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Selective and Efficient Cycloisomerization of Alkynols Catalyzed by a New Ruthenium Complex with a Tetradentate Nitrogen–Phosphorus Mixed Ligand

Pei Nian Liu,[a, b] Fu Hai Su,[a] Ting Bin Wen,[a] Herman H.-Y. Sung,[a] Ian D. Williams,[a] and Guochen Jia*[a]

Abstract: The new ruthenium complex $[Ru(N_3P)(OAc)][BPh_4]$ (**4**), in which N_3P is the N,P mixed tetradentate ligand *N*,*N*-bis[(pyridin-2-yl)methyl]-[2-(diphenylphosphino)phenyl]methanamine was synthesized. The complex was found to be catalytically active for the *endo* cycloisomerization of alkynols. The catalytic reactions can be used to synthesize five-, six-, and seven-membered *endo*-cyclic enol ethers in good to excellent yields. A catalytic cycle involving a vinylidene intermediate was proposed for the catalytic reactions. Treatment of complex **4** with PhC≡CH and H_2O gave the alkyl complex $[Ru(CH_2Ph)(CO)(N_3P)][BPh_4]$ (**30**), which supports the assumption that the catalytic reactions involve addition of a hydroxyl group to the C=C bond of vinylidene ligands.

Keywords: alkynes · isomerization · N,P ligands · ruthenium · vinylidene

Introduction

Oxygen-containing heterocycles are important structural components presented in a diverse range of naturally occurring and biologically active molecules.[1] The widespread occurrence of oxygen heterocycles and the limitations associated with the traditional synthetic methodologies for heterocycles[1a,b] have stimulated considerable interest in developing efficient homogeneous catalytic methods for the synthesis of such heterocyclic compounds.[2] Cycloisomerization of alkynols represents a direct means for the synthesis of cyclic enol ethers with the advantage of 100% atom efficiency, which fulfills the requirements for green chemistry[3] and provides a straightforward and efficient approach to numerous oxygen-containing heterocycles.[4]

Cycloisomerization of alkynols can lead to either *exo*- or *endo*-cyclic enol ethers.[5] There have been growing efforts to develop efficient and selective catalysts for this challenging transformation. Cycloisomerization of alkynols to give *exo*-cyclic enol ethers was firstly described for reactions catalyzed by HgO and $BF_3{\cdot}Et_2O$.[6] Other complexes, such as $Pd(OAc)_2$,[7] Ag_2CO_3,[8] AuCl,[9] and organolanthanide complexes $[Ln\{N(SiMe_3)_2\}_3]$ (Ln = La, Sm, Y, Lu)[10] were also demonstrated to be effective to mediate the *exo* cycloisomerization of alkynols. $[RuCl_2(p\text{-cymene})(PPh_3)]$[11] and palladium catalysts, such as $PdCl_2$,[12] $Pd(OAc)_2$,[13] and K_2PdI_4,[14] were found to catalyze the *exo* cycloisomerization/isomerization tandem reactions of enynols to form *endo*-cyclic enol ethers or furans.

The *endo* cycloisomerization of alkynols could afford *endo*-cyclic enol ethers, which are very useful synthetic intermediates in the construction of diverse oxygen-containing heterocycles.[15–19] As the pioneering work, McDonald and co-workers have developed the *endo* cycloisomerization of alkynols by employing molybdenum or tungsten carbonyls as the catalysts.[20] The molybdenum catalyst is effective for the synthesis of five-membered cyclic enol ethers from 4-hydroxy-1-alkynes,[5,17,18,21] whereas the tungsten catalyst can also effect the formation of six-[15,16,20–22] and seven-membered[23] cyclic enol ethers from 5-hydroxy-1-alkynes and 6-

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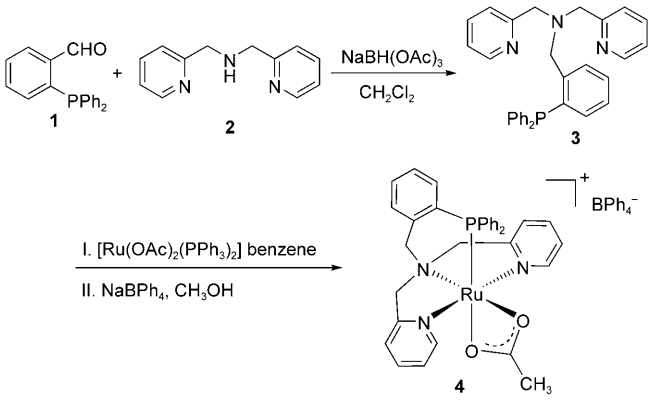
hydroxy-1-alkynes. Although a rather large amount of catalyst loading (25–40 mol%) was usually required in these catalytic reactions, the catalytic reaction has been successfully applied for the synthesis of various natural products,[15] such as glycals,[16] nucleosides,[17] and clinically valuable drugs.[18] More recently, Trost, Saa, and Zacuto et al. reported the cycloisomerization of 4-hydroxy-1-alkynes and 5-hydroxy-1-alkynes (homo and bis(homopropargylic) alcohols) catalyzed by ruthenium complexes, such as $[Ru(Cp)(L)_n]^+$/phosphine ligands (20–40 mol%) and $[RuCl(Cp)(PPh_3)_2]$/amine,[24] and the rhodium complex $[RhCl(PR_3)_3]$/phosphine ligands (30–55 mol%).[25] It was reported very recently that $AgNO_3$, Pd^{II}/Cu^{I}, or Au^{I} complexes can catalyze the cycloisomerization of *cis*-4-hydroxy-5-alkynylpyrrolidinones and *cis*-5-hydroxy-6-alkynylpiperidinones.[26] In a related work, Qing et al. have studied the $[PdCl_2(MeCN)_2]$-mediated *endo* cycloisomerization of 2-alkynyl-3-trifluoromethyl allylic alcohols to give tetrahydrofuran derivatives.[27] The development of more efficient and selective catalysts for the *endo* cycloisomerization of alkynols still remains a challenging objective.

Reported herein is our work in the design and synthesis of a new ruthenium complex with a P/N tetradentate ligand and its application for the cycloisomerization of alkynols. The catalytic reactions exhibit very high regioselectivity to give exclusively *endo* products in good to excellent yields.

Results and Discussion

Synthesis of the catalytic precursor $[Ru(N_3P)(OAc)][BPh_4]$: The synthetic route to the catalytic precursor $[Ru(N_3P)(OAc)][BPh_4]$ (**4**) N_3P = *N*,*N*-bis[(pyridin-2-yl)methyl][2-(diphenylphosphino)phenyl]methanamine) is outlined in Scheme 1. Reductive amination of compound **1** with di(2-picolyl)amine (**2**) in the presence of sodium triacetoxyborohydride produced the tetradentate ligand **3** (abbreviated as N_3P), which could be isolated in 85% yield. Treatment of ligand **3** with $[Ru(OAc)_2(PPh_3)_2]$ and $NaBPh_4$ produced the new ruthenium complex $[Ru(N_3P)(OAc)][BPh_4]$ (**4**), which was isolated as a yellow solid in 63% yield.



Scheme 1. Synthesis of complex **4**.

Complex **4** has been characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy and mass spectroscopic methods. Consistent with the structure shown in Scheme 1, the ^1H NMR spectrum (in CD_2Cl_2) displays the methyl signal of the acetate ligand at $\delta = 2.00$ ppm and the proton signal of the methylene linked to the aryl group at $\delta = 3.37$ ppm. The four protons of the methylenes linked to the pyridyls exhibit two doublets at $\delta = 3.83$ and 4.37 ppm. The $^{13}C\{^1H\}$ NMR spectrum (in CD_2Cl_2) shows the signals of the acetate ligand at $\delta = 24.3$ and 189.7 ppm and the signals of the three methylenes at $\delta = 67.5$, 67.6, and 68.7 ppm. The $^{31}P\{^1H\}$ NMR spectrum displays a singlet at $\delta = 63.4$ ppm.

The structure of **4** has also been confirmed by X-ray diffraction. Single crystals of complex **4** suitable for the X-ray crystallographic study were readily obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of complex **4**. The crystal data and refinement details are given in Table 1 and selected bond lengths and angles are listed in Table 2. Figure 1 shows the X-ray structure of the complex cation of **4**. The coordination geometry of ruthenium in **4** can be described as a distorted octahedron with a tetradentate N_3P ligand and a bidentate acetate ligand. The two pyridine rings of the N_3P ligand are *trans* to each other. One of the oxygen atoms of the acetate ligand is *trans* to the P atom and the other

Table 1. Crystal data and structure refinement for complexes **4** and **30**.

	4	**30**
empirical formula	$C_{57}H_{51}BN_3O_2PRu{\cdot}CH_2Cl_2$	$C_{63}H_{55}BN_3OPRu$
M_w	1037.78	1012.95
T [K]	100(2)	173(2)
λ [Å]	0.71073	1.54178
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P21/c$
a [Å]	11.5070(15)	16.6548(2)
b [Å]	13.4495(17)	11.33680(10)
c [Å]	16.409(2)	26.4042(2)
α [°]	82.474(2)	90
β [°]	82.791(2)	102.0530(10)
γ [°]	77.904(2)	90
V [Å^3]	2449.0(5)	4875.53(8)
Z	2	4
ρ [g cm^{-3}]	1.407	1.380
crystal size [mm^3]	$0.38\times0.25\times0.20$	$0.30\times0.28\times0.15$
θ range [°]	1.82 to 26.00	5.79 to 71.65
index ranges	$-14\le h\le 14$	$-19\le h\le 20$
	$-16\le k\le 16$	$-13\le k\le 11$
	$-20\le l\le 20$	$-30\le l\le 32$
no. of reflns collected	20681	15205
no. of independent reflns	9454	8913
	(R(int) = 0.0256)	(R(int) = 0.0284)
completeness to $\theta = 25.00°$ [%]	98.5	96.3
max. and min. transmission	1.00 and 0.94	1.00 and 0.83
data/restraints/parameters	9454/0/633	8913/0/631
GOF on F^2	1.044	1.023
final R indices [$I>2\sigma(I)$]	$R1 = 0.0338$,	$R1 = 0.0310$,
	$wR2 = 0.0767$	$wR2 = 0.0850$
R indices (all data)	$R1 = 0.0402$,	$R1 = 0.0334$,
	$wR2 = 0.0790$	$wR2 = 0.0864$
largest diff peak and hole [e Å^{-3}]	0.582 and −0.497	0.389 and −0.451

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Table 2. Selected bond lengths and angles in complex **4**.

Ru1–N1	2.0797(18)	Ru1–N10	2.0478(18)
Ru1–N20	2.0523(18)	Ru1–O51	2.1866(14)
Ru1–O52	2.1406(14)	Ru1–P1	2.2446(6)
C50–O51	1.270(3)	C50–O52	1.266(3)
C1–C2	1.509(3)	N1–C1	1.505(2)
N1–C20	1.499(3)	N1–C10	1.502(3)
C10–C11	1.504(3)	C20–C21	1.510(3)
O52-Ru1-O51	60.61(6)	O52-Ru1-P1	107.91(4)
N1-Ru1-O52	160.20(6)	N1-Ru1-O51	99.60(6)
O51-Ru1-P1	168.00(4)	N20-Ru1-N1	83.37(7)
N10-Ru1-N20	165.29(7)	N1-Ru1-P1	91.88(5)
N10-Ru1-P1	94.86(5)	N20-Ru1-P1	91.59(5)
N20-Ru1-O52	95.26(6)	N10-Ru1-O52	95.32(6)
N20-Ru1-O51	86.34(6)	N10-Ru1-O51	89.97(6)
N10-Ru1-N1	83.22(7)	C50-O51-Ru1	89.14(12)
C50-O52-Ru1	91.33(13)	O52-C50-O51	118.91(19)
C3-P1-Ru1	107.14(7)	C1-N1-Ru1	119.43(13)
N1-C1-C2	112.73(16)	C20-N1-Ru1	104.41(12)
N1-C20-C21	111.72(18)	C10-N1-Ru1	102.74(12)
N1-C10-C11	110.06(17)	C41-P1-Ru1	120.07(7)
C31-P1-Ru1	117.95(7)	C21-N20-Ru1	112.34(14)
C25-N20-Ru1	129.20(16)	C11-N10-Ru1	111.83(14)
C15-N10-Ru1	129.08(15)		

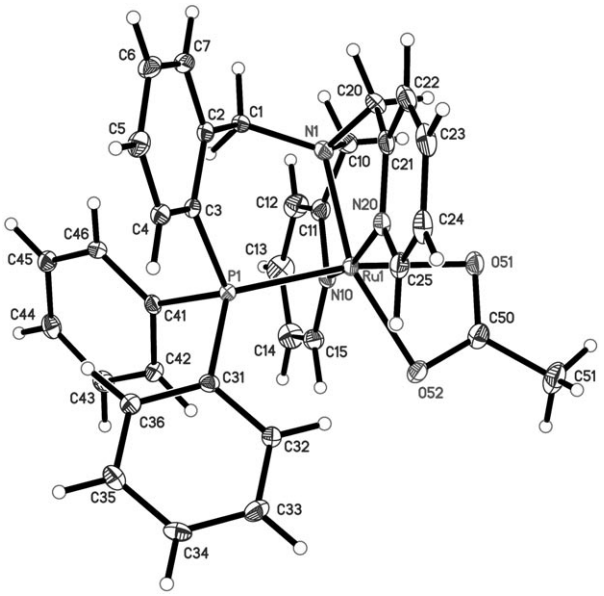
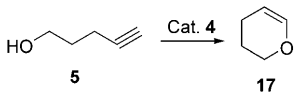


Figure 1. ORTEP diagram for the cation of complex **4**.

one *trans* to the tertiary amine N atom. The Ru–O (acetyl) bond lengths (2.1866(14) and 2.1406(14) Å) are similar to those of other Ru^{II}–η^2-acetate complexes.[28] The solid-state structure is in agreement with the solution NMR spectroscopic data.

Catalytic reactions: The catalytic properties of complex **4** for the cycloisomerization of alkynols was initially tested with 5-pentyn-1-ol (**5**) as the substrate in various solvents. In a typical reaction, a mixture of **5** (0.50 mmol) and catalyst (0.005 mmol) in a solvent was heated at 80 °C for 2 h and the conversion of the substrate was then analyzed by ^{1}H NMR spectroscopy. The results are listed in Table 3. As shown in Table 3, the reactions proceeded well in solvents

Table 3. Cycloisomerization of 5-pentyne-1-ol **5** under various conditions.[a]



5 **17**

Entry	Solvent	Loading of cat. **4** [mol %]	t [h]	Conv. [%][b]
1	acetone	1	2	84
2	$CHCl_3$	1	2	85
3	benzene	1	2	100
4	CH_3CN	1	2	9
5	CH_2Cl_2	1	48	22[c]
6	THF	1	1	100
7	THF	0.5	7	70
8	THF	2	7	3[d]

[a] The reactions were carried out by using 0.50 mmol of **5** and 0.5 mL of solvent under N_2 at 80 °C, unless otherwise noted. [b] Determined by ^{1}H NMR spectroscopy. [c] The reaction was carried out at 50 °C. [d] The reaction was carried out at room temperature.

such as acetone, chloroform, and benzene to give exclusively six-membered *endo*-enol ether **17** (Table 3, entries 1–3). However, the reaction in CH_3CN gave a poor conversion probably due to the strong coordination ability of CH_3CN with ruthenium (entry 4). The conversion of the reaction is also poor (only 22 % conversion) if the reaction was carried out in boiling CH_2Cl_2 (ca. 50 °C; entry 5). THF was found to be the best solvent for the reaction and complete cycloisomerization of 5-pentyn-1-ol could be accomplished in refluxing THF in 1 h with a catalyst loading of only 1 mol % (entry 6). In contrast, 25 mol % or more of tungsten carbonyl,[20,21] 5–10 mol % of $[Ru(Cp)(L)_n]^+$/phosphine ligands (20–40 mol %),[24] or 2.5–7.5 mol % of rhodium complex $[RhCl(PR_3)_3]$/phosphine ligands (30–55 mol %)[25] were required for a similar transformation. Our catalytic system is still effective even when the catalyst loading is decreased to 0.5 mol %, although a longer reaction time is required. For example, approximately 70 % conversion of **5** was achieved after 7 h of reaction (entry 7). However, we noted that the catalytic reaction proceeded very slowly at room temperature (entry 8).

We then explored the substrate scope of the cycloisomerization reactions catalyzed by complex **4** in THF at 80 °C and the results are summarized in Table 4. With only 1 mol % of the catalyst, both aliphatic and aromatic alkynols **5**–**8** were converted exclusively to the corresponding six-membered *endo*-enol ethers **17**–**20** in high yields within 1 h (Table 4, entries 1–4), which indicated that the reactivity of primary and secondary hydroxyl groups is similar. With 5 mol % of the catalyst, cycloisomerization of propargyl alcohol **9** also occurred to give the *endo*-cyclic enol ether **21** in 90 % yield in 1 h (entry 5), and no byproduct was detected in the reaction.

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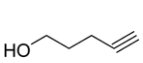
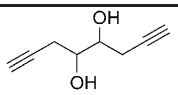
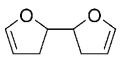
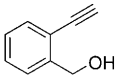
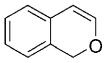
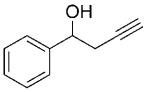
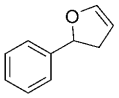
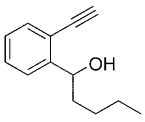
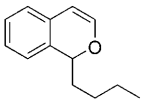
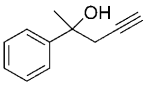
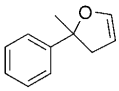
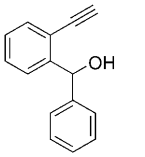
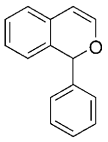
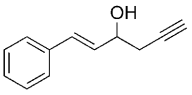
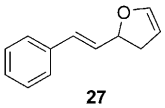
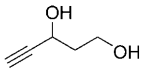
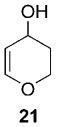
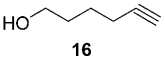
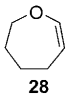
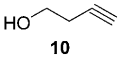
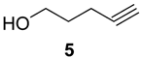
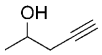
Table 4. Cycloisomerization of various alkynols by using catalyst **4**.[a]

Entry	Substrate	Product	Loading of **4** [mol%]	*t* [h]	Yield [%][b]	Entry	Substrate	Product	Loading of **4** [mol%]	*t* [h]	Yield [%][b]
1	 **5**	 **17**	1	1	91[c]	8	 **12**	 **24**	5	44	83
2	 **6**	 **18**	1	1	98[d]	9	 **13**	 **25**	5	17	98
3	 **7**	 **19**	1	1	97	10	 **14**	 **26**	5	15	89
4	 **8**	 **20**	1	1	94	11	 **15**	 **27**	5	20	93
5	 **9**	 **21**	5	1	90[d]	12	 **16**	 **28**	5	20	91[d]
6	 **10**	 **22**	5	20	78[d]	13[e]	 **5**	 **17**	1	2	90[c]
7	 **11**	 **23**	5	17	80[d]						

[a] The reactions were catalyzed by complex **4** by using 0.5 mmol substrate and THF (0.5 mL) under N_2 at 80 °C, unless otherwise noted. [b] Isolated yields. [c] Yields were determined by ^{1}H NMR spectroscopic integration with CH_3NO_2 as the internal standard. [d] Yields were determined by ^{1}H NMR spectroscopic integration with *t*BuOH as the internal standard. [e] The reaction was carried out by using **5** (10 mmol) and THF (10 mL) at 80 °C.

Our catalytic system also effects the cycloisomerization of 4-hydroxy-1-alkynols to give five-membered cyclic enol ethers. With 5 mol% of the catalyst, cycloisomerization of 4-hydroxy-1-alkynols generally gave the five-membered cyclic enol ethers in high yields, although a longer reaction time is required relative to the formation of six-membered enol ethers. For example, cycloisomerization of aliphatic alkynols **10** and **11** gave the corresponding *endo*-cyclic enol ethers **22** and **23** in 78 and 80% yields, respectively, (Table 4, entries 6 and 7). When 4,5-dihydroxy-1,7-octadiyne (**12**) was used, the reaction produced bicyclic compound **24** in 83% yield (entry 8). Catalytic cycloisomerization of alkynols **13** and **14**, which bear sterically hindered tertiary hydroxyl groups, also proceeded smoothly to afford the five-membered products **25**–**26** in high yields (entries 9 and 10). Under similar conditions, 4-hydroxy-6-phenyl-1,5-enyne (**15**) was also transformed into the five-membered *endo*-cyclic enol ether **27** in 93% yield, which suggests that the presence of the alkenyl group did not exhibit any obvious adverse effect on the catalytic reaction (entry 11). We were delighted to note that the reaction of compound **16** proceeded smoothly to give the seven-membered product **28** in excellent yield (entry 12). To evaluate the practical applicability of this catalytic reaction, we have carried out the catalytic reaction by using 10 mmol (0.84 g) of 5-pentyn-1-o1 (**5**). In the presence of 1 mol% of complex **4**, the reaction gave the cyclized product **17** in 90% yield in 2 h (entry 13).

We have tried the catalytic reaction of 10-undecyn-1-ol, with the hope of obtaining a 12-membered enol ether. However, the catalytic reaction did not proceed. In addition, no reaction was observed for 3-hexyn-1-ol, which is expected to give a four-membered enol ether.

Mechanism: The *endo* cycloisomerization reactions of terminal alkynols catalyzed by Mo and W systems were generally believed to involve the initial formation of vinylidene intermediates that undergo intramolecular nucleophilic addition of an OH group to the vinylidene ligand to afford an *endo*-cyclic enol ether linked to the transition metals, followed by protonation of the metal–carbon bond.[29] The mechanism is supported by DFT studies,[30] although experimental evidence for the mechanism is still rare.[31] Since it is well-

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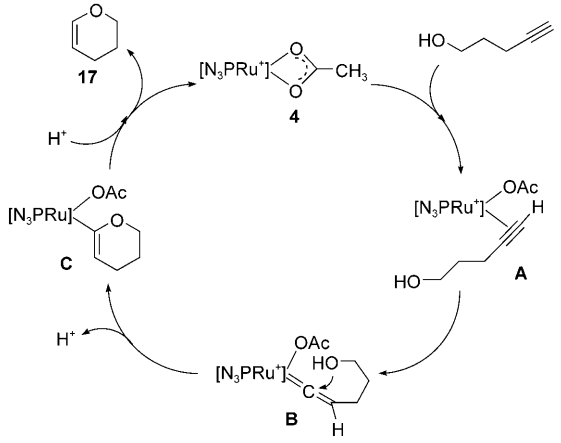
known that ruthenium(II) complexes can react with terminal alkynes to give vinylidene complexes[32] and ruthenium vinylidene complexes can be attacked by weak nucleophiles, such as alcohols,[24,33] water,[34] and carboxylic acids,[35] it is likely that the reactions catalyzed by complex **4** proceed through a vinylidene intermediate.

A plausible mechanism for the *endo* cycloisomerization of alkynols catalyzed by complex **4** is depicted in Scheme 2 by using substrate **5** as an example. The alkynol reacts with

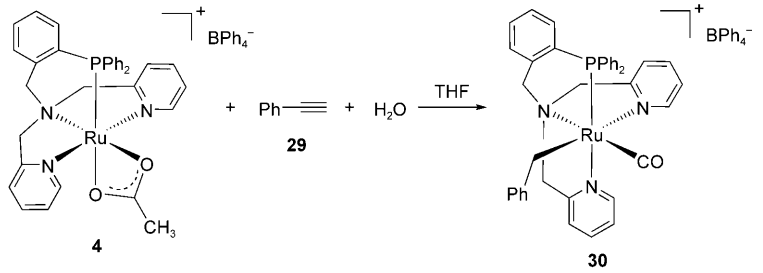


Scheme 2. The proposed working mechanism of the catalytic reaction.

complex **4** to give initially an η^2-alkyne complex **A** which could then rearrange to the vinylidene intermediate **B**. Intramolecular attack by the hydroxyl group on the α-carbon atom of the vinylidene ligand in **B** followed by deprotonation would afford the vinyl complex **C**. Protolysis of the metal–carbon bond would then give the *endo*-cyclic enol ether **17** and regenerate complex **4**. Nucleophilic attack on vinylidene intermediates has been proposed for several ruthenium-catalyzed reactions of terminal alkynes, for example, coupling of allyl alcohols with alkynes,[24,33d–m] addition of carboxylic acids to terminal alkynes to give enol esters,[35] hydration of terminal alkynes to give aldehydes,[34] hydrophosphination of alkynes,[36] and reactions of hydrazines with terminal alkynes to give nitriles.[37] It should be noted that the mechanism involving nucleophilic attack on simple η^2-alkyne complexes rather than vinylidene intermediates has also been suggested for some of the transformations, for example, in the addition reactions of amides to alkynes,[38] and in the addition of carboxylic acids to terminal alkynes.[39] The catalytic reactions in this study are closely related to the formation of unsaturated lactones by *endo* cyclization of α,ω-alkynoic acids catalyzed by [Ru(PhC=C(Ph)C≡CPh)(PMe*i*Pr$_2$)(Tp)] (Tp = hydrotris(pyrazolyl)borate).[35e]

Consistent with the catalytic cycle, no reaction was observed when using internal alkynols, such as 5-decyn-1-ol and 3-hexyn-1-ol, as the catalytic reaction substrates. Unfortunately, we have failed to isolate and identify experimentally the active species involved in the catalytic reactions. In an effort to gain indirect evidence for the involvement of a vinylidene intermediate in the catalytic reactions, we have carried out the reaction of complex **4** with phenylacetylene (**29**) in the presence of H_2O. The reaction was found to give the benzyl carbonyl complex **30** (Scheme 3). Thus C≡C bond cleavage occurred in the reaction. Several related metal-assisted C≡C bond-cleavage reactions of 1-alkynes with water leading to the formation of complexes containing a carbonyl and an η^1-alkyl with one less carbon atom have been reported, especially for metal complexes of ruthenium,[40] osmium,[41] and iridium.[42] The related reactions of metal acetylides or vinylidenes with water are also known.[43]

The structure of **30** has been determined by an X-ray diffraction study. The crystal data and refinement details of complex **30** are given in Table 1 and selected bond lengths and angles are listed in Table 5. A view of the molecular geometry for the complex cation of **30** is shown in Figure 2. The geometry around ruthenium in **30** can be viewed as a distorted octahedron. The tertiary amine N atom is *trans* to the CO ligand. The two pyridyl units in **30** are *cis* to each other, which is different from the *trans* arrangement in com-



Scheme 3. Reaction of complex **4** with phenylacetylene and H_2O to afford complex **30**.

Table 5. Selected bond lengths and angles in complex **30**.

Ru1−C1	1.825(2)	Ru1−N20	2.1253(15)
Ru1−N10	2.1627(15)	Ru1−C2	2.1692(17)
Ru1−N1	2.1934(15)	Ru1−P1	2.2890(4)
O1−C1	1.162(3)	C2−C3	1.495(2)
C1-Ru1-C2	91.99(8)	C1-Ru1-N1	174.55(7)
C1-Ru1-N10	96.16(7)	C1-Ru1-P1	89.94(6)
C1-Ru1-N20	97.22(7)	C2-Ru1-N1	92.51(6)
N10-Ru1-C2	167.87(7)	N20-Ru1-C2	86.68(6)
C2-Ru1-P1	91.40(5)	N10-Ru1-N1	78.92(6)
N1-Ru1-P1	93.02(4)	N20-Ru1-N1	79.98(6)
N10-Ru1-P1	97.56(4)	N20-Ru1-N10	83.40(6)
N20-Ru1-P1	172.64(5)	O1-C1-Ru1	176.20(18)
C3-C2-Ru1	114.27(12)	C8-C3-C2	121.33(17)
C4-C3-C2	121.52(17)		

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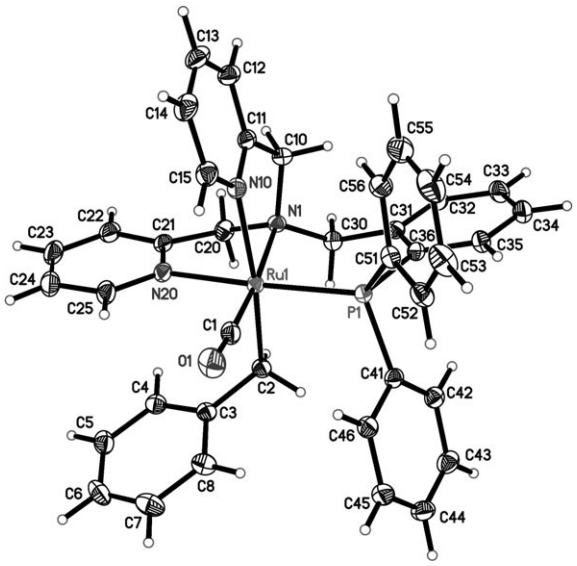
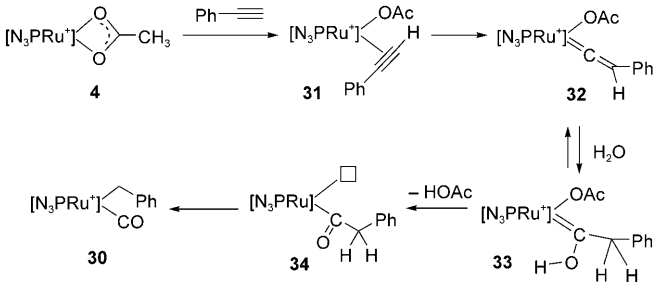


Figure 2. ORTEP diagram for the complex cation of **30**.

plex **4**. The benzyl group is *trans* to one of the two pyridyl nitrogen atoms.

The solid-state structure of complex **30** is supported by the ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ NMR, and HRMS spectroscopic data. In the ^{1}H NMR spectrum of **30** (in CD_2Cl_2), the methylene protons of the benzyl group gave rise to two signals at $\delta = 1.38$ and 2.50 ppm. The six protons of the three methylenes of the tetradentate ligand exhibit six doublets at $\delta =$ 3.41, 3.65, 3.86, 4.37, 4.43, and 4.84 ppm. In the $^{13}C\{^{1}H\}$ NMR spectrum (in CD_2Cl_2), the signal of $RuCH_2$ appears as a doublet at $\delta = 21.3$ ppm, and the signal of the CO ligand was observed at $\delta = 204.6$ ppm. The $^{31}P\{^{1}H\}$ NMR spectrum shows a singlet at $\delta = 55.9$ ppm. The mass spectrum displays the parent peak of the cation $[Ru(CH_2Ph)(CO)(N_3P)]^+$ (**30**$^+$) at m/z: 694.2952 (calcd: 694.1556).

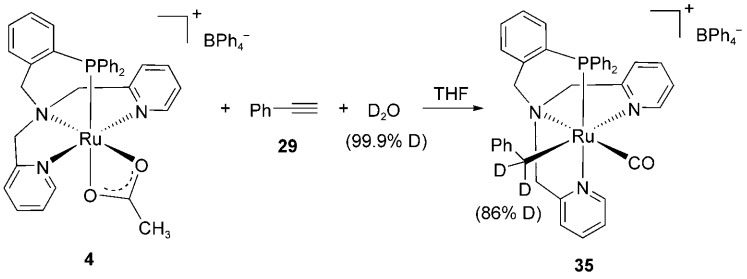
Scheme 4 shows a plausible mechanism for the formation of complex **30**. Complex **4** could react with phenylacetylene to give an alkyne complex **31** that rearranges to the vinylidene intermediate **32**, which could react with H_2O to afford intermediate **33**. Losing HOAC from **33** would afford intermediate **34**, which could undergo a deinsertion reaction to afford complex **30**. A similar mechanism has been proposed



Scheme 4. The mechanism of the reaction of complex **4** with phenylacetylene and H_2O to afford complex **30**.

previously for similar transformations, for example, in the reaction of $[RuCl_2(=C=CHPh)(PNP)]$ with water to give $[RuCl(CH_2Ph)(CO)(PNP)]$ (PNP = $EtN(CH_2CH_2PPh_2)_2$),[40b] the reaction of $[Os(C{\equiv}CPh)_2(CO)(P\mathit{i}Pr_3)_2]$ with H_2O to give $[Os(C{\equiv}CPh)(CH_2Ph)(CO)_2(P\mathit{i}Pr_3)_2]$,[43d] the reaction of $[IrCl_2(Cp^*)]_2$ (Cp^* = pentamethylcyclopentadienyl) with terminal alkynes RC≡CH and water to give $[IrCl(CH_2R)(Cp^*)(CO)]$,[42e] and in catalytic hydration reactions.[34] We have also tried the reaction of complex **4** with phenylacetylene in the presence of methanol with a hope to obtain a carbene complex related to **33**. Unfortunately, the expected ruthenium carbene complex could not be isolated.

In support of the mechanism, we found that reaction of complex **4** with phenylacetylene and approximately 50 equivalents of D_2O (99.9 atom% D) gave the partially deuterated complex **35** (Scheme 5). An analysis of the ^{1}H



Scheme 5. Reaction of complex **4** with phenylacetylene and D_2O to afford complex **35**.

and ^{2}D NMR spectra suggests that the methylene carbon atom of the benzyl group has approximately 86% deuterium. The formation of **35** is consistent with the mechanism profile outlined in Scheme 4. Incorporation of 86% rather than 50% deuterium at the methylene carbon atom is likely due to reversible formation of **33** from **32**. It is also possible that the terminal alkyne is enriched with deuterium before forming **32** due to H/D exchange between the terminal alkyne and D_2O in the presence of the ruthenium complex.

Formation of **30**–**35** provides indirect evidence that complex **4** can react with terminal alkynes to give a vinylidene intermediate that can be attacked by weak nucleophiles, such as water and alcohols.

Conclusion

We have synthesized a new ruthenium complex **4** that is an effective catalyst for the catalytic *endo* cycloisomerization of a range of alkynols. The cycloisomerization is highly selective and effective to give exclusively *endo*-cyclic enol ethers of five-, six-, and seven-membered rings in high yields under nonbasic conditions. The ruthenium catalytic precursor is air-stable and can be easily prepared. The catalytic reaction can be carried out with a low loading of catalyst without additional co-catalyst. The isolation of complex **30** from the

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reaction of complex **4** with PhC≡CH and H_2O supports that the catalytic cycle involves a vinylidene intermediate and hydroxyl-group addition. Further investigations are underway to expand the applications of complex **4** in other catalytic reactions.

Experimental Section

General: All manipulations were carried out under a nitrogen atmosphere by using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium benzophenone (hexane, diethyl ether, THF, benzene) or calcium hydride (dichloromethane). The starting material $[Ru(OAc)_2(PPh_3)_2]$[44] and substrates **7–9**,[45] and **12-15**[46] were prepared according to literature methods. Other chemicals were used as received from Aldrich. Elemental analyses were performed by M-H-W Laboratories (Phoenix, AZ). Mass Spectra were collected on a MALDI Micro MX Mass Spectrometer (MALDI), an API QSTAR XL System (ESI), or a GCT Premier Mass Spectrometer (CI). ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were collected on a Bruker AV 400 MHz NMR spectrometer. ^2D NMR spectra were collected on a JEOL EX 400 MHz NMR spectrometer. ^1H and ^{13}C NMR chemical shifts are relative to TMS or the residue of deuterium solvents, and ^{13}P NMR chemical shifts are relative to 85% H_3PO_4.

***N,N*-Bis[(pyridin-2-yl)methyl][2-(diphenylphosphino)phenyl]methanamine (3)**: A mixture of 2-(diphenylphosphino)benzaldehyde (**1**, 0.85 g, 2.93 mmol), $NaBH(OAc)_3$ (1.04 g, 4.09 mmol), and 2,2′-dipicolylamine (**2**, 0.44 mL, 2.44 mmol) in CH_2Cl_2 (30 mL) was stirred at room temperature for 12 h to give a light-yellow solution with a white precipitate. The reaction mixture was filtered through Celite to remove the white solid. The light-yellow filtrate was washed with a saturated aqueous solution of sodium hydrogen carbonate and brine. The organic extract was dried with magnesium sulfate. After filtration, the solvent was pumped away under vacuum and the residue was purified by chromatography with a silica-gel column to afford the product as a tacky solid (85%, 0.98 g). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162.0 MHz, 25°C): $\delta=-16.6$ ppm (s); ^1H NMR ($CDCl_3$, 400.1 MHz, 25°C): $\delta=8.48$ (d, $J=4.8$ Hz, 2H; Py), 7.82–7.79 (m, 1H), 7.59–7.54 (m, 2H), 7.39–7.26 (m, 9H), 7.23–7.19 (m, 4H), 7.15–7.09 (m, 3H), 6.88–6.85 (m, 1H), 3.99 (s, 2H; CH_2Ph), 3.80 ppm (s, 4H; $2CH_2Py$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz, 25°C): $\delta=159.0$, 148.7, 136.9, 136.7, 136.6, 136.4, 133.9, 133.7, 129.3, 129.2, 128.9, 128.6, 128.5, 127.2, 123.0, 121.9, 59.6 (ArCH_2N), 56.8 (PyCH_2N), 56.6 ppm (PyCH_2N); HRMS (ESI+): *m/z*: calcd for $C_{31}H_{29}N_3P^+$: 474.2094; found: 474.1947 $[M+H]^+$.

Complex 4: A mixture of $[Ru(OAc)_2(PPh_3)_2]$ (0.89 g, 1.2 mmol) and **3** (0.74 g, 1.56 mmol) in benzene (50 mL) was stirred at room temperature for 12 h to give a yellow solution with an orange precipitate. The mixture was concentrated to approximately 10 mL. The solid was collected by filtration, washed with benzene, THF, and Et_2O, and dried under vacuum. The resulting yellow solid was redissolved in CH_3OH (30 mL), and then a solution of $NaBPh_4$ (0.86 g, 2.5 mmol) in CH_3OH (10 mL) was added dropwise. After completion of the addition, the reaction mixture was stirred at room temperature for 1 h. The mixture was concentrated to approximately 5 mL. The solid was collected by filtration, washed with methanol and Et_2O, and dried under vacuum to afford **4** as a yellow solid (63%, 0.72 g). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, 25°C): $\delta=63.5$ ppm (s); ^1H NMR (CD_2Cl_2, 400.1 MHz, 25°C): $\delta=8.40$ (d, $J=4.4$ Hz, 2H; Py), 7.40–7.15 (m, 23H), 7.06–6.88 (m, 17H), 6.73–6.63 (m, 4H), 4.37 (d, $J=15.2$ Hz, 2H; PyCH_2), 3.83 (2H, $J=15.6$ Hz; PyCH_2), 3.37 (s, 2H; ArCH_2), 2.00 ppm (s, 3H; $COCH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz, 25°C): $\delta=189.7$, 165.1, 164.6, 164.1, 163.6, 163.2, 154.0, 136.8, 136.6, 136.4, 132.8, 132.7, 132.1, 131.6, 130.8, 130.7, 130.6, 130.3, 129.9, 129.3, 128.9, 128.8, 126.1, 124.0, 122.3, 121.2, 68.7 (ArCH_2), 67.6 (PyCH_2), 67.5 (PyCH_2), 24.3 ppm ($COCH_3$); elemental analysis calcd (%) for $C_{57}H_{52}BN_3O_2PRu\cdot0.5H_2O$: C 71.17, H 5.45, N 4.37; found: C 71.26, H 5.51, N 4.48; ESI-MS (CH_2Cl_2): *m/z*: 575 $[M-BPh_4-OAc]^+$.

Complex 30: A mixture of complex **4** (0.15 g, 0.16 mmol), phenylacetylene (0.16 mL, 1.5 mmol), and H_2O (0.20 mL, 11 mmol) in THF (6 mL) was stirred at 80°C for 10 h. The reaction mixture was cooled to room temperature and Na_2SO_4 was added. Two hours later, the solid was removed by filtration and the filtrate was concentrated to 1–2 mL and Et_2O was added to give a white precipitate. The solid was collected by filtration, washed with a mixed solvent of CH_2Cl_2 and Et_2O (1:5), and dried under vacuum to afford **30** as a white solid (69%, 0.11 g). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, 25°C): $\delta=55.9$ ppm (s); ^1H NMR (CD_2Cl_2, 400.1 MHz, 25°C): $\delta=8.12$ (d, $J=5.6$ Hz, 1H); 7.82 (t, $J=2.8$ Hz, 1H); 7.32–7.63 (m, 19H); 7.15–7.21 (m, 3H); 6.88–7.06 (m, 16H); 6.62–6.72 (m, 5H); 6.47 (d, $J=7.2$ Hz, 2H); 4.84 (d, $J=13.6$ Hz, 1H; RuCH_2Ar); 4.43 (d, $J=16.0$ Hz, 1H; RuCH_2Py); 4.37 (d, $J=17.6$ Hz, 1H; RuCH_2Py); 3.86 (dd, $J=13.6$, 2.0 Hz, 1H; RuCH_2Ar); 3.65 (d, $J=16.0$ Hz, 1H; RuCH_2Py); 3.41 (d, $J=17.2$ Hz, 1H; RuCH_2Py); 2.50 (dd, $J=9.6$, 8.4 Hz, 1H; RuCH_2Ph); 1.38 ppm (d, $J=10.0$ Hz, 1H; RuCH_2Ph); $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 25°C): $\delta=204.7$ (Ru*C*O), 204.5, 165.2, 164.7, 164.2, 163.7, 157.8, 155.1, 153.1, 151.5, 151.2, 141.1, 141.0, 138.0, 136.7, 136.5, 135.0, 134.5, 134.3, 134.2, 133.6, 133.5, 133.1, 132.5, 132.4, 130.9, 130.5, 130.2, 130.1, 130.0, 129.3, 129.2, 128.8, 128.7, 127.9, 127.7, 127.5, 126.6, 126.2, 125.1, 125.0, 122.4, 121.8, 70.6 (RuCH_2Py), 66.5 (RuCH_2Py), 63.9, 63.8 (RuCH_2Ar), 21.3, 21.2 ppm (RuCH_2Ph); elemental analysis calcd (%) for $C_{63}H_{55}BN_3OPRu$: C 74.70, H 5.47, N 4.15; found: C 74.35, H 5.35, N 4.08; HRMS (MALDI, Matrix: CHCA): *m/z*: calcd for $C_{39}H_{35}N_3OPRu^+$: 694.1556; found: 694.2952 $[M-BPh_4]^+$.

[D_2]complex 35: A mixture of complex **4** (0.10 g, 0.11 mmol), phenylacetylene (0.11 mL, 1.0 mmol), and D_2O (0.10 mL, 5.0 mmol) in THF (4 mL) was stirred at 80°C for 10 h. The reaction mixture was cooled to room temperature and Na_2SO_4 was added. After 2 h, the solid was removed by filtration and the filtrate was concentrated to approximately 1 mL and Et_2O was added to give a white precipitate. The solid was collected by filtration, washed with a mixed solvent of CH_2Cl_2 and Et_2O (1:5), and dried under vacuum to afford **35** as a white solid (61%, 62 mg). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, 25°C): $\delta=55.7$ ppm (s); ^1H NMR (400.1 MHz, CD_2Cl_2, 25 °C): $\delta=8.13$ (d, $J=4.4$ Hz, 1H); 7.82 (d, $J=6.4$ Hz, 1H); 7.32–7.65 (m, 19H); 7.12–7.20 (m, 3H); 6.86–7.04 (m, 16H); 6.59–6.74 (m, 5H); 6.47 (d, $J=6.8$ Hz, 2H); 4.87 (d, $J=13.6$ Hz, 1H; RuCH_2Ar); 4.49 (d, $J=15.6$ Hz, 1H; RuCH_2Py); 4.41 (d, $J=17.2$ Hz, 1H; RuCH_2Py); 4.00 (dd, $J=13.6$ Hz, 2.0 Hz, 1H; RuCH_2Ar); 3.88 (d, $J=16.0$ Hz, 1H; RuCH_2Py); 3.60 ppm (d, $J=17.2$ Hz, 1H; RuCH_2Py); ^2D NMR (61.3 MHz, $(CH_3)_2CO$ (set as $\delta=2.20$ ppm), 25°C): $\delta=1.66$ (s, 1H; RuCD_2Ph); 0.99 ppm (s, 1H; RuCD_2Ph); HRMS (MALDI, Matrix: CHCA): *m/z*: calcd (%) for $C_{39}H_{33}D_2N_3OPRu^+$: 696.1681; found: 696.2880 $[M-BPh_4]^+$.

Typical procedure for the catalytic cycloisomerization of alkynols: Catalyst **4** (0.005 or 0.025 mmol, as indicated in Table 4) was added to a solution of alkynol (0.5 mmol) in THF (0.5 mL). The resulting solution was stirred at 80°C and monitored by TLC or ^1H NMR spectroscopy. When the maximum conversion was reached, the desired product was isolated by flash column chromatography on silica gel. For products of low boiling points, the yields were determined by ^1H NMR spectroscopic integration with CH_3NO_2 or *t*BuOH as the internal standards.

2,3-Dihydro-2-styrylfuran (27): ^1H NMR (400.1 MHz, CD_2Cl_2, 25°C): $\delta=$ 7.31–7.13 (m, 5H; Ph), 6.52 (d, $J=16.0$ Hz, 1H; PhC*H*CH), 6.27–6.18 (m, 2H; PhCHC*H*, OC*H*CHCH$_2$), 5.05–5.01 (m, 1H; CHCHC*H*(CH$_2$)O), 4.84 (q, $J_1=5.2$, $J_1=2.8$ Hz, 1H; OCHC*H*CH$_2$), 2.80–2.73 (m, 1H; OCHCHCH_2), 2.42–2.36 ppm (m, 1H; OCHCHCH_2); $^{13}C\{^1H\}$ NMR (100.6 MHz, CDCl$_3$, 25°C): $\delta=145.0$ (O*C*HCHCH$_2$), 136.5, 131.0, 129.1, 128.5, 127.7, 126.5, 99.1 (OCH*C*HCH$_2$), 81.7 (CHCH*C*H(CH$_2$)O]), 35.5 ppm (OCHCH*C*H$_2$); HRMS (CI+): *m/z*: calcd for $C_{12}H_{13}O^+$: 173.0961; found: 173.0984 $[M+H]^+$.

Crystallographic structure analysis of complexes 4 and 30: The diffraction intensity data of **4** was collected with a Bruker Smart APEX CCD diffractometer with monochromatized $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å) at 173 K. Lattice determination and data collection were carried out by using SMART v.5.625 software. Data reduction and absorption corrections were performed by using SAINT v 6.26 and SADABS v 2.03. The diffraction intensity data of **30** was collected with an Oxford Diffraction

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Gemini S Ultra with monochromatized $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å) at 173 K. Lattice determination, data collection, and reduction were carried out by using CrysAlisPro 171.32.5. Absorption corrections (semi-empirical from equivalents) were performed by using the SADABS built-in the CrysAlisPro program suite. Structure solution and refinement for all three compounds were performed by using the SHELXTL v.6.10 software package. They were solved by the direct methods and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms.

CCDC-747458 (complex **4**) and CCDC 747459 (complex **30**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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