Heterocycle Synthesis

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

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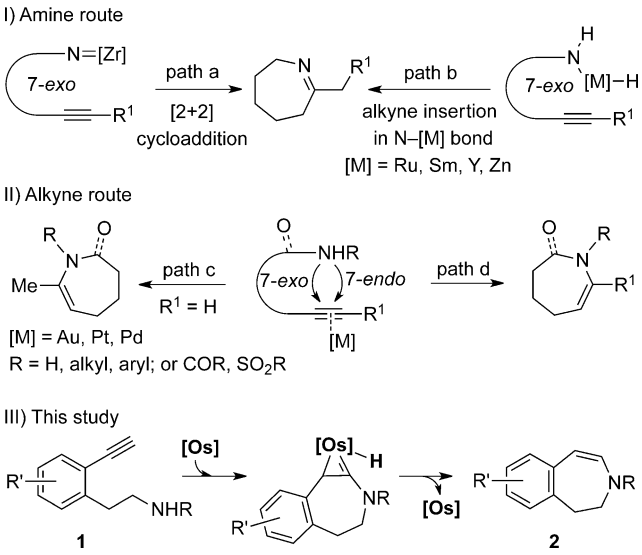
Dedicated to Professor Antonio Echavarren on the occasion of his 60th birthday

Abstract: *A novel osmium-catalyzed cyclization of o-alkynyl phenethylamines to give 3-benzazepines is reported. The procedure allows the straightforward preparation of a broad range of dopaminergic 3-benzazepine derivatives. Mechanistic investigations revealed that the process takes place via osmacyclopropene intermediates, which were isolated and characterized by X-ray crystallography.*

The design of efficient procedures for the preparation of seven-membered 3-benzazepines is a significant challenge, since they are among the most reliable structural scaffolds in terms of affinity and selectivity for the D_1 receptor, which is the most important and abundant receptor in mammalian brains for the dopamine neurotransmitter.[1] In this context, transition-metal-mediated C–N bond-formation strategies offer advantages in comparison with classical approaches to the synthesis of heterocycles, such as mild reaction conditions, readily accessible starting materials, and user-friendly procedures.[2] For example, the intramolecular hydroamination and hydroamidation of alkynes is a successful atom-economical approach for the formation of N-heterocycles.[3] Unfortunately, only a few efficient syntheses of seven-membered rings are known, mainly because of the scarcity of specific transition-metal catalysts that have been developed for these reactions and the poor 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) the amine route and II) the alkyne route (Scheme 1). The first is initiated by N–H activation and includes the participation of a zirconium–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 by the formation of ruthenium–, samarium–, yttrium–, and zinc–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 gold-catalyzed 7-*exo*-dig cyclization of terminal alkynyl tosylamides (path c, Scheme 1),[8] the formation of diazepanones and oxazepines by means of the platinum- and gold-mediated 7-*endo*-dig cyclization of alkynyl amides and diynamides,[9] and the gold- and palladium-catalyzed 7-*endo*-dig cyclization of *o*-alkynyl phenylacetamides to the corresponding benzazepinones (path d, Scheme 1).[10] We now report a new osmium-catalyzed 7-*endo*-dig cyclization of terminal *o*-alkynyl phenethylamines **1** to give 2,3-dihydro-1*H*-benzo[*d*]azepines **2** (commonly known as 3-benzazepines). The reaction proceeds by a novel mechanism (Scheme 1, III) involving two osmacyclopropene intermediates, both of which have been isolated and characterized by X-ray diffraction analysis.



Scheme 1. Metal-catalyzed intramolecular hydroamination and hydroamidation reactions towards seven-membered nitrogenated heterocycles.

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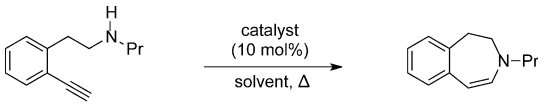
In the search for a specific catalyst and the optimum experimental conditions for this challenging cyclization, we initially used ruthenium, rhodium, and platinum catalysts with *N*-(2-ethynylphenethyl)propane-1-amine (**1a**) as a model substrate (Table 1). We began with the complex [CpRuCl-

Table 1: Optimization of the reaction.[a]



1a **2a**

Entry	Catalyst	Solvent	Yield [%][b]
1	$[CpRuCl(PPh_3)_2]$	pyridine	24
2	$[Cp^*RuCl(PPh_3)_2]$	pyridine	20
3	$[CpRuCl(PPh_3)_2]$	toluene	–
4	$[CpRuCl(PPh_3)_2]$	toluene/pyridine (1 equiv)	20
5	$[CpRuCl(PPh_3)_2]$	toluene/2-picoline (1 equiv)	13
6	$[CpRu(py)_3]PF_6$	pyridine	5
7	$[CpRu(CH_3CN)_3]PF_6$/ligand[c]	DMF	–
8	$[\{Rh(cod)Cl\}_2]/(4\text{-}FC_6H_4)_3P$	pyridine	–[d]
9	$PtCl_2$	DCE	–[e]
10	$[CpOs(py)_3]PF_6$ (**3**)	pyridine	57 (51)[f]
11	$[CpOs(CH_3CN)_2(P\mathit{i}Pr_3)]PF_6$ (**4**)	pyridine	52

[a] Typical reaction conditions: 90 °C, 24 h, [**1a**] = 0.05 M. [b] The yield was calculated by ^1H NMR spectroscopy by using trimethoxybenzene as an internal standard. [c] 5,5′-Bis(trifluoromethyl)-2,2′-bipyridine was used as a ligand. [d] Starting material was recovered. [e] A complex mixture was obtained. [f] The yield of the isolated product is given in parenthesis. cod = 1,5-cyclooctadiene, Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl, DCE = 1,2-dichloroethene, DMF = *N*,*N*-dimethylformamide, py = pyridine.

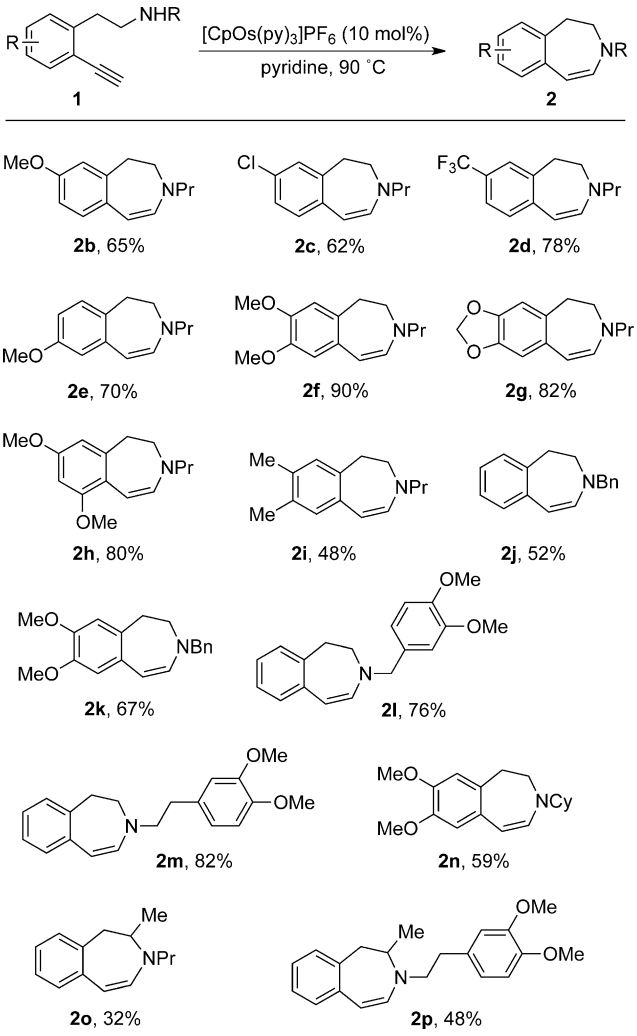
$(PPh_3)_2]$, which was found be the optimal catalyst for the 5- and 6-*endo* cyclization of aromatic homo- and bis-homopropargylic amines and amides to give indoles, dihydroisoquinolines, and dihydroquinolines.[3c] Encouragingly, the regioselective 7-*endo* cyclization of **1a** in pyridine occurred to give the desired 3-benzazepine **2a**, albeit in low yield (Table 1, entry 1). A similar result was found with the bulkier and more electron rich catalyst $[Cp^*RuCl(PPh_3)_2]$ (Table 1, entry 2). The presence of pyridine is mandatory; its removal was detrimental for the reaction (Table 1, entry 3), even though a stoichiometric amount was sufficient (entry 4). The reaction yield decreased when the bulkier derivative 2-picoline was used (Table 1, entry 5), thus showing the importance of 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 the combination $[CpRu(CH_3CN)_3]PF_6$/bipyridine, recently used for the anti-Markovnikov hydration of alkynes,[12] were detrimental to the reaction (Table 1, entries 6 and 7). Finally, reactions performed with $[\{RhCl(cod)\}_2]/(4\text{-}FC_6H_4)_3P$ (Table 1, entry 8) and $PtCl_2$ (entry 9) were unsuccessful.

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 for reactions catalyzed by ruthenium and other metals.[14] However, recent findings have demonstrated that it is a promising alternative to classical metal catalysts, in particular for promoting some environmentally friendly reactions.[15] Five years ago, we showed that the complex $[CpOs(py)_3]PF_6$ (**3**) is a more efficient catalyst than tungsten, ruthenium, and rhodium complexes for the regioselective 7-*endo* heterocyclization of aromatic alkynols to give benzoxepines.[16] Beller and co-workers recently reported a highly regioselective and general osmium-mediated hydroformylation of olefins to afford aldehydes.[17] These reactions prompted us to employ osmium complexes as catalysts, in view of the low 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 fairly good yield (Table 1, entry 10). Similar results were observed with the more electron rich catalyst $[CpOs(CH_3CN)_2(P\mathit{i}Pr_3)]PF_6$ (**4**; Table 1, entry 11). Hence, the reaction conditions shown in entry 10 of Table 1 were chosen for subsequent examination of the scope of this transformation.

We first examined the electronic effect of substituents, which are typically important for dopaminergic properties, on the efficiency of the method. The heterocyclization generally proceeded in fairly good yield with monosubstituted electron-rich and electron-poor substrates (with a substituent *para* or *meta* to the alkyne) to give 3-benzazepines **2b**–**e** (Scheme 2). To our delight, the dialkoxy-substituted derivatives **1f**–**h** smoothly and cleanly underwent the *7-endo* heterocyclization to give the corresponding 3-benzazepines **2f**–**h** in good to excellent yield. The higher yields as compared to those observed for the monoalkoxy derivatives are most likely due to the higher stability of the products under the reaction conditions.[18] By contrast, the less electron rich dimethyl phenethylamine **1i** was converted into the dialkyl-substituted 3-benzazepine **2i** in moderate yield.

We subsequently evaluated the influence of different substituents on the amine to favor future manipulation of the 3-benzazepines. Thus, whereas *N*-benzyl derivatives **1j** and **1k** of the parent phenethylamine or a dimethoxy analogue gave the corresponding 3-benzazepines **2j**,**k** in moderate yield, the more electron rich *N*-(3,4-dimethoxy)benzyl or *N*-(3,4-dimethoxy)phenethyl derivatives **1l** and **1m** of the parent phenethylamine underwent smooth cyclization to the corresponding 3-benzazepines **2l**,**m** in fairly good yield. Phenethylamines **1n**–**p** bearing bulkier secondary *N*-alkyl substituents also cyclized to the corresponding 3-benzazepines **2n**–**p**, although in low to moderate yield.

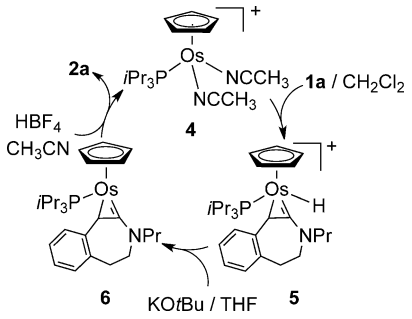
Pyridine plays a major role in the catalysis. To isolate some reaction intermediates from which we could obtain information about the reaction mechanism, we decided to study the stoichiometric reaction of the phosphine catalyst **4**



Scheme 2. Osmium-catalyzed heterocyclization of *o*-alkynyl phenethylamines **1b–p** to give 3-benzazepines **2b–p**. Isolated yields are indicated. Bn = benzyl, Cy = cyclohexyl.

with **1a** in the absence of the heterocycle (Scheme 3). The treatment of solutions of **4** in dichloromethane with the substrate (1.1 equiv) at room temperature for 5 h led to the osmacyclopropene derivative **5**, which was isolated as an off-white solid in 60% yield.

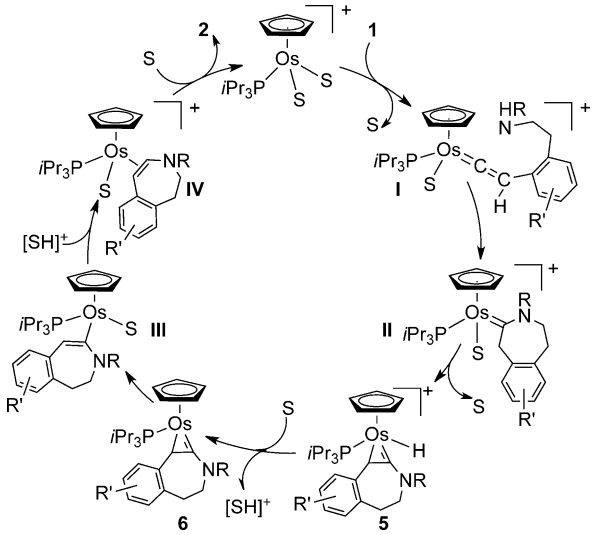
The X-ray crystal structure of **5**[19] proved the formation of the osmacyclopropene moiety, which implies the oxidation of the metal center by two units. Thus, the distribution of ligands



Scheme 3. Stoichiometric reactions.

around the metal center is that expected for a cyclopentadienyl osmium(IV) species and can be described as a four-legged-piano-stool geometry, in which the cyclopentadienyl group occupies the three-membered face, and the two C atoms of the metallacycle, the hydride ligand, and the phosphine ligand lie in the plane of the four-membered face. The Os–C(1) 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 structure, the $^{13}C\{^1H\}$ NMR spectrum contained a low-field C(1) resonance at 207.5 ppm and a high-field C(2) resonance at −12.7 ppm. The most noticeable signal in the ^1H NMR spectrum was that corresponding to the hydride ligand and was observed at −13.73 ppm as a doublet with an H–P coupling constant of 33 Hz.

Complex **5** is certainly a species involved in 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, entry 11). The formation of this intermediate can be rationalized according to Scheme 4, which summarizes



Scheme 4. Proposed catalytic cycle.

a mechanistic proposal for the catalysis on the basis of the stoichiometric cycle shown in Scheme 3. The addition of the substrate to the metal center should lead to tautomerization of the carbon–carbon triple bond to initially afford the vinylidene complex **I**. Thus, according to the electrophilic and nucleophilic nature of the C_α and C_β atoms, respectively, the N–H bond of the amine functionality could add to the carbon–carbon double bond of the allene[21] to give the azacycloalkylidene **II**, which could evolve into **5** by oxidative addition of one of the C_β–H bonds of the seven-membered ring.

The metal–alkylidene to metal–alkene rearrangement is present in many catalytic transformations, and it is particularly favored when the alkylidene has a C_β–H bond, as in this case.[22] In this case, complex **5** is the key intermediate in the

osmium–alkylidene to osmium–alkene transformation (**II**→**5**→**6**→**III**→**IV**), which is promoted by pyridine. The hydride ligand in **5** is fairly acidic, as a consequence of the cationic nature of the complex. Thus, it should undergo deprotonation under the action of the basic solvent to afford **6**. This compound would be in equilibrium with the η^1-cycloalkenyl intermediate **III**. The transformation of the metallacyclopropene into the alkenyl metal complex 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 cation, generated previously by the deprotonation of **5**, could afford the osmium–alkene complex **IV** to regenerate the catalyst and release the reaction product.

Intermediate **6** was also isolated and characterized by X-ray diffraction analysis.[19] As expected, the addition of KO*t*Bu (1.0 equiv) to solutions of **5** in THF at room temperature led to deprotonation of the metal center and the formation of **6**, which was isolated as an orange solid in 88% yield. The most interesting feature is the orientation of the C(2)–H bond, which, in contrast to the structure of **5**, points away from the cyclopentadienyl ligand. The inversion of the configuration of C(2) is 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 4, the addition of $HBF_4{\cdot}OEt_2$ (1.0 equiv) to solutions of **6** in acetonitrile led to the release of **2a** and regeneration of **4** (Scheme 3). 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 no influence on the metallacyclopropene. 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) ($\delta = 214.7$ ppm) and C(2) resonances ($\delta = -5.9$ ppm) 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 has been discovered that enables the straightforward preparation of a wide range of dopaminergic 3-benzazepines. The process takes place via osmacyclopropene intermediates, which have been isolated and characterized by X-ray diffraction analysis.

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[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. For ORTEP diagrams of complexes **5** and **6**, see the Supporting Information.

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