A Triflamide-Tethered N-Heterocyclic Carbene-Rhodium(I) Catalyst for Hydroalkoxylation Reactions: Ligand-Promoted Nucleophilic Activation of Alcohols

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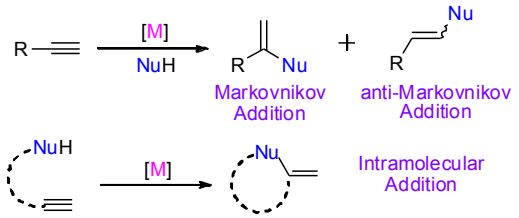
A Triflamide-tethered NHC–Rh(I) Catalyst for Hydroalkoxylation Reactions: Ligand Promoted Nucleophilic Activation of Alcohols

Abir Sarbajna,[a] Pragati Pandey,[a] S. M. Wahidur Rahaman,[a] Kuldeep Singh,[a] Akshi Tyagi,[a] Pierre H. Dixneuf,[b] and Jitendra. K. Bera*[a]

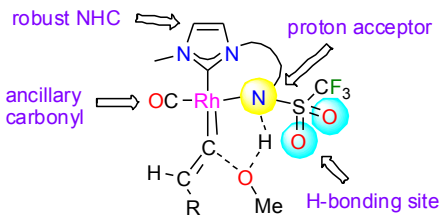
A triflamide-tethered NHC-bound Rh(I) dicarbonyl catalyst is found highly effective for both intermolecular hydroalkoxylation and intramolecular heteroannulation reactions. The involvement of both amido nitrogen and triflato oxygen of the triflamide functionality for alcohol activation and 1,2-hydrogen shift respectively is proposed.

Metal catalyzed nucleophilic addition across an alkyne bond is a synthetically important reaction offering an atom-economic route to a diverse array of compounds.[1] Significant advancements have been made toward selective formation of the Markovnikov(M)/anti-Markovnikov(AM) products for direct intermolecular addition of amines, acids, thiols and various other nucleophilic substrates to alkynes. Endo/exo-dig cyclic products are accessed via intramolecular heteroannulations (Scheme 1).[2] However, addition reactions of weak nucleophiles such as water and alcohol remain a challenging task.[3]



Scheme 1. Nucleophilic addition across a terminal alkyne.

Enol ethers are an important functionality in organic synthesis being used widely in cross coupling and ring–closing metathesis, cycloaddition reactions and for the synthesis of pharmaceuticals.[4] While metal catalyzed intramolecular hydroalkoxylations are well reported,[5] intermolecular reaction between alcohol and alkyne is difficult[6] and often demands strong base or harsh conditions.[7] Kirchner reported the addition of allylic alcohols to phenylacetylene by [RuCl(tris(pyrazolyl)borate)(pyridine)$_2$] catalyst.[8] A [PdMo$_3$S$_4$(1,4,7-triazacyclononane)$_3$Cl]$^{3+}$ cubane cluster with CF_3SO_3Ag was reported to catalyze the AM hydroalkoxylation of alkynic acid esters.[9] Kakiuchi first reported intermolecular AM hydroalkoxylation of terminal acetylenes by a 8–quinolinolato ligated rhodium(I) dicarbonyl complex.[10] In most cases, products were obtained with high *Z* selectivity.[11] Computational studies by Wang and co-workers revealed that the 8–quinolinolato oxygen atom facilitates alcohol deprotonation to a more potent O-nucleophile which readily adds to Rh-vinylidene followed by proton transfers.[12] N–heterocyclic carbene (NHC) derived ligands are widely used in organometallic catalysis owing to their ability to form robust compounds with a variety of metal ions and for their relatively easy steric and electronic tunability.[13] We postulated that a NHC with pendant basic group would be ideally suited for alcohol activation and promote its nucleophilic attack to the metal-vinylidene.[14] Herein we report the design, synthesis and catalytic activity of a Rh(I)-NHC dicarbonyl complex featuring a tethered triflamide group for intermolecular addition of alcohol to terminal alkynes and intramolecular cycloisomerization of alkynols (Scheme 2). The involvement of both the amido nitrogen and the triflato oxygen in alcohol activation and proton transfer steps is highlighted.



Scheme 2. Catalyst design.

Reaction of 2–isopropyl–1–(trifluoromethylsulfonyl)-aziridine and 1–mesitylimidazole afforded a zwitterionic imidazolium salt (**LH**) in high yield (90%). Subsequent reaction of **LH** with AgOAc in presence of K_2CO_3 in refluxing THF gave a neutral disilver complex **1** in 82% yield (Scheme 3a, Figure S2). Transmetallation of **1** with [Rh(*μ*–Cl)(COD)]$_2$ (COD = 1,5–cyclooctadiene) dimer afforded **2** in 90% yield. The molecular structure revealed a neutral square planar Rh complex chelate bound to **L** *via* carbene carbon and triflamido nitrogen. The metal coordination sphere is completed by a COD (Scheme 3b). The Rh1–C2 and Rh1–N3 bond lengths are 2.012(2) and 2.227(2) Å respectively. When CO was bubbled into a dichloromethane solution of **2** for 30 minutes, a yellow amorphous solid **3** was isolated in quantitative yield. Although the crystal structure could not be obtained, **3** was identified as [Rh(CO)$_2$L]. The carbene carbon was observed at *δ* 172.1 ppm as a doublet (*J* = 48 Hz) in the ^{13}C NMR spectrum. Two carbonyls resonate at 171 and 165 ppm. Sharp absorptions were observed at 2079 and 2005 cm^{-1} for carbonyls in **3**, which

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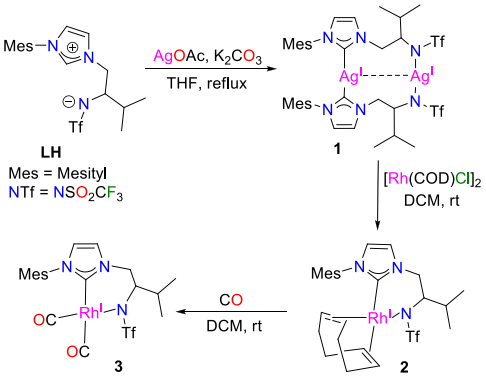
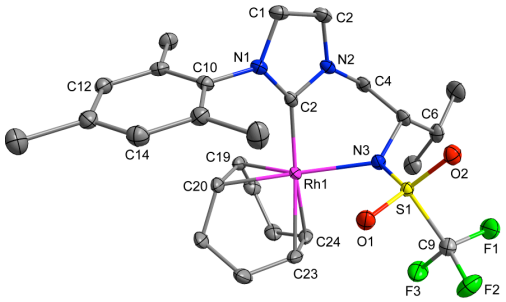
were absent in **2**. Electrospray ionization mass spectrometry (ESI–MS) showed a single peak at *m*/*z* 562.041 (*z*=1) assigned for $[\mathbf{3}+H]^+$.

(a)

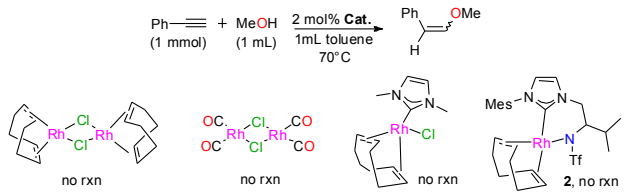


(b)



Scheme 3. (a) Synthesis of complexes **1**, **2** and **3**. (b) Molecular structure of **2** with the anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms are omitted for clarity.

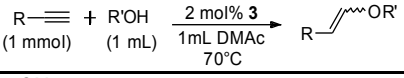
The catalytic utility of several Rh compounds was tested towards intermolecular hydroalkoxylation to understand the role of participating and ancillary ligands. Both $[Rh(\mu\text{–}Cl)(COD)]_2$ and $[Rh(\mu\text{–}Cl)(CO)_2]_2$ were found ineffective at 2 mol% catalyst loading using 1 mmol phenylacetylene and methanol (1 mL) in toluene co–solvent (1 mL) (Scheme 4). This suggests that a ligand framework is probably required for catalyst activity. However, both [RhL'(COD)Cl] and [RhL'$(CO)_2$Cl] (L'=*N,N'*–dimethylimidazoline–2–ylidene) were found ineffective. Even **2** with an appended triflamide did not show any catalytic activity. However, when the COD ligand is replaced by two carbonyls in **3**, modest yield of (2–methoxyvinyl)benzene (41%, Table S2) was obtained after 24 h at 70°C. A host of other solvents such as THF, acetonitrile, 1,4-dioxane and DMSO were screened but did not increase the yield significantly (41–51%, Table S3). However, the use of amide based solvents dimethylformamide and *N,N*–dimethylacetamide (DMAc) led to a considerable increase in the product formation.[15] Quantitative conversion was achieved after 48 h by using a methanol–DMAc solvent combination (Table S3). The C–O bond formation took place regioselectively at terminal carbon of the phenylacetylene and showed *E* isomer as the major product. The progress of the reaction was monitored by ^{1}H NMR analysis. Initially the *Z* isomer was predominant (kinetic product), but the thermodynamic *E* product gradually increased over time (See, Figure S4). Use of stronger bases such as Et_3N and pyridine led to decreased yields.[16]

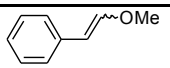
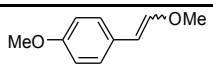
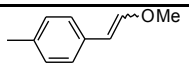
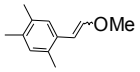
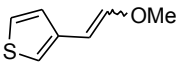
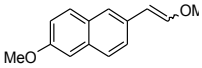
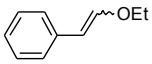
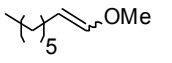
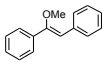


Scheme 4. Evaluation of Rh(I) catalysts for intermolecular hydroalkoxylation.

The substrate scope for **3** was tested under optimized reaction conditions and the results are collected in Table 1. For electron rich aromatic alkynes 1–ethynyl–4–methoxybenzene, 1–ethynyl–4–methylbenzene and 1–ethynyl–2,4,5–trimethylbenzene, high yields were obtained (entries 2–4, Table 1). 3–ethynylthiophene was converted to 3–(2–methoxyvinyl)thiophene in quantitative yield (entry 5). The best result was obtained for 2–ethynyl–6–methoxynaphthalene with 97% *E*-selectivity (entry 6, Table 1). The reaction was extended to ethanol and quantitative conversion to (2–ethoxyvinyl)benzene was obtained with 3:2 *E*/*Z* selectivity (entry 7, Table 1). The reaction also showed poor activity for aliphatic alkyne 1–octyne (entry 8, Table 1). All catalysis reactions were limited to terminal alkynes. For an internal alkyne diphenylacetylene, no addition product was detected implying the intermediacy of a metal-vinylidene for AM hydroalkoxylation.[10] The prerequisite of *π*-acidic carbonyl ligands for catalyst activity could be rationalized owing to their ability to favor the metal-vinylidene formation and increase electrophilicity of the vinylidene carbon.

Table 1. Substrate scope of intermolecular hydroalkoxylation reaction.[a]



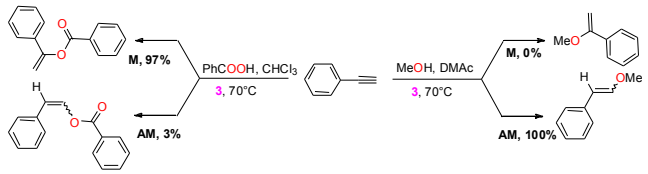
		
1, 86%, 82*E*:18*Z*	2, 99%, 63*E*:37*Z*	3, 98%, 66*E*:34*Z*
		
4, 95%, 72*E*:28*Z*	5, 99%, 71*E*:29*Z*	6, 99%, 97*E*:3*Z*
		
7, 99%, 60*E*:40*Z*	8, 12%, n.d.	9, 0%

[a] Alkyne (1 mmol) and alcohol (1 mL) were sequentially added to a 1 mL DMAc solution of **3** (0.02 mmol) and the closed reaction vessel was heated at 70°C for 24h. Isolated yields are reported. *E*/*Z* ratio determined by NMR and GC analyses in presence of internal standard mesitylene (1 mmol). n.d. = not determined.

We further carried out reactions with a series of alcohols under optimized conditions. Methanol and ethanol afforded excellent yields (*vide supra*), but sterically demanding aliphatic alcohols n-butanol, ^{i}butanol, n-hexanol and n-octanol were found unreactive. When ^{i}PrOH was used, dehydrogenation took place

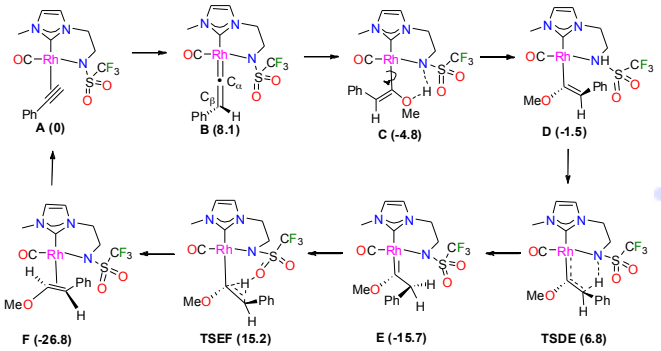
and acetone was obtained. For benzyl alcohol, the reaction showed no product formation. Interestingly, moderate yield of 35% was obtained for phenol in presence of a catalytic amount of 2,6-lutidine. The inability of bulkier alcohols to give hydroalkoxylated product suggests that the ligand-appended triflamide unit participates in the alcohol activation through hydrogen bonding interactions. Surprisingly, CF_3CH_2OH was also found unreactive under the reaction conditions. Although the acidity of CF_3CH_2OH is higher than ethanol, the conjugate base $CF_3CH_2O^-$ is not sufficiently nucleophilic to attack the Rh-vinylidene. High solvation of fluorinated alcohols may also contribute to its lack of activity.[17]

The hydroalkoxylation proceeds in a slightly alkaline DMAc solvent. We pondered whether **3** could activate terminal alkyne with acidic nucleophile. Remarkably, the selectivity in the addition of benzoic acid across phenylacetylene was completely reversed as M product was obtained in near quantitative yield (Scheme 5). In a separate experiment, when phenylacetylene, **3** and methanol were refluxed along with a few drops of ethereal hydrochloric acid, quantitative formation of the M hydration product acetophenone was observed similar to the acidic nucleophile. The contrast in product regioselectivity for acidic/basic nucleophiles demonstrates that a switch between metal-*π*–alkyne and metal-vinylidene intermediates could be achieved by changing the nucleophile and/or by controlling the acidity of the reaction medium.



Scheme 5. Selectivity of addition products.

Mechanistic investigation by deuterium labeling experiments was difficult due to rapid exchange of protons between methanol and phenylacetylene. DFT calculations at BPW91 level of theory were carried out using Gaussian 09 to rationalize a probable mechanism depicted in Scheme 6.[18] At first, alkyne substitution to one of the carbonyls in **3** takes place (**A**) directed by the strong *trans* effect of NHC. Rearrangement of terminal alkyne to vinylidene on a metal site has been studied extensively by computational and experimental techniques.[19] For Kakiuchi's catalyst, indirect 1,2–hydrogen shift promoted by 8–quinolinolato oxygen atom was proposed to be the most favorable pathway.[12] Nevertheless, a Rh–vinylidene intermediate **B** was computed to be endergonic by 8.1 kcal/mol. Next, we optimized a low lying intermediate **C** where the methanol proton migrates to the triflamide nitrogen (N–H = 1.06, O…H = 1.73 Å). The C_α–O bond length is 1.43 Å. A relevant transition state could not be located suggesting a facile proton movement without much of a kinetic barrier. NBO analyses showed negative charges on both Rh (-0.449) and C_β (-0.446) whereas C_α (+0.221) was electrophilic. Hence, a proton transfer from protonated ligand to C_α was not considered. Due to a large C_β–H separation, a rotamer intermediate along Rh–C_α was optimized. **D** facilitates a hydrogen migration from amido N to C_β *via* **TSDE** (E_a = 8.3 kcal/mol). Intermediate **E** is a Fischer type carbene containing two diastereomeric β–hydrogen atoms which undergoes 1,2–β–hydrogen shift to form a thermodynamically more stable metal-alkene complex.[20] A relevant transition state **TSEF** was located (rate limiting step) which revealed the involvement of a triflato oxygen for hydrogen shift (O···H = 1.85, C_α–H= 1.25, C_β–H = 1.56 Å), resulting in an enol ether coordinated Rh complex **F**. Overall, the addition reaction of phenylacetylene to methanol is exothermically driven as a weak π bond is broken and a strong σ bond is formed.

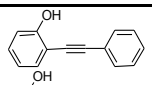
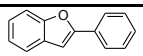
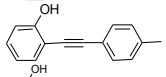
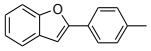
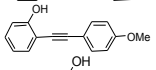
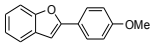
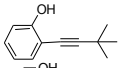
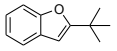
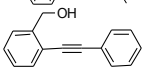
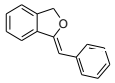
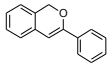
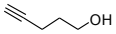


Scheme 6 Mechanism for intermolecular hydroalkoxylation catalyzed by **3**. Energies are shown in parentheses in kcal/mol relative to **A**.

We further evaluated the catalytic potential of **3** for intramolecular reactions. 2–(phenylethynyl)phenol was used as a model substrate and the reaction was performed in chloroform at 70°C. The 2–phenylbenzofuran was obtained in moderate yield (56%), but could be improved significantly on adding 5 mol% of Cs_2CO_3 as an additive (95%, entry 1, Table 2). Other aromatic alkynol derivatives also showed excellent yields although 2–(t-butylethynyl)phenol was less reactive (entries 2–4, Table 2). The reaction was extended to (2–(phenylethynyl)phenyl)methanol where two products are possible. NMR analysis showed that the *5–exo–dig* cyclized product formed exclusively (entry 5, Table 2). Intramolecular cycloisomerization is limited to internal alkynols, since a terminal alkynol (entry 6) rearranges to the corresponding metal-vinylidene that is rapidly trapped by an alcohol to afford a stable Fischer carbene complex.[21] This suggests that *π*–activation mechanism at the Rh center is the preferred pathway for intramolecular reactions that is in contrast to the intermediacy of metal-vinylidene for intermolecular reactions. Nonetheless, catalyst **3** is active for both inter and intramolecular hydroalkoxylations.

In conclusion, we have synthesized a triflamide-tethered NHC-Rh(I)$(CO)_2$ complex **3** which is an effective and versatile catalyst for both inter- and intramolecular hydroalkoxylation of terminal alkynes and alkynols respectively. The AM selectivity of the addition product was reversed for acidic nucleophiles. The potential of both amido nitrogen and triflato oxygen of the appended triflamide functionality for alcohol activation and hydrogen shift is realized. Further studies for water addition by a triflamide appendage are being actively pursued in our laboratory.

Table 2. Substrate scope for intramolecular hydroalkoxylation reaction.[a]

Entry	Substrate	Product	Yield (%)[b]
1			95
2			92
3			99
4			72
5			88
			0
6		n.r.	n.r.

[a] Alkynol (1 mmol) and Cs_2CO_3 (0.05 mmol) were sequentially added to a 3 mL $CHCl_3$ solution of the catalyst **3** (0.02 mmol) and the closed reaction vessel was heated at 70°C for 24h. [b] Isolated yields are reported. n.r. = no reaction.

Experimental Section

General procedure for intermolecular hydroalkoxylation: Alkyne (1 mmol), mesitylene (internal standard, 1 mmol) and MeOH (1 mL) were sequentially added to a 1 mL DMAc solution of the catalyst **3** (0.02 mmol) and the closed reaction vessel was heated at 70ºC for 24h. After completion of the reaction, the solutions were diluted to 10 mL with Et_2O and washed with LiCl solution (0.1 M, 2×10 mL). The organic phase was dried with saturated brine solution (20 mL) and Na_2SO_4, and the solvent was removed in vacuo. Products were analyzed using GC–MS and ^1H NMR spectroscopy.

Intramolecular hydroalkoxylation: Alkynol (1 mmol), mesitylene (internal standard, 1 mmol) and Cs_2CO_3 (0.05 mmol) were sequentially added to a 2 mL chloroform solution of the catalyst **3** (0.02 mmol) and the closed reaction vessel was heated at 70ºC for 24h. After completion of reaction, the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (eluent: hexane: ethyl acetate = 10:1) to give desired product.

Acknowledgements

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Keywords: alkyne hydroalkoxylation • nucleophilic addition • ligand design • triflamide • cyclization

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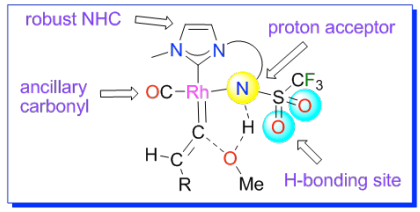
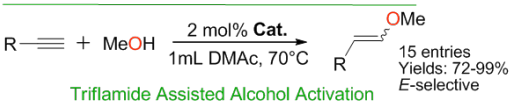
Alcohol Activation

A triflamide-tethered NHC-bound $Rh(I)(CO)_2$ catalyst is highly effective for both intermolecular hydroalkoxylation and intramolecular heteroannulation reactions.





Triflamide Assisted Alcohol Activation

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