CHEMISTRY
A European Journal

A Journal of
ChemPubSoc Europe

Accepted Article

Title: Efficient Endo Cycloisomerization of Terminal Alkynols Catalyzed by a New Ruthenium Complex with 8-(Diphenylphosphino)-quinoline Ligand and Mechanism Investigation

Authors: Tao Cai, Yu Yang, Wei-Wei Li, Wen-Bing Qin, and Ting-Bin Wen

To be cited as: *Chem. Eur. J.* 10.1002/chem.201703971

Link to VoR: http://dx.doi.org/10.1002/chem.201703971

Supported by
ACES

WILEY-VCH

10.1002/chem.201703971

WILEY-VCH

Efficient *Endo* Cycloisomerization of Terminal Alkynols Catalyzed by a New Ruthenium Complex with 8-(Diphenylphosphino)-quinoline Ligand and Mechanism Investigation

Tao Cai,[a] Yu Yang,[a] Wei-Wei Li,[a] Wen-Bing Qin,[a] and Ting-Bin Wen*[a]

Abstract: Several new ruthenium complexes supported by the P,N-donor ligand 8-(diphenylphosphino)quinoline (DPPQ) were synthesized, including $RuCl_2(DPPQ)_2$ (**1**), $[Ru(\mu\text{-}Cl)(DPPQ)_2]_2(BPh_4)_2$ (**2**) and $[RuCl(DPPQ)_2Py](BF_4)$ (**3**). Complex **2**, with only 1 mol% loading, was found to be catalytically active for the *endo* cycloisomerization of various terminal alkynols to *endo*-cyclic enol ethers in moderate to excellent yields. In particular, the 7- and 8-*endo* heterocyclization can be achieved efficiently to give the seven-membered 3-benzoxepine and eight-membered 3-benzo[*d*]oxocine derivatives. The stoichiometric reactions of **2** with various alkynol substrates have been carried out to investigate the mechanism, which led to a series of seven-, six-, and five-membered oxacyclocarbene ruthenium complexes including $[RuCl(DPPQ)_2\{=CCH_2C_6H_4CH_2CH_2O\}](BPh_4)$ (**12**) and $[RuCl(DPPQ)_2\{=CCH_2(CH_2)_nCH_2O\}](BPh_4)$ (n = 3, **12'**; n = 2, **13**; n = 1, **14**). The quantitative transformation of oxacyclocarbene **12** into catalyst **2** and 3-benzoxepine **5a** as well as the efficient catalytic activity of **12** for the *endo*-cyclization of **4a** demonstrated that **12** is a key intermediate involved in the catalytic cycle. Moreover, comparative studies on the modeling reactions and catalytic activity of the series of oxacyclocarbene complexes indicated that the different catalytic activity of **2** for the *endo*-cycloisomerization of different types of alknynols can be related to the reactivity of the respective ruthenium oxacyclocarbene intemediates.

Introduction

The widespread occurrence of oxygen-containing heterocycles in natural products and biologically active molecules[1] have stimulated considerable interest in developing efficient homogeneous catalytic methods for the synthesis of such heterocyclic compounds.[2,3] The catalytic cycloisomerization of alkynols represents an atom-economic pathway to afford cyclic enol ethers, which are very useful synthetic intermediates in the construction of diverse oxygen-containing heterocycles.[4] Various transition metals like molybdenum,[5] tungsten,[6] copper,[7] palladium,[8] platinum,[9] silver,[10] gold,[11] ruthenium,[12] rhodium,[13] and osmium[14] have been explored as catalysts for these cycloisomerization reactions. In general, molybdenum, tungsten, ruthenium, osmium and rhodium systems were proposed to proceed through intramolecular nucleophilic addition of the hydroxyl group to a transition metal vinylidene intermediate, while copper, gold, platinum and palladium systems were proposed to proceed through hydroxyl group addition to one carbon of a η^2-alkyne intermediate. Cycloisomerization of alkynols through metal vinylidene intermediates can regioselectively lead to endo-cyclic enol ethers, while those reactions proceed through metal-alkyne π-complex can lead to either *exo*- or *endo*-cyclic enol ethers.

In the past decades, there have been growing efforts in the *endo* cycloisomerization of alkynyl alcohols to *endo*-cyclic enol ethers through metal vinylidene intermediates. However, it appears that most of the studies so far mainly focus on the methodologies for the synthesis of five- and six-membered oxacycles. Pioneer work in this area using molybdenum and tungsten carbonyl complexes as the catalysts has been developed by McDonald and co-workers to successfully cycloisomerize a range of alkynols into dihydrofuran and dihydropyran derivants.[5,6a,6b,6d,6f] Other seminal studies were carried out by Trost later, using catalytic vinylidene species generated from the cationic ruthenium system $(CpRuCl(PAr_3)_2/n\text{-}Bu_4N(PF_6)$[12a] or rhodium system $([Rh(cod)Cl]_2/PAr_3)$[13a] in the *endo* cycloisomerization of homopropargyl and bis-homopropargyl alcohols. A related rhodium-catalyzed efficient heterocyclization of 2-ethynyl-anilines or -phenols (aromatic homopropargylic alcohols) to indoles or benzofurans has been also described.[15] Shortly after, Saá and Zacuto found that $CpRuCl(PPh_3)_2$ complex accompanied with amines or PPh_3 ligand can be also used for the effective *endo* cycloisomerization of aromatic homo- and bis-homopropargylic alcohols or amino-substituted bis-homopropargylic alcohols to afford benzofurans or dihydropyrans.[12c,12e] By contrast, transition-metal catalyzed *endo* cycloisomerization of alkynols into the larger seven- and eight-membered oxacycles as well as their nine- and ten-membered counterparts remains a challenging objective, which is still limited to a few scattering reports on the 7- and 8-*endo* cycloisomerization only. In 2010, Jia and coworkers reported the smooth cycloisomerization of various alkynols with C≡C attached to aryl or alkyl groups into five- and six-membered *endo*-cyclic enol ethers in good to excellent yields catalyzed by the new ruthenium complex $[Ru(N_3P)(OAc)](BPh_4)$ with a tetradentate N_3P ligand (N_3P = N,N-bis[(pyridin-2-yl)methyl]-[2-(diphenylphosphino)phenyl]methanamine),[12d] wherein one example of 7-*endo* cycloisomerization of the 5-hexyn-1-ol into the 2,3,4,5-tetrahydrooxepine was also described. Almost at the same time, Esteruelas *et al.* developed the 7-*endo* cycloisomerization of aromatic alkynols (including one example of benzylic alkynyl alcohol) to benzoxepine derivatives as well as one example of 8-*endo* cyclization of aromatic alkynol by employing $[CpOs(py)_3](PF_6)$ complex as the catalysts.[14a] In addition, heterocyclization of alkynols into seven-membered oxepines has been also achieved by McDonald in 2004 *via* tungsten-vinylidene intermediates, however, the specific alkynyldiol substrates in the presence of acetonide protecting

[a] T. Cai, Y. Yang, W.-W. Li, W.-B. Qin and Prof. Dr. T.-B. Wen
Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, Fujian 361005, P.R. China
E-mail: chwtb@xmu.edu.cn

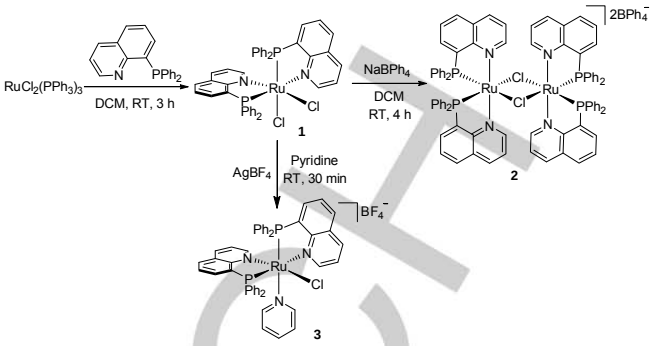
Supporting information for this article is given via a link at the end of the document.

group were required.[6f,6k] Therefore, the development of new efficient catalysts for the selective synthesis of larger oxygen-containing heterocyclic compounds are highly desirable, especially for the seven- and eight-membered candidates in view of their importance in organic synthesis as well as their attractive biological significance.[16]

On the other hand, 8-quinolylphosphine ligands possess two donor groups with different electronic characters, a phosphino group with a strong π-acidity and a quinoline group as a moderate σ-donor, and can act as unsymmetrical bidentate ligands to form a five-membered chelate ring with transition metals.[17] Such an electronic differentiation of this ligand may stabilize unusual oxidation states or coordination geometries for the metal centers, and thus may confer novel structural, spectroscopic, and photophysical properties as well as intriguing reactivities to the complexes.[18] Palladium and nickel complexes with 8-quinolylphosphine ligands have been proved to be catalytically active for the reductive carbonylation of nitrobenzene[18a], ethylene polymerization,[18b,18d] and methoxycarbonylation of olefins.[18e] For ruthenium, only two reports have described the syntheses and electrochemical property studies of a series of ruthenium bipyridine or polypyridine complexes bearing 8-quinolylphosphine ligands.[18c,18f] In the search of efficient catalysts for the *endo*-cycloisomerization of alkynols, we have now synthesized several new ruthenium complexes with the heterobidentate P,N-donor ligand 8-(diphenylphosphino)quinoline (DPPQ), including $RuCl_2(DPPQ)_2$ (**1**), $[Ru(\mu\text{-}Cl)(DPPQ)_2]_2(BPh_4)_2$ (**2**) and $[RuCl(DPPQ)_2Py](BF_4)$ (**3**). Complex **2**, with only 1 mol% loading, was found to be catalytically active for the *endo* cycloisomerization of various alkynols to the corresponding *endo*-cyclic enol ethers in moderate to excellent yields. In particular, the 7-*endo* and 8-*endo* heterocyclization of aromatic alkynols can be achieved efficiently to give seven-membered 3-benzoxepine and eight-membered 3-benzo[*d*]oxocine derivatives. The stoichiometric reactions of catalyst **2** with various alkynol substrates and the comparative studies on the modeling reactions of the oxacyclocarbene ruthenium complexes thus obtained have been carried out to investigate the mechanism for the *endo* cycloisomerization reaction. Herein, we reported the details of these studies.

Results and Discussion

Preparation and characterization of DPPQ ruthenium complexes $RuCl_2(DPPQ)_2$ (1), $[Ru(\mu\text{-}Cl)(DPPQ)_2]_2(BPh_4)_2$ (2), and $[RuCl(DPPQ)_2Py](BF_4)$ (3): The synthetic routes to complexes **1**-**3** are outlined in Scheme 1. The ruthenium complex $RuCl_2(DPPQ)_2$ (**1**) can be readily obtained by treatment of $RuCl_2(PPh_3)_3$ with DPPQ in a ratio of 1:2 in CH_2Cl_2 at room temperature, which was isolated as a red solid in 96% yield. Complex **1** is almost insoluble in toluene and only slightly soluble in CH_2Cl_2 and $CHCl_3$. We have also performed the reaction of $RuCl_2(PPh_3)_3$ with 1.0 equiv of DPPQ ligand in an attempt to obtain the mono-DPPQ product $RuCl_2(DPPQ)(PPh_3)$, however, the reaction led to an intractable mixture containing the *bis*-DPPQ complex **1** and other unknown species, even when a diluted solution of DPPQ ligand was added dropwise to a solution of $RuCl_2(PPh_3)_3$ in either CH_2Cl_2 or toluene.



Scheme 1. Preparation of complexes **1**, **2** and **3**

Complex **1** has been characterized by NMR spectroscopy, elemental analysis as well as X-ray single crystal diffraction. A view of the molecular structure of **1** is shown in Figure 1 with selected bond lengths and angles. The coordination geometry around the ruthenium center can be described as a distorted octahedron with the two chloride ligands in a *cis*-arrangement (Cl(1)-Ru(1)-Cl(2), 92.33(3)°). The two DPPQ ligands chelate to Ru nearly perpendicularly to each other with the P atom of one of the DPPQ ligands *trans* to one Cl (P(1)-Ru(1)-Cl(1), 171.59(3)°), while the N atom *trans* to the P atom of the other DPPQ ligand (N(1)-Ru(1)-P(2), 177.78(7)°). Consistent with the solid state structure, the ^{31}P NMR spectrum (in $CDCl_3$) of **1**

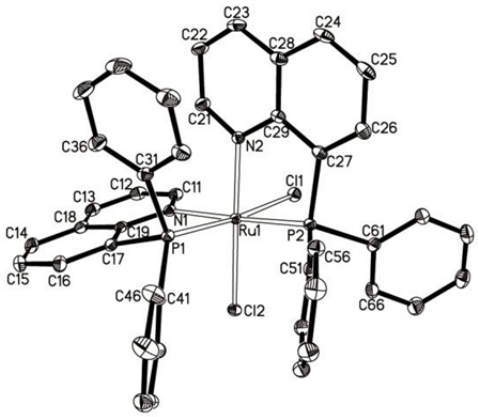


Figure 1. Molecular structure of **1** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru(1)-N(1) 2.189(2), Ru(1)-N(2) 2.084(2), Ru(1)-P(1) 2.2510(8), Ru(1)-P(2) 2.2470(8), Ru(1)-Cl(1) 2.4904(7), Ru(1)-Cl(2) 2.4550(7); N(1)-Ru(1)-P(2) 177.78(7), P(1)-Ru(1)-Cl(1) 171.59(3), N(2)-Ru(1)-Cl(2) 177.63(7), N(2)-Ru(1)-Cl(1) 85.39(7), N(1)-Ru(1)-Cl(1) 90.82(7), P(2)-Ru(1)-Cl(1) 87.79(3), Cl(2)-Ru(1)-Cl(1) 92.33(3), N(2)-Ru(1)-N(1) 94.75(9), N(2)-Ru(1)-P(2) 83.42(7), N(2)-Ru(1)-P(1) 91.90(7), N(2)-Ru(1)-P(1) 81.46(7), P(2)-Ru(1)-P(1) 99.82(3), N(1)-Ru(1)-Cl(2) 84.65(7), P(2)-Ru(1)-Cl(2) 97.13(3), P(1)-Ru(1)-Cl(2) 90.28(3).

exhibited two doublet signals at 62.2 and 53.9 (J(PP) = 33.4 Hz) ppm, indicating the presence of two inequivalent phosphorous nuclei.

Treatment of **1** with sodium tetraphenylborate in CH_2Cl_2 for 4 h at room temperature gave an orange solution, from which the dicationic dimeric complex $[Ru(\mu\text{-}Cl)(DPPQ)_2]_2(BPh_4)_2$ (**2**) was isolated almost quantitatively. Apparently, the cationic monochloro species $[RuCl(DPPQ)_2]^+$ generated via chloride abstraction dimerized in the solution to give complex **2**. In contrast, when **1** was treated with 1.0 equiv of $AgBF_4$ in pyridine at room temperature for 30 min, the pyridine coordinated monocatonic complex $[RuCl(DPPQ)_2Py](BF_4)$ (**3**) was isolated as an orange solid in 98% yield. Both complexes **2** and **3** have been characterized by multinuclear NMR spectroscopy and elemental analysis. The structures of **2** and **3** have also been confirmed by X-ray diffraction studies.

Figure 2 shows the X-ray structure for the cation of complex **2**, which reveals a doubly-chloro-bridged dinuclea structure. The crystal of **2** belongs to the centrosymetric space group *C*2/*c*, and the structure has a crystallographic C_2 symmetry with the 2-fold axis passing through Cl(1) and Cl(2), and thus the asymmetric unit contains only half a molecule of **2**. The coordination geometry around each ruthenium center can be described as a distorted octahedron. The two N atoms of the two chelated DPPQ ligands are *trans* to each other, occupying the axial positions. and the two P atoms are *cis*-disposed and lie in the equatorial plane together with the two bridging chlorides. Consequently, the four DPPQ ligands in complex **2** are chemically equivalent, as was also reflected by the ^{31}P NMR spectrum of **2**, which displayed a singlet only at 63.5 ppm (in CD_2Cl_2).

The structure for the cation of **3** is shown in Figure 3, which is similar to that of **1**, with the Cl *trans* to the P atom in **1** replaced by a pyridine. Again, as was the case for **1**, the ^{31}P NMR spectrum of **3** exhibited two doublet signals for the two inequivalent DPPQ ligands at 58.5 and 57.6 (J(PP) = 33.8 Hz) ppm (in $CDCl_3$).

Endo Cycloisomerization of Alkynols Catalyzed by Ruthenium DPPQ Complexes: Recently, Esteruelas[14] and co-workers reported that the osmium complex $[CpOs(py)_3](PF_6)$ is a more efficient catalyst for the regioselective 7-*endo* heterocyclization of aromatic alkynols or *o*-alkynyl phenethylamines to give 3-benzoxepines and dopaminergic 3-benzazepines than the ruthenium catalysts $[CpRu(py)_3](PF_6)$, $[CpRu(CH_3CN)_3](PF_6)$ and some tungsten, rhodium catalysts. Given the rarity of efficient catalysts for the 7-*endo* cycloisomerization of alkynyl alcohols reported in the literature and the success of ruthenium catalysts in the related 5- and 6-*endo* cycloisomerization reactions, we were prompted to investigate the catalytic activity of our DPPQ ruthenium complexes for such 7-*endo* reactions. Moreover, from an economic viewpoint, it is also quite appealing to develop much cheaper ruthenium catalysts for such reaction compared to osmium.

The aromatic alkynol 2-(2-ethynylphenyl)ethanol (**4a**) was chosen as the model substrate to test the catalytic activity of complexes **1-3** (Table 1). Initially, the reactions were investigated in 1,2-dichloroethane(DCE) at 90 ^oC under argon for 13 h with the same loading of ruthenium for complexes **1-3** (2.0 mol% of Ru). Considering that complex **3** may easily dissociate the coordinated pyridine ligand to initiate the reaction,

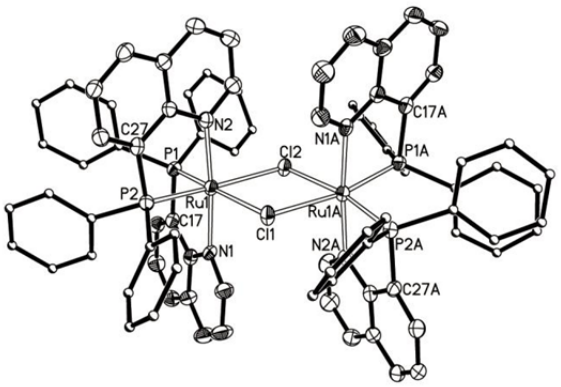


Figure 2. Molecular structure for the cation of **2** with thermal ellipsoids drawn at 30% probability. Counter anion and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru(1)-N(1) 2.124(4), Ru(1)-N(2) 2.136(4), Ru(1)-P(1) 2.2482(12), Ru(1)-P(2) 2.2604(13), Ru(1)-Cl(1) 2.5077(11), Ru(1)-Cl(2) 2.4982(11); N(1)-Ru(1)-N(2) 175.27(13), P(1)-Ru(1)-Cl(1) 168.95(4), P(2)-Ru(1)-Cl(2) 170.02(4), N(1)-Ru(1)-P(1) 83.49(10), N(2)-Ru(1)-P(1) 94.35(10), N(1)-Ru(1)-P(2) 92.28(11), N(2)-Ru(1)-P(2) 83.76(10), P(1)-Ru(1)-P(2) 96.31(5), N(1)-Ru(1)-Cl(2) 93.94(10), N(2)-Ru(1)-Cl(2) 90.34(10), P(1)-Ru(1)-Cl(2) 92.16(5), N(1)-Ru(1)-Cl(1) 90.53(10), N(2)-Ru(1)-Cl(1) 92.26(10), P(2)-Ru(1)-Cl(1) 93.20(5), Cl(2)-Ru(1)-Cl(1) 78.95(4), Ru(1)-Cl(1)-Ru(1A) 100.79(6), Ru(1)-Cl(2)-Ru(1A) 101.31(6). (Symmetry code for A: –x, y, -z+1/2)

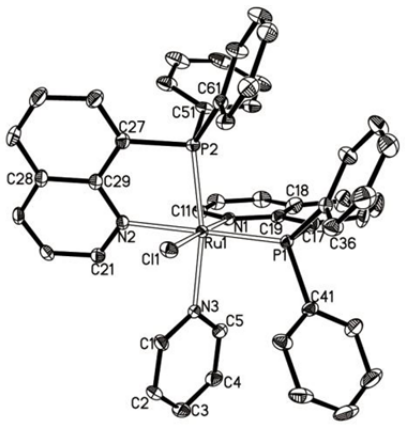
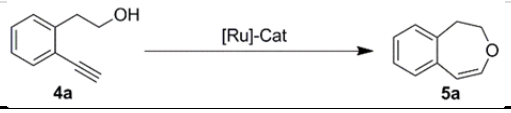


Figure 3. Molecular structure for the cation of **3** with thermal ellipsoids drawn at 30% probability. Counter anion and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru(1)-N(1) 2.076(3), Ru(1)-N(3) 2.182(3), Ru(1)-N(2) 2.193(3), Ru(1)-P(1) 2.2556(10), Ru(1)-P(2) 2.2856(10), Ru(1)-Cl(1) 2.4337(11); N(1)-Ru(1)-N(3) 89.63(11), N(1)-Ru(1)-N(2) 94.60(11), N(3)-Ru(1)-N(2) 87.87(11),N(1)-Ru(1)-P(1) 83.85(9), N(3)-Ru(1)-P(1):91.46(8), N(2)-Ru(1)-P(1) 178.32(8), N(1)-Ru(1)-P(2) 92.24(9), N(3)-Ru(1)-P(2) 168.70(8), N(2)-Ru(1)-P(2) 80.88(8), P(1)-Ru(1)-P(2) 99.81(4), N(1)-Ru(1)-Cl(1) 178.65(8), N(3)-Ru(1)-Cl(1) 89.57(8), N(2)-Ru(1)-Cl(1) 86.45(8), P(1)-Ru(1)-Cl(1) 95.08(4), P(2)-Ru(1)-Cl(1) 88.75(4).

the cycloisomerization of **4a** with **3** was first examined, which, to our delight, selectively gave the desired 7-*endo* cyclization product 3-benzoxepine **5a** in 73% yield (entry 1). More encouragingly, when the dimeric complex **2** was employed as the catalyst, the yield of **5a** was improved to 81% (entry 2), indicating that dissociation of the dimeric complex **2** into catalytically active 16-electron monomeric species could readily occur in the reaction of **2** with **4a** under these conditions. The dichloride complex **1** could also catalyze the reaction, but with a much lower yield of product **5a** (entry 3) due to the fact as expected that dissociation of a chloride ligand from **1** to generate the coordinatively unsaturated species is more difficult than the dissociation of the dimeric structure in **2** and the pyridine ligand in **3**. Having established complex **2** as the most efficient catalyst, different solvents were screened for the reactions, suggesting that DCE is the best choice. The reactions also proceeded well in tetrahydrofuran (THF) or $CHCl_3$ to give 3-benzoxepine **5a** in 64% and 75% yields, respectively (entries 4 and 5). However, the reactions in 1,4-dioxane, toluene or N,N-dimethylformamide (DMF) gave only trace amounts of product **5a** (entries 6-8), probably due to the poor solubility of the cationic complex **2** in the former two solvents and the coordination of DMF with ruthenium. The reaction temperature was then examined with **2** as the catalyst in DCE solvent. Higher temperature (110 °C) was found to decrease the yield of **5a** (69%, entry 9) due to the formation of a complex mixture of organic products containing **5a**, while lower temperature (60 °C) led to the incomplete conversion of **4a** (about only 50% conversion) and the formation of a new phosphine-containing complex (the oxacyclocarbene complex **12**, *vide infra*) (Entry 10). Thereafter, the reaction time was also carefully checked. When the reaction in DCE was heated at 90 °C for 2 h, 5 h, 8 h and 11 h, incomplete conversion of substrate **4a** were observed in all case and the yields of product **5a** monitored by GC were 36%, 64%, 72% and 78%, respectively (entries 11-14). At last, it was found that reducing the loading of catalyst **2** to 0.5 mol% (1.0% of Ru) resulted in the incomplete conversion of substrate **4a** and a significant drop in the yield of product **5a** (46%, entry 15).

Table 1. Screening of catalysts and optimization of reaction conditions for 7-*endo* heterocyclization of **4a**.



4a **5a**

Entry	Cat. (mol %)	Solvent	T (°C)	t (h)	Yield[a]
1	**3** (2.0)	DCE	90	13	73
2	**2** (1.0)	DCE	90	13	81 (56[b])
3	**1** (2.0)	DCE	90	13	29
4	**2** (1.0)	THF	90	13	64
5	**2** (1.0)	$CHCl_3$	90	13	75
6	**2** (1.0)	1,4-dioxane	90	13	trace
7	**2** (1.0)	toluene	90	13	trace
8	**2** (1.0)	DMF	90	13	trace
9	**2** (1.0)	DCE	110	13	69
10	**2** (1.0)	DCE	60	13	50[c]
11	**2** (1.0)	DCE	90	2	36
12	**2** (1.0)	DCE	90	5	64
13	**2** (1.0)	DCE	90	8	72
14	**2** (1.0)	DCE	90	11	78
15	**2** (0.5)	DCE	90	13	46

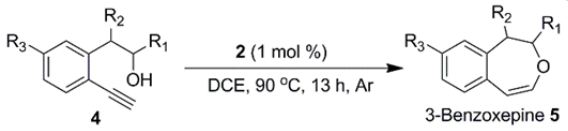
Typical conditions: [**4a**] = 0.16 M, oil bath, the reactions were catalyzed by using 0.1 mmol substrate and solvent (0.6 mL) under Ar, unless otherwise noted. [a] Yield determined by GC methods calculated by using dibromomethane as internal standard. [b] Isolated yield (the relatively low isolated yield of **4a** is due the low boiling point) [c] Conversion of **4a** determined by ^{1}H NMR, and formation of the oxacyclocarbene complex **12** was detected from ^{31}P NMR. DCE = 1,2-dichloroethane. DMF = N,N-dimethylformamide.

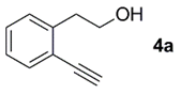
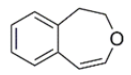
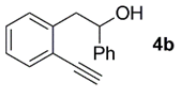
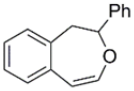
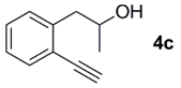
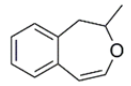
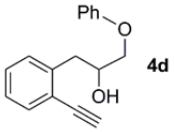
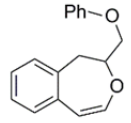
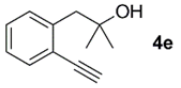
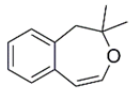
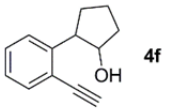
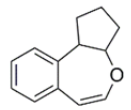
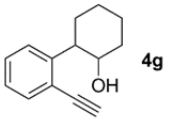
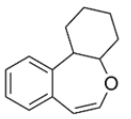
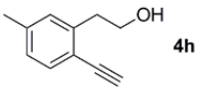
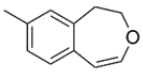
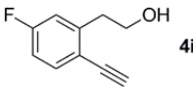
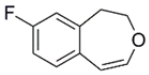
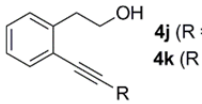
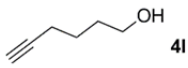
With the optimized conditions in hand, the substrate scope of the 7-*endo* cycloisomerization reactions catalyzed by complex **2** (1 mol % loading) was explored in DCE at 90 °C. A variety of aromatic alkynols **4** were converted into their corresponding seven-membered 3-benzoxepines **5** in moderate to good yields (Table 2). Besides the parent primary aromatic alkynol **4a**, secondary aromatic alkynols such as **4b**-**4d** were also exclusively converted to the corresponding 3-benzoxepines **5b**-**5d** in moderate to excellent yields (entries 2-4). Other secondary alkynols such as cyclopentanol derivative **4f** and cyclohexanol derivative **4g**, and even the sterically hindered tertiary alkynol **4e** all smoothly afforded the corresponding products (entries 5-7) in high yields. Moreover, both aromatic alkynols with electron-donating or electron-withdrawing substituents such as Me (**4h**) and F (**4i**) on the aromatic rings were well tolerated to provide the corresponding 3-benzoxepines in good yields (entries 8 and 9). However, nonterminal alkynols such as 2-(2-(phenylethynyl)phenyl)ethanol (**4j**) and 2-(2-((trimethylsilyl)ethynyl)phenyl)ethanol (**4k**) failed to give the corresponding *endo* cycloisomerization products (entry 10), which indirectly indicate that the cyclization occurs via a vinylidene intermediate.[12d,14a,19] These results are comparable with those reported for the reactions catalyzed by the osmium catalyst $[CpOs(py)_3](PF_6)$ (10 mol% loading, pyridine, 90 °C), [14a] in that the aromatic alkynols **4a**, **4b**, **4c** and **4g** were converted into the corresponding 3-benzoxepines **5** in 60%, 58%, 65% and 56% yields, respectively, in 0.5-1.5 h.

In an attempt to extend the 7-*endo* cycloisomerization reactions to aliphatic alkynols, the reaction of hex-5-yn-1-ol (**4l**) in the presence of **2** under the typical conditions was investigated. Unfortunately, the reaction failed to provide the corresponding *endo* cyclized oxepine product **5l** (entry 11). Instead, exclusive formation of the corresponding oxacyclocarbene complex **12'** (*vide infra*) was detected by ^{31}P NMR. Of note, successful *endo* cycloisomerization of **4l** into oxepine **5l** catalyzed by the complex $[Ru(N_3P)(OAc)](BPh_4)$ has

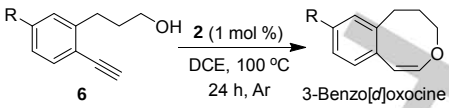
10.1002/chem.201703971

Table 2. The substrate scope of the cycloisomerization reactions catalyzed by complex **2**.



Entry	Alkynol **4**	3-benzoxepine **5**	Yield[a]
1	 **4a**	 **5a**	81%[b]
2	 **4b**	 **5b**	57%
3	 **4c**	 **5c**	77%
4	 **4d**	 **5d**	91%
5	 **4e**	 **5e**	86%
6	 **4f**	 **5f**	76%
7	 **4g**	 **5g**	61%
8	 **4h**	 **5h**	63%
9	 **4i**	 **5i**	55%
10	 **4j** (R = Ph) **4k** (R = $SiMe_3$)		s.m.
11	 **4l**	 **5l**	---[c]

Typical conditions: 1 mol% **2**, [**4**] = 0.16 M, oil bath, 90 °C, 13 h, the reactions were catalyzed by using 0.1 mmol substrate and solvent (0.6 mL) under Ar, unless otherwise noted. [a] Isolated yield. [b] Yield determined by GC methods calculated by using dibromomethane as internal standard. [c] Exclusive formation of the corresponding oxacyclocarbene complex **12'** was detected by ^{31}P NMR.



	R	Isolated Yield
6a, 7a	H	62%
6b, 7b	Me	66%
6c, 7c	F	58%

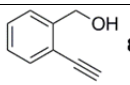
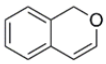
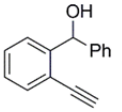
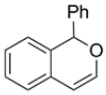
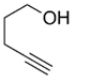
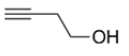
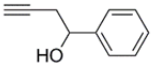
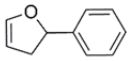
Scheme 2. 8-*endo* cycloisomerization of aromatic alkynol **6** to 3-benzo[d]oxocine **7** catalyzed by complex **2**.

been reported by Jia and co-workers.[12d] However, the superior capacity of complex **2** for the catalytic *endo* heterocyclization reactions can be demonstrated by the even more challenging regioselective 8-*endo* cyclization of aromatic alkynols, although a longer reaction time (24 h) and a slightly higher temperature (100 °C) were required (Scheme 2). Again, with 1 mol% loading of catalyst **2**, not only the 2-ethynylphenyl alkynol (**6a**) but also other related derivatives with an electron-donating methyl group (**6b**) or the electron-withdrawing fluoride (**6c**) *para* to the alkyne on the aromatic ring were all successfully cycloisomerized to the corresponding *endo*-cyclic eight-membered 3-benzo[*d*]oxocine derivatives **7a-7c**, and the product was isolated in quite good yields of 62%, 66% and 58%, respectively. Notably, Esteruelas has also reported the 8-*endo* cyclization of the parent alkynol **6a** catalyzed by $[CpOs(py)_3](PF_6)$ in pyridine solvent at 130 °C for 4 h to give 3-benzo[*d*]oxocine **7a** in 40% yield with 10 mol% loading of catalyst.[14a] In this regard, complex **2** competes favorable with respect to the osmium catalyst in terms of the catalytic activity for the 8-*endo* cycloisomerizations of aromatic alkynols.

We have also investigated the catalytic activity of **2** for the 6- and 5-*endo* cycloisomerization of bis-homopropargylic and homopropargylic alcohols. It was found that the reactions in DCE gave poor conversion of the substrates. However, when a THF solution of the alkynol substrate in the presence of 1 mol% of complex **2** sealed in a Schlenk tube was heated at 100 °C for 24 h, the 6- and 5-*endo* cycloisomerization can also be achieved to provide the *endo*-cyclic enol ethers in moderate to good yields. The results are summarized in Table 3. For example, the aromatic bis-homopropargylic alcohol **8a** was smoothly converted into isochromene **10a** in a high 75% yield (entry 1), while the secondary alkynol **8b** gave the corresponding isochromene **10b** in only a moderate 46% yield probably due to the steric hinderance (entry 2). Cycloisomerization of the aliphatic bis-homopropargylic pent-4-yn-1-ol (**8c**) was also realized to give the 6-*endo*-cyclic dihydropyran **10c** in 51% yield (entry 3). Under similar conditions, the aliphatic homopropargylic but-3-yn-1-ol (**9a**) was transformed to the 5-*endo*-cyclic dihydrofuran **11a** in 42% yield (entry 4), whereas 5-*endo* cyclization of the phenyl substituted secondary alkynol **9b** provided dihydrofuran **11b** in a good 64% yield (entry 5). Again, 7-*endo* cycloisomerization of hex-5-yn-1-ol (**4l**) cannot be achieved under this condition. Although the catalytic activity of **2** for the 6-*endo* and 5-*endo* cycloisomerization reactions is relatively lower than those of the reported ruthenium complex $[Ru(N_3P)(OAc)](BPh_4)$[12d] and the $CpRuCl(PPh_3)_2$/amine system,[12c] these results have manifested the versatility of complex **2** as the catalyst for *endo* cycloisomerization of alkynols.

10.1002/chem.201703971

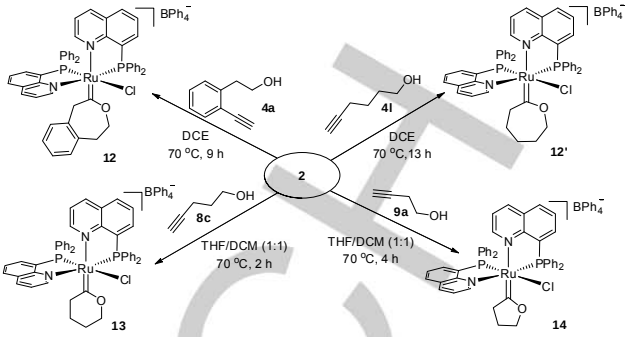
Table 3. 6-*endo* and 5-*endo* heterocyclization of alkynols catalyzed by complex **2**.

Entry	Alkynol **8** and **9**	Product **10** and **11**	Yield[a]
1	 **8a**	 **10a**	75%
2	 **8b**	 **10b**	46%
3	 **8c**	 **10c**	51%[b]
4	 **9a**	 **11a**	42%[b]
5	 **9b**	 **11b**	64%

Typical conditions: 1 mol% of **2**, [**8**] or [**9**] = 0.16 M, oil bath, 100 °C, 24 h, the reactions were catalyzed by using 0.1 mmol substrate in THF (0.6 mL) under Ar in a Schlenk tube sealed with a Teflon lined cap, unless otherwise noted. [a] Isolated yield. [b] In d_8-THF, yield determined by ^{1}H NMR spectroscopic integration with dibromomethane as the internal standard.

Mechanism study: The mechanism of the *endo* cycloisomerization reactions of terminal alkynols catalyzed by Mo,[5] W,[6] Ru,[12] Rh[13a] and Os[14a] systems were generally believed to involve the initial formation of a vinylidene intermediate that undergoes intramolecular nucleophilic addition of an OH group to the vinylidene ligand to afford a vinylic intemediate with an endocyclic enol ether linked to the transition-metal (or in some cases, interconvertible with the oxocyclocarbene intermediate[14a,20]), which then followed by protonation of the metal–carbon bond to give the endocyclized product. Although experimental evidence for the mechanism is still rare,[20,21] the mechanism for the Mo and W systems is supported by DFT studies.[6i,22] In order to isolate some reaction intermediates from which we could obtain information about the mechanism of our *endo* cycloismerization reactions, the stoichiometric reactions of complex **2** with alkynols were studied.

As mentioned before, during our examining the reaction temperature for the catalytic cycloisomerization of 2-(2-ethynylphenyl)ethanol (**4a**), formation of a new phosphine-containing complex could be detected by ^{31}P NMR when the reaction was conducted at a lower temperature (60 °C) (Table 1, entry 10). Thus the reaction of **2** with 10 equiv of **4a** in DCE at 70 °C was carried out. Indeed, the reaction proceeded smoothly to produce the above-mentioned newly formed complex quantitatively within 9 h, which was isolated in 95% yield and identified to be the 3-benzoxepine derivatized seven-membered ruthenium oxacyclocarbene complex **12** (Scheme 3). Numerous oxacyclocarbene complexes have been prepared previously from the reactions of various transition-metal complexes with terminal ω-alkynols,[20,23-26] including a number of ruthenium oxacyclocarbene complexes.[20,25]



Scheme 3. Stoichiometric reactions of **2** with various alkynols.

The structure of complex **12** has been confirmed by X-ray diffraction. Figure 4 shows the X-ray structure for the cation of **12**, from which we can see that the Ru center adopts distorted octahedral geometry consisting of two DPPQ ligands chelating to Ru nearly perpendicularly, one chlorine ligand, and one oxacarbene ligand. The P atom of one of the DPPQ ligands is *trans* to the Cl ligand (P(1)-Ru(1)-Cl(1), 167.48(3)°), while the N atom *trans* to the P atom of the other DPPQ ligand (N(1)-Ru(1)-P(2), 172.67(7)°). The N atom of the other DPPQ ligand is *trans* to the oxocarbene ligand (N(2)-Ru(1)-C(1), 168.70(11)°). The Ru=C bond length of 1.937(3) Å is similar to those of other reported ruthenium oxacyclocarbene complexes.[20,25,27]

Complex **12** was also characterized by multinuclear NMR spectroscopy and elemental analysis. Consistent with the solid state structure, the ^{31}P{^{1}H} NMR spectrum (in CD_2Cl_2) of **12** showed two doublet signals at 58.6 and 49.5 ppm (*J*(PP) = 31.3 Hz) for the two inequivalent phosphine groups. Due to the

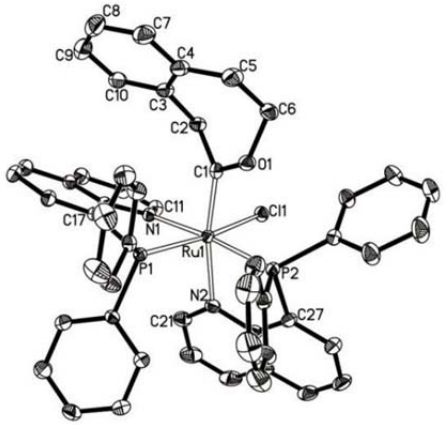
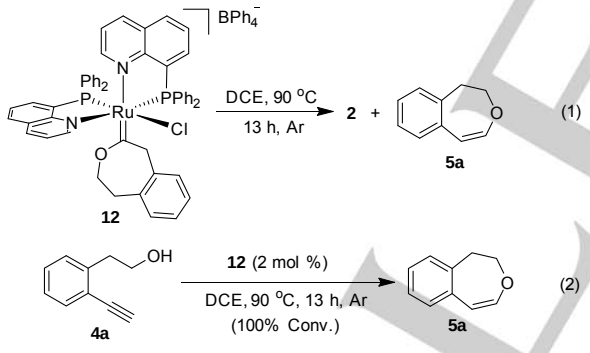


Figure 4. Molecular structure for the cation of **12** with thermal ellipsoids drawn at 30% probability. Counter anion and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru(1)-C(1) 1.937(3), Ru(1)-N(1) 2.204(3), Ru(1)-N(2) 2.215(3), Ru(1)-P(2) 2.2798(10), Ru(1)-P(1) 2.2946(11), Ru(1)-Cl(1) 2.4653(12), O(1)-C(1) 1.323(4), O(1)-C(6) 1.471(4), C(1)-C(2) 1.506(4), C(5)-C(6) 1.491(5); C(1)-Ru(1)-N(1) 93.63(11), C(1)-Ru(1)-N(2) 168.70(11), N(1)-Ru(1)-N(2) 91.21(10), C(1)-Ru(1)-P(2) 93.47(9), N(1)-Ru(1)-P(2) 172.67(7), N(2)-Ru(1)-P(2) 81.47(8), N(1)-Ru(1)-P(1) 79.84(7), N(2)-Ru(1)-P(1) 97.74(8), P(2)-Ru(1)-P(1) 101.59(4), N(1)-Ru(1)-Cl(1) 87.66(7), N(2)-Ru(1)-Cl(1) 81.62(8), P(2)-Ru(1)-Cl(1) 90.71(4), P(1)-Ru(1)-Cl(1) 167.48(3).

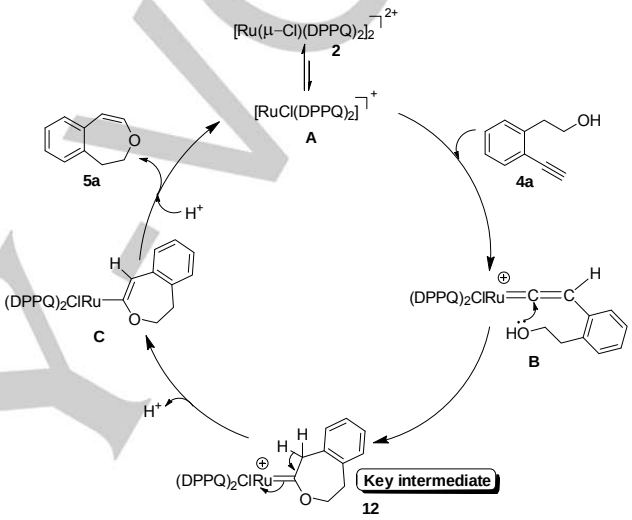
chirality at the metal center, the two protons of each methylene group of the oxacyclocarbene ring (Ru=CCH_2, Ru=COCH_2 and Ru=COCH$_2$CH_2) are diastereotopic, giving rise to complicated ^{1}H NMR spectrum with three pairs of multiplet signals in the aliphatic region between 3.05 and 4.85 ppm, similar to what were reported for other chiral ruthenium oxacyclocarbene complexes.[20,25f-25j,25l,25m] The ^{13}C{^{1}H} NMR spectrum displayed a Ru=*C* signal at 321.6 ppm (*^{2}J(PC) = 11.2 Hz*), in agreement with those observed for other ruthenium oxacyclocarbene complexes.[25,26] The ^{13}C{^{1}H} signals for the Ru=CO*C*H$_2$, Ru=COCH$_2$*C*H$_2$ and Ru=C*C*H$_2$ were observed at 73.0, 55.4, and 32.3 ppm, respectively. Reported examples of seven-membered oxacyclocarbene complexes are rather limited, specifically synthesized from the reacions of Ru,[25f,25h,25k] Os,[26b] and Re[26a] complexes with the aliphatic alkynols. To our knowledge, complex **12** represents the first example of benzo-oxacycloheptylidene transition-metal complexes.

Moreover, quantitative transformation of complex **12** to give complex **2** and 3-benzoxepine **5a** was observed, as indicated by the ^{31}P and ^{1}H NMR spectroscopy, when a solution of **12** was heated in DCE at 90 °C within 13 h (Scheme 4, Eq 1). Furthermore, complex **12** is also catalytically active for the 7-endo cyclization of **4a**. Thus, when a DCE slution of **4a** in the presense of 2 mol% **12** was heated at 90 °C, complete conversion of **4a** to **5a** was achieved within 13 h, and the product was isolated in 58% yield (Scheme 4, Eq 2). These results clearly indicate that oxacyclocarbene complex **12** is certainly an intermediate involved in the cycloisomerization of **4a** catalyzed by **2**.



Scheme 4. Transformation of complex **12** into complex **2** and 3-benzoxepine **5a** and 7-*endo* cycloisomerization of alkynol **4a** to afford **5a** catalyzed by **12**.

On the basis of these results, a plausible mechanism for the *endo* cycloisomerization of alkynols catalyzed by complex **2** is described in Scheme 5 by using substrate **4a** as an example. Dissociation of the dimeric complex **2** in the solution can generate the 16-electron monocationic species **A**, which reacts with alkynol **4a** to form the vinylidene intermediate **B** tethering with a hydroxyl chain. Due to the electrophilic and nucleophilic nature of the C_α and C_β atoms of the vinylidene ligand, respectively, intramolecular addition of the O-H group to the C=C double bond of the vinylidene ligand could give the seven-membered ruthenium oxacyclocarbene intermediate **12**,[25] which then undergoes deprotonation to afford the vinyl complex **C**. Finally, protonation of the metal-carbon bond in **C** would give the organic compound **5a** and regenerate **A**. The conversion of metal-carbene to metal-vinyl is present in many catalytic transformations, and it is particularly favored when the carbene has a C_β-H bond.[28,29] In this case, the C_β-proton of the oxacyclocarbene intermediate **12** is fairly acidic due to the cationic nature of the complex. Thus, it should undergo deprotonation to afford **C** with the aid of the basic media presented in the solution (probably could be the trace amounts of water, the hydroxy group of substrate **4a** or the ether functionality of product **5a**).



Scheme 5. Proposed mechanism of 7-endo cycloisomerization of 2-(2-ethynylphenyl)ethanol by catalyst **2**.

Despite of the numerous oxacyclocarbene complexes reported in the literature and the widely accepted idea that they are relevant to transition metal-catalyzed endo cycloisomerization of terminal alkynols,[5b,12a,14a,20,21a,23] isolation or even observation of the oxacyclocarbene complexes formed from the reactions of the catalysts and the substrates has rarely been achieved. McDonald and co-workers have trapped the molybdenum oxocyclocarbene intermediate using benzaldehyde to give the 5-phenyl-3-benzylidene-1-oxacyclopent-2-ylidene molybdenum complex from the stoichiometric version of the catalytic reaction of 1-phenylbut-3-yn-1-ol with Et_3N:$Mo(CO)_5$.[5b] In the absence of the Et_3N, they also described the reactions of $W(THF)(CO)_5$ with 4-alkyne-1-ols to result in the tungsten dihydropyranylidene complexes, and the subsequent stoichiometric transformation of them into α-stannyl dihydropyrans upon treated with tributyltin triflate and trimethylamine.[21a] In particular, Jia and co-workers[20] have isolated the oxacyclocarbene ruthenium complex $\{Ru(N_3P)[=C(CH_2)_3O](OAc)\}(BPh_4)$ from the reaction of the catalyst $[Ru(N_3P)(OAc)](BPh_4)$ with the 3-butyn-1-ol substrate, but the presence of extra base DIPEA (N,N-diisopropylethanamine) was need to facilitate the formation of

10.1002/chem.201703971

the oxacyclocarbene. Moreover, they also showed that the oxocyclocarbene complex can be detected in the catalytic reaction and the isoltated one is catalytically active for the cycloisomerization. Our above-mentioned results provided the most direct evidences for the first time to show the intermediacy of an oxacyclocarbene complex in the catalytic *endo*-cycloisomerization of alkynols.

In this context, it is noted that although complex **2** is not active for the cycloisomerization of the aliphatic alkynol hex-5-yn-1-ol (**4l**), exclusive formation of a new complex with ^{31}P NMR signals similar to that of complex **12** was detected (Table 2, entry 11). Thus, treatment of of **2** with 10 equiv of **4l** in DCE at 70 °C afforded the seven-membered oxacycloheptylidene ruthenium complex **12'** exclusively, which was isolated in 89% yield. Under similar reaction conditions, the six- and five-membered ruthenium oxacyclocarbenes **13** and **14** were also smoothly obtained in 90% and 92% yields, respectively, from the reactions of complex **2** with pent-4-yn-1-ol (**8c**) or but-3-yn-1-ol (**9a**) in DCM/THF (V:V = 1:1) at 70 °C for 2 h or 4 h (Scheme 3). Previous studies have revealed that the intramolecular addition of the hydroxy group to the C_α of the vinylidene intermediate is generally disfavoured with increasing the length of the spacer between the triple bond and the hydroxyl group in the starting alkynol due to the higher flexibility of the longer hydroxy alkyl substituent.[23,25f] Thus, longer reaction time is needed for the formation of the seven-membered oxacyclocarbene complexes **12** and **12'** than those for the six- and five-membered complexes **13** and **14**. It is also noted that reaction of the aromatic alkynol **4a** to generate seven-membered oxacyclocarbene **12** took place faster than that of the aliphatic alkynol **4l** (9 h *vs* 13 h). Apparently, the presence of the phenyl ring tethering the ortho terminal alkyne and the hydroxy alkyl substituent in the aromatic alkynol somehow reduces the flexibility of the hydroxy alkyl substituent in the vinylidene intermediate, which then favours intramolecular attack of the hydroxy group to the C_α.

Complexes **12'**, **13** and **14** were characterized by multinuclear NMR spectroscopy and elemental analysis. Taking **12'** for example, the $^{31}P\{^1H\}$ NMR spectrum showed two doublet signals at 57.6 and 49.1 ppm (J(PP) = 31.7 Hz) in CD_2Cl_2. The ^{1}H NMR spectrum displayed characteristic signals for the five pairs of C*H*$_2$ proton resonances in the aliphatic region between 4.37 and 0.83 ppm. The $^{13}C\{^1H\}$ NMR spectrum displayed a Ru=*C* signal at 326.5 ppm (*^{2}J(CP) = 11.2 Hz*), which is similar to that of complex **12** and those reported for other ruthenium oxacyclocarbene complexes.[20,25] The $^{13}C\{^1H\}$ signals for the five methylene resonances were observed at 77.5, 65.6, 50.1, 28.5 and 19.5 ppm, respectively. The structures of complexes **12'**, **13** and **14** have been also confirmed by X-ray diffraction, which are similar to that of **12**. Figures 5-7 showed the X-ray structures for the cation of complexes **12', 13** and **14**, with the Ru=C bond lengths being 1.948(3),1.935(5) and 1.930(4) Å, respectively.

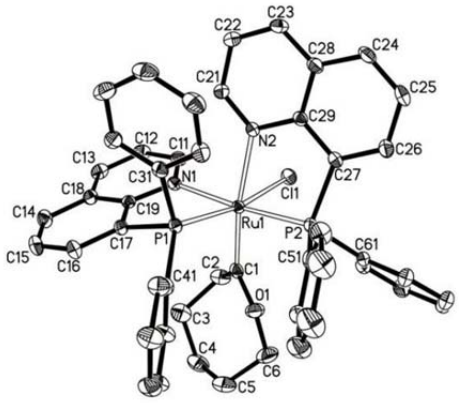


Figure 5. Molecular structure for the cation of **12'** with thermal ellipsoids drawn at 30% probability. Counter anion and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru(1)-C(1) 1.948(3), Ru(1)-N(1) 2.194(2), Ru(1)-N(2) 2.203(2), Ru(1)-P(2) 2.2764(9), Ru(1)-P(1) 2.2833(14), Ru(1)-Cl(1) 2.4540(13), O(1)-C(1) 1.321(4), O(1)-C(6) 1.466(4), C(1)-C(2) 1.498(4), C(2)-C(3) 1.538(5), C(3)-C(4) 1.522(6), C(4)-C(5) 1.509(6), C(5)-C(6) 1.504(6); C(1)-Ru(1)-N(1) 91.16(11), C(1)-Ru(1)-N(2) 170.39(10), N(1)-Ru(1)-N(2) 92.49(9), C(1)-Ru(1)-P(2) 93.93(9), N(1)-Ru(1)-P(2) 174.78(6), N(2)-Ru(1)-P(2) 82.30(7), N(1)-Ru(1)-P(1) 80.29(7), N(2)-Ru(1)-P(1) 94.50(7), P(2)-Ru(1)-P(1) 100.36(4), N(1)-Ru(1)-Cl(1) 89.25(7), N(2)-Ru(1)-Cl(1) 80.99(7), P(2)-Ru(1)-Cl(1) 89.62(4), P(1)-Ru(1)-Cl(1) 168.45(3).

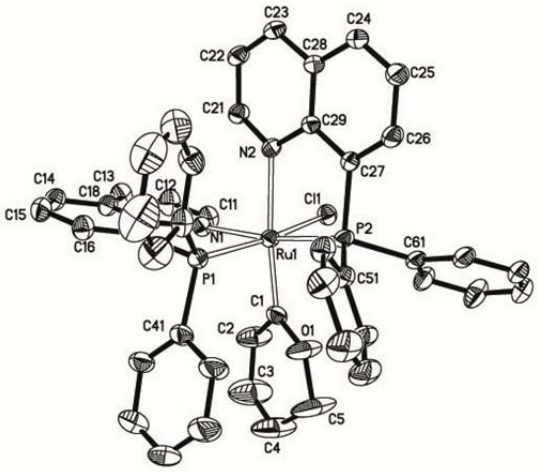


Figure 6. Molecular structure for the cation of **13** with thermal ellipsoids drawn at 30% probability. Counter anion and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru(1)-C(1) 1.935(5), Ru(1)-N(1) 2.210(3), Ru(1)-N(2) 2.212(4), Ru(1)-P(2) 2.2844(12), Ru(1)-P(1) 2.2915(15), Ru(1)-Cl(1) 2.4694(15), O(1)-C(1) 1.292(6), O(1)-C(5) 1.467(7), C(1)-C(2) 1.491(7), C(2)-C(3) 1.413(10), C(3)-C(4) 1.403(12), C(4)-C(5) 1.402(12); C(1)-Ru(1)-N(1) 93.39(17), C(1)-Ru(1)-N(2) 173.49(17), N(1)-Ru(1)-N(2) 89.16(13), C(1)-Ru(1)-P(2) 94.89(14), N(1)-Ru(1)-P(2) 171.70(10), N(2)-Ru(1)-P(2) 82.67(10), N(1)-Ru(1)-P(1) 81.57(10), N(2)-Ru(1)-P(1) 95.48(10), P(2)-Ru(1)-P(1) 97.69(5), N(1)-Ru(1)-Cl(1) 87.06(10), N(2)-Ru(1)-Cl(1) 83.47(10), P(2)-Ru(1)-Cl(1) 93.45(4), P(1)-Ru(1)-Cl(1) 168.60(4).

10.1002/chem.201703971

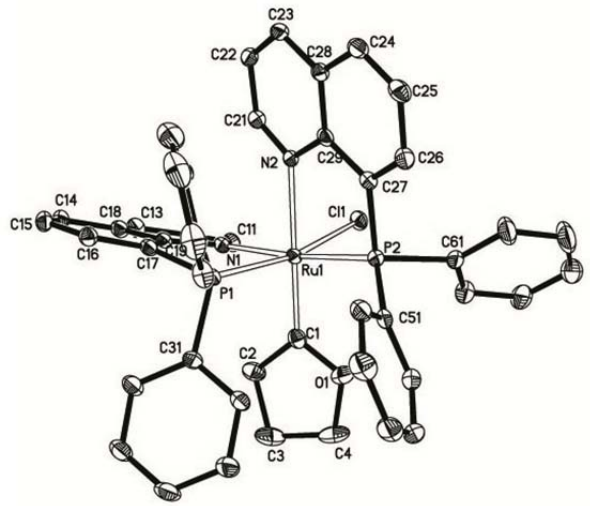
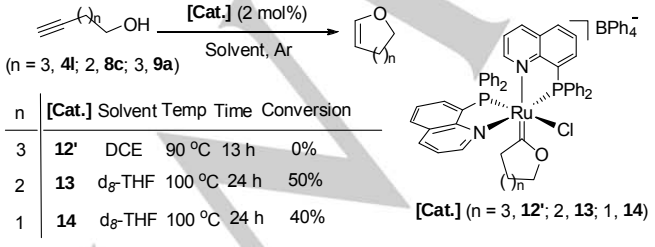


Figure 7. Molecular structure for the cation of **14** with thermal ellipsoids drawn at 30% probability. Counter anion and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru(1)-C(1) 1.930(4), Ru(1)-N(1) 2.187(3), Ru(1)-N(2) 2.215(3), Ru(1)-P(2) 2.2993(10), Ru(1)-P(1) 2.2903(11), Ru(1)-Cl(1) 2.4480(11), O(1)-C(1) 1.319(5), O(1)-C(4) 1.477(5), C(1)-C(2) 1.512(5), C(2)-C(3) 1.523(6), C(3)-C(4) 1.506(8); C(1)-Ru(1)-N(1) 87.46(14), C(1)-Ru(1)-N(2) 179.45(14), N(1)-Ru(1)-N(2) 92.93(11), C(1)-Ru(1)-P(2) 98.16(12), N(1)-Ru(1)-P(2) 174.34(8), N(2)-Ru(1)-P(2) 81.45(8), N(1)-Ru(1)-P(1) 81.17(8), N(2)-Ru(1)-P(1) 88.66(8), P(2)-Ru(1)-P(1) 99.30(4), N(1)-Ru(1)-Cl(1) 87.85(8), N(2)-Ru(1)-Cl(1) 84.67(8), P(2)-Ru(1)-Cl(1) 90.92(4), P(1)-Ru(1)-Cl(1) 166.85(4).

In agreement with the results of the catalytic reactions, no reaction occurred when a solution of **12'** was heated in DCE at 90°C or 110 °C for 13 h, and even in the presence of base such as Et_3N and Cs_2CO_3, which is stark contrast to the facile tansformation of complex **12** into the 3-benzoxepine **5a**. On the other hand, cycloisomerization of corresponding alkynols employing complexes **12'**, **13** or **14** as catalysts were also conducted (Scheme 6). Again, no appreciable reaction could be observed when the reaction of hex-5-yn-1-ol (**4l**) in the presence of 2.0 mol% complex **12'** in DCE was heated at 90 °C for 13 h. On the contrary, in a d_8-THF solution, cycloisomerization of pent-4-yn-1-ol (**8c**) or but-3-yn-1-ol (**9a**) in the presence of 2.0 mol% **13** or **14** could be detected after the reaction solution were heated at 100 °C for 24 h, although only partial conversion was achived (50 and 40% for **8c** and **9a**, respectively).



n	[Cat.]	Solvent	Temp	Time	Conversion
3	**12'**	DCE	90 °C	13 h	0%
2	**13**	d_8-THF	100 °C	24 h	50%
1	**14**	d_8-THF	100 °C	24 h	40%

Scheme 6. *Endo*-cycloisomerization of alkynols catalyzed by oxacyclocarbene ruthenium complexes.

The results obtained above naturally raise the question about what factors are responsible for the different reactivity of the oxacyclocarbene intermediates in the catalytic reactions, in particular the marked difference between **12** and **12'**. Initially, we envisioned that facile tansformation of oxacyclocarbene **12** into the 3-benzoxepine **5a** might be related to the stronger acidity of the C_β-protons due to the benzylic character. However, the control experiments of **12'** in the presence of base have shown that the acidity issue is very unlikely. At this stage, it appears likely that the failure for the transformation of oxacyclocarbene **12'** can be rationalized in terms of the conformational flexibility of the seven-membered aliphatic oxacyclic ring, which disfavored the deprotonation of the C_β-protons by baisc media. Consistent with this assumption, the oxacyclocarbene **12** with a less flexible benzo-oxacyclic ring can be readily deprotonated and evolve into catalyst **2** and 3-benzoxepine **5a**. In the cases of aliphatic oxacyclocarbene complexes **13** and **14**, deprotonation of the C_β-protons could be also achieved under the action of weak basic THF solvent due to the reduced conformational flexibility of the smaller oxacycle, albeit not very efficiently as reflected by the relatively low conversion of substrates **8c** and **9a** in the catalytic reactions (Table 3 and Scheme 6).

Conclusions

In summary, we have prepared several new ruthenium complexes with the heterobidentate P,N-donor ligand DPPQ, including $RuCl_2(DPPQ)_2$ (**1**), $[Ru(\mu\text{-}Cl)(DPPQ)_2]_2(BPh_4)_2$ (**2**) and $[RuCl(DPPQ)_2Py](BF_4)$ (**3**). Complex **2** was found to be catalytically active for *endo* cycloisomerization of a range of terminal alkynols to form corresponding endo-cyclic enol ethers in moderate to excellent yields. In particular, with only 1 mol% loading of **2**, the 7-*endo* and 8-*endo* heterocyclization of aromatic alkynols can be achieved efficiently to give the seven-membered 3-benzoxepine and eight-membered 3-benzo[*d*]oxocine derivatives. The stoichiometric reactions of catalyst **2** with various alkynol substrates such as the aromatic alkynol **4a** and the aliphatic alkynols **4l**, **8c** or **9a** have been carried out to study the mechanism for the endo-cycloisomerization reactions, which led to the isolation of a series of seven-, six-, and five-membered oxacyclocarbene ruthenium complexes including $[RuCl(DPPQ)_2\{=CCH_2C_6H_4CH_2CH_2O\}](BPh_4)$ (**12**) and $[RuCl(DPPQ)_2\{=CCH_2(CH_2)_nCH_2O\}](BPh_4)$ (n = 3, **12'**; n = 2, **13**; n = 1, **14**). Complex **12** represents the first example of benzo-oxacycloheptylidene transition-metal complexes. The quantitative transformation of complex **12** into catalyst **2** and 3-benzoxepine **5a** as well as the efficient catalytic activity of **12** for the endo-cyclization of **4a** demonstrated that complex **12** is an intermediate involved in the catalytic cycle, which provided the most direct evidences for the first time to show the intermediacy of an oxacyclocarbene complex in the catalytic endo-cycloisomerization of alkynols. Moreover, comparative studies on the modeling reactions and catalytic activity of the series of oxacyclocarbene complexes indicated that the different catalytic activity of complex **2** for the endo-cycloisomerization of different

types of alknynols can be related to the reactivity of the respective ruthenium oxacyclocarbene intemediates.

Experimental Section

General: All manipulations were carried out under an argon atmosphere by using standard schlenk techniques, unless otherwise noted. Solvents were distilled from sodium/benzophenone (toluene, tetrahydrofuran, diethyl ether and n-hexane) or calciumhydride(CH_2Cl_2,1,4-dioxane,1,2-dichloroethane) under argon prior to use. All other reagents were used as received from commercial sources without further purification,unless otherwise noted. The starting material 8-(diphenylphosphino)quinoline,[30] and $RuCl_2(PPh_3)_3$[31] were prepared according to literature methods. NMR spectroscopic experiments were carried out on Bruker AV400 and Bruker AV500.^{1}H and $^{13}C\{^1H\}$ NMR chemical shifts are relative to TMS, and $^{31}P\{^1H\}$ NMR is relative to 85% H_3PO_4 as the external standard. Elemental analyses data were obtained on an Elementar Analysensysteme GmbH Vario EL III instrument. Mass spectra (HRMS) were obtained on Bruker En Apex ultra 7.0T FT-MS by the Public Instrument Platform. Reactions were monitored by using a GC – 9106.

Preparation of complex 1: A mixture of $RuCl_2(PPh_3)_3$ (1.0 g, 1.04 mmol) and 8-(diphenylphosphino)quinoline (0.65 g, 2.08 mmol) in dichloromethane (20 mL) was stirred at room temperature for 3 h to give a red solution along with a red precipitate. The volume of the reaction mixture was reduced to *ca.*10 mL and diethyl ether (20 mL) was added slowly to the residue with stirring. The mixture was stirred for *ca.* 5 min. to complete further precipitation. The solid was collected by filtration, washed with diethyl ether (3 x 10 mL) and dried under vacuum. Yield: 0.8 g (96%). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 62.2 (d, *J* (PP) = 33.4 Hz), 53.9 (d, *J* (PP) = 33.4 Hz); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.83 (d, *J* = 4.0 Hz, 1H, *quinolyl*), 8.43 – 8.34 (m, 4H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.71 – 7.67 (m, 3H), 7.63 – 7.51 (m, 4H), 7.36 – 7.25 (m, 7H), 7.03 (t, *J* = 7.7 Hz, 2H), 6.97 (t, *J* = 7.3 Hz, 1H), 6.84 (t, *J* = 7.4 Hz, 1H), 6.77 (t, *J* = 7.5 Hz, 2H), 6.55 (t, *J* = 7.6 Hz, 2H), 6.36 (dd, *J* = 7.9, 5.3 Hz, 1H), 6.17 (t, *J* = 7.2 Hz, 2H). $^{13}C\{^1H\}$ NMR spectrum was not collected due to the poor solubility of the compound. elemental analysis calcd (%) for $C_{42}H_{32}Cl_2N_2P_2Ru$•$2CHCl_3$: C, 50.94; H, 3.30; N, 2.70; found: C, 51.04; H, 3.65; N, 2.92 (Crystals of **1** grown from $CHCl_3$/Hexane were used for EA analysis and the presence of $CHCl_3$ in the sample has been confirmed by an X-ray diffraction study (See Supporting Information)).

Preparation of complex 2: A mixture of **1** (0.94 g, 1.17 mmol) and sodium tetraphenylborate (0.80 g, 2.34 mmol) in dichloromethane (25 mL) was stirred at room temperature for 4 h to give a red solution. The solvent was removed under reduced pressure. Addition of diethyl ether (20 mL) to the residue produced an orange-red solid, which was collected by filtration, washed with THF (2 x 10 mL), MeOH (10 mL), diethyl ether (10 mL) and dried under vacuum. Yield: 1.26 g (99%). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2) δ 63.5 (s); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.82 (d, *J* = 4.6 Hz, 4H, *quinolyl*), 8.29-8.26 (m, 8H), 7.90-7.86 (m, 8H), 7.48 (s(br), 16H, B*Ph*$_4$-*ortho* and other aromatic), 7.38-7.34 (m, 4H), 7.13-7.07 (m, 24H, B*Ph*$_4$-*meta* and other aromatic), 6.98 – 6.83 (m, 12H, B*Ph*$_4$-*para* and other aromatic), 6.74 (s(br), 8H), 6.52 (dd(unresolved), *J* = 7.6, 5.5 Hz, 4H), 6.41 (t, *J* = 7.2 Hz, 8H), 5.59 (s(br), 8H); $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2) δ 164.1 (dd, *J* = 98.7, 49.1 Hz, P*Ph*$_2$-*ipso*), 157.0, 156.6 (t, *J* = 9.6 Hz, *quinolyl*), 139.5, 138.1, 136.1 (B*Ph*$_4$-*ortho*), 133.5, 133.3, 130.5, 130.4, 130.2, 130.7, 129.9, 129.8, 129.7, 129.5, 129.2, 129.0 (br), 128.3 (br), 128.1 (br, B*Ph*$_4$-*ipso*), 125.7 (br, B*Ph*$_4$-*meta*), 122.5, 121.9 (B*Ph*$_4$-*para*); elemental analysis calcd (%) for $C_{132}H_{104}B_2Cl_2N_4P_4Ru_2$: C, 73.24; H, 4.84; N, 2.59; found: C, 73.65; H, 5.01; N, 2.38

Preparation of complex 3: A mixture of complex **1** (330 mg, 0.42 mmol) and $AgBF_4$ (85 mg, 0.42 mmol) in pyridine (10 mL) was stirred at room temperature for 30 min to give an orange solution and undissolved salt, which were seperated by filtration on a pad of Celite®. The solution was removed to about 1 mL, addition of Et_2O (15 mL) produced orange-yellow solid, which was collected by filteration, washed with Et_2O (2x10 mL), and dried under vacuum. Yield: 384 mg (98%). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$) δ 58.5 (d, *J* (PP)= 33.8 Hz), 57.6 (d, *J* (PP)= 33.8 Hz); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.30 (d, *J* = 5.8 Hz, 1H, *quinolyl*), 8.63 (dt, *J* = 8.5, 1.5 Hz, 1H), 8.45 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 1H), 8.30 – 8.28 (m, 1H), 8.25 (dt (unresolved t), *J* = 8.5, 1.5 Hz, 1H), 8.21 (dt (unresolved t), *J* = 8.0, 1.5 Hz, 1H), 8.10 (dt, *J* = 8.0, 1.8 Hz, 1H), 8.07 – 8.02 (m, 2H), 7.74 – 7.70 (m, 3H), 7.63 – 7.56 (m, 2H), 7.55 – 7.51 (m, 2H), 7.41 (ddd, *J* = 9.8, 7.1, 1.2 Hz, 1H), 7.37 – 7.32 (m, 3H), 7.20 – 7.13 (m, 3H), 7.09 – 6.98 (m, 8H), 6.77 (dd, *J* = 8.3, 5.4 Hz, 1H), 6.71 (t, *J* = 6.6 Hz, 1H), 6.61 (td, *J* = 8.1, 2.1 Hz, 2H), 6.03 (ddd, *J* = 10.3, 8.5, 1.7 Hz, 2H); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) δ 156.8, 156.6 (*quinolyl*), 154.0, 152.7, 152.4 (d, *J* = 16.3 Hz, *quinolyl*), 150.2, 139.1, 139.0, 137.5, 137.2 (d, *J* = 41.8 Hz, P*Ph*$_2$), 136.8, 134.5 (d, *J* = 9.8 Hz, P*Ph*$_2$),, 133.0, 132.9 – 127.6 (m), 125.9, 125.0, 123.5, 122.9; elemental analysis calcd (%) for $C_{47}H_{37}BClF_4N_3P_2Ru$•$CH_2Cl_2$: C, 56.85; H, 3.88; N, 4.14; found: C, 56.99; H, 4.10; N, 4.49 (Crystals of **3** grown from CH_2Cl_2/Hexane were used for EA analysis and the presence of CH_2Cl_2 in the sample has been confirmed by an X-ray diffraction study (See Supporting Information)).

Complex 12: A mixture of complex **2** (210 mg, 0.1 mmol) and 2-(2-ethynylphenyl)ethanol (146 mg,1.0 mmol) in 1,2-dichloroethane (10 mL) was stirred at 70 °C for 9 h, then cooled to room temperature. The solvent was removed to ca. 1 mL under reduced pressure and diethyl ether (10 mL) was added to the residue to produce a yellow solid, which was collected by filtration, washed with diethyl ether (2x6 mL), tetrahydrofuran (6 mL) and dried under vacuum. Yield: 226 mg (95%). ^{31}P NMR (202 MHz, CD_2Cl_2) δ 58.6 (d, *J* (PP)= 31.3 Hz), 49.5 (d, *J* (PP) = 31.3 Hz); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 10.73 (s (br), 1H, *quinolyl*), 8.73 (d, *J* = 8.2 Hz, 1H, *quinolyl*), 8.24 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 8.3 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.05 – 7.98 (m, 2H), 7.95 – 7.89 (m, 2H), 7.79 (t, *J* = 7.6 Hz, 1H, P*Ph*$_2$-*para*), 7.63 (t, *J* = 7.5 Hz, 1H, P*Ph*$_2$-*para*), 7.48 (dt, *J* = 15.2, 7.8 Hz, 2H), 7.39 – 7.35 (m, 10H, B*Ph*$_4$-*ortho* and other aromatic), 7.31 (t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 3.7 Hz, 1H), 7.18 – 6.99 (m, 18H, B*Ph*$_4$-*meta* and other aromatic), 6.89 (t, *J* = 7.2 Hz, 4H, B*Ph*$_4$-*para*), 6.82 (dd, *J* = 8.2, 5.0 Hz, 1H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.65 (dd, *J* = 7.8, 1.3 Hz, 2H), 6.35 (dd, *J* = 11.5, 7.7 Hz, 2H), 6.17 (dd, *J* = 10.7, 7.8 Hz, 2H), 5.56 (d, *J* = 7.6 Hz, 1H), 4.85-4.73 (m, 1H, Ru=COC*H*$_2$), 4.40 (d, *J* = 15.0 Hz, 1H, Ru=CC*H*$_2$), 4.37-4.34 (m, 1H, Ru=COC*H*$_2$), 4.23 (d, *J* = 15.0 Hz, 1H, Ru=CC*H*$_2$), 3.15-3.05 (m, 2H, Ru=COCH$_2$C*H*$_2$); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) δ 321.6 (t, *J* (PC) = 11.2 Hz, Ru=*C*),164.1 (dd, *J* = 98.9, 49.1 Hz, *quinolyl*), 155.6, 152.5, 152.3, 151.7, 151.6, 139.6, 138.5, 137.8, 137.4, 136.5, 136.1 (B*Ph*$_4$-*ortho*), 135.8–127.3 (m), 126.6, 125.6 (B*Ph*$_4$-*meta*), 124.4, 122.1, 121.7 (B*Ph*$_4$-*para*), 73.0 (Ru=CO*C*H$_2$), 55.4 (Ru=C*C*H$_2$), 32.3 (Ru=COCH$_2$*C*H$_2$); elemental analysis calcd (%) for $C_{76}H_{62}BClN_2OP_2Ru$: C, 74.30; H, 5.09; N, 2.28; found: C, 74.69; H, 5.36; N, 2.50

Complex 12': A mixture of complex **2** (210 mg, 0.1 mmol) and hex-5-yn-1-ol (115 uL, 1.0 mmol) in 1,2-dichloroethane (10 mL) was stirred at 70 °C for 13 h to give an orange solution, then the solvent was removed to ca. 1 mL under reduced pressure. Addition of diethyl ether (10 mL) to the residue produced a yellow solid, which was collected by filtration, washed with diethyl ether (2x6 mL), tetrahydrofuran (5 mL) and dried under vacuum at least 3 h. Yield: 204 mg (89%).^{31}P NMR (202 MHz, CD_2Cl_2) δ 57.6 (d, *J* = 31.7 Hz), 49.1 (d, *J* = 31.7 Hz); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 10.69 (dd (unresolved), *J*(HH) ≈ 5.2 Hz, *J*(PH) ≈ 2.3 Hz, 1H, *quinolyl*), 8.65 (d, *J* = 8.3 Hz, 1H, *quinolyl*), 8.23 (dd, *J* = 16.8, 8.2 Hz, 2H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.02 – 8.00 (m, 3H), 7.93 (dd, *J* = 8.0, 5.2 Hz, 1H), 7.79

(t, *J* = 7.5 Hz, 1H, P*Ph*$_2$-*para*), 7.74 (t, *J* = 7.5 Hz, 1H, P*Ph*$_2$-*para*), 7.49 (dd, *J* = 13.9, 6.4 Hz, 2H), 7.43 – 7.28 (m, 13H, B*Ph*$_4$-*ortho* and other aromatic), 7.26 – 7.19 (m, 3H), 7.12 – 6.97 (m, 12H, B*Ph*$_4$-*meta* and other aromatic), 6.90 – 6.87 (m, 5H, B*Ph*$_4$-*para* and other aromatic), 6.68 (t, *J* = 6.8 Hz, 2H), 6.59 (dd, *J* = 10.8, 8.2 Hz, 2H), 6.19 – 6.06 (m, 2H), 4.37 (dd, *J* = 11.7, 5.9 Hz, 1H), 4.04 (dd, *J* = 11.0, 9.5 Hz, 1H), 3.05 (dd, *J* = 13.7, 9.3 Hz, 1H), 2.35 (t, *J* = 11.5 Hz, 1H), 1.67 – 1.59 (m, 1H), 1.44 (dd, *J* = 6.1, 3.9 Hz, 1H), 1.42 – 1.36 (m, 1H), 1.04 – 0.95 (m, 1H), 0.95 – 0.83 (m, 2H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 326.5(t, *J* (PC) =11.2 Hz, Ru=*C*), 164.1(dd, *J* = 98.2, 49.3 Hz, P*Ph*$_2$-*ipso*), 155.8, 152.4, 152.1, 151.9, 151.8, 139.4, 138.5, 137.9, 135.9 (B*Ph*$_4$-*ortho*), 135.54, 135.47, 133.4 – 127.3 (m), 125.6 (B*Ph*$_4$-*meta*), 124.1, 122.2, 121.7 (B*Ph*$_4$-*para*), 77.5 (RuO*C*H$_2$), 65.6 (RuOCH$_2$*C*H$_2$), 50.1 (RuOCH$_2$CH$_2$*C*H$_2$), 28.5 (RuCH$_2$*C*H$_2$), 19.5 (Ru*C*H$_2$); elemental analysis calcd (%) for $C_{72}H_{62}BClN_2OP_2Ru$•2CH_2Cl_2: C, 65.82; H, 4.93; N, 2.07; found: C, 66.04; H, 5.30; N, 2.33 (Crystals of **12'** grown from CH_2Cl_2/Hexane were used for EA analysis and the presence of CH_2Cl_2 in the sample has been confirmed by an X-ray diffraction study (See Supporting Information)).

Complex 13: A mixture of complex **2** (210 mg, 0.1 mmol) and pent-4-yn-1-ol (0.1 mL, 0.1 mmol) in dichloromethane/tetrahydrofuran (15 mL, V:V = 1:1) was stirred at 70 °C for 2 h to give an orange solution. After cooling down to room temperature, the solvent was removed to ca. 2 mL under reduced pressure and diethyl ether (10 mL) was added to the residue to give a yellow solid, which was collected by filtration, washed with diethyl ether (2 x 6 mL), tetrahydrofuran (6 mL) and dried under vacuum at least 3 h. Yield: 200 mg (90%). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ 58.3 (d, *J* (PP) = 31.9 Hz), 51.1 (d, *J* (PP) = 31.9 Hz); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 10.74 (d (unresolved), *J* = 5.2 Hz, 1H, *quinolyl*), 8.63 (d, *J* = 8.1 Hz, 1H, *quinolyl*), 8.23 (d, *J* = 7.8 Hz, 2H), 8.07 (t, *J* = 8.0 Hz, 2H), 7.98 (d, *J* = 7.9 Hz, 2H), 7.93 (dd, *J* = 8.1, 5.2 Hz, 1H, *quinolyl*), 7.78 (t, *J* = 7.9 Hz, 1H, P*Ph*$_2$-*para*), 7.73 (t, *J* = 7.8 Hz, 1H, P*Ph*$_2$-*para*), 7.51 – 7.30 (m, 13H, B*Ph*$_4$-*ortho* and other aromatic), 7.25 – 7.21 (m, 3H), 7.12 – 6.97 (m, 14H, B*Ph*$_4$-*meta* and other aromatic), 6.93 – 6.86 (m, 5H, B*Ph*$_4$-*para* and other aromatic), 6.73 (dd (unresolved), *J* ≈ 9.0, 6.4 Hz, 2H), 6.46 (t, *J* = 9.4 Hz, 2H), 6.32 (t, *J* = 9.0 Hz, 2H), 4.16 – 4.04 (m, 1H, Ru=C(O-)CH$_2$CH$_2$CH$_2$C*H*$_2$-), 3.79-3.76 (m, 1H, Ru=C(O-)CH$_2$CH$_2$CH$_2$C*H*$_2$-), 3.67–3.51 (m, 1H, Ru=C(O-)C*H*$_2$), 2.04–1.89 (m, 1H, Ru=C(O-)C*H*$_2$), 1.64-1.58 (m, 1H, Ru=C(O-)CH$_2$C*H*$_2$), 1.48–1.40 (m, 1H, Ru=C(O-)CH$_2$C*H*$_2$), 1.36-1.31 (m, 1H, Ru=CCH$_2$C*H*$_2$), 1.22–1.12 (m, 1H, Ru=CCH$_2$C*H*$_2$); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ 319.9 (t, *J* (PC)= 9.9 Hz, Ru=*C*), 164.1 (dd, *J* = 98.5, 49.4 Hz, P*Ph*$_2$-*ipso*), 155.9 (P*Ph*$_2$), 152.1 (P*Ph*$_2$), 151.0 (d, *J* = 10.0 Hz, *quinolyl*), 139.4 (*quinolyl*), 138.7, 137.7, 137.5, 136.8 (d, *J* = 50.1 Hz, *quinolyl*), 136.5 (B*Ph*$_4$-*ortho*), 135.7 (d, *J* = 9.9 Hz, P*Ph*$_2$), 134.4 (dd, *J* = 51.2, 40.8 Hz, *quinolyl-ipso*), 132.5 (t (unresolved), *J* ≈ 9.1 Hz, B*Ph*$_4$-*ipso*), 132.2, 132.1, 132.0, 131.7, 131.5, 131.0, 30.6, 130.5, 130.4, 130.3, 130.0, 129.8, 129.5 (d, *J* = 8.2 Hz, *quinolyl*), 128.57, 128.51, 128.47, 128.16, 128.06, 128.02, 127.92, 127.6 (d, *J* = 9.9 Hz), 127.5 (d, *J* = 6.2 Hz), 125.6 (B*Ph*$_4$-*meta*), 124.1, 122.3, 121.7 (B*Ph*$_4$-*para*), 75.4 (Ru=C(O-)CH$_2$CH$_2$CH$_2$C*H*$_2$-), 47.5 (Ru=C*C*H$_2$), 21.3 (Ru=C(O-)CH$_2$*C*H$_2$),16.6 (Ru=CCH$_2$*C*H$_2$); elemental analysis calcd (%) for $C_{71}H_{60}BClN_2OP_2Ru$: C, 73.10; H, 5.18; N, 2.40; found: C, 73.44; H, 5.43; N, 2.62

Complex 14: A mixture of complex **2** (210 mg, 0.1 mmol) and but-3-yn-1-ol (75 uL,1.0 mmol) in dichloromethane/tetrahydrofuran (15 mL, V:V=1:1) was stirred at 70 °C for 4 h to give an orange solution, and then cooled to room temperature. The solvent was removed to ca. 2 mL under reduced pressure and diethyl ether (10 mL) was added to the residue to produce a yellow solid, which was collected by filtration, washed with diethyl ether (2x6 mL), tetrahydrofuran (6 mL) and dried under vacuum at least 3 h. Yield: 210 mg (92%). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2) δ 57.8 (d, *J* (PP) = 30.8 Hz), 50.9 (d, *J*(PP) = 30.8 Hz); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 10.71 (dd (unresolved), *J*(PH) ≈ *J*(HH) ≈ 5.2 Hz, 1H, *quinolyl*), 8.65 (d, *J* = 8.2 Hz, 1H), 8.24 (t, *J* = 9.2 Hz, 2H), 8.13 – 8.09 (m, 2H), 7.93 (dd, *J* = 8.1, 5.2 Hz, 1H, *quinolyl*), 7.93 (dd, *J* = 10.5, 8.0 Hz, 2H), 7.81 (t, *J* = 7.6 Hz, 1H, P*Ph*$_2$-*para*), 7.74 (t, *J* = 7.5 Hz, 1H, P*Ph*$_2$-*para*), 7.46 (dd, *J* = 16.0, 8.0 Hz, 2H), 7.42–7.30 (m, 13H, B*Ph*$_4$-*ortho* and other aromatic), 7.19 (t, *J* = 6.6 Hz, 2H), 7.13–7.07 (m, 3H), 7.04 (t, *J* = 7.3 Hz, 10H, B*Ph*$_4$-*meta* and other aromatic), 6.94–6.85 (m, 5H, B*Ph*$_4$-*para* and other aromatic), 6.73 (t, *J* = 6.8 Hz, 2H), 6.40 (dd, *J* = 11.0, 8.1 Hz, 2H), 6.23 (dd, *J* = 11.0, 7.5 Hz, 2H), 4.48 (dd, *J* = 16.5, 8.6 Hz, 1H, Ru=C(O-)CH$_2$CH$_2$C*H*$_2$-), 4.27 (dd, *J* = 15.4, 8.9 Hz, 1H, Ru=C(O-)CH$_2$CH$_2$C*H*$_2$-), 3.34 – 3.21 (m, 1H, Ru=C(O-)C*H*$_2$), 2.08 (ddd, *J* = 19.6, 9.3, 5.9 Hz, 1H, Ru=C(O-)C*H*$_2$), 1.82–1.74 (m, 1H, Ru=C(O-)CH$_2$C*H*$_2$), 1.39-1.34 (m, 1H, Ru=C(O-)CH$_2$C*H*$_2$); ^{13}C{^{1}H} NMR(126 MHz, CD_2Cl_2) δ 314.14(t, *J* (PC)= 12.2 Hz, Ru=*C*), 164.1 (dd, *J* = 98.4, 49.5 Hz, P*Ph*$_2$-*ipso*), 156.1, 152.3, 152.1, 152.0, 151.93, 151.87, 139.5, 138.8, 137.93, 137.87, 135.9 (B*Ph*$_4$-*ortho*), 135.5, 135.4, 134.2-127.4(m), 125.6 (B*Ph*$_4$-*meta*), 124.0, 122.3, 121.7 (B*Ph*$_4$-*para*), 83.1 (Ru=CO*C*H$_2$-), 53.0 (Ru=COCH$_2$*C*H$_2$CH$_2$-), 20.8 (Ru=C*C*H$_2$-); elemental analysis calcd (%) for $C_{70}H_{58}BClN_2OP_2Ru$•CH_2Cl_2: C, 68.91; H, 4.89; N, 2.26; found: C, 69.31; H, 5.30; N, 2.49

Typical procedure for the catalytic reactions: Catalyst **2** (0.001 mmol) was added to a solution of alkynol (0.1 mmol) in DCE or THF. The resulting solution was stirred at 90 °C or 100 °C and monitored by TLC or ^{1}H NMR spectroscopy. When the conversion of sustrates was complete, the desired product was isolated by flash column chromatography on silica gel. For some products of low boiling points, the yields were determined by GC methods or ^{1}H NMR spectroscopic integration with CH_2Br_2 as the internal standards in d_8-THF.

Crystallograhic Analysis. Crystals suitable for X-ray diffraction were grown from a $CHCl_3$ solution (for **1**), or CH_2Cl_2 solution (for **2**, **3**, **12**, **12'**, **13**, and **14**) layered with *n*-hexane. Data collections were performed on an Oxford Gemini S Ultra or a Rigaku R-AXIS SPIDER IP CCD area detector using graphite-monochromated Mo Kα radiation (λ =0.71073 Å). Multiscan absorption corrections (SADABS) were applied. All of the data were corrected for absorption effects using the multi-scan technique. The structures were solved by direct methods, expanded by difference Fourier syntheses, and refined by full-matrix least-squares on F^2 using the Bruker SHELXTL-97 program and Olex 2. Non-H atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms. The Cell parameters, data collection, and structure solution and refinement for complexes **1**, **2**, **3**, **12, 12', 13** and **14** are given in Tables S1–S3 (See Supporting Information). CCDC 1469353 (**1**)**,** 1469355 (**2**)**,** 1469359 (**3**)**,** 1469354 (**12**)**,** 1564337 (**12'**)**,** 1469356 (**13**) and 1469357 (**14**) contain the 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.

Acknowledgements

This work was supported by the National Basic Research Program of China (973 Program 2012CB821600), and Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT).

Keywords: alkynes • cycloisomerization • ruthenium • oxacyclocarbene complex • 8-(diphenylphosphino)quinoline

Reference

[1] a) A. Mitchinson, A. Nadin, *J. Chem. Soc., Perkin Trans. 1*, **2001**, 2303-2340; b) G. Wuitschik, E. M. Carreira, B. Wagner, H. Fischer, I. Parrilla, F. Schuler, M. Rogers-Evans, K. Müller, *J. Med. Chem.* **2010**, *53*, 3227-3246; c) B. Das, P. Jangili, *Synlett* **2016**, *27*, 924-928.

[2] Selected examples: a) Z. Zhang, C. Liu, R. E. Kinder, X. Han, H. Qian, R. A. Widenhoefer, *J. Am. Chem. Soc.* **2006**, *128*, 9066–9073; b) A. Boyer, N. Isono, S. Lackner, M. Lautens, *Tetrahedron* **2010**, *66*, 6468-6482; c) V. Christov, I. E. Ismailov, I. K. Ivanov, *Molecules* **2015**, *20*, 7263-7275; d) A. A. Peshkov, A. A. Nechaev, O. P. Pereshivko, J. L. Goeman, J. Van der Eycken, V. A. Peshkov, E. V. Van der Eycken, *Eur. J. Org. Chem.* **2015**, 4190-4197.

[3] Selected reviews see: a) S. Ma, *Acc. Chem. Res.* **2003**, *36*, 701–707; b) I. Nakamura, Y. Yamamoto, *Chem. Rev*. **2004**, *104*, 2127-2198; c) B. Alcaide, P. Almendros, J. M. Alonso, *Org. Biomol. Chem.* **2011**, *9*, 4405-4416; d) A. V. Gulevich, A. S. Dudnik, N. Chernyak, V. Gevorgyan, *Chem. Rev.* **2013**, *113*, 3084-3213; e) X.-F. Wu, H. Neumann, M. Beller, *Chem. Rev.* **2013**, *113*, 1-35; f) C. Díez-Poza, A. Barbero, *Eur. J. Org. Chem.* **2017**, DOI: 10.1002/ejoc.201700644.

[4] Selected reviews see: a) B. M. Trost, *Acc. Chem. Res.* **2002**, *35*, 695–705;b) F. Alonso, I. P. Beletsaya, M. Yus, *Chem. Rev*. **2004**, *104*, 3079–3159; c) B. M. Trost, M. U. Frederiksen, M. T. Rudd, *Angew. Chem. Int. Ed.* **2005**, *44*, 6630-6666; *Angew. Chem.* **2005**, *117*, 6788-6825.

[5] a) F. E. McDonald, C. B. Connolly, M. M. Gleason, T. B. Towne, K. D. Treiber, *J. Org. Chem*. **1993**, *58*, 6952–6953; b) F. E. McDonald, C. C. Schultz, *J. Am. Chem. Soc.* **1994**, *116*, 9363-9364; c) F. E. McDonald, M. M. Gleason, *Angew. Chem. Int. Ed. Engl*. **1995**, *34*, 350–352; *Angew. Chem*. **1995**, *107*, 356–358; d) F. E. McDonald, M. M. Gleason, *J. Am. Chem. Soc*. **1996**, *118*, 6648–6659; e) F. E. McDonald, *Chem. Eur. J.* **1999**, *5*, 3103-3106.

[6] a) F. E. McDonald, K. S. Reddy, Y. Díaz, *J. Am. Chem. Soc.* **2000**, *122*, 4304-4309; b) F. E. McDonald, K. S. Reddy, *Angew.Chem. Int. Ed*. **2001**, *40*, 3653–3655; *Angew. Chem*. **2001**, *113*, 3765–3767; c) F. E. McDonald, K. S. Reddy, *J. Organomet. Chem*. **2001**, *617–618*, 444–452; d) P. Wipf, T. H. Graham, *J. Org. Chem*. **2003**, *68*, 8798–8807; e) M. H. Davidson, F. E. McDonald, *Org. Lett.* **2004**, *6*,1601–1603; f) E. Alcázar, J. M. Pletcher, F. E. McDonald, *Org. Lett.* **2004**, *6*, 3877-3880; g) B. Koo, F. E. McDonald, *Org. Lett.* **2005**, *7*, 3621–3624; h) J. Barluenga, A. Diéguez, F. Rodríguez, F. J. Fañanás, *Angew. Chem. Int. Ed.* **2005**, *44*, 126-128; *Angew. Chem*. **2005**, *117*, 128 –130; i) J. Barluenga, A. Diéguez, F. Rodríguez, F. J. Fañanás, T. Sordo, P. Campomanes, *Chem. Eur. J*. **2005**, *11*, 5735-5741; j) S. B. Moilanen, D. S. Tan, *Org. Biomol. Chem.* **2005**, *3*, 798-803; k) B. Koo, F. E. McDonald, *Org. Lett.* **2007**, *9*, 1737-1740; l) J. Wu, M. Wang, L. Wang, J. Wang, L. Jiang, *J. Org. Chem.* **2013**, *78*, 10812-10820;

[7] H. X. Siyang, X. R. Wu, X. Y. Ji, X. Y. Wu, P. N. Liu, *Chem. Commun.* **2014**, *50*, 8514-8517.

[8] a) B. Gabriele, G. Salerno, A. Fazio, R. Pittelli, *Tetrahedron* **2003**, *59*, 6251-6259; b) J. Zhang, X. Zhao, L. Lu, *Tetrahedron Lett.* **2007**, *48*, 1911-1913; c) C. V. Ramana, R. Mallik, R. G. Gonnade, *Tetrahedron* **2008**, *64*, 219-233; d) C. V. Ramana, B. Induvadana, B. Srinivas, K. Yadagiri, M. N. Deshmukh, R. G. Gonnade, *Tetrahedron* **2009**, *65*, 9819-9832; e) F. Wang, Z. Miao, R. Chen, *Org. Biomol. Chem.* **2009**, *7*, 2848-2850.

[9] a) B. Liu, J. K. De Brabander, *Org. Lett.* **2006**, *8*, 4907-4910; b) J. Barluenga, A. Mendoza, F. Rodríguez, F. J. Fañanás, *Chem. Eur. J.* **2008**, *14*, 10892-10895; c) N. T. Patil, R. D. Kavthe, V. S. Raut, V. V. N. Reddy, *J. Org. Chem.* **2009**, *74*, 6315-6318; d) N. T. Patil, R. D. Kavthe, V. S. Shinde, B. Sridhar, *J. Org. Chem*. **2010**, *75*, 3371-3380; e) P. A. Allegretti, E. M. Ferreira, *Org. Lett.* **2011**, *13*, 5924-5927; f) P. Pardo, A. Fernández, F. J. Fañanás, F. Rodríguez, *Adv. Synth. Catal.* **2012**, *354*, 2141-2145; g) A. Galván, J. Calleja, F. J. Fañanás, F. Rodríguez, *Angew. Chem. Int. Ed.* **2013**, *52*, 6038-6042; *Angew. Chem.* **2013**, *125*, 6154-6158.

[10] a) E. Parker, N. Leconte, T. Godet, P. Belmont, *Chem. Commun.* **2011**, *47*, 343-345; b) M. Maheswara, Y. Y. Lee, E. J. Kang, *Synlett* **2012**, *23*, 2481-2484; c) M. Dell'Acqua, B. Castano, C. Cecchini, T. Pedrazzini, V. Pirovano, E. Rossi, A. Caselli, G. Abbiati, *J. Org. Chem.* **2014**, *79*, 3494-3505;

[11]a) P.-S. Wang, K.-N. Li, X.-L. Zhou, X. Wu, Z.-Y. Han, R. Guo, L.-Z. Gong, *Chem. Eur. J.* **2013**, *19*, 6234-6238; b) L. Cala, A. Mendoza, F. J. Fananas, F. Rodriguez, *Chem. Commun.* **2013**, *49*, 2715-2717; c) Y.-F. Yu, C. Shu, B. Zhou, J.-Q. Li, J.-M. Zhou, L.-W. Ye, *Chem. Commun.* **2015**, *51*, 2126-2129; d) B. Wagner, W. Hiller, H. Ohno, N. Krause, *Org. Biomol. Chem.* **2016**, *14*, 1579-1583; e) S. Doherty, J. G. Knight, D. O. Perry, N. A. B. Ward, D. M. Bittner, W. McFarlane, C. Wills, M. R. Probert, *Organometallics* **2016**, 35, 1265-1278.

[12] a) B. M. Trost, Y. H. Rhee, *J. Am. Chem. Soc*. **2002**, *124*, 2528-2533; b) B. M. Trost, M. T. Rudd, M. G. Costa, P. I. Lee, A. E. Pomerantz, *Org. Lett.* **2004**, *6*, 4235-4238; c) A. Varela-Fernández, C. González-Rodríguez, J. A. Varela, L. Castedo, C. Saá, *Org. Lett.* **2009**, *11*, 5350-5353; d) P. N. Liu, F. H. Su, T. B. Wen, H. H. Y. Sung, I. D. Williams, G. Jia, *Chem. Eur. J*. **2010**, *16*, 7889-7897; e) M. J. Zacuto, D. Tomita, Z. Pirzada, F. Xu, *Org. Lett*. **2010**, *12*, 684-687. .

[13] a) B. M. Trost, Y. H. Rhee, *J. Am. Chem. Soc*. **2003**, *125*, 7482-7483; b) D. Y. Li, H. J. Chen, P. N. Liu, *Angew. Chem. Int. Ed.* **2016**, *55*, 373-377; *Angew. Chem.* **2016**, *128*, 381-385.

[14] a) A. Varela-Fernández, C. García-Yebra, J. A. Varela, M. A. Esteruelas, C. Saá, *Angew. Chem. Int. Ed.* **2010**, *49*, 4278-4281; *Angew. Chem.* **2010**, *122*, 4374-4377; For a closely related example of osmium-catalyzed 7-endo heterocyclization of *o*-alkynyl phenethylamines, see: b) A. Álvarez-Pérez, C. González-Rodríguez, C. García-Yebra, J. A. Varela, E. Oñate, M. A. Esteruelas, C. Saá, *Angew. Chem. Int. Ed.* **2015**, *54*, 13357-13361; *Angew. Chem.* **2015**, *127*, 13555-13559.

[15] B. M. Trost, A. McClory, *Angew. Chem. Int. Ed.* **2007**, *46*, 2074 –2077; *Angew. Chem.* **2007**, *119*, 2120 –2123.

[16] a) J. Liu, A. Steigel, E. Reininger, R. Bauer, *J. Nat. Prod.* **2000**, *63*, 403-405; b) L. I. Belen'kii in *Comprehensive Heterocyclic Chemistry III*, *Vol. 3*, Elsevier, Amsterdam, **2008**, pp. 45-95, and references therein. c) J. R. Kesting, D. Staerk, M. V. Tejesvi, K. R. Kini, H. S. Prakash, J. W. Jaroszewski, *Planta Med*. **2009**, *75*, 1104-1106.

[17] a) H. A. Hudali, J. V. Kingston, H. A. Tayim, *Inorg. Chem*. **1979**,*18*,1391-1394; b) D. G. Allen, G. M. McLaughlin, G. B. Robertson, W. L. Steffen, G. Salem, S. B. Wild, *Inorg. Chem*. **1982**, *21*, 1007-1014; c) G. Salem, S. B. Wild, *Inorg. Chem*. **1992**, *31*, 581-586.

[18] a) P. Wehman, H. M. A. van Donge, A. Hagos, P. C. J. Kamer, P. W. N. M. van Leeuwen, *J. Organomet. Chem*. **1997**, *535*, 183-193; b) W.H. Sun, Z. Li, H. Hu, B. Wu, H. Yang, N. Zhu, X. Leng, H. Wang, *New J. Chem.* **2002**, *26*, 1474–1478; c) T. Suzuki, T. Kuchiyama, S. Kishi, S. Kaizaki, H. D. Takagi, M. Kato, *Inorg. Chem.* **2003**, *42*, 785-795; d) D. Sirbu, G. Consiglio, S. Gischig, *J. Organomet. Chem*. **2006**, *691*,1143-1150; e) P. A. Aguirre, C. A. Lagos, S. A. Moya, C. Zúñiga, C. Vera-Oyarce, E. Sola, G. Peris, J. C. Bayón, *Dalton Trans*., **2007**, *0*, 5419-5426; f) G. Nakamura, M. Okamura, M. Yoshida, T. Suzuki, H. D. Takagi, M. Kondo, S. Masaoka, *Inorg. Chem*. **2014**, *53*, 7214-7266; g) L. Canovese, F. Visentin, T. Scattolin, C. Santo, V. Bertolasi, *Dalton Trans*., **2015**, *44*, 15049-15058; h) L. Huang, F. Rominger, M. Rudolph, A. S. K. Hashmi, *Chem. Commun*., **2016**, *52*, 6435-6438;

[19] For reviews on the use of vinylidenes in catalysis, see: a) M. I.Bruce, *Chem. Rev*. **1991**, 91, 197–257; b) C. Bruneau, P. H. Dixneuf, *Angew. Chem.Int. Ed. 2006*, 45, 2176–2203; *Angew. Chem*. **2006**, *118*, 2232–2260; c) B. M. Trost, A. McClory, *Chem. Asian J*. **2008**, 3, 164–194.

[20] P. N. Liu, T. B. Wen, K. D. Ju, H. H. Y. Sung, I. D. Williams, G. Jia, *Organometallics* **2011**, *30*, 2571-2580

[21] a) F. E. McDonald, J. L. Bowman, *Tetrahedron Lett.* **1996**, *37*, 4675-4678; b) F. E. McDonald, H. Y. H. Zhu, *Tetrahedron* **1997**, *53*, 11061-11068.

[22] a) Y. Sheng, D. G. Musaev, K. S. Reddy, F. E. McDonald, K. Morokuma, *J. Am. Chem Soc.* **2002**, *124*, 4149–4157; b) T. Nowroozi-Isfahani, D. G. Musaev, F. E. McDonald, K. Morokuma, *Organometallics* **2005**, *24*, 2921-2929; c) T. Sordo, P. Campomanes, A. Dieguez, F. Rodriguez, F. J. Fananas, *J. Am. Chem. Soc.* **2005**, *127*, 944-952;

[23] B. Weyershausen, K. H. Dötz, *Eur. J. Inorg. Chem*. **1999**, 1057−1066 and references therein;

[24] a) J. M. O'Connor, K. Hiibner, A. Closson, P. Gantzel, *Organometallics* **2000**, *20*,1482-1485; b) M. Peruzzini, D. Akbayeva, C. Bianchini, I. de los Rios, A. Ienco, N. Mantovani, L. Marvelli, R. Rossi, *Inorg. Chim. Acta*, **2002**, *339*, 202-208;c) L. Marvelli, N. Mantovani, A. Marchi, R. Rossi, M. Brugnati, M. Peruzzini, P. Barbaro, I. de los Rios, V. Bertolasi, *Dalton Trans*. **2004**, 713-722; d) S. El-Tarhuni, L. M. Manhães, C. Morrill, J. Raftery, J. K. Randhawa, M. W. Whiteley, *J. Organomet. Chem.* **2016**, *811*, 20-25;

[25] a) H. Le Bozec, K. Ouzzine, P. H. Dixneuf, *Organometallics* **1991**, *10*, 2768-2772; b) R. L. Beddoes, R. W. Grime, Z. I. Hussain, M. W. Whiteley, *J. Organomet. Chem.* **1996**, *526*, 371-378; c) W.-H. Leung, E. Y. Y. Chan, I. D. Williams, W.-T. Wong, *Organometallics* **1997**, *16*, 3234-3240; d) L.P. Barthel-Rosa, K. Maitra, J. Fischer, J. H. Nelson, *Organometallics* **1997**,*16*,1714-1723; e) H. D. Hansen, J. H. Nelson, *Organometallics* **2000**, *19*, 4740-4755; f) M. P. Gamasa, J. Gimeno, B. M. MartínVaca, R. Isea, A. Vegas, *J. Organomet. Chem*. **2002**, *651*, 22−33; g) A. Keller, B. Jasionka, T. Gzowiak, A. Ershov, R. Matusiak, *Inorg. Chim. Acta* **2003**, *344*, 49-60; h) S. Pavlik, K.Mereiter, M. Puchberger, K. Kirchner, *J. Organomet. Chem*. **2005**, *690*, 5497-5507; i) H. Kopf, C. Pietraszuk, E. Hübner, N. Burzlaff, *Organometallics* **2006**, *25*, 2533-2546; j) Y. –H. Lo, T. –H. Wang, C. –Y. Lee, Y. –H. Feng, *Organometallics* **2012**, *31*, 6887−6899; k) C. E. Welby, T. O. Eschemann, C. A. Unsworth, E. J. Smith, R. J. Thatcher, A. C. Whitwood, J. M. Lynam, *Eur. J. Inorg. Chem.* **2012**, *2012*,1493-1506; l) T. Li, C. Fu, Z. Liu, S. Guo, Z. Liu, T.-B. Wen, *Organometallics* **2015**, *34*, 3292-3302; m) I. G. Arada, J. Díez, M. P. Gamasa, E. Lastra, *J. Organomet. Chem*. **2015**, *797*,101-109;

[26] a) C. Bianchini, A. Marchi, N. Mantovani, L. Marvelli, D. Masi, M. Peruzzini, R. Rossi, *Eur. J. Inorg. Chem.* **1998**, 211–219; b) J. Gimeno, M. González-Cueva, E. Lastra, E. Pérez-Carreño, S. García-Granda, *Inorg. Chim. Acta* **2003**, *347*, 99–106.

[27] a) C. –W. Chang, Y. –C. Lin, G. –H. Lee, Y. Wang, *Organometallics* **2000**, *19*, 3211-3219; b) Y. –C. Wang, Y. -C. Lin, Y. H. Liu, *Chem. Asian J.* **2012**, *7*, 2703-2710.

[28] a) W. G. Hatton, J. A. Gladysz, *J. Am. Chem. Soc*. **1983**, *105*, 6157–6158; b) C. Roger, G. S. Bodner, W. G. Hatton, J. A. Gladysz, *Organometallics* **1991**, *10*, 3266–3274.

[29] a) R. Castro-Rodrigo, M. A. Esteruelas, S. Fuertes, A. M. López, S. Mozo, E. Oñate, *Organometallics* **2009**, *28*, 5941–5951; b) M. Besora, S. F. Vyboishchikov, A. Lledós, F. Maseras, E. Carmona, M. L. Poveda, *Organometallics* **2010**, *29*, 2040–2045; c) S. Bajo, M. A. Esteruelas, A. M. López, E. Oñate, *Organometallics* **2014**, *33*, 4057–4066.

[30] T. Pullmann, B. Engendahl, Z. Zhang, M. Hölscher, A. Zanotti-Gerosa, A. Dyke, G. Franciò, W. Leitner, *Chem. Eur. J.* **2010**, *16*, 7517-7526.

[31] R. W. Mitchell, A. Spencer, G. Wilkinson, *J. Chem. Soc., Dalton Trans.* **1973**, 846-854.

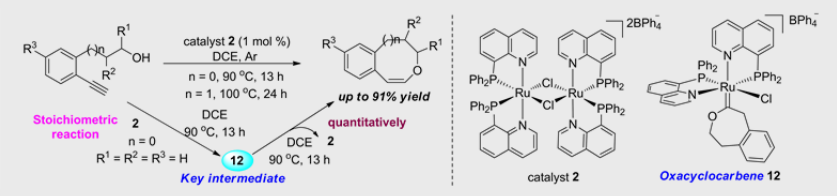
10.1002/chem.201703971

WILEY-VCH

Entry for the Table of Contents (Please choose one layout)

Layout 2:

FULL PAPER



The new ruthenium complex $[Ru(\mu\text{-}Cl)(DPPQ)_2]_2(BPh_4)_2$ (**2**) (DPPQ = 8-(diphenylphosphino)quinoline), with only 1 mol% loading, was found to be catalytically active for the *endo*-cycloisomerization of various alkynols to endo-cyclic enol ethers in moderate to excellent yields. In particular, the 7-*endo* and 8-*endo* heterocyclization of aromatic alkynols can be achieved efficiently. The oxacyclocarbene complex **12** was isolated as the key intermediate.

*Tao Cai, Yu Yang, Wei-Wei Li, Wen-Bing Qin, and Ting-Bin Wen**

Page No. – Page No.

Efficient *Endo* Cycloisomerization of Terminal Alkynols Catalyzed by a New Ruthenium Complex with 8-(Diphenylphosphino)quinoline Ligand and Mechanism Investigation