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[Cp*RhCl₂]₂-Catalyzed Alkyne Hydroamination to 1,2-Dihydroquinolines

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Supporting Information Placeholder

ABSTRACT: [Cp*RhCl₂]₂ catalyzes the formation of 1,2-dihydroquinolines from the reaction of two terminal alkynes and an aniline. This reaction is believed to proceed via an alkyne hydroamination followed by an alkyne insertion.

The 1,2-dihydroquinoline unit occurs in a vast number of pharmaceuticals and other biologically active compounds,¹ as well as several natural products, such as, angustureine and the alkaloids. They are also used as intermediates in organic and natural product synthesis,² and have the additional advantage that they can be reduced to 1,2,3,4-tetrahydroquinolines which also have great importance as pharmaceuticals and agrochemicals.³ A straightforward synthetic route towards 1,2-dihydroquinolines would therefore be of interest.⁴ The application of transition metal mediated C-H bond functionalization in C-C and C-N bond formation reactions is now widely recognized.⁵ In particular, functional group directed arene C-H bond activation followed by coupling with alkynes has been shown to be attractive for the construction of valuable organic motifs.⁶ For instance, imine has been used as a directing group for C-H bond functionalization mediated by rhodium complexes, including [Cp*RhCl₂]₂, **1**.⁷

In our work on alkyne hydroamination reactions,⁸ we recently reported that **1** can efficiently catalyze the reaction of a terminal alkyne with an aniline to afford a ketimine; our proposed catalytic cycle is shown below (Scheme 1).⁹ **Error! Bookmark not defined.**^b

The final step in this catalytic cycle is the formation of an enamine which, we believed, rearranges rapidly under the reaction conditions to the ketimine, the species isolated. It occurred to us that the final imine-enamine equilibrium could be shifted towards the enamine via protonation of the imine ni-

trogen.⁹ A number of metal systems are known to catalyze alkyne hydroamination with enamine to afford the 1,2-dihydroquinoline unit,¹⁰ although they do have drawbacks such as the need for an excess of the alkyne,⁹ **Error! Bookmark not defined.**^{a,b} or higher temperatures.⁹ **Error! Bookmark not defined.**^{c,d,f} We therefore envisaged that we could switch from the formation of ketimine to that of 1,2-dihydroquinoline in our system through a change in the pH.

Scheme 1

Indeed, the reaction of PhCCH, **2a**, and 3-methoxyaniline, **3a**, in an ~2:1 molar ratio at 100 °C in the presence of 2 mol% of **1** and 5 mol% of NH₄PF₆ afforded dihydroquinoline derivative, **4aa** in 55% isolated yield. The identity of the product was established on the basis of NMR and mass spectroscopic data, and the structure confirmed by a single crystal X-ray crystallographic study (SI). An optimisation study showed that an increase in the amount of catalyst and/or NH₄PF₆ did not improve the yield significantly (Table 1, entries 2-3) but replacement of NH₄PF₆ with acids such as TFA or HBF₄, however, improved it dramatically (entries 4-5). The use of coordinating solvents like THF, IPA or methanol was detrimental (entries 9-11). Control experiments showed that both **1** and HBF₄ are necessary (entries 6-7).

The catalyst system is tolerant to a wide variety of substrates; a complete list of the substrate scope tested is given in the SI, and a selected list is presented in Table 2. Both electron-donating and electron-withdrawing substituents on the phenylacetylene

were tolerated, as were acid-sensitive groups like -OR and -OH. The reaction also worked with aliphatic alkynes and various 3-alkoxyanilines. Extension to other anilines, such as, aniline and 3-methylaniline, however, gave comparatively lower yields. The reaction failed with anilines containing electron-withdrawing substituents at the *meta*-position (3-chloroaniline), secondary anilines (*N*-methyl 3-methoxyaniline) and internal alkynes (PhC≡CPh).

Table 1. Optimization of conditions for the reaction **2a** + **3a** → **4aa**.

Entry	1 (mol %)	Additive (mol %)	solvent	T (°C)	Isolated yield (%)
1	2	NH ₄ PF ₆ (5)	Toluene	100	55
2	5	NH ₄ PF ₆ (10)	Toluene	100	65
3	2	NH ₄ PF ₆ (12)	Toluene	100	58
4	2	HBF ₄ (5)	Toluene	100	86
5	2	TFA (5)	Toluene	100	70
6	2	-	Toluene	100	-
7	-	HBF ₄ (5)	Toluene	100	-
8	2	HBF ₄ (5)	DCE	80	78
9	2	HBF ₄ (5)	THF	40	-
10	2	HBF ₄ (5)	IPA	80	-
11	2	HBF ₄ (5)	MeOH	80	-

Conditions: **3a** (1.0 mmol), **2a** (2.1 mmol), **1**/ additive in a solvent (3 mL), heated for 24 h.

Although the intermediacy of an enamine in such reactions has been proposed for the other metal systems, **Error! Bookmark not defined.** we have also sought to exclude other possible pathways, including ones in which a part of the pathway does not involve a metal-bound species. Two of these are depicted in Scheme 2. Path A involves an ortho alkenylation, a hydroamination and then a [3,3] sigmatropic shift; metal-catalyzed hydroamination and ortho C-H bond insertion of arylamines have both been well studied.¹² We have found, however, that **5** failed to react with **2a** to afford **4aa**, thus ruling out this pathway.

Path B involves the metal-catalyzed formation of an imine, its insertion into a metal-alkynyl species, followed by ortho C-H bond activated cyclization; a similar pathway has been proposed previously for Ag and Au. **Error! Bookmark not defined.** Although we did observe that **7** reacted with **2a** to give **4aa**, and that the reaction required both **1** and HBF₄·OEt₂, the intermediate **8a** was not observed. This was also true for the less reactive aniline, which would be expected to be arrested at the formation of the analogue of **8a** as the C-H bond activated cyclization would not be favored without an activating group on the aniline; only the corresponding imine was observed as a minor product. Further confirmation of this was obtained through the syntheses of the analogues **8b** and **8c**; under the same reaction conditions, **8b** did afford the corresponding 1,2-dihydroquinoline **4aa'**, but in a significantly reduced yield (compare Table 2 entries 9 and 10, and Table S3 entries 17-23),

while **8c** failed to react (Scheme 3). These results served to rule out path B.

Table 2. Selected results for the formation of 1,2-dihydroquinoline from the reaction of alkyne with aniline.

Entry	Alkyne (2x); R=	Aniline(2y); R'=	Product, %yield ^[a]
1	Ph (2a)	OMe (3a)	4aa , 86
2	HOCH ₂ -4-C ₆ H ₄ (2g)	OMe (3a)	4ga , 73
3	HO-3-C ₆ H ₄ (2h)	OMe (3a)	4ha , 71
4	H ₃ CO-4-C ₆ H ₄ (2j)	OMe (3a)	4ja , 89
5	Cl-4-C ₆ H ₄ (2n)	OMe (3a)	4na , 75
6	F-4-C ₆ H ₄ (2p)	OMe (3a)	4pa , 85
7	-(CH ₂) ₂ CH ₃ (2q)	OMe (3a)	4qa , 73
8	Ph (2a)	OEt (3b)	4ab , 83
9	Ph (2a)	O ⁱ Pr (3d)	4ad , 79
10	Ph (2a)	OBn (3g)	4ag , 80
11 ^b	-(CH ₂) ₂ CH ₃ (2q)	CH ₃ (3j)	4rj , 48
12 ^b	-(CH ₂) ₂ CH ₃ (2q)	H (3k)	4rk , 34

Conditions: Arylamine (1.0 mmol), alkyne (2.1 mmol), **1** (0.02 mmol) and HBF₄·OEt₂ (0.05 mmol) in toluene (3 mL), heated at 100 °C for 24 h.^[b] Isolated yields.^[c] 30-40% ketimine was observed.

It is therefore likely that the reaction here proceeded via the formation of an enamine intermediate followed by ortho C-H bond activation and alkyne insertion (Scheme 4). Formation of the intermediate **B** may be envisaged as proceeding via an electrophilic substitution. The *meta*-alkoxy and NH₂ substituents on the aniline make the position ortho to the amine group electron-rich and thus favoring substitution there. Displacement of the coordinated enamynyl alkene by an alkyne, followed by alkyne insertion, affords the intermediate **D**. A 1,2-alkene insertion of the enamine would give **E** which can then undergo protonolysis to yield the final product **4** and regenerate the active catalyst.

In conclusion, we have described a single-step synthesis of 1,2-dihydroquinolines from the reaction of arylamines with terminal alkynes, catalyzed by the rhodium complex **1**. This reaction involved two separate catalytic cycles – the first involving alkyne hydroamination to form a ketimine as reported earlier, and the second involving transformation of the ketimine through ortho C-H bond activation and alkyne insertion. The

acidic conditions employed favored the enamine in the imine-enamine equilibrium which resulted from the first catalytic cycle.

Scheme 3

Scheme 4

Experimental procedure

General. All reactions and manipulations were performed under argon by using standard Schlenk techniques. The catalyst **1** was prepared according to the published method.¹² ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded in chloroform- d_3 except **4ga** and **4ha** which were recorded in methanol- d_4 , on a JEOL ECA400 or ECA400SL spectrometer; chemical shifts reported were referenced to residual solvent resonances. High resolution mass spectra (HRMS) were recorded in ESI mode on a Waters UPLC-Q-TOF mass spectrometer.

Crystallographic analyses. Diffraction-quality crystals of **4aa** and **4ga** were obtained by slow evaporation of hexane/dichloromethane solutions. X-ray data were collected on a Bruker AXS APEX system, using Mo $\text{K}\alpha$ radiation and at 103 K, with the SMART suite of programs.¹³ Data were processed and corrected for Lorentz and polarization effects with SAINT,¹⁴ and for absorption effects with SADABS.¹⁵ Structural solution and refinement were carried out with the SHELXTL suite of programs.¹⁶ The structures were solved by direct methods and completed with difference maps following refinement. Hydrogen atoms were placed in calculated positions and refined with a riding model. There were two molecules in the asymmetric unit of **4ga**. One molecule exhibited disorder of the benzo ring and the other exhibited disorder of the OMe and CH_2OH groups. These were modelled with two alternative sites of equal occupancies each, with appropriate restraints.

General procedure for the synthesis of 3-alkoxyanilines

In a 2-neck RB flask, 3-nitrophenol (0.5 g, 3.59 mmol) was dissolved in dry DMF (5 mL). To this solution 1-iodoethane (316

μL , 3.95 mmol) and K_2CO_3 (0.5 g, 3.59 mmol) were added and the reaction mixture was stirred at room temperature. After completion of the reaction, reaction solvent was removed under reduced pressure. Then the mixture was diluted with water and extracted with chloroform (3 $\times$ 15 mL), dried over MgSO_4 and the solvent evaporated.

In a 2-neck RB flask, the above obtained 3-ethoxynitrobenzene was dissolved in ethanol (15 mL), followed by the addition of acetic acid (675 μL). The reaction mixture was refluxed for 20 min. To the refluxing solution Fe powder (1.45 g, 25 mmol) was added portionwise, followed by $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (162 mg, 0.58 mmol). After completion of the reaction, the mixture was filtered, diluted with ether (25 mL) and water (15 mL), and the layers separated. The aqueous layer was extracted with ether (3 $\times$ 15 mL), dried over MgSO_4 , and the solvent was removed by evaporation. The crude product obtained was purified by silica gel (60–120 mesh) column chromatography to give pure **3b** (256 mg, 52%). A similar procedure was used for the other 3-alkoxyanilines. The amount of reagents used, product formed (with yield) and HRMS for the products are given in the SI.

General procedure for the preparation of 1,2-dihydroquinolines

In a carius tube, **1** (12 mg, 0.02 mmol) and $\text{HBF}_4 \cdot \text{OEt}_2$ (7 mg, 0.05 mmol) were dissolved in toluene (3.0 mL). To this suspension, 3-methoxyaniline (123 mg, 1.0 mmol) and PhCCH (214 mg, 2.1 mmol) were added. The reaction mixture was heated at 100 °C for 24 h, and then the reaction solvent was rotary evaporated to give the crude product as brown oil. Purification using flash column chromatography on silica with ethyl acetate/hexane (5% v/v) as eluent gave **4aa** (281 mg, 86 %). Similar procedures were used with the other alkynes and anilines for other **4**. The amount of reagents used, product formed (with yield) and HRMS for the products are given in the SI.

Synthesis of compound 5

3-methoxyaniline (615 mg, 5.0 mmol), PhCCH (510 mg, 5.0 mmol) and montmorillonite K-10 (500 mg) were placed in a round bottomed flask equipped with magnetic stirrer and reflux condenser. The reaction mixture was then heated at 140 °C for 12 h. After cooling to rt, it was filtered, washed through with diethyl ether (20 mL), and the solvent was from the combined filtrate and washings was removed by evaporation. The crude product obtained was purified by silica gel (60–120 mesh) column chromatography using hexane:ethyl acetate (90:10, v/v) as eluent to obtain pure **5** (618 mg, 55%). HRMS: Found (calc); 226.1232 (226.1232).

Reactions with phenylacetylene

In a carius tube, **1** (10 mg, 0.016 mmol) and $\text{HBF}_4 \cdot \text{OEt}_2$ (7 mg, 0.04 mmol) were dissolved in toluene (3 mL). To this suspension, **5** (180 mg, 0.8 mmol) and PhCCH (91 mg, 0.85 mmol) were added. The mixture was heated at 100 °C for 24 h, and ^1H NMR analysis showed that there was no product formation.

An analogous reaction with **7** in place of **5** afforded, after flash column chromatographic separation (ethyl acetate/hexane, 5% v/v) of the crude, **4aa** (55 mg, 86 %). A similar reaction using **8b** (212 mg, 0.8 mmol) but without the PhCCH afforded, after a similar workup, **4aa'** (89 mg, 42 %). HRMS: Found (calc); 266.1541 (266.1545).

Supporting Information

Details of optimization and substrate scope studies, characterization data of all new compounds, and X-ray crystallography

report. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Conflicts of interest

The authors declare no competing financial interests.

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