2CO_3. [d] 1 mL of NMP was used. [e] 3 equiv of PhBr, 4 equiv K_2CO_3.

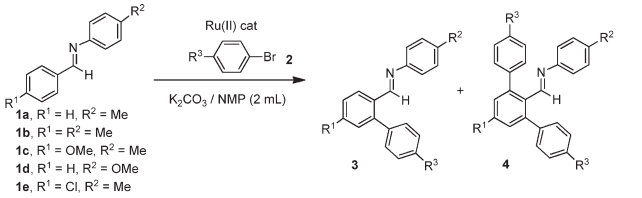


Whereas in NMP at 120 °C for 48 h $[RuCl_2(p\text{-cymene})]_2$ **A** gives a low conversion of 45%, catalyst **A** with 2 equiv of KOAc per Ru atom leads to 85% conversion (Table 1, entries 1, 2). With in situ prepared $Ru(OAc)_2(p\text{-cymene})$ **B**[40] in NMP at 160 °C after 48 h, complete diarylation was reached (entry 3), and the diarylated imine **4a** was isolated in 75% yield. The addition of one PPh_3 per Ru atom to $[RuCl_2(p\text{-cymene})]_2$ allows to reach complete diarylation of imine **1a** at 120 °C for 20 h (entry 4). Interestingly, the association of KOAc and PPh_3 ligand with catalyst **A** (1 KOAc/1 PPh_3/ 1 Ru) led to the best system for diarylation of imine at 100 °C (entry 6 vs 5). It is noteworthy that an increase of the OAc ligand is more important than that of PPh_3 ligand (entries 7 and 8).[45] The cooperative actions of both KOAc and PPh_3 for the production of **4a** are thought to favor first the cyclometalation assisted with acetate ligand,[38,39] and other carboxylates[19] via an autocatalytic process,[49] and then the oxidative addition of PhBr with PPh_3 by increasing electron density at Ru(II) center.

Aldimines **1b** and **1c** have first been diarylated with a variety of arylbromides with $Ru(OAc)_2(p\text{-cymene})$ in situ generated by reaction of $[RuCl_2(p\text{-cymene})]_2$ **A** with 2 equiv of KOAc and without phosphine. At 160 °C in NMP for 48 h, the diarylation was almost quantitative and pure diarylated aldimines **4a**−**4h** were isolated in 50−75% yield after flash chromatography (Scheme 1, entries 1−7). The presence of a donating group (R^1 = OMe, Me, entries 6, 7) slightly decreases the conversion. These results show that the conditions (160 °C, 48 h) provide a good way to produce and isolate diarylated aldimines without phosphine ligand.

Then, the association of the PPh_3 and acetate ligands on Ru(II) catalyst was shown to be more advantageous to diarylate the aldimines **1a** and **1e** (Scheme 1, entries 8−11) with respect

Scheme 1. Direct Arylation of Aldimines with in Situ Prepared $Ru(OAc)_2(p\text{-cymene})$: Influence of the PPh_3 Ligand



[Cat] = $[RuCl_2(p\text{-cymene})]_2$ (5 mol%) / **KOAc (20 mol%)**[a] **160°C, 48h**

Entry	R^1	R^2	R^3	Conv (%)	Yield[b] (%)	Mono/di **3** / **4**
1	H	Me	H (**4a**)	100	75	0:100
2	H	Me	Me (**4d**)	99	51	4:96
3	H	Me	F (**4e**)	100	55	0:100
4	H	Me	OMe (**4f**)	100	52	9:91
5	H	OMe	H (**4h**)	94	71	8:92
6	Me	Me	H (**4b**)	89	65	0:100
7	OMe	Me	H (**4c**)	91	68	15:85

[Cat] = $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol%) / **KOAc (5 mol%) / PPh_3 (5 mol%)**[c] **100°C, 20h**

Entry	R^1	R^2	R^3	Conv (%)	Yield[b] (%)	Mono/di **3** / **4**
8	H	Me	H (**4a**)	100	73	0:100
9	H	Me	Me (**4d**)	97	86	0:100
10	Cl	Me	H (**4i**)	100	88	0:100
11	H	Me	COMe (**4j**)	99[d]	63	0:100

[a] Ar-Br **2** (2.5 equiv)/K_2CO_3 (3 equiv). [b] Isolated yields. [c] Ar-Br **2** (3 equiv)/K_2CO_3 (4 equiv). [d] 36 h reaction.

to $Ru(OAc)_2$ system (Scheme 1, entries 1−7) under much milder conditions. The diarylation of imine **1a** in NMP at 100 °C was completed in 20 h and **4a** was isolated in 73% yield. (Entry 8) Whatever is the para substituent (R^3 = H, Me, COMe) on the arylbromide with aldimines **1a**, **1e**, the diarylated imines **4d**, **4i**, and **4j** were isolated in 63−88% yield (entries 9−11).

The direct diarylation of ketimines was then explored in NMP in which the cooperative action of acetate ligand alone, without PPh_3 ligand, was shown to be profitable (Scheme 2).

Attempts were made without phosphine at 160 °C for 48 h in NMP and high conversion was obtained; only the diarylated products were isolated in 56−80% yields (Scheme 2, entries 1, 2, 4−8), and these conditions provide the best way to reach diarylated ketimines. Indeed the addition of PPh_3 to the Ru-OAc catalytic system led to full conversion at 120 °C for 48 h but actually favored the monoarylation (entry 3). It thus appears that the bulkiness of the Ru(II)-PPh_3 catalyst disfavors the diarylation of ketimines, likely because of the interaction of the (ketimine)methyl and the first introduced aryl group that should prevent the planarity of the molecule required for the second arylation (formation of the cyclometalated intermediate). The PPh_3 ligand that was revealed to decrease the arylation temperature[45] cannot play its role here.

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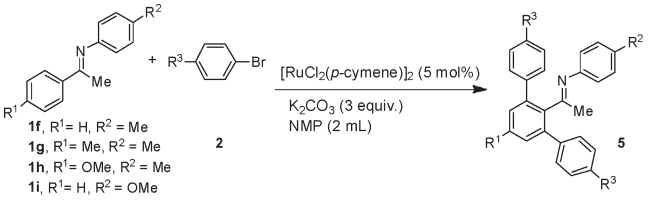
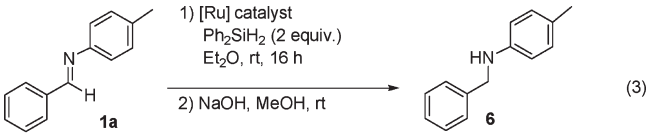
Scheme 2. Direct Arylation of Ketimines with Ru-OAc Catalyst



Entry	R^1	R^2	R^3		conditions	Temp (°C)	Time (h)	Conv (%)	Yield[a] (%)	Mono/di
1	H	Me	H	(**5a**)	KOAc (20 mol%)	160	48	92	70	0:100
2	H	Me	Me	(**5f**)	KOAc (20 mol%)	160	48	100	56	0:100
3	H	Me	Me	(**5f**)	KOAc(5 mol%)[b] PPh_3 (5 mol%)	120	48	100	-	58:42
4	H	Me	F	(**5d**)	KOAc (20 mol%)	160	48	100	81	0:100
5	H	Me	*t*-Bu	(**5e**)	KOAc (20 mol%)	160	48	100	78	0:100
6	Me	Me	H	(**5b**)	KOAc (20 mol%)	160	48	100	78	0:100
7	OMe	Me	H	(**5c**)	KOAc (20 mol%)	160	48	100	78	0:100
8	H	OMe	H	(**5g**)	KOAc (20 mol%)	160	48	96	74	0:100

[a] Isolated yield. [b] Ar-Br (3 equiv), K_2CO_3 (4 equiv).

The recent significant contribution for reduction of imines using iron catalysts by Beller and coworkers[50,51] prompted us to investigate sequential catalytic direct diarylation/hydrosilylation of imines, but using Ru(II) species in both steps. To reach bulky ortho-diarylated secondary amines, we have first explored the hydrosilylation of the simple imine **1a** in the presence of Ph_2SiH_2 in ether (eq 3).[52−54]



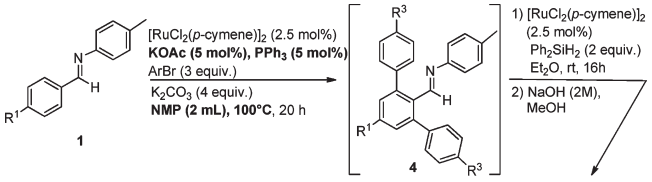
[Ru] = $RuCl_2$(p-cymene)]$_2$ (2.5 mol%), conv= 100%
[Ru] = $Ru(OAc)_2$(p-cymene) (5 mol%), conv= 15%

$Ru(OAc)_2$(*p*-cymene) and [$RuCl_2$(*p*-cymene)]$_2$ were selected as catalyst precursors for hydrosilylation of imines as they are also catalyst precursors for the first catalytic arylation. Surprisingly, $Ru(OAc)_2$(*p*-cymene) is quite inactive leading to only 15% conversion. By contrast, [$RuCl_2$(*p*-cymene)]$_2$ alone appears as an excellent hydrosilylation catalyst of the imine **1a** into amine **6a** with 2 equiv of H_2SiPh_2 at room temperature (r.t.) for 16 h (eq 3).[55−58] Notably, when [$RuCl_2$(*p*-cymene)]$_2$ is associated with PPh_3 (PPh_3/Ru:1/1), the conversion decreased to 10−20%.

The sequential catalytic diarylation/hydrosilylation of imine **1a** has then been carried out. Imine **1a** was diarylated according to the optimized catalytic conditions (Table 1, entry 6). After a short purification of the diarylated imine **4a** that is preferable as both acetate and PPh_3 inhibit the hydrosilylation reaction, 2 equiv of Ph_2SiH_2 and 2.5 mol % of [$RuCl_2$(*p*-cymene)]$_2$ were then added to the crude product in ether. The reaction was completed at r.t. after 16 h, and the diarylated amine **6a** was isolated in 78% yield (Scheme 3). Similarly, the imines **1a**, **1b**, and **1e** were diarylated and then hydrosilylated with [$RuCl_2$(arene)]$_2$ catalysts and the corresponding amines **6b**−**6h** were isolated in 70−86% yields, based on initial imines.

In summary, the above results demonstrate that the diarylation of aldimines with a variety of arylbromides can be performed at best with Ru(II) catalysts with the cooperative actions of both acetate and PPh_3 ligands. For the arylation of ketimines, PPh_3 additive inhibits the diarylation, and thus in situ generated $Ru(OAc)_2$(*p*-cymene) catalyst using longer reaction times was preferable. It is shown that simple [$RuCl_2$(*p*-cymene)]$_2$ catalyst efficiently promotes hydrosilylation of arylated imines into amines at room temperature. The sequential catalytic diarylation/hydrosilylation reactions directly generate secondary bulky amines from simple imines easily obtained from aldehydes and ketones.

Scheme 3. Sequential Direct Diarylation/Hydrosilylation



Entry	R^1	R^3		Yield(%)
1	H	Me	(**6a**)	78
2	H	H	(**6b**)	82
3	H	F	(**6c**)	76
4	Cl	H	(**6d**)	86
5	Cl	Me	(**6e**)	71
6	Me	H	(**6f**)	72
7	Me	Me	(**6g**)	71
8	Me	F	(**6h**)	82

EXPERIMENTAL SECTION

In a typical experiment, in a dried Schlenk tube were introduced [$RuCl_2$(*p*-cymene)]$_2$ (2.5 mol %), KOAc (5 mol %), PPh_3 (5 mol %), K_2CO_3 (1 mmol), imine **1a** (0.25 mmol), bromobenzene (0.75 mmol), NMP (2 mL), and tetradecane (10 μL) as an internal standard. The reaction mixture was heated at 100 °C for 20 h. The product, which was quickly purified by filtration on a short column of alumina, was added to [$RuCl_2$(*p*-cymene)]$_2$ (2.5 mol %), diphenylsilane (2 equiv), and diethyl ether (1 mL). The reaction mixture was stirred at r.t. for 16 h. After methanolysis [MeOH (1 mL) and NaOH (2M, 5 mL)], the desired amine was isolated by chromatography on silica gel. Further experimental details are provided in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information. General procedures for the preparation of diarylated imines and amines, ^{1}H and ^{13}C NMR data for all the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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