Catalytic Cyclization of *o*-(Alkynyl)Phenethylamines via Osmacyclopropene Intermediates: A Direct Access to Dopaminergic 3-Benzazepines

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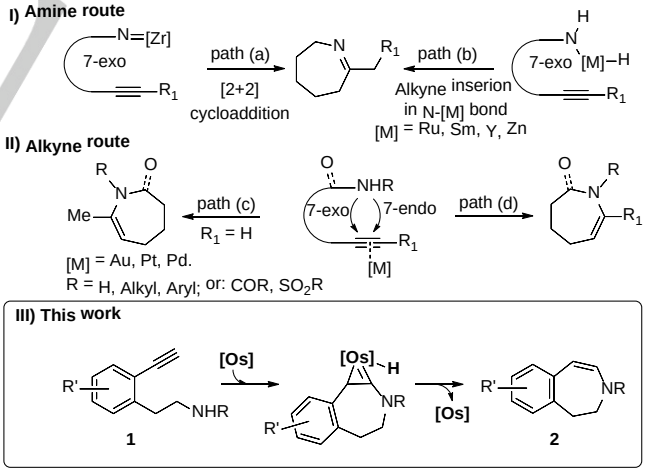
Dedication This article is dedicated to Prof. Antonio Echavarren on occasion of his 60th birthday

Abstract: A novel osmium-catalyzed cyclization of *o*-(alkynyl)phenethylamines to 3-benzazepines is reported. The procedure allows the easy preparation of a broad range of dopaminergic 3-benzazepine derivatives. The investigation of the mechanism has revealed that the process takes place through osmacyclopropene intermediates, which have been isolated and X-ray characterized.

The design of efficient procedures for the preparation of seven-membered 3-benzazepines is challenging, since they remain as one of the most reliable structural scaffold in terms of affinity and selectivity against the D_1 receptor, which is the most important and abundant in the mammalian brains for the dopamine neurotransmitter.[1] In this context, transition metal-mediated C-N bond formation strategies offer advantages in comparison with the classical synthesis of heterocycles, such as mild reaction conditions, readily accessible starting materials, and user friendly procedures.[2] For instance, the intramolecular hydroamination and hydroamidation of alkynes has been a successful atom economic approach for the formation of N-heterocycles.[3] Unfortunately, only a few efficient syntheses of seven-membered rings are known. This is mainly due to the scarce number of specific transition metal catalysts developed for these reactions and the little understanding of the mechanism of the processes, as a consequence of the very low number of intermediates that have been isolated and characterized.[4]

Typically, two general mechanisms have been considered:[5] (I) amine route, and (II) alkyne route (Scheme 1). The first of them is initiated by N-H activation and includes the participation of Zr-imido species, which afford cyclic imines by [2+2] cycloaddition between the C-C triple bond of the alkyne moiety and the imido N-M double bond (path a, Scheme 1),[6] or the formation of Ru-, Sm-, Y- and Zn-amido intermediates, which evolve by insertion of the C-C triple bond into the N-M single bond (path b, Scheme 1).[7] The alkyne route implies the initial π-coordination of the C-C triple bond to the metal center, and it has been proposed for the Au-catalyzed 7-*exo*-dig cyclization of terminal alkynyltosylamides (path c, Scheme 1),[8] the formation of diazepanones and oxazepines by means of Pt- and Au-mediated 7-*endo*-dig cyclization of alkynylamides and diynamides,[9] and the Au- and Pd-catalyzed 7-*endo*-dig cyclization of *o*-(alkynyl)phenylacetamides to the corresponding benzazepinones (path d, Scheme 1).[10] We now report a new Os-catalyzed 7-*endo*-dig cyclization of terminal *o*-(alkynyl)phenethylamines (**1**) to 2,3-dihydro-1*H*-benzo[*d*]azepines (**2**; commonly 3-benzazepines) that proceeds via a novel mechanism (III in Scheme 1) involving two metalacyclopropene intermediates, both of which have been isolated and characterized by X-ray diffraction analysis.



Scheme 1. Metal-catalyzed intramolecular hydroaminations and hydroamidations towards seven-membered nitrogenated heterocycles.

In the search for a specific catalyst and the optimum experimental conditions to perform this challenging cyclization, ruthenium, rhodium and platinum catalysts were initially employed, using N-(2-ethynylphenethyl)propane-1-amine (**1a**) as model substrate (Table 1). We began with complex $CpRuCl(PPh_3)_2$, which has been found be the optimal catalyst for the 5- and 6-*endo* cyclization of aromatic homo- and bis-homopropargylic amines and amides to indoles,

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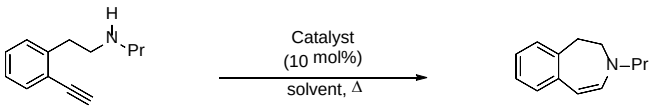
dihydroisoquinolines and dihydroquinolines.[3c] Encouragingly, the regioselective 7-*endo* cyclization of **1a** in pyridine occurred to give the desired 3-benzazepine **2a**, albeit in a low yield (run 1). Similar result was found with the bulkier and electron richer catalyst Cp*RuCl(PPh_3)$_2$ (run 2). The presence of pyridine is mandatory since its removal is detrimental for the reaction (run 3), even though a stoichiometric amount is enough (run 4). The reaction yield decreased when the bulkier 2-picoline was used (run 5), showing the importance of the pyridine as both a base and a ligand.[11] Modification of the electronic nature of the catalyst by using the ruthenium salt [CpRu(py)$_3$]PF_6 or a combination [CpRu(CH_3CN)$_3$]PF_6/ bypyridine, recently used for the anti-Markovnikov hydration of alkynes,[12] were detrimental for the reaction (runs 6 and 7). Finally, reactions performed with [RhCl(COD)]$_2$/(4-FC_6H_4)$_3$P (run 8) and $PtCl_2$ (run 9) were unsuccessful.

Table 1. Optimization of the reaction[a]



1a **2a**

Run	Catalyst	Solvent	Yield (%)[b]
1	CpRuCl(PPh_3)$_2$	Py	24
2	Cp*RuCl(PPh_3)$_2$	Py	20
3	CpRuCl(PPh_3)$_2$	Toluene	---
4	CpRuCl(PPh_3)$_2$	Toluene/ Py (1 equiv)	20
5	CpRuCl(PPh_3)$_2$	Toluene/Pic (1 equiv)	13
6	[CpRu(py)$_3$]PF_6	Py	5
7	[CpRu(CH_3CN)$_3$]PF_6/ Ligand[c]	DMF	--
8	[Rh(cod)Cl]$_2$/(4- FC_6H_4)$_3$P	Py	--[d]
9	$PtCl_2$	DCE	--[e]
10	[CpOs(py)$_3$]PF_6 (**3**)	Py	57(51)[f]
11	[CpOs(CH_3CN)$_2$(P^iPr_3)]PF_6 (**4**)	Py	52

[a] *Typical reaction conditions*: catalyst (10 mol %), 90 ºC, 24 h, [**1a**] = 0.05 M. [b] Yields calculated by ^{1}H NMR using trimethoxybenzene as internal standard. [c] Ligand 5,5'-bis(tri-fluoromethyl)-2,2'-bipyridine. [d] Starting material recovered. [e] Complex mixture. [f] In parenthesis, isolated yield. Pic = 2-picoline.

Osmium has received little attention in catalysis, although its stoichiometric chemistry is very rich.[13] Traditionally, it has been used to stabilize models of reactive intermediates proposed in reactions catalyzed by ruthenium and other metals.[14] However, recent findings have demonstrated that it is a promising alternative to the classical metal catalysts, in particular for promoting some environmental friendly reactions.[15] Five years ago, we showed that complex [CpOs(py)$_3$]PF_6 (**3**) is a more efficient catalyst than tungsten, ruthenium, and rhodium for the regioselective 7-*endo* heterocyclization of aromatic alkynols into benzoxepines.[16] Beller and co-workers have recently reported a high regioselective and general osmium-mediated hydroformylation of olefins to aldehydes.[17] These precedents prompted us to employ osmium complexes as catalysts, in view of the little efficiency of the tested ruthenium complexes. Gratifyingly, when the cyclization of **1a** was performed in the presence of a catalytic amount of complex **3**, the 3-benzazepine **2a** was formed in a fairly good yield (run 10). Similar results were achieved by using the electron richer catalyst [CpOs(CH_3CN)$_2$(P^iPr_3)]PF_6 (**4**; run 11). Hence the reaction conditions shown in run 10 were chosen for subsequent examination of the substrate scope of this transformation.

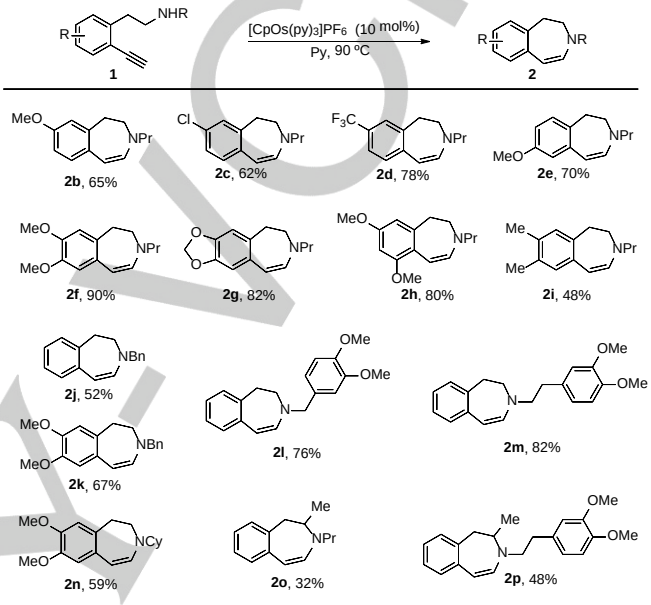


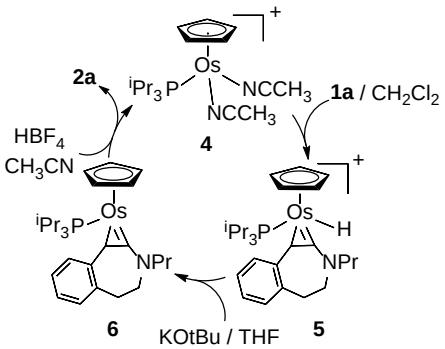
Figure 1. Os-catalyzed heterocyclization of *o*-(alkynyl)phenethylamines **1b**-**1p** towards 3-benzazepines **2b**-**p**[a,b]

We firstly examined the electronic effect of substituents, typically involved in dopaminergic properties, on the efficiency of the method. As illustrated in Chart 1, the heterocyclizations generally proceed in fairly good yields with monosubstituted electron rich and electron poor (*para*- or *meta*-substituents to the alkyne) to give 3-benzazepines **2b-e**. To our delight, disubstituted alkoxy derivatives **1f-h** smoothly and cleanly undergo the *7-endo* heterocyclization to the corresponding 3-benzazepines **2f-h** in good-to-excellent yields as compared to the monoalkoxy derivatives due, most likely, to the higher stability under the reaction conditions.[18] By contrast, the less electron rich dimethyl phenethylamine **1i** gave a moderate yield of dialkylated 3-benzazepine **2i**.

We subsequently evaluated the influence of different substituents on the amine, in order to favor future manipulations on the 3-benzazepines. Thus, while *N*-benzyl derivatives of parent or dimethoxy phenethylamines **1j** and **1k** gave moderate yields of the corresponding 3-benzazepines **2j,k**, the electron-richer *N*-(3,4-dimethoxy) benzyl or phenethyl derivatives of parent phenethylamine **1l** and **1m** cyclized smoothly to the corresponding 3-benzazepines **2l** and **2m** in fairly good yields. Phenethylamines bearing bulkier secondary *N*-alkyl substituents **1n-p**, also cyclized to the corresponding 3-benzazepines **2n-p**, although in low to moderate yieds.

Pyridine plays a main role in the catalysis. In order to isolate some reaction intermediates which allow us to obtain information about the reaction mechanism, we decided to study the

stoichiometric reaction of the phosphine catalyst **4** with **1a** in the absence of the heterocycle (Scheme 2). Treatment of dichloromethane solutions of **4** with 1.1 equiv of substrate, at room temperature for 5 h, led to the osmacyclopropene derivative **5**, which was isolated as an off-white solid in 60 % yield.

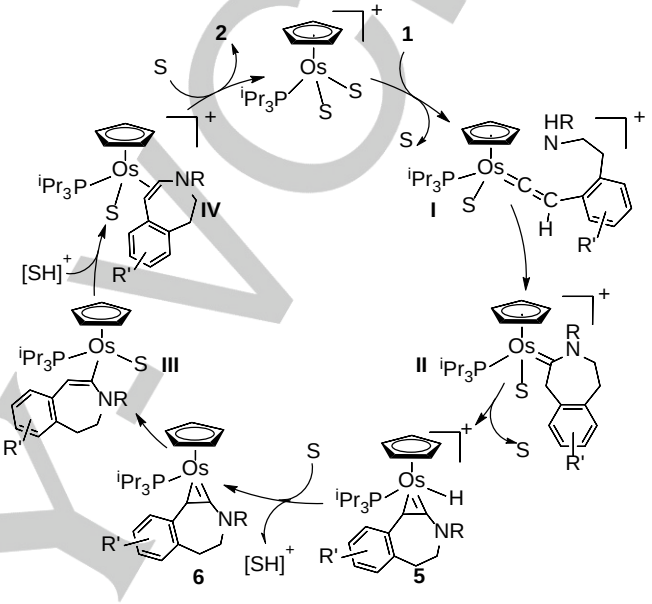


Scheme 2. Stoichiometric reactions.

The X-ray structure of **5**[19] proves the formation of the osmacyclopropene moiety, which implies the oxidation of the metal center by two units. Thus, the distribution of ligands around the metal center is the expected one for a cyclopentadienyl-osmium (IV) species and can be described as a four-legged piano-stool geometry, with the cyclopentadienyl group occupying the three membered face whereas the C(1) and C(2) atoms of the metalacycle, the hydride ligand, and the phosphine lie in the four-membered face. The Os-(C1) and Os-C(2) bond lengths of 1.941(6) and 2.219(8) Å, respectively, compare well with those found in other osmacyclopropene compounds,[20] and support the double and single character of the bonds. In agreement with this, the $^{13}C\{^1H\}$ NMR spectrum contains a low field C(1)-resonance at 207.5 ppm and a high field C(2)-resonance at -12.7 ppm. In the ^1H NMR spectrum the most noticeable signal is the corresponding to the hydride ligand, which is observed at -13.73 ppm as a doublet with a H-P coupling constant of 33 Hz.

Complex **5** is certainly a species of the catalytic cycle. As a proof of concept, it catalyzed the heterocyclization of **1a** to give **2a** in 62% yield, after 24 h, under the same experimental conditions as those employed for the reaction with **4** (Table 1, run 11). The formation of this intermediate can be rationalized according to Scheme 3, which summarizes a mechanistic proposal for the catalysis, on the basis of the stoichiometric cycle shown in Scheme 2. The addition of the substrate to the metal center should produce the tautomerization of the carbon-carbon triple bond to initially afford the vinylidene **I**. Thus, according to the respective electrophilic and nucleophilic nature of the C_α and C_β atoms, the carbon-carbon double bond of the allene could add the N-H bond of the amine function[21] to give the azacycloalkylidene **II**, which should evolve into **5** by oxidative addition of one of the C_β-H bonds of the seven-membered ring.

The M-alkylidene to M-olefin rearrangement is present in many catalytic transformations, and it is particularly favored when the alkylidene has a C_β-H bond as here.[22] Complex **5** is the key intermediate in the M-alkylidene to M-olefin transformation involved in this case (**II→5→6→III→IV**), which is promoted by pyridine. The hydride ligand in **5** if fairly acidic, as a consequence of the cationic nature of the complex. Thus, it should undergo deprotonation by action of the basic solvent, to afford **6**. This compound would be in equilibrium with the η^1-cycloalkenyl intermediate **III**. In this context, it should be noted that the metalacyclopropene to metal-alkenyl transformation implies a simple C_α-C_β dissociation. Once intermediate **III** has been formed, protonation of the C_α atom of the alkenyl ligand by the pyridinium, generated previously by deprotonation of **5**, could afford olefin derivative **IV**, regenerating the catalyst and releasing the reaction product.



Scheme 3. Proposed catalytic cycle.

Intermediate **6** was also isolated and characterized by X-ray diffraction analysis.[19] As expected, the addition of 1.0 equiv of KO*t*Bu to tetrahydrofurane solutions of **5**, at room temperature, produces the deprotonation of the metal center and the formation of **6**, which was isolated as an orange solid in 88% yield. Figure 1b shows a view of its structure. The most interesting feature is the disposition of the C(2)-H bond which, in contrast to **5**, points away from the cyclopentadienyl ligand. The inversion of the configuration of C(2) is a strong indirect evidence in favor of the η^1-alkenyl intermediate **III**, since the process requires the rupture of the Os-C(2) bond of **6**. Furthermore, in agreement with the cycle shown in Scheme 3, the addition of 1.0 equiv of HBF_4•OEt_2 to acetonitrile solutions of **6** releases **2a** and regenerates **4** (Scheme 2). The geometry around the metal center of **6** is close to octahedral, with the cyclopentadienyl ligand occupying three sites of a face. The reduction of the metal center as a consequence of its deprotonation has not any influence in the metalacyclopropene. Thus, the Os-C(1) and Os-C(2) bond lengths of 1.926(2) and 2.208(2)Å, respectively, are statistically identical to those of **5**, whereas the chemical shifts for the C(1) (δ, 214.7) and C(2) (δ, -5.9) resonances in the $^{13}C\{^1H\}$ NMR spectrum are also similar to those of **5**.

In conclusion, an efficient osmium-catalyzed heterocyclization of *o*-(alkynyl)phenethylamines, which allows the easy preparation of a wide range of dopaminergic 3-benzazepines, has been discovered. The process takes place

via osmacyclopropene intermediates, which have been isolated and characterized by X-ray diffraction analysis.

Acknowledgements

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Keywords: benzazepines • cyclization • osmium catalysts • osmacyclopropenes • phenethylamines

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[18] ^{1}H NMR monitoring showed no significant variation in the kinetics of formation of unsubstituted 3-benzazepine **2a** and dialkoxy derivative **2f**.

[19] CCDC 1408065 (**5**) and 1408066 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For ORTEP diagrams of complexes **5** and **6**, see Supporting Information.

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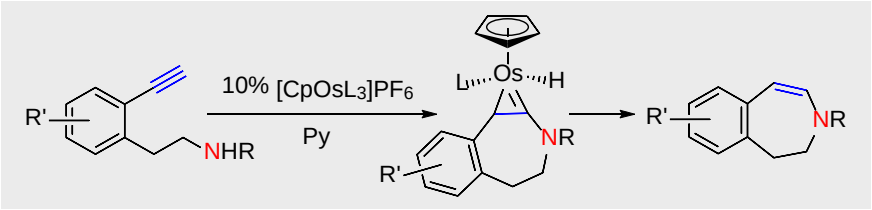

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