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J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.6b08863 • Publication Date (Web): 02 Nov 2016

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Ruthenium Sulfonamide-Catalyzed Direct Dehydrative Condensation of Benzylic C–H Bonds with Aromatic Aldehydes

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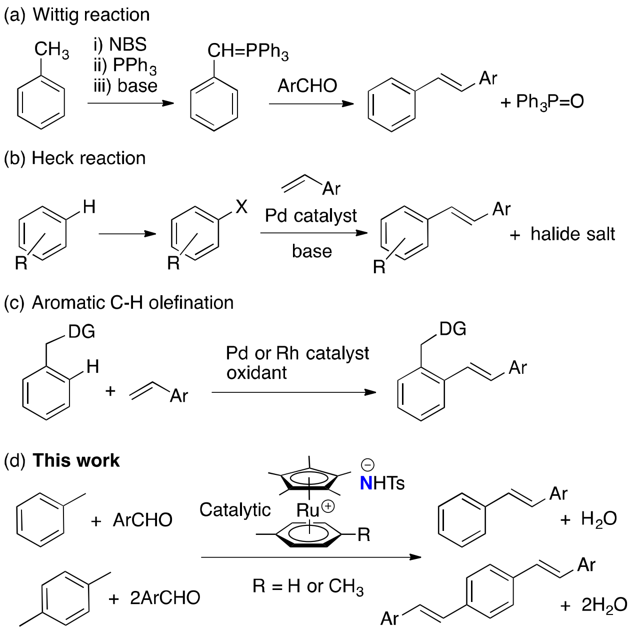
Supporting Information Placeholder

ABSTRACT: The first catalytic dehydrative condensation of the benzylic C–H bonds of toluene and *p*-xylene with aromatic aldehydes is reported herein. This protocol provides highly atom-economical access to stilbene and *p*-distyrylbenzene derivatives, whereby water is the sole byproduct. The reaction is based on the deprotonation–functionalization of benzylic C–H bonds through η^6-complexation of the arenes, which is realized for the first time using a catalytic amount of a transition metal activator. The key to the success of this method is the use of a sulfonamide anion as a catalyst component, which appears to facilitate not only the deprotonation of the benzylic C–H bonds but also the formation of a C–C bonds *via* an electrophilic tosylimine intermediate.

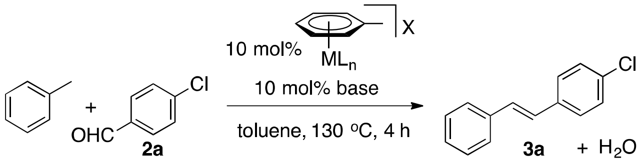
Stilbene and *p*-distyrylbenzene moieties are useful structural motifs in pharmaceuticals and optoelectronic materials~~,~~.[1-3] ~~and t~~The development of new atom-economical methods for their preparation is therefore of considerable academic and industrial interest.[4] Conventional synthetic routes to stilbenes rely predominantly on Wittig[5] and Heck reactions,[6] both of which, although successful, present certain drawbacks. On one hand, the Wittig reaction (Scheme 1a) requires multiple steps and hazardous reagents to generate phosphorus ylide intermediates, and it produces stoichiometric quantities of halogen- and phosphorus-containing byproducts. ~~The~~ ~~s~~Syntheses via the Heck reaction (Scheme 1b), on the other hand, produce less waste, but may present regioselectivity issues when introducing the halogen (X) group on the aromatic ring. The recently emerged catalytic aromatic C–H olefination reactions (Scheme 1c),[7] which use directing groups (DGs) such as carboxylic acids and carboxylic amides to ensure high regioselectivity, represent a more selective and direct approach to stilbenes. These oxidative C–H olefin coupling reactions can be highly atom-economical and cost-effective, provided that molecular oxygen or air are used as the terminal oxidant.[8] However, in many cases, relatively expensive oxidants such as Ag(I) or Cu(II) salts are required in stoichiometric amounts.

Scheme 1. Synthetic approaches toward Stilbenes



Herein, we report a new catalytic process that yields stilbenes and *p*-distyrylbenzenes in a highly atom-economical fashion *via* the direct dehydrative condensation of the benzylic C–H bonds of toluene and *p*-xylene with aromatic aldehydes (Scheme 1d). The reaction appears to proceed through the benzylic deprotonation-functionalization of toluene and *p*-xylene activated through π-coordination to a cationic Cp*Ru complex. Although existing examples of side-chain functionalization of π-coordinated aromatics have needed stoichiometric amounts of transition metal activators,[9,10] we now demonstrate for the first time a catalytic version of such transformation using a novel cooperative catalysis of a cationic Cp*Ru(η^6-arene) complex and a sulfonamide anion $NHTs^-$ (Ts = *p*-toluenesulfonyl).

Table 1. Screening of Active Catalyst Components.

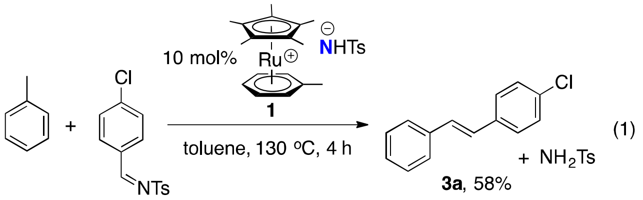


Entry	ML_n	X^-	Base	Yield (%)[a]
1	Cp^*Ru^+	$NHTs^-$	none	50
2	Cp^*Ru^+	OTf^-	none	0
3	Cp^*Ru^+	Cl^-	none	0
4	Cp^*Ru^+	Cl^-	KNHTs	40
5	Cp^*Ru^+	Cl^-	KNHMs	24
6	Cp^*Ru^+	Cl^-	KNMeTs	2
7	Cp^*Ru^+	Cl^-	KN^tBuTs	2
8	Cp^*Ru^+	Cl^-	KHMDS	1
9	Cp^*Ru^+	Cl^-	KO^tBu	2
10	Cp^*Ru^+	Cl^-	K_3PO_4	2
11[b]	$CpRu^+$	PF_6^-	KNHTs	8
12[b]	Cp^*Fe^+	PF_6^-	KNHTs	5
13[b]	$CpFe^+$	PF_6^-	KNHTs	9
14[b,c]	$(PCP)Ru^+$	OTf^-	KNHTs	0
15[b]	$Mn(CO)_3^+$	PF_6^-	KNHTs	0
16[b]	$Cr(CO)_3$	none	KNHTs	0

[a] Determined by GC. [b] Reaction time 19 h. [c] PCP = 1,5-bis(diphenylphosphino)pent-3-yl.

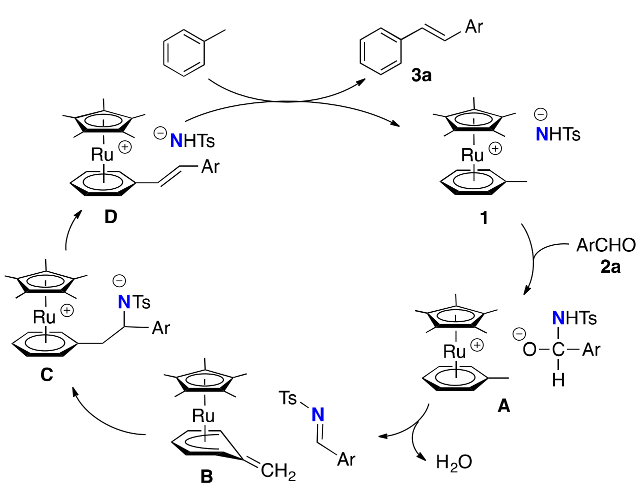
Our initial discovery of ~~the~~ this ~~dehydration~~ dehydrative condensation of toluene with an aromatic aldehyde in the presence of [Cp*Ru(η^6-toluene)][NHTs] (**1**; Cp* = η^5-C_5Me_5)[11] and the subsequent screening tests for the optimal catalyst composition are detailed in Table 1. When a mixture of **1** and a 10-fold excess of *p*-chlorobenzaldehyde (**2a**) in toluene was heated ~~at~~ to 130 °C, *p*-chlorostilbene (**3a**) was produced in 50% yield relative to **2a** (entry 1), indicating that the solvent toluene ~~used as solvent~~ was ~~also~~ ~~acted as a reactant and was~~ subjected to a catalytic condensation with the aldehyde. As expected, analogous ruthenium complexes containing less basic triflate or chloride counteranions displayed no catalytic activity for this reaction (entries 2 and 3). However, the catalyst generated *in situ* from [Cp*Ru(η^6-toluene)]Cl and KNHTs was similarly effective as the pre-isolated $NHTs^-$ salt **1** (entries 1 and 4). Screening of several potassium bases in combination with precatalyst [Cp*Ru(η^6-toluene)]Cl (entries 4-10) revealed that primary sulfonamide anions, in particular $NHTs^-$, play an essential role in this catalytic process. The η^6-toluene complexes of the $[CpRu]^+$, $[CpFe]^+$, and $[Cp^*Fe]^+$ fragments (entries 11–13) were much less effective than that of the $[Cp^*Ru]^+$ fragment, while the η^6-toluene complexes of $[(PCP)Ru]^+$,[12] $[Mn(CO)_3]^+$, and $[Cr(CO)_3]$ were totally inactive (entries 14-16).

The pronounced difference between the catalytic activity of the primary and secondary tosylamide anions (Table 1; *cf.* entries 4, 6, and 7) indicates that the role of the $NHTs^-$ anion is not restricted to act as a base. We envisaged that the $NHTs^-$ anion might react with the aldehyde to form a tosylimine intermediate and hence facilitate the C–C bond formation step of the catalytic cycle, considering that tosylimines are generally more electrophilic than the corresponding aldehydes.[13] As a support for this hypothesis, the condensation reaction between pre-synthesized tosylimine *p*-$ClC_6H_4CH{=}NTs$ and toluene was effected by 10 mol% of catalyst **1** to afford the *p*-chlorostilbene **3a** in 58%yield (eq 1).



(1)

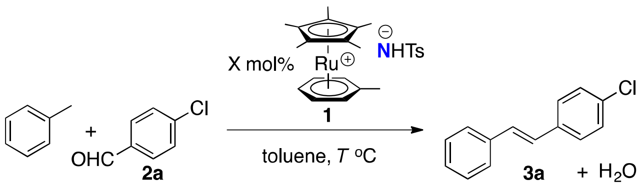
Scheme 2. Proposed Catalytic Cycle



Scheme 2 depicts a proposed catalytic cycle for the dehydrative condensation of toluene with the aldehyde **2a** *via* a tosylimine intermediate. The initial interaction between **1** and the aldehyde would occur by nucleophilic addition of the $NHTs^-$ anion to form the intermediate **A** containing a hemiaminolate anion. Benzylic deprotonation[14] from the $[Cp^*Ru(\eta^6\text{-toluene})]^+$ cation by the oxy anion in **A** ~~with~~ and subsequent elimination of water could form the tosylimine and η^5-methylenecyclohexadienyl intermediate **B**.[15] A nucleophilic attack of the *exo*-methylene carbon in **B** to the tosylimine followed by a 1,2-elimination of the $NHTs^-$ anion would form an η^6-stilbene complex **D**, which could subsequently undergo ligand exchange with toluene to complete the catalytic cycle.

Having identified **1** as a desired catalyst and with a likely mechanistic scenario in hand, we next examined optimization of reaction conditions using catalyst **1** and the aldehyde **2a** as a test substrate (Table 2). Raising the reaction temperature from 130 °C to 150 °C showed a considerable increase in the reaction rate and the yield of stilbene **3a** (entries 1 and 2). Although there was a glaring discrepancy between the conversion of **2a** and the yield of **3a** in entries 1-3, a dramatically improved selectivity for the production of **3a** was obtained when the reaction was conducted with molecular sieves 4Å (MS 4Å; entry 4). Complete conversion of **2a** and 98% yield of **3a** was achieved with 5 mol% catalyst loading in 24 h (entry 5), although further reduction of catalyst loading (2.5 mol%) resulted in a slower reaction (entry 6).

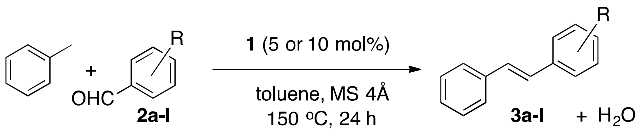
Table 2. Optimization of Reaction Conditions.



Entry	X	*T*	time (h)	additive	conv. (%)[a]	yield (%)[a]
1	10	130	4	none	88	50
2	10	150	4	none	100	72
3	5	150	4	none	71	58
4	5	150	4	MS 4Å	70	70
5	5	150	24	MS 4Å	100	98
6	2.5	150	24	MS 4Å	57	51

[a] Determined by GC analysis.

Table 3. Scope of Aromatic Aldehydes in the Catalytic Dehydrative Condensation with Toluene.[a]



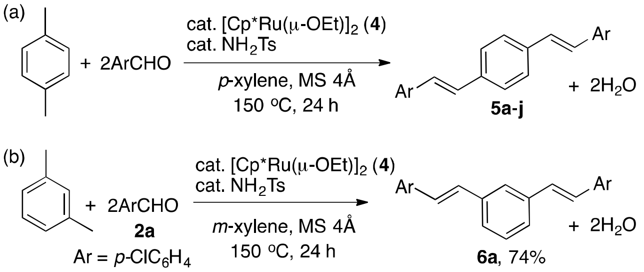
Entry	R	Ru mol%	conv. (%)[b]	product	yield (%)
1	*p*-Cl	5	100	**3a**	95
2	*p*-F	5	100	**3b**	90
3	*p*-CF_3	5	100	**3c**	94
4	*p*-Br	5	91	**3d**	85
5	*m*-Cl	5	100	**3e**	92
6	*p*-CN	10	78	**3f**	60
7	H	10	100	**3g**	87
8	*p*-Me	10	100	**3h**	88
9	*o*-Me	10	100	**3i**	85
10	*o*-Cl	5	21	**3j**	5
11	*p*-NO_2	5	26	**3k**	8
12	*p*-MeO	10	30	**3l**	20

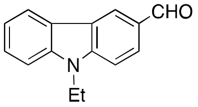
[a] Isolated yields are reported. [b] Determined by GC.

With optimized conditions in hand, we explored the scope of aromatic aldehydes in the dehydrative condensation with toluene (Table 3). Aromatic aldehydes with electron-withdrawing halogen and -CF_3 groups in para or meta positions were smoothly transformed into the corresponding stilbenes **3a-e** in good yield with 5 mol% of Ru catalyst (entries 1-5), while *p*-cyanobenzaldehyde, parent benzaldehyde, and *p*- and *o*-tolualdehydes were less reactive and required 10 mol% catalyst loading to afford the corresponding stilbenes in acceptable yield (entries 6-9). The aldehydes with *o*-chloro, *p*-NO_2, and *p*-OMe functionalities were not very compatible in this reaction (entries 10-12).

We next extended our protocol to include substrates other than toluene, namely, *p*-xylene (Table 4a). For this purpose, the combination of $[Cp^*Ru(\mu\text{-}OEt)]_2$ (**4**)[16] and NH_2Ts was found to be a convenient precatalyst that could generate the catalyst $[Cp^*Ru(\eta^6\text{-}p\text{-xylene})]NHTs$ in situ[17] and facilitate the condensation of *p*-xylene with 2 equiv of aromatic aldehydes to afford a series of *p*-distyrylbenzene derivatives (**5a**–**5j**) in good yields. The compound **5j**, bearing a carbazole functionality, is known as a useful host material for blue organic light-emitting diodes.[18] In these experiments, the *p*-distyrylbenzene products, which are generally highly crystalline, precipitated as microcrystalline solids from the reaction medium and could thus be easily isolated by filtration.[19] Hence, the present catalytic protocol provides an operationally simple procedure for the synthesis of relatively simple *p*-distyrylbenzene derivatives. Additionally, we also demonstrate a reaction of *m*-xylene with the benzaldehyde **2a**, which affords the *m*-distyrylbenzene derivative **6a** in 74% yield (Table 4b).[20]

Table 4. Dehydrative Condensation of *p*- and *m*-Xylene with Aromatic Aldehydes.[a,b]



Entry	ArCHO	Product	Yield (%)[b]
1	*p*-ClC_6H_4CHO	**5a**	81
2	*p*-FC_6H_4CHO	**5b**	93
3	*p*-$CF_3C_6H_4CHO$	**5c**	71
4	*m*-ClC_6H_4CHO	**5d**	94
5	*p*-NCC_6H_4CHO	**5e**	73
6	PhCHO	**5f**	49
7	*p*-MeC_6H_4CHO	**5g**	80
8	*o*-MeC_6H_4CHO	**5h**	91
9	*p*-$MeOC_6H_4CHO$	**5i**	70
10		**5j**	~~48~~78

[a] Catalyst loading: 5 mol% **4** and 10 mol% $TsNH_2$ relative to ArCHO. [b] Isolated yields are reported.

In summary, we have developed a ruthenium-sulfonamide-catalyzed direct dehydrative condensation between the benzylic C–H bonds of toluene and *p*-xylene and aromatic aldehydes. This method provides highly atom-economical access to relatively simple stilbene and *p*-distyrylbenzene derivatives, both of which are valuable structural motifs in pharmaceuticals and optoelectronic materials. This catalytic process represents the first benzylic deprotonation-functionalization of η^6-coordinated arenes promoted by a catalytic quantity of a transition metal activator.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures and product characterization data (PDF).

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This study was supported by the JSPS KAKENHI grants JP15K05457 and JP15K05459. This work was also partially supported by the JSPS KAKENHI grants JP16H01038 (“Precisely Designed Catalysts with Customized Scaffolding”) and 15H00958 (“Stimuli-responsive Chemical Species for the Creation of Functional Molecules”). The authors are also grateful to the TOYOTA Motor Corporation for financial support.

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(17) Reaction of **4** with 2 equiv of NH_2Ts in *p*-xylene afforded a mixture of $[Cp^*Ru(\eta^6\text{-}p\text{-xylene})][Cp^*Ru(NHTs)_2]$ and $[Cp^*Ru(\eta^6\text{-}p\text{-xylene})]NHTs$ in 1:4 molar ratio. See Supporting Information for details.

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(19) The stilbene derivatives *p*-$MeC_6H_4CH{=}CHAr$, resulting from the 1:1 condensation reaction between *p*-xylene and ArCHO, were formed as minor products (for details, see Supporting Information).

(20) Other methylarene substrates such as *p*-chloro- and *p*-methoxytoluene did not react with **2a** under similar conditions.