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2012

Kumaran, E., & Leong, W. K. (2012). Rhodium(III)-Catalyzed Hydroamination of Aromatic Terminal Alkynes with Anilines. Organometallics, 31(3), 1068–1072.

https://hdl.handle.net/10356/101028

https://doi.org/10.1021/om201134j

Rhodium(III) Catalysed Hydroamination of Aromatic Terminal Alkynes with Anilines

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*Abstract: The dinuclear Rh(III) species [Cp*RhCl$_2$]$_2$ catalyses the hydroamination reaction between an aromatic terminal alkyne (ArCCH) and an aniline (Ar'NH$_2$), in the presence of a salt additive, to afford the ketimine Ar'N=C(Me)(Ar). A reaction pathway has been proposed on the basis of experimental and computational studies.*

Introduction

Amines and imines are important intermediates in the synthesis of natural products, pharmacological agents and N-heterocycles, and in a number of industries including fine chemicals, agrochemicals and dyes.[1] Practical synthetic routes to imines include the condensation of ketones with primary amines. This method is, however, not suitable for aromatic ketimines because of the poor reactivity of arylketones, the propensity towards aldol-type side reactions with methyl ketones,[2] and the poor (40-55%) yields.[3] The direct addition of amine N-H bonds to unsaturated substrates like alkynes and alkenes provide a simple, efficient, and atom-economic route to the synthetically useful ketimines and enamines. It is also superior to the other available methods like imination of ketones,[2,3] or the aminomercuration/demercuration of alkynes.[4] Catalytic hydroamination of alkynes have also been successfully utilized as key steps in a variety of total synthesis of naturally occurring molecules.[5]

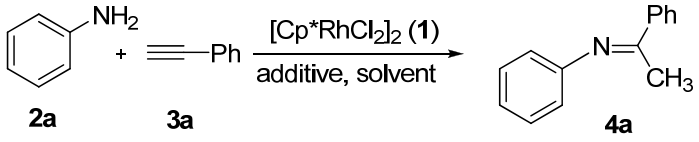
A number of metal complexes are known to catalyse the intermolecular hydroamination of terminal alkynes,[6] and the regioselective hydroamination of alkynes to form aromatic ketimines has been achieved with ruthenium,[6e] and gold catalysts.[6j] Rhodium complexes have also been reported to catalyse hydroamination reactions, including the inter-

and intramolecular hydroamination of alkenes,[7] and the intramolecular cyclization of aminoalkynes.[8] The first reported rhodium catalysed intermolecular alkyne hydroamination by Beller also appears to be the only one to-date which afforded Markovnikov products;[9] a closely related example was the Markovnikov addition of hydrazine reported by Messerle.[10] Other reports on rhodium catalysed intermolecular alkyne hydroamination all led to the anti-Markovnikov product.[11] In particular, we noticed that all the rhodium catalysts reported have involved a Rh(I) species. In addition, the sole example of Markovnikov addition did not work well with phenylacetylene, affording only a 10% yield of product, because of competing oligomerisation.[9]

In here, we wish to report our investigations into the first successful example of a Rh(III) species acting as a catalyst precursor, for the efficient synthesis of aromatic ketimines based on the regioselective Markonikvov hydroamination of terminal aromatic alkynes with anilines. The catalyst precursor is the relatively simple, easily accessible and air-stable dinuclear rhodium complex $[Cp^*RhCl_2]_2$ (**1**).

Results and discussion

Complex **1** catalyses the reaction between aniline (**2a**) and phenylacetylene (**3a**), in the presence of an additive, to form the ketimine **4a**, via a Markovnikov alkyne hydromamination (Scheme 1).



Scheme 1

An optimization study showed that a number of additives (AgOTf, $AgPF_6$, $AgSbF_6$, $LiPF_6$, $NaPF_6$, HBF_4 or NH_4PF_6) were active, although Bu_4NPF_6 was not (Table 1; more variations in SI); as a control, use of the additive NH_4PF_6 alone did not catalyse the reaction. This points to a cationic complex as the active catalyst. Our subsequent studies utilized a

catalyst loading of 0.5 mol% and a 1.5 mol% loading of NH_4PF_6; a higher catalyst loading did not improve the yield much, although it did accelerate the reaction rate. Strongly coordinating solvents such as THF, methanol and isopropanol were detrimental to the reaction; higher (> 80 ^oC) temperatures gave slightly lower yields, and the reaction failed to proceed at ambient temperature.

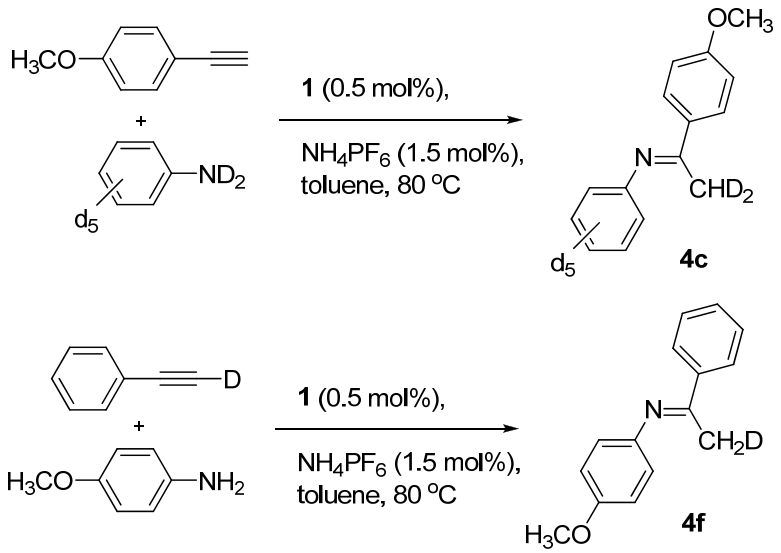
Table 1. Effects of variations in additive and solvent for **1**-catalysed hydroamination of phenylacetylene with aniline.

S/No	Solvent	**1** (mol%)	Additive (mol%)	T (^oC)	Yield (%)
1	Toluene	1.0	NH_4PF_6 (2.0)	80	69
2	Toluene	1.0	NH_4PF_6 (3.0)	80	89
3	Toluene	1.0	NH_4PF_6 (5.0)	80	85
4	Toluene	1.0	Bu_4NPF_6(3.0)	80	-
5	Toluene	1.0	AgOTf (3.0)	80	81
6	THF	1.0	NH_4PF_6 (3.0)	80	-
7	Toluene	1.0	NH_4PF_6 (3.0)	30	-
8	Toluene	1.0	NH_4PF_6 (3.0)	110	83
9	Toluene	0.5	NH_4PF_6 (1.5)	80	87
10	Toluene	0.2	NH_4PF_6 (0.6)	80	53
11	Toluene	-	NH_4PF_6 (3.0)	80	-

The substrate scope has also been studied; this is summarised in Table 2, for both imines which were sufficiently stable for isolation (left columns) and those which were converted to the amine by $NaBH_4$ reduction and isolated as such (right columns). Both electron-donating and –withdrawing substituents on the alkyne and the aniline are tolerated. However, the reaction failed with aliphatic amines or alkynes, nor with internal alkynes.

Mechanistic considerations

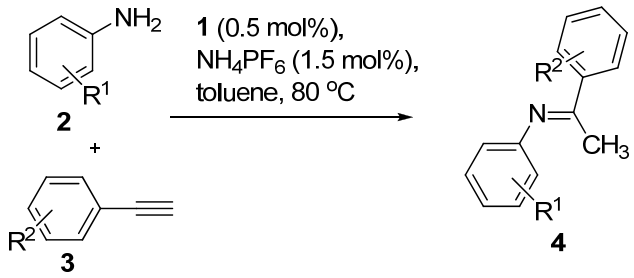
Isotopic labelling experiments employing (a) d_7-aniline and *4*-methoxyphenyl acetylene, and (b) *4*-methoxyaniline and PhCCD, afforded **4c** with two, and **4f** with one, respectively, of the CH_3 protons being deuterated (Scheme 2). These results clearly indicate that all the three H atoms in the CH_3 group are derived solely from the terminal alkyne ≡CH and the aniline NH_2.

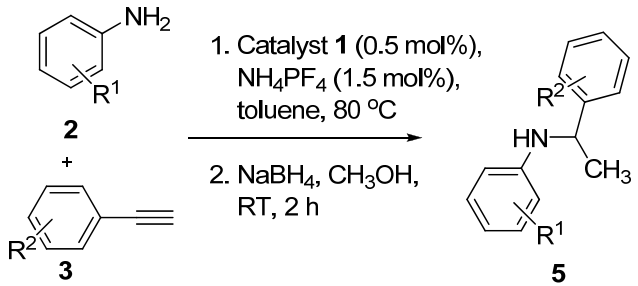


Scheme 2

There are a number of possibilities for the reaction pathway. One involves an insertion into the N-H bond,[8c,11a-b] but this is known mainly for the group 4 metals and lanthanides,[12] and would also involve a Rh(V) species which is likely to lose HCl (and hence loss of deuterium in the labelling experiments). Complex **1** does not react with alkyne, NH_4PF_6 or both, even upon heating. It does, however, react immediately at room temperature with $PhNH_2$ to form $Cp^*RhCl_2(NH_2Ph)$ (**6**), which is also an active catalyst for the reaction. It is therefore reasonable to assume that the initial reaction involved the formation of **6** followed by loss of a chloride to the cationic species $[Cp^*RhCl(NH_2Ph)]^+$ (**A**). A plausible reaction pathway for the catalytic cycle is that depicted in Figure 1.

Table 2. Substrate scope study for isolated imine (left) and imine converted to, and isolated as, the amine (right).





Entry	R^1	R^2	Yield (%)[†]
1	H	H	**4a** (89)
2	H	*4*-CH_3	**4b** (90)
3	H	*4*-OCH_3	**4c** (92)
4	H	*4*-Cl	**4d** (84)
5	*4*-CH_3	H	**4e** (91)
6	*4*-OCH_3	H	**4f** (93)
7	*4*-OCH_3	*3*-CH_3	**4g** (89)
8	*4*-OCH_3	*4*-CH_3	**4h** (91)
9	*4*-OCH_3	*4*-Cl	**4i** (92)
10	*4*-OCH_3	*4*-OCH_3	**4j** (93)

[†]Yields reported are isolated yields.

Entry	R^1	R^2	Yield (%)[†]
11	H	*2*-CH_3	**5a** (66)
12	H	*2*-OCH_3	**5b** (77)
13	H	*3*-CH_3	**5c** (77)
14	H	*3*-OCH_3	**5d** (61)
15	H	*3*-Cl	**5e** (65)
16	H	*3*-F	**5f** (71)
17	H	*4*-Br	**5g** (81)
18	H	*4*-F	**5h** (76)
19	H	*4*-CH_2OH	**5e** (55)
20	H	*4*-^{t}Bu	**5j** (79)
21	H	*2*-CH_3,*4*-OCH_3	**5k** (78)
22	H	$C_{10}H_8$	**5l** (73)
23	H	*6*-OCH_3-*1*-naphthyl	**5m** (81)
24	*4*-OCH_3	*2*-OCH_3	**5n** (76)
25	*4*-OCH_3	*3*-OCH_3	**5o** (74)
26	*3*-OCH_3	H	**5p** (80)
27	*3,5*-$(OCH_3)_2$	H	**5q** (67)
28	*4*-OCH_3	H	**5r** (83)
29	*4*-Br	H	**5s** (78)
30	*4*-Cl	H	**5t** (82)

We have also examined computationally the energetics involved, using DFT at the B3LYP/LANL2DZ level of theory, for the reaction between PhCCH and $PhNH_2$; the computed free energies ($\Delta G^{\ominus}$) are also given in Figure 1. The first step, involving binding of the alkyne to **A** to afford **B**, has a slightly positive $\Delta G^{\ominus}$. The computed structure of **B** is interesting as it appears to be quite similar to that proposed by Messerle for a similar cationic alkyne complex,[8e] but the binding of the alkyne is so asymmetric that it is essentially an alkene-like carbonium ion; the ipso and α carbons carry positive Mulliken charges. That the binding of the alkyne is endergonic is consistent with the suppression of the reaction in coordinating solvents; we have computed a $\Delta G^{\ominus}$ of -32 kJ mol^{-1} for the binding of isopropanol to **A**.

The second step (step **B** → **C**) involves attack of a second aniline molecule on the bound alkyne; the isomeric form of **C** in which the amino group is *trans* to the Rh lies 67 kJ mol^{-1} higher. The possibility of direct migration of the Rh-bound aniline to the alkyne has a computed $\Delta G^{\ominus}$ of -16 kJ mol^{-1} but binding of the aniline to the metal centre would be expected to lower its nucleophilicity.[13] Consistent with this is our observation that although **6** is also an active catalyst for the reaction, it does not give any ketimine when reacted with alkyne and NH_4PF_6 without the addition of aniline.

The following step, **C** → **D**, is essentially an enammonium-iminium rearrangement. This has been shown to occur via an intramolecular *1,3*-H shift, and is consistent with our deuterium labelling experiments.[14] As for the case of **C**, there are also two isomeric forms for **D** which differ in their stereochemistry about the C=N bond. The energies shown in Figure 1 for the last two steps are those for the *cis* isomer; the corresponding values for the *trans* isomer are -64 and +12 kJ mol^{-1}, respectively, which does not allow us to determine which, or both, is the likely identity for **D**. The final step is dissociation of the iminium, presumably as the enamine which then tautomerizes to the corresponding, more stable, imine product. This

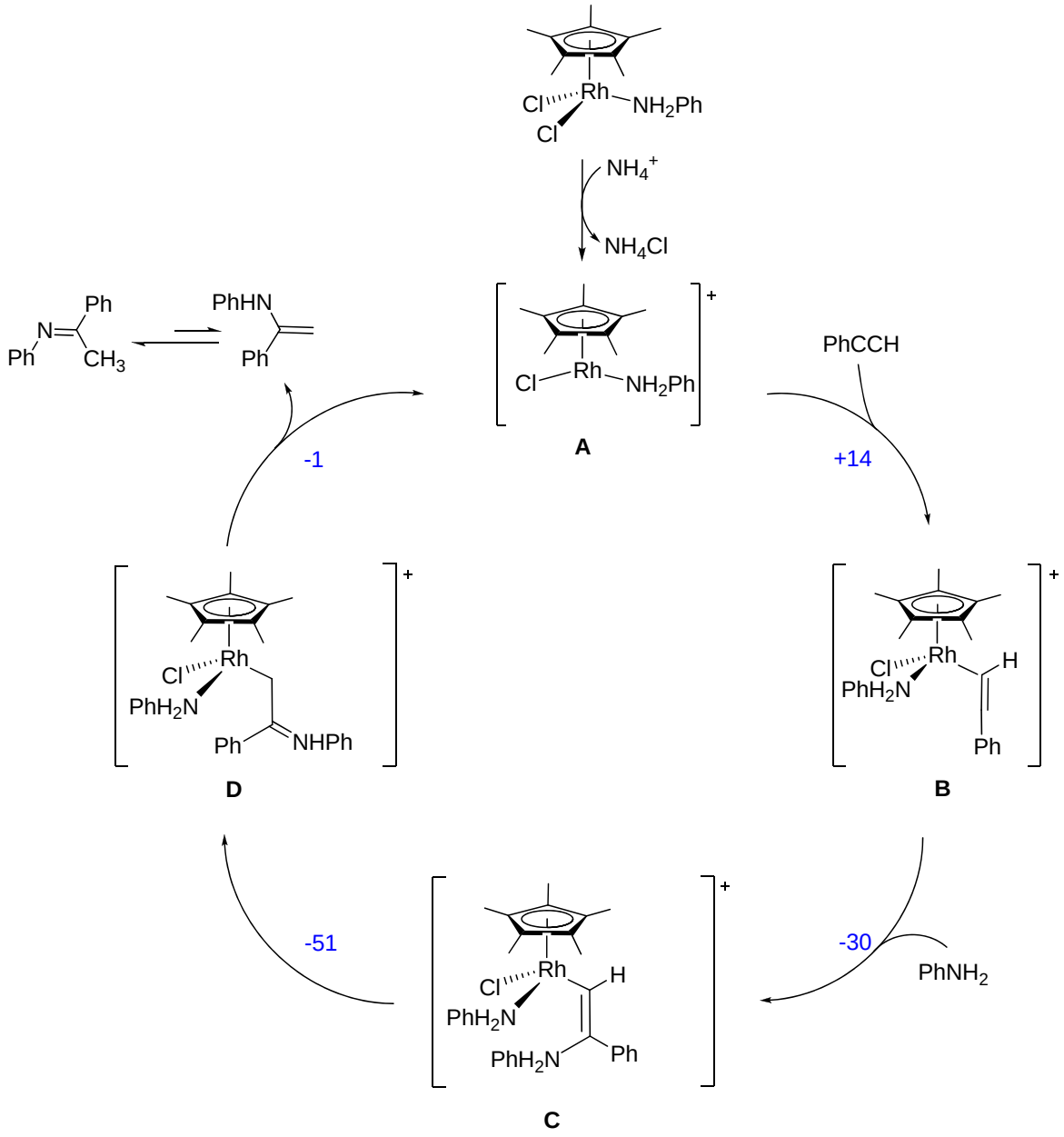


Figure 1. Proposed reaction pathway for the catalytic reaction involving PhCCH and $PhNH_2$. Gibbs free energies (in kJ mol^{-1}) for the various steps in the cycle are also given.

final tautomerisation also involves an intramolecular *1,3*-H shift,[15] which is again consistent with the deuterium labelling experiments.

Concluding remarks

We have shown that the readily available Rh(III) complex $[Cp^*RhCl_2]_2$ is a good catalyst precursor for alkyne hydroamination involving aromatic terminal alkynes and anilines. A reaction pathway involving cationic intermediates has been proposed on the basis of experimental and computational evidence. This involves binding of both alkyne and aniline, nucleophilic attack by a second aniline on the coordinated alkyne, followed by an intramolecular *1,3*-H shift to form an Rh-bound iminium, before its release from the catalyst.

In particular, one important aspect of the proposed reaction pathway is that all the intermediates contain a Cp*RhCl(aniline) moiety. The implication is that Rh(III) complexes of the general formula Cp*Rh(X)(L) should be potential catalysts for alkyne hydroamination. Our work on this is ongoing and our results will be reported shortly.

Experimental section

All chemicals from commercial sources were used without further purification and solvents were dried over the appropriate drying agents and distilled under argon. The catalyst **1** was prepared according to the published method.[16] All reactions and manipulations were carried out under argon by using standard Schlenk techniques. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded in $CDCl_3$ on a JEOL ECA400 or ECA400SL spectrometer and the chemical shifts were referenced to the residual proton resonance. GC/MS was recorded in EI mode on a Thermofinnigan DSQII mass spectrometer. High resolution mass spectra (HRMS) were recorded in ESI mode on a Waters UPLC-Q-TOF mass spectrometer.

General procedure for the hydroamination of alkynes with anilines

In a typical experiment, aniline (240 μL, 2.5 mmol) and a slight excess of phenylacetylene (302 μL, 2.75 mmol) were added using syringe to a suspension of the **1** (7.8

mg, 0.5 mol%) and NH_4PF_6 (6.2 mg, 1.5 mol%) in toluene (10 mL) in a carius tube under argon at room temperature. The mixture was degassed (3 cycles of freeze-pump-thaw) and then stirred at 80 ^oC for 12 h, after which the solvent was removed under vacuum and the crude product washed with chilled (-10 ^oC), dry hexane (3×5 mL). A similar procedure was used for the other imines **4**. Characterisation data are given in the Supporting Information.

General procedure for the reduction of imine using $NaBH_4$

For reactions in which the imine is unstable, the crude imine product obtained from the hydroamination reaction was dissolved in dry methanol. To this was added sodium borohydride (1.2 eq) and the mixture stirred at room temperature for 2 h. The solvent was then evaporated and the residue was quenched with water and then extracted with ethyl acetate (3×15 mL). The combined extracts were dried over magnesium sulphate, and then the solvent was evaporated under reduced pressure. The crude amine product **5** was purified by column chromatography using ethylacetate/hexane (15:85, v/v) as eluent. Characterisation data are given in the Supporting Information.

Deuterium labelling experiments

A sample of 4-methoxyaniline (20 mg, 0.16 mmol) and a slight excess of phenylacetylene-d (19 μL, 0.18 mmol) were added using syringe to a suspension of **1** (1 mg, 1 mol%) and NH_4PF_6 (1 mg, 3 mol%) in toluene (2 mL). The mixture was degassed (3 cycles of freeze-pump-thaw) and then stirred at 80 ^oC for 12 h, after which the solvent was removed under vacuum and the crude product was characterized by ^1H NMR and HRMS.

Similarly, aniline-d_7 (20 μL, 0.2 mmol) was reacted with 4-methoxypheneylacetylene (29 μL, 0.22 mmol) in the presence of **1** (1.2 mg, 1 mol%) and NH_4PF_6 (1 mg, 3 mol%) in toluene at 80 ^oC for 12 h, after which the solvent was removed under vacuum and the crude product was characterized by ^1H NMR and HRMS.

Preparation of $Cp^*RhCl_2(NH_2Ph)$ (6)

Aniline (10 μL, 0.105 mmol) and **1** (30 mg, 0.048 mmol) were dissolved in dichloromethane (2 ml) and stirred for a few minutes, and then the solvent was removed under vacuum and the residue obtained washed with hexane (1 ml). ^{1}H NMR ($CDCl_3$): 1.41 (s, 15H, 5×CH_3, Cp*), 4.98 (bs, 2H, NH_2), 7.09 (t, $^3J_{HH}$ = 6.64 Hz, 1H, para), 7.27-7.32 (m, 4H, ortho and meta). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 9.05 (CH_3, Cp*), 94.06 (d, $^1J_{RhC}$ = 34.5 Hz, ring C, Cp*), 120.41, 124.62, 129.44 & 142.17 (Ph). FAB MS: 402. Anal. Calcd for $C_{16}H_{22}Cl_2NRh$: C 47.78, H 5.51, N 3.48. Found: C 47.36, H 5.15, N 3.69. A single crystal X-ray crystallographic study of **6** has also been carried out; details are given in the SI.

Reaction of 6 with phenylacetylene

In a carius tube were placed **6** (25 mg, 0.062 mmol), NH_4PF_6 (15 mg, 0.093 mmol) and toluene (3 ml). Phenylacetylene (13 μL, 0.12 mmol) was added and the mixture was stirred at 80 ^{o}C for 8 h. Analysis by ^{1}H NMR spectroscopy showed no formation of the ketimine product. A similar reaction containing aniline (100 μL, 1.07 mmol), phenylacetylene (110 μL, 1.07 mmol), **6** (5 mg, 0.012 mmol) and NH_4PF_6 (3 mg, 0.018 mmol) afforded the ketimine product in 85% yield.

Computational studies. The reaction energetics were studied using DFT theory utilising the Becke's three parameter hybrid function,[17] and Lee-Yang-Parr's gradient-corrected correlation function (B3LYP),[18] together with the LanL2DZ (Los Alamos Effective Core Potential Double-ζ) basis set. Spin-restricted calculations were used for geometry optimization, and harmonic frequencies were then calculated to characterize the stationary points as equilibrium structures with all real frequencies, and to evaluate zero-point energy (ZPE) corrections. All calculations were performed using the Gaussian 03 suite of program.[19]

Acknowledgment. This work was supported by Nanyang Technological University and the Ministry of Education (Research Grant No. T208B1111) and one of us (E. K.) thanks the university for a Research Scholarship.

Supporting Information Available: Further experimental details and characterisation for **4** and **5**, crystallographic data for **6**, and optimised geometry of **A-D**. Ordering information is given on any current masthead page.

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Rhodium(III) Catalysed Hydroamination of Aromatic Terminal Alkynes with Anilines

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The dinuclear Rh(III) species $[Cp^*RhCl_2]_2$ catalyses the hydroamination reaction between an aromatic terminal alkyne (ArCCH) and an aniline ($Ar'NH_2$), in the presence of a salt additive, to afford the ketimine Ar'N=C(Me)(Ar). A reaction pathway has been proposed on the basis of experimental and computational studies.