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Mechanism Investigations of the Endo Cycloisomerization of Alkynols through Isolation and Characterization of Ruthenium Complexes from the Reactions of Alkynes with a Ruthenium Complex

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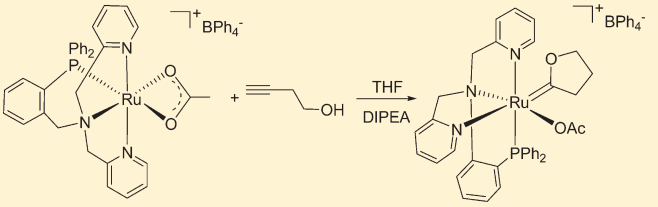
Supporting Information

ABSTRACT: In our efforts to probe the reaction mechanism of the endo cycloisomerization of alkynols catalyzed by the complex [Ru(N_3P)(OAc)](BPh$_4$) (**1**; NP_3 = *N*,*N*-bis[(pyridin-2-yl)methyl][2-(diphenylphosphino)phenyl]methanamine), the reactions of **1** with alkynes were investigated. Several complexes related to intermediates in the catalytic reactions were isolated and characterized. In the presence of DIPEA (*N*,*N*-diisopropylethanamine), complex **1** reacted with 3-butyn-1-ol to afford the Ru−oxocyclocarbene complex {Ru(N_3P)[=C(CH_2)$_3$O](OAc)}(BPh$_4$) (**4**). Under anhydrous conditions, the reaction of complex **1** with *tert*-butylacetylene afforded [Ru(N_3P)(η^3-^{t}BuC≡CC=CHBu^t)](BPh$_4$) (**8**). In the presence of water, the reaction of complex **1** with *tert*-butylacetylene afforded [Ru(N_3P)(CO)(η^1-CH_2Bu^t)](BPh$_4$) (**13**). All the reactions are likely to proceed through ruthenium vinylidene intermediates. These results support that ruthenium vinylidene complexes are involved as the key intermediates in the cycloisomerization of alkynols catalyzed by complex **1**.



INTRODUCTION

Endocyclic enol ethers are very useful synthetic starting materials for the construction of diverse oxygen-containing heterocycles which are important structural units in a number of naturally occurring and biologically active molecules.[1−6] Catalytic endo cycloisomerization of alkynols represents the most straightforward approach to obtain endocyclic enol ethers,[7] with the advantages of high efficiency and 100% atom economy.[8] In the pioneering work in this area, McDonald and his co-workers discovered that molybdenum[4,5,9] and tungsten[2,3,8−10] carbonyl complexes can effectively catalyze the endo cycloisomerization of a range of alkynols. Such catalytic endocycloisomerization of alkynols has been successfully applied to the synthesis of various natural products,[2] glycals,[3] nucleosides,[4] and clinically valuable drugs.[5] Endo cycloisomerization of alkynols catalyzed by Mo and W complexes was generally believed to involve initial formation of a vinylidene intermediate, and the following intramolecular nucleophilic addition of the OH group to the vinylidene ligand would generate an endocyclic enol ether linked to the transition metal. Then protonation of the metal−carbon bond would afford the product endocyclic enol ether.[11] The mechanism is supported by DFT studies,[12] although experimental evidence for the mechanism is still scarce.[13]

In the past several years, other systems such as CpRuL$_n^+$/20−40 mol % phosphine ligands,[14] [Rh(PR_3)$_3$Cl]/30−55 mol % phosphine ligands,[15] $AgNO_3$ (10 mol %), Pd(II)/Cu(I), Au(I) (17−30 mol %),[16] and Pd(MeCN)$_2$Cl$_2$[17] were also found to be catalytically active for the endo cycloisomerization of alkynols. Endo cycloisomerization of alkynols catalyzed by the Rh and Ru systems was proposed to proceed through vinylidene intermediates, while those catalyzed by Ag(I), Au(I), Cu(I), and Pd(II) complexes were proposed to proceed through η^2-alkyne complex intermediates.

Ruthenium complexes containing a tripodal tetradentate ligand are appealing in catalysis, since the coordination of ruthenium with a tetradentate ligand offers rigid frameworks and two mutually cis coordination sites for substrates in an octahedral mononuclear complex.[18] Moreover, high structural stability can be achieved due to the chelate effect,[19] which offers a good opportunity to investigate catalytic reaction mechanisms through isolating relatively stable intermediates.[20]

Recently, we have reported the preparation of the new ruthenium complex [Ru(N_3P)(OAc)](BPh$_4$) (**1**; N_3P = *N*,*N*-bis[(pyridin-2-yl)methyl][2-(diphenylphosphino)phenyl]methanamine) and its catalytic properties for the cycloisomerization of a variety of alkynols with C≡C attached to aryl or alkyl groups (Scheme 1).[21] The reactions catalyzed by complex **1** exhibit high regioselectivity and reactivity to give exclusively endo products in good to excellent yields without any additive. Herein, we report our results in the investigation of the mechanism of the catalytic reactions through isolation and characterization of several ruthenium complexes related to the

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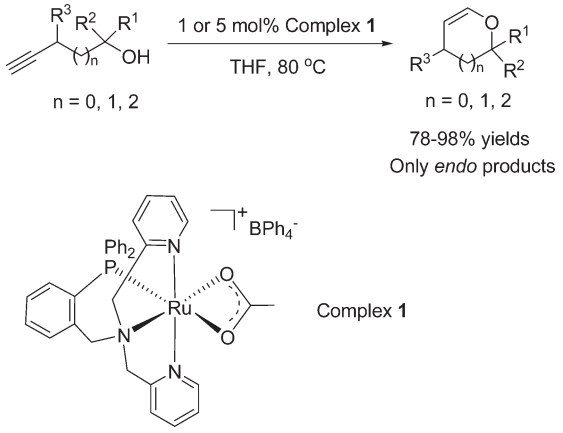
Scheme 1. Endo Cycloisomerization of Alkynols Catalyzed by Complex 1



reaction intermediates in the endo cycloisomerization of alkynols catalyzed by complex **1**.

RESULTS AND DISCUSSION

Reaction of Complex 1 with 3-Butyn-1-ol. Because ruthenium(II) complexes can react with terminal alkynes to generate vinylidene complexes[22] which can be attacked by weak nucleophiles such as alcohols,[11,23] water,[24] and carboxylic acids;[25] it seems reasonable to assume that the endo cycloisomerization of alkynols catalyzed by complex **1** proceeds through a vinylidene intermediate. A plausible mechanism of the catalytic reactions mediated by complex **1** is depicted in path I of Scheme 2 using 3-butyn-1-ol (**2**) as an example of the substrate. The alkynol **2** can react with complex **1** to give initially the η^2-alkyne complex **A**, which could then rearrange to the vinylidene intermediate **B**. Intramolecular attack by the hydroxyl group on the α-carbon of the vinylidene ligand in **B** followed by deprotonation would afford the vinyl complex **C**. Protonation of the metal−carbon bond in **C** would then give the endocyclic enol ether **3** and regenerate complex **1**. As reactions involving direct nucleophilic attack on η^2-alkyne rather than vinylidene ligands have also been suggested for some of the related transformations, for example, in addition reactions of amides to alkynes[26] and in addition reactions of carboxylic acids to terminal alkynes,[27] it is also possible that **C** can be formed from alkyne complex **A** without the involvement of vinylidene intermediate **B**.

In our initial attempts to probe the mechanism of the endo cycloisomerization of alkynols catalyzed by complex **1**, the reactions of complex **1** with stoichiometric amounts of various alkynols were carried out. Unfortunately, we have failed to isolate or identify experimentally the active intermediates involved in the catalytic reactions. In an effort to gain indirect evidence for the involvement of the vinyl intermediate **C** in the catalytic reactions, the reaction of complex **1** with 3-butyn-1-ol (**2**) was carried out in the presence of *N*,*N*-diisopropylethanamine (DIPEA), which may neutralize the proton generated in the formation of **C** and thus quench the reaction of **C** to **1** and **3**.

The reaction of complex **1** with alkynol **2** in the presence of DIPEA in refluxing THF for 1 h afforded the new Ru−oxocyclocarbene complex $[Ru(N_3P)(=C_4H_6O)(OAc)](BPh_4)$ (**4**) (Scheme 3). Several reactions of ruthenium complexes with alkynols to give oxocyclocarbene complexes have been reported.[28]

The Ru−oxacyclocarbene complex **4** has been characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy, 2D-NMR experiments, including H,H-COSY, HSQC, and HMQC, and mass spectrometry. Consistent with the structure shown in Scheme 3, the ^1H NMR spectrum of complex **4** (in CD_2Cl_2) displays the methyl signal of the acetyl group at 1.97 ppm. With the help of 2D-NMR experiments, the signals of the six protons of the five-membered tetrahydrofuranylidene are located in the ^1H NMR spectrum as a quartet at 4.25 ppm and a multiplet at 3.95−4.01 ppm for C^1H_2, two multiplets at 1.81−1.90 and 1.66−1.75 ppm for C^2H_2, and two multiplets at 1.92−2.04 and 3.65−3.72 ppm for C^3H_2. In the $^{13}C\{^1H\}$ NMR spectrum of complex **4**, the carbon signals of the acetyl group appears at 25.1 and 177.2 ppm. The four carbon atoms of the five-membered oxa ring show three singlets at 81.7 (C^1), 22.5 (C^2), and 53.2 (C^3) ppm and a doublet at 312.7 ppm (C^4, J_{CP} = 14 Hz), which indicates the presence of Ru=C.[28] Consistent with this structure, the $^{31}P\{^1H\}$ NMR spectrum displays a singlet at 53.4 ppm and the HRMS spectrum shows the parent peak of the complex cation of **4** at *m*/*z* 704.1570 (calcd 704.1611).

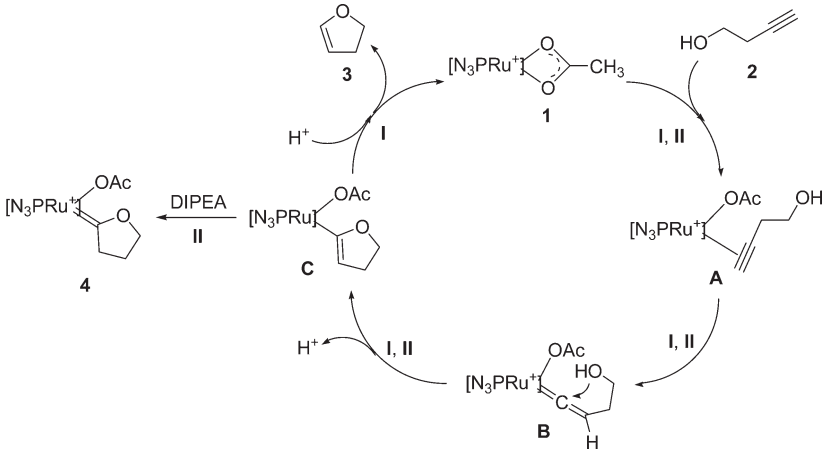
The structure of **4** has been confirmed by an X-ray diffraction study. Yellow single crystals of complex **4** suitable for X-ray diffraction analysis were obtained via slow diffusion of Et_2O into a CH_2Cl_2 solution of complex **4**. The crystal data and refinement details are given in Table 1, and selected bond lengths and angles are given in Table 2. An ORTEP view of the cation of complex **4** is shown in Figure 1. The coordination geometry around ruthenium in **4** can be viewed as a distorted octahedron with a tetradentate N_3P ligand, an acetyl ligand, and an oxocarbene ligand. The tertiary amine N atom is trans to the acetyl ligand. The two pyridyl units in **4** are cis to each other. The P atom is trans to a pyridyl N atom, and the carbene ligand is trans to the other pyridyl N atom. The Ru=C bond length (Ru(1)−C(3) = 1.906(4) Å) is similar to those of other Ru−alkoxycarbene complexes.[28] The solid-state structure is in agreement with the solution NMR spectroscopic data.

A plausible mechanism for the formation of complex **4** from complex **1** and alkynol **2** is shown in path II of Scheme 2. Complex **1** could coordinate alkyne **2**, followed by rearrangement to give the vinylidene intermediate **B**. Subsequent intramolecular addition of the hydroxyl group to the α-carbon of the vinylidene ligand in **B** could generate intermediate **C**, accompanied by the loss of a proton which could be neutralized by DIPEA. The reaction of **C** to form **1** and **3** could be quenched because protonation of the metal−carbon bond in **C** could not proceed due to the low acidity of DIPEA-H^+. On the other hand, complex **C** could be protonated to give complex **4**.

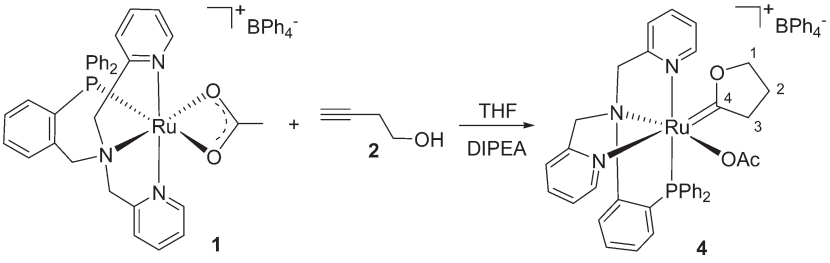
In the cycloisomerization of alkynol **2** catalyzed by complex **1** without DIPEA, complex **4** could be detected by $^{31}P\{^1H\}$ NMR spectroscopy. Moreover, complex **4** is also catalytically active in the cycloisomerization of alkynol. For example, when a THF solution of 4-pentyn-1-ol (**5**) was refluxed in the presence of 1 mol % complex **4** for 5 h, 100% conversion of **5** to product **6** was achieved (Scheme 4). This result demonstrates that complex **4** could be converted to intermediate **C** under the conditions for catalytic cycloisomerization of alkynol.

Reaction of Complex 1 with *tert*-Butylacetylene (7) in the Absence of Water. In the proposed mechanism for endo cycloisomerization of alkynols catalyzed by complex **1** (Scheme 2, path I) and for the formation of complex **4** from the reaction of **1** with 3-butyn-1-ol (**2**) (Scheme 2, path II), vinylidene complexes have been suggested as important intermediates. To gain more

Scheme 2. Proposed Mechanisms of the Complex 1 Catalyzed Endo Cycloisomerization of Alkynols and the Formation of Complex 4



Scheme 3. Reaction of Complex 1 with Alkynol 2 in the Presence of DIPEA To Afford Complex 4



evidence for the involvement of vinylidene intermediates, the reaction of complex **1** with *tert*-butylacetylene (**7**) was performed. When a THF solution containing complex **1** and **7** was refluxed for 1 h, complex **1** disappeared completely and the new butenynylruthenium complex $[Ru(N_3P)(\eta^3\text{-}^tBuC_3CHBu^t)](BPh_4)$ (**8**) was produced, which can be isolated in 77% yield (Scheme 5). Related reactions of ruthenium complexes with alkynes to afford butenynylruthenium complexes have been reported.[29] Butenynylruthenium complexes have also been suggested as intermediates in the catalytic dimerization of terminal acetylenes.[18e,30]

The structure of complex **8** has been unambiguously confirmed by single-crystal X-ray analysis as well as its spectroscopic data. The ^{1}H NMR spectrum of complex **7** showed ^{t}Bu resonances at 0.76 (H^1) and 1.29 ppm (H^8) and the resonance of proton H^3 at 4.80 ppm. The $^{13}C\{^1H\}$ spectrum exhibits the resonances of tertiary carbons of ^{t}Bu at 35.3 (C^2) and 33.7 (C^7) ppm and the resonances of methyl groups at 29.7 (C^1) and 32.5 (C^8) ppm. The resonance of the double-bonded carbon tethered with a proton was observed at 133.6 ppm. The resonances of C^4, C^5, and C^6 were found at 144.7, 48.9, and 123.7 ppm, respectively. The mass spectrum of complex **8** showed a strong signal of complex cation of **8** with m/z 738.4191 (calcd 738.2546).

Yellow single crystals of complex **8** suitable for single-crystal X-ray diffraction analysis were obtained at 4 °C by slow diffusion of Et_2O into a CH_2Cl_2 solution containing complex **8**. The crystal data and refinement details are given in Table 1, and selected bond lengths and angles are given in Table 3. Figure 2 shows the X-ray structure of complex **8**. The coordination geometry around ruthenium in **8** is approximately octahedral, and the compound contains a tetradentate N_3P ligand and an η^3-Bu^{t}C$_3$CHBu^t ligand. The η^3-Bu^{t}C$_3$CHBu^t ligand is trans to the tertiary amine N atom and a pyridine N atom and the P atom is trans to another pyridine N atom. The bond lengths of Ru(1)−C(35) (2.212(5) Å), Ru(1)−C(36) (2.139(5) Å), and Ru(1)−C(37) (2.074(6) Å) and the bond angles of C(36)−C(35)−C(31) (142.7(6)°), C(35)−C(36)−C(37) (143.8(5)°), C(36)−C(37)−C(38) (139.3(6)°), and C(37)−C(38)−C(39) (127.4(6)°) are similar to those of other Ru−η^3-RC$_3$CHR′ complexes.[29] The solid-state structure is in agreement with the solution NMR spectroscopic data.

A plausible mechanism for the reaction of complex **1** with *tert*-butylacetylene to afford complex **8** is depicted in Scheme 6.[31] First, complex **1** could react with acetylene **7** to generate the η^2-alkyne complex **9**, which would rearrange to the vinylidene intermediate **10**. One more molecule of acetylene **7** might react with **10** to form intermediate **11**, which could undergo an intramolecular C−C coupling reaction to afford the 16-electron ruthenium complex **12**, which could evolve to complex **8** after coordination of ruthenium with the C≡C moiety.

Reaction of 1 with *tert*-Butylacetylene in the Presence of H_2O. In our previous effort to gain indirect evidence for the involvement of the transformation in the catalytic reactions, we have carried out the reaction of complex **1** with phenylacetylene in the presence of H_2O. The reaction was found to give a benzyl carbonyl complex, which is most likely formed by nucleophilic attack of water at a vinylidene intermediate followed by an deinsertion reaction. Several related metal-assisted C≡C bond

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Table 1. Crystal Data and Structure Refinement Details for Complexes 4, 8, 13, and 19

	4·1.5CH_2Cl_2	**8**·CH_2Cl_2	**13**·CH_2Cl_2·0.25(hexane)	**17**·4THF
empirical formula	$C_{62.5}H_{60}BCl_3N_3O_3PRu$	$C_{68}H_{69}BCl_2N_3PRu$	$C_{63.5}H_{64.5}BCl_2N_3OPRu$	$C_{126}H_{130}B_2N_6O_6P_2Ru_2$
formula wt	1150.33	1142.01	1099.43	2110.06
temp (K)	173(2)	173(2)	173(2)	173(2)
wavelength (Å)	0.710 73	1.541 78	1.541 78	1.541 78
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$C2/c$	$P2_1/c$	$C2/c$	$P\bar{1}$
unit cell dimens				
a (Å)	33.168(3)	22.9187(16)	33.8739(9)	14.3083(7)
b (Å)	9.0552(8)	13.7663(3)	12.3263(4)	15.0767(7)
c (Å)	36.835(3)	21.4402(10)	27.7974(6)	15.4095(7)
α (deg)	90	90	90	112.824(5)
β (deg)	92.1830(10)	117.178(7)	93.945(2)	104.771(4)
γ (deg)	90	90	90	107.571(4)
V (Å^3)	11055.1(16)	6017.6(5)	11579.0(5)	2646.2(2)
Z	8	4	8	1
calcd density (Mg/m^3)	1.382	1.261	1.261	1.324
abs coeff (mm^{-1})	0.507	3.495	3.626	3.065
F(000)	4760	2384	4580	1104
θ range for data collecn (deg)	1.68−27.50	4.68−66.99	4.92−66.99	5.92−71.55
no. of rflns collected	32 951	20 042	16 943	13 956
no. of indep rflns	12 229 (R(int) = 0.0569)	9764 (R(int) = 0.0984)	9833 (R(int) = 0.0546)	9512 (R(int) = 0.0237)
completeness to θ = 25.00° (%)	97.2	91.1	95.2	94.9
max, min transmissn	1.00, 0.83	1.00, 0.58	1.00, 0.73	1.00, 0.81
no. of data/restraints/params	12 229/1/670	9764/0/690	9833/4/664	9512/0/649
goodness of fit on F^2	1.040	1.036	1.012	1.055
final R indices ($I > 2\sigma(I)$)	R1 = 0.0650, wR2 = 0.1366	R1 = 0.0694, wR2 = 0.1701	R1 = 0.0548, wR2 = 0.1233	R1 = 0.0317, wR2 = 0.0778
largest diff peak, hole (e Å^{-3})	0.978, −1.107	1.553, −1.121	1.458, −1.556	0.893, −1.024

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 4

Bond Distances			
Ru(1)−C(3)	1.906(4)	Ru(1)−O(1)	2.070(3)
Ru(1)−N(1)	2.114(3)	Ru(1)−N(10)	2.116(3)
Ru(1)−N(20)	2.175(3)	Ru(1)−P(1)	2.2843(10)
C(3)−C(4)	1.510(5)	C(4)−C(5)	1.520(6)
C(5)−C(6)	1.502(7)	C(6)−O(3)	1.478(5)
C(3)−O(3)	1.328(4)		
Bond Angles			
C(3)−Ru(1)−O(1)	98.20(13)	C(3)−Ru(1)−N(1)	94.41(13)
O(1)−Ru(1)−N(1)	161.56(11)	C(3)−Ru(1)−N(10)	88.66(14)
O(1)−Ru(1)−N(10)	87.72(12)	N(1)−Ru(1)−N(10)	79.16(12)
C(3)−Ru(1)−N(20)	170.18(13)	O(1)−Ru(1)−N(20)	84.65(11)
N(1)−Ru(1)−N(20)	80.78(12)	N(10)−Ru(1)−N(20)	82.05(12)
C(3)−Ru(1)−P(1)	93.42(11)	O(1)−Ru(1)−P(1)	98.27(8)
N(1)−Ru(1)−P(1)	94.32(8)	N(10)−Ru(1)−P(1)	173.30(9)
N(20)−Ru(1)−P(1)	95.47(9)	O(3)−C(3)−Ru(1)	125.8(3)
C(4)−C(3)−Ru(1)	126.5(3)	C(3)−C(4)−C(5)	104.3(3)
C(6)−C(5)−C(4)	102.9(4)	O(3)−C(6)−C(5)	103.9(3)
C(3)−O(3)−C(6)	113.0(3)	O(3)−C(3)−C(4)	107.4(3)

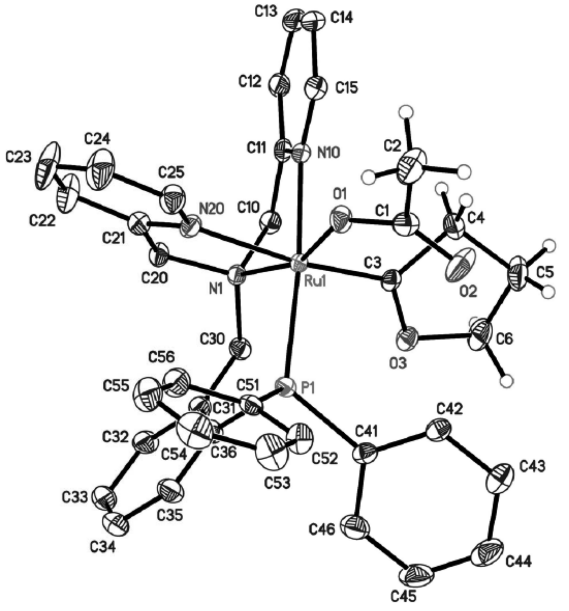
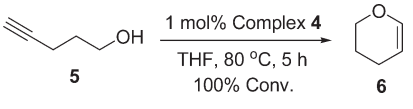


Figure 1. ORTEP diagram of the complex cation **4**$^+$.

cleavage reactions of 1-alkynes with water have been reported to afford complexes containing a carbonyl and an η^1-alkyl with one fewer carbon atom, especially for metal complexes of ruthenium,[32] osmium,[33] and iridium.[34] The related reactions of metal acetylides or vinylidenes with water have been also reported.[35]

As complex **1** can also catalyze the endo cycloisomerization of alkynols with C≡C attached to aliphatic chains, it would be of interest to see if a similar reaction will also occur for the reaction of **1** with aliphatic alkynes in the presence of water. For this purpose, the reaction of complex **1** with *tert*-butylacetylene in the presence of H_2O was carried out. After refluxing in THF for 8 h, the new complex **13** was produced and was isolated in 87% yield (Scheme 7).

Scheme 4. Complex 4 Catalyzed Endo Cycloisomerization of Alkynol 5 To Afford 6



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Scheme 5. Reaction of Complex 1 and *tert*-Butylacetylene (7) To Afford Complex 8

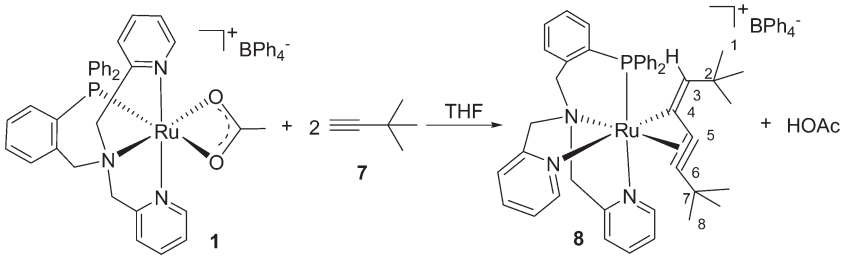


Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 8

Bond Distances			
Ru(1)−C(37)	2.074(6)	Ru(1)−C(36)	2.139(5)
Ru(1)−C(35)	2.212(5)	Ru(1)−N(1)	2.156(5)
Ru(1)−N(2)	2.139(5)	Ru(1)−N(3)	2.172(4)
Ru(1)−P(1)	2.2658(15)	C(31)−C(35)	1.493(8)
C(35)−C(36)	1.263(8)	C(36)−C(37)	1.392(8)
C(37)−C(38)	1.335(8)	C(38)−C(39)	1.510(8)
Bond Angles			
C(37)−Ru(1)−C(36)	38.6(2)	C(37)−Ru(1)−N(2)	82.3(2)
C(36)−Ru(1)−N(2)	85.5(2)	C(37)−Ru(1)−N(1)	171.8(2)
C(36)−Ru(1)−N(1)	138.00(19)	N(2)−Ru(1)−N(1)	90.16(18)
C(37)−Ru(1)−N(3)	102.9(2)	C(36)−Ru(1)−N(3)	140.0(2)
N(2)−Ru(1)−N(3)	76.62(17)	N(1)−Ru(1)−N(3)	78.28(17)
C(37)−Ru(1)−C(35)	72.1(2)	C(36)−Ru(1)−C(35)	33.7(2)
N(2)−Ru(1)−C(35)	94.1(2)	N(1)−Ru(1)−C(35)	105.5(2)
N(3)−Ru(1)−C(35)	170.07(19)	C(37)−Ru(1)−P(1)	88.26(17)
C(36)−Ru(1)−P(1)	95.05(16)	N(2)−Ru(1)−P(1)	164.03(12)
N(1)−Ru(1)−P(1)	99.84(13)	N(3)−Ru(1)−P(1)	93.15(13)
C(35)−Ru(1)−P(1)	95.21(16)	C(36)−C(35)−Ru(1)	70.0(4)
C(31)−C(35)−Ru(1)	147.3(5)	C(35)−C(36)−Ru(1)	76.3(4)
C(37)−C(36)−Ru(1)	68.2(3)	C(38)−C(37)−Ru(1)	147.2(5)
C(36)−C(37)−Ru(1)	73.2(3)	C(36)−C(35)−C(31)	142.7(6)
C(35)−C(36)−C(37)	143.8(5)	C(36)−C(37)−C(38)	139.3(6)
C(37)−C(38)−C(39)	127.4(6)		

Complex **13** has been characterized by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR and mass spectroscopy. The ^{1}H NMR spectrum of complex **13** in CD_2Cl_2 shows the resonance of ^{t}Bu at 0.54 ppm and the resonance of the methylene tethered with ^{t}Bu at 0.90 ppm as a doublet (J_{HH} = 10.8 Hz) and at 1.59 ppm as a triplet (J_{HH} = J_{HP} = 10.8 Hz). In the ^{13}C{^{1}H} NMR spectrum, the signal of the CO ligand was observed at 207.0 ppm as a doublet (J_{CP} = 18 Hz) due to coupling with the phosphorus atom in the tetradentate ligand. Furthermore, the mass spectrum showed the ion peak of the complex cation of **13** at *m*/*z* 674.3293 (calcd 674.1869).

The structure of **13** has also been confirmed by X-ray diffraction. A colorless single crystal suitable for single-crystal X-ray diffraction analysis was obtained by slow diffusion of hexane into a CH_2Cl_2 solution of complex **13**. A view of the molecular structure of complex cation of **13** is shown in Figure 3. Crystal data and refinement details are given in Table 1, and selected bond lengths and bond angles of complex **13** are given in Table 4. The geometry around ruthenium in **13** can be viewed as a distorted octahedron. The tertiary amine N atom is trans to the CO ligand. The two pyridyl units in **13** are cis to each other, and the CH_2CMe_3 group is trans to one of the two pyridyl nitrogen atoms. For the two protons of the methylene in Ru−CH_2Bu^{t}, the

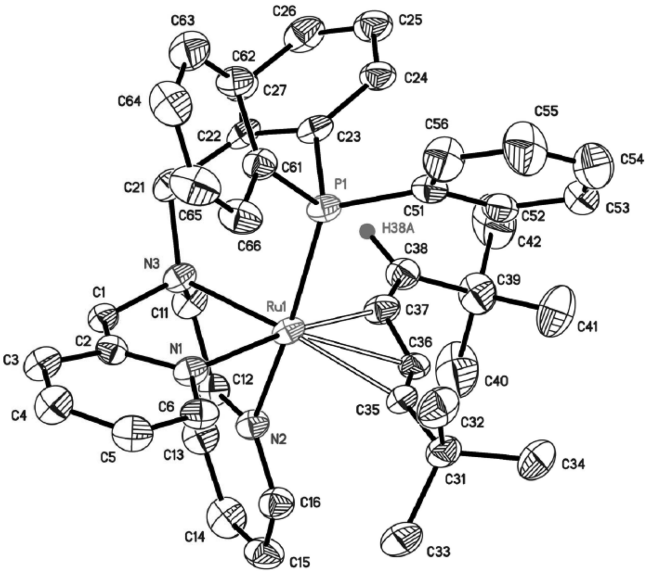
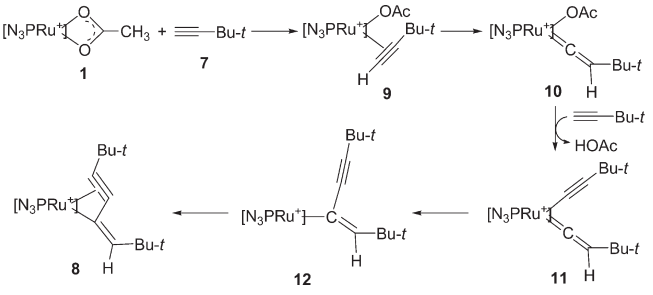


Figure 2. ORTEP diagram of the complex cation 8^{+}.

Scheme 6. Proposed Mechanism for the Reaction of Complex 1 and *tert*-Butylacetylene To Afford Complex 8



two H−C−Ru−P dihedral angles are 3 and 109°, respectively. The structural feature may account for why one proton of Ru−CH_2Bu^{t} couples with the phosphorus atom (J_{HP} = 10.8 Hz) while the other does not in the ^{1}H NMR spectrum.

Scheme 8 shows a plausible mechanism for the formation of complex **13**. Complex **1** could react with *tert*-butylacetylene to give vinylidene complex **10** via intermediate **9**. **10** could be attacked by H_2O to give intermediate **14**. After tautomerization and the loss of the acetyl ligand, the resulting intermediate **15** could undergo a deinsertion reaction to afford complex **13**.

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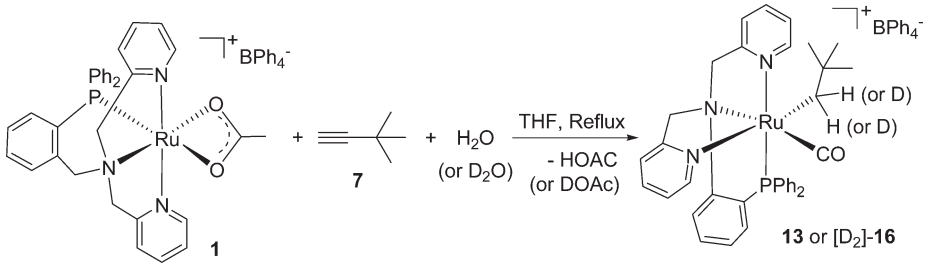
Scheme 7. Reaction of Complex 1 with *tert*-Butylacetylene (7) and H_2O (or D_2O) To Afford Complex 13 (or the $[D_2]$ Complex 16)



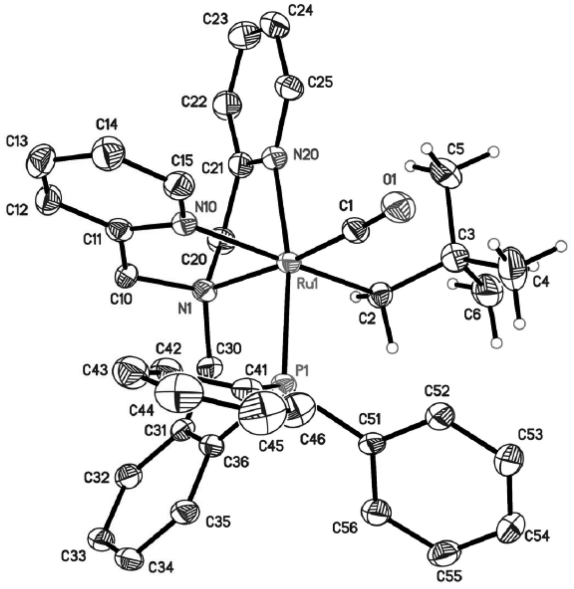


Figure 3. ORTEP diagram of complex $\mathbf{13}^+$.

A similar mechanism has been proposed previously, for example, in the reaction of $[RuCl_2(=C=CHPh)(PNP)]$ with water to give $[RuCl(CH_2Ph)(CO)(PNP)]$ (PNP = $EtN(CH_2CH_2PPh_2)_2$),[31b] the reaction of $[Os(C{\equiv}CPh)_2(CO)(PiPr_3)_2]$ with H_2O to give $[Os(C{\equiv}CPh)(CH_2Ph)(CO)_2(P^iPr_3)_2]$,[32d] and the reaction of $[IrCl_2(Cp^*)]_2$ (Cp^* = pentamethylcyclopentadienyl) with terminal alkynes RC≡CH and water to give $[IrCl(CH_2R)(Cp^*)(CO)]$.[34e] Addition of water to coordinated alkyne has also been proposed in catalytic hydration reactions.[24]

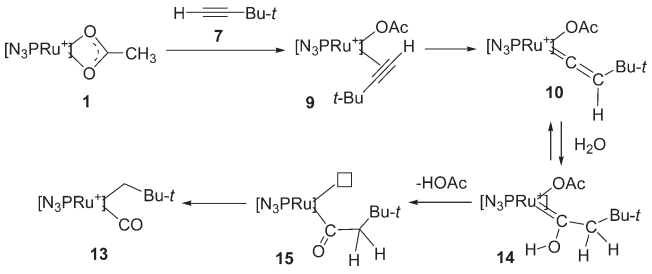
In support of the mechanism, the reaction of complex **1** with *tert*-butylacetylene and approximately 50 equiv of D_2O (99.9 atom % D) gave the deuterated complex **16** (Scheme 7). The ^1H and ^2D NMR data of $[D_2]$-**16** suggest that the methylene of the CH_2-CMe_3 group has approximately 95% deuterium. Formation of $[D_2]$-**16** is consistent with the mechanism profile outlined in Scheme 8. Incorporation of 95% rather than 50% deuterium at the methylene carbon atom is likely due to reversible formation of **14** from **10**. It is also possible that the terminal alkyne is enriched with deuterium before forming **10** due to H/D exchange between the terminal alkyne and excess D_2O in the presence of the ruthenium complex.

We have monitored the reaction of complex **1** with *tert*-butylacetylene and H_2O by $^{31}P\{^1H\}$ NMR, which revealed that complex **8** was also formed initially. After 6 h, complex **8** was completely transformed to complex **13**. Presumably, the η^3-butenynyl ligand in **8** could be protonated by water to regenerate complex **1**,

Table 4. Selected Bond Lengths (Å) and Angles (deg) in Complex 13

Bond Distances			
Ru(1)−C(1)	1.794(4)	Ru(1)−N(20)	2.145(3)
Ru(1)−N(10)	2.154(4)	Ru(1)−C(2)	2.186(5)
Ru(1)−N(1)	2.198(4)	Ru(1)−P(1)	2.3028(10)
O(1)−C(1)	1.176(5)	C(2)−C(3)	1.521(6)
C(3)−C(6)	1.520(8)	C(3)−C(4)	1.529(8)
C(3)−C(5)	1.540(7)		
Bond Angles			
C(1)−Ru(1)−N(20)	99.13(16)	C(1)−Ru(1)−N(10)	96.17(19)
N(20)−Ru(1)−N(10)	81.56(14)	C(1)−Ru(1)−C(2)	92.7(2)
N(20)−Ru(1)−C(2)	91.11(16)	N(10)−Ru(1)−C(2)	169.25(16)
C(1)−Ru(1)−N(1)	174.45(18)	N(20)−Ru(1)−N(1)	77.18(13)
N(10)−Ru(1)−N(1)	79.26(14)	C(2)−Ru(1)−N(1)	91.49(16)
C(1)−Ru(1)−P(1)	90.68(13)	N(20)−Ru(1)−P(1)	169.46(10)
N(10)−Ru(1)−P(1)	93.62(9)	C(2)−Ru(1)−P(1)	92.29(11)
N(1)−Ru(1)−P(1)	92.75(9)	O(1)−C(1)−Ru(1)	177.0(5)
C(3)−C(2)−Ru(1)	128.9(3)	C(6)−C(3)−C(2)	108.7(4)
C(2)−C(3)−C(4)	112.7(5)	C(2)−C(3)−C(5)	111.3(4)

Scheme 8. Proposed Mechanism for the Reaction of Complex 1 with *tert*-Butylacetylene (7) and H_2O To Generate Complex 13



which could react with *tert*-butylacetylene and H_2O to give **13**. In fact, complex **8** reacted with H_2O in THF at 80 °C to give complex **17** as red single crystals (Scheme 9). The structure of complex **17** has been confirmed by X-ray diffraction analysis (Figure 4). The crystal data and refinement details of complex **17** are given in Table 1, and selected bond lengths and bond angles are given in Table 5. Unfortunately, its NMR spectroscopic data could not be collected, due to its extremely

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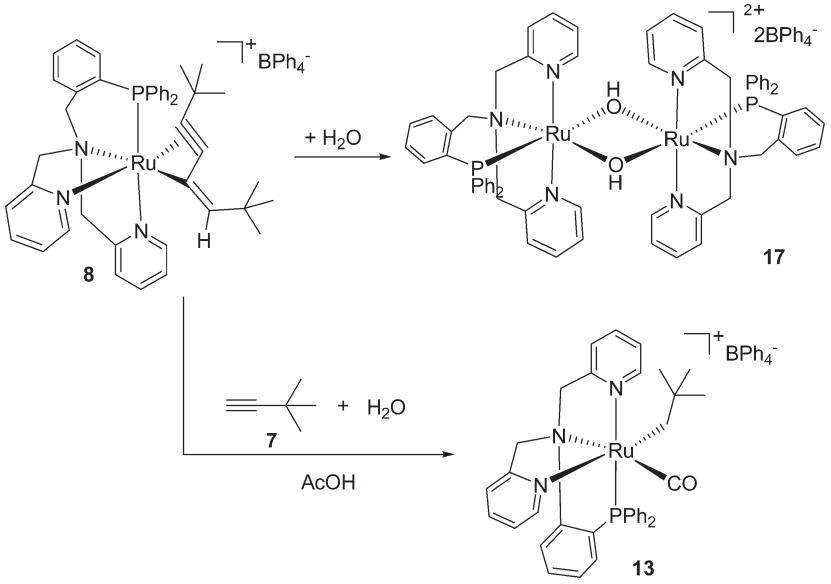
Scheme 9. Reactions of Complex 8



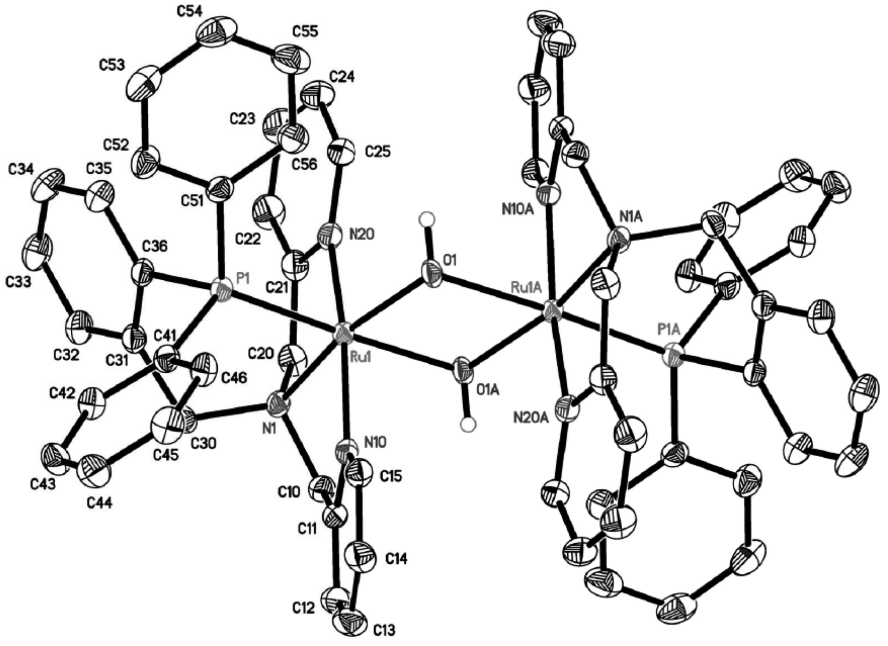


Figure 4. ORTEP diagram of complex $\mathbf{17}^{2+}$.

poor solubility in common solvents. As expected, isolated complex **8** reacted with *tert*-butylacetylene and H_2O to produce complex **13**. The transformation is accelerated by adding HOAc. Apparently, HOAc can easily protonate the η^3-butenynyl ligand in complex **8** to regenerate complex **1**.

CONCLUSION

Vinylidene complexes have been suggested as the key intermediates in the endo cycloisomerization of alkynols catalyzed by complex **1**. In this work, we have successfully isolated and characterized complexes **4**, **8**, and **13** from the reactions of **1** with alkynes. Production of these complexes can also be interpreted via vinylidene intermediates. The experimental results provide indirect evidence that the catalytic cycloisomerization of alkynols catalyzed by complex **1** involves vinylidene complexes as the key intermediates.

EXPERIMENTAL SECTION

General Considerations. 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

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Table 5. Selected Bond Lengths (Å) and Angles (deg) in Complex 17

Bond Distances			
Ru(1)−N(10)	2.0650(16)	Ru(1)−N(1)	2.0958(16)
Ru(1)−N(20)	2.1019(17)	Ru(1)−O(1)	2.1468(13)
Ru(1)-O(1A)	2.1681(13)	Ru(1)−P(1)	2.2502(5)
Bond Angles			
N(10)−Ru(1)−N(1)	80.94(6)	N(10)−Ru(1)−N(20)	162.96(7)
N(1)−Ru(1)−N(20)	82.58(7)	N(10)−Ru(1)−O(1)	96.01(6)
N(1)−Ru(1)−O(1)	168.69(6)	N(20)−Ru(1)−O(1)	99.33(6)
N(10)−Ru(1)−O(1A)	84.77(6)	N(1)−Ru(1)−O(1A)	90.28(6)
N(20)−Ru(1)−O(1A)	91.02(6)	O(1)−Ru(1)−O(1A)	78.58(6)
N(10)−Ru(1)−P(1)	96.28(5)	N(1)−Ru(1)−P(1)	92.68(5)
N(20)−Ru(1)−P(1)	88.77(5)	O(1)−Ru(1)−P(1)	98.49(4)
O(1A)-Ru(1)−P(1)	176.98(4)	Ru(1)−O(1)−Ru(1A)	101.42(6)

calcium hydride (dichloromethane). $[Ru(N_3P)(OAc)](BPh_4)$ (**1**) was prepared according to the literature method.[21] 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) and an API QSTAR XL System (ESI). ^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 $^{13}C\{^1H\}$ NMR chemical shifts are relative to TMS or the residue of deuterium solvents, and $^{31}P\{^1H\}$ NMR chemical shifts are relative to 85% H_3PO_4.

Complex 4. A mixture of $[Ru(N_3P)(OAc)](BPh_4)$ (**1**; 0.15 g, 0.16 mmol), 3-butyn-1-ol (**2**; 60 μL, 0.76 mmol), and DIPEA (130 μL, 0.76 mmol) in THF (5 mL) was stirred under N_2 at 80 °C for 1 h. The mixture was cooled to room temperature and concentrated to approximately 3 mL. The precipitated solid was collected by filtration, washed with THF, Et_2O, and hexane, and dried under vacuum to afford complex **4** as a yellow solid (68%, 0.11 g). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, 25 °C): δ 53.4 ppm (s). ^1H NMR (400.1 MHz, CD_2Cl_2, 25 °C): δ 8.72−8.70 (m, 1H), 8.38 (d, J = 4.8 Hz, 1H), 7.70−7.66 (m, 2H), 7.63−7.57 (m, 2H), 7.44−7.34 (m, 14H), 7.29−7.17 (m, 3H), 7.06−6.99 (m, 12H), 6.87 (t, J = 7.2 Hz, 4H), 6.78−6.74 (m, 2H), 6.57 (d, J = 7.8 Hz, 1H), 4.64 (d, J = 13.0 Hz, 1H; ArCH_2), 4.25 (q, J_1 = 16.4, J_2 = 8.7 Hz; Ru=C(O−)$CH_2CH_2CH_2$−), 4.06 (d, J = 17.4 Hz, 1H; PyCH_2), 4.01−3.95 (m, 1H; Ru=C(O−)$CH_2CH_2CH_2$−), 3.76 (d, J = 13.2 Hz, 1H; ArCH_2), 3.72−3.65 (m, 1H; Ru=C(O−)CH_2), 3.40 (d, J = 15.4 Hz, 1H; PyCH_2), 3.22 (d, J = 15.4 Hz, 1H; PyCH_2), 3.06 (d, J = 17.4 Hz, 1H; PyCH_2), 2.04−1.92 (m, 1H; Ru=C(O−)CH_2), 1.97 (s, 3H; COCH_3), 1.90−1.81 (m, 1H; Ru=C(O−)CH_2CH_2), 1.75−1.66 (m, 1H; Ru=C-(O−)CH_2CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.6 MHz, 25 °C): δ 312.7 (d, J = 14 Hz, Ru=C), 177.2 (CH_3CO), 165.4, 157.4, 156.6, 149.0, 138.4, 137.8, 136.4, 135.8, 134.5, 134.4, 132.6, 132.5, 132.1, 129.9, 129.4, 128.2, 128.1, 127.9, 127.7, 126.1, 122.3, 120.1, 81.7 (Ru=C(O−)CH_2CH_2-CH_2−), 74.2 (PyCH_2), 67.7 (d, J = 4 Hz, ArCH_2), 65.9 (PyCH_2), 53.2 (Ru=C(O−)$CH_2CH_2CH_2$−), 25.1 (CH_3CO), 22.5 (Ru=C(O−)CH_2-CH_2CH_2−) ppm. Anal. Calcd for $C_{61}H_{57}BN_3O_3PRu\cdot0.5$(hexane): C, 72.10; H, 6.05; N, 3.94. Found: C, 72.64; H, 5.94; N, 3.97. HRMS (ESI): m/z calcd for $C_{37}H_{37}N_3O_3PRu^+$ 704.1611, found 704.1570 $[M - BPh_4]^+$.

Complex 8. A mixture of complex **1** (0.3 g, 0.3 mmol) and *tert*-butylacetylene (**7**; 0.38 mL, 3.0 mmol) in THF (12 mL) was stirred under N_2 in a sealed tube at 90 °C for 20 min. The reaction mixture was cooled to room temperature, and the solution was concentrated to 1 mL; then Et_2O (10 mL) was added to give a precipitate. The solvent was removed by filtration, and the solid was dissolved in CH_2Cl_2 (1 mL); then Et_2O (10 mL) was added to the solution to afford a precipitate. The solid was collected by filtration, washed with Et_2O, and dried under vacuum to afford complex **8** as a yellow solid (71%, 0.21 g). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, 25 °C): δ 50.2 ppm (s). ^1H NMR ($CDCl_3$, 400.1 MHz, 25 °C): δ 9.75 (d, J = 5.2 Hz, 1H), 7.74 (d, J = 5.4 Hz, 1H), 7.49−7.39 (m, 10H), 7.36−7.18 (m, 7H), 7.10−6.99 (m, 11H), 6.89−6.80 (m, 8H), 6.72−6.65 (m, 3H), 6.41 (d, J = 7.8 Hz, 1H), 4.80 (s, 1H; C=CHC$(CH_3)_3$), 4.70 (d, J = 13.1 Hz, 1H; ArCH_2), 4.54 (d, J = 15.0 Hz, 1H; PyCH_2), 4.07 (d, J = 13.2 Hz, 1H; ArCH_2), 3.68 (d, J = 16.7 Hz, 1H; PyCH_2), 3.64 (d, J = 14.7 Hz, 1H; PyCH_2), 3.10 (d, J = 14.7 Hz, 1H; PyCH_2), 1.29 (s, 9H; C≡CC$(CH_3)_3$), 0.76 (s, 9H; C=CHC$(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 164.9, 164.4, 163.9, 163.4, 155.7, 148.6, 144.7 (C≡CC=CH), 141.2, 136.8, 136.4, 134.7, 133.6 (C=CHC$(CH_3)_3$), 132.7, 132.6, 130.9, 129.5, 129.3, 129.0, 128.7, 128.3, 128.1, 127.9, 127.6, 127.2, 125.7, 123.7 (C≡CC=CH), 123.4, 122.0, 121.4, 70.5 (PyCH_2), 67.8 (ArCH_2), 64.8 (PyCH_2), 48.9 (C≡CC=CH), 35.3 (C=CHC$(CH_3)_3$), 33.7 (C≡CC$(CH_3)_3$), 32.5 (C≡CC$(CH_3)_3$), 29.7 (C=CHC$(CH_3)_3$). Anal. Calcd for $C_{67}H_{69}BN_3OPRu$: C, 74.85; H, 6.47; N, 3.91. Found: C, 74.99; H, 6.19; N, 4.08. HRMS (MALDI, matrix CHCA): m/z calcd for $C_{43}H_{47}N_3PRu^+$ 738.2546, found 738.4191 $[M - BPh_4]^+$.

Complex 13. A mixture of complex **1** (0.10 g, 0.10 mmol), *tert*-butylacetylene (**7**; 0.25 mL, 2.0 mmol), and H_2O (0.2 mL) in THF (8 mL) was stirred under N_2 in a sealed tube at 90 °C for 6 h. The reaction mixture was cooled to room temperature, and Na_2SO_4 was added. After 2 h, the solid was removed by filtration, the filtrate was concentrated to approximately 1 mL, and Et_2O (7 mL) 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 complex **13** as a white solid (76%, 76 mg). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, 25 °C): δ 56.7 ppm (s). ^1H NMR (400.1 MHz, $(CD_3)_2CO$, 25 °C): δ 8.81 (d, J = 5.5 Hz, 1H), 8.25 (d, J = 5.3 Hz, 1H), 7.76−7.68 (m, 2H), 7.64−7.42 (m, 9H), 7.39−7.35 (m, 8H), 7.29−7.21 (m, 3H), 7.19−7.14 (m, 4H), 7.02−6.98 (m, 2H), 6.93 (t, J = 7.4 Hz, 8H), 6.78 (t, J = 7.2 Hz, 4H), 5.07 (d, J = 14.1 Hz, 1H; ArCH_2), 5.05 (d, J = 16.1 Hz; PyCH_2), 4.73 (d, J = 17.2 Hz; PyCH_2), 4.45 (d, J = 16.1 Hz; PyCH_2), 4.32 (dd, J_1 = 14.1 Hz, J_2 = 1.0 Hz, 1H; ArCH_2), 4.23 (d, J = 17.2 Hz; PyCH_2), 1.59 (t, J = 10.8 Hz, 1H; RuCH_2), 0.90 (d, J = 10.8 Hz, 1H; RuCH_2), 0.54 (s, 9H; $CH_2C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 25 °C): δ 207.0 (d, J = 18 Hz), 165.1, 164.7, 164.2, 163.7, 156.6, 156.0, 152.0, 150.2, 141.7, 141.5, 138.3, 137.8, 137.5, 136.4, 135.7, 135.2, 133.9, 133.7, 133.6, 133.0, 132.3, 131.9, 131.8, 130.6, 129.9, 129.6, 128.8, 128.7, 128.6, 128.5, 126.6, 126.2, 126.1, 124.8, 124.7, 122.9, 122.4, 121.7, 70.6 (PyCH_2), 66.8 (PyCH_2), 62.6 (d, J = 4 Hz, ArCH_2), 37.3 ($C(CH_3)_3$), 33.6 ($C(CH_3)_3$ and RuCH_2). Anal. Calcd for $C_{61}H_{59}BN_3OPRu$: C, 73.78; H, 5.99; N, 4.23. Found: C, 73.45; H, 6.02; N, 4.09. HRMS (MALDI, matrix CHCA): m/z calcd for $C_{37}H_{39}N_3OPRu^+$ 674.1869, found 674.3293 $[M - BPh_4]^+$.

[D_2] Complex 16. A mixture of complex **1** (0.10 g, 0.10 mmol), *tert*-butylacetylene (**7**; 0.25 mL, 2.0 mmol) and D_2O (0.2 mL) in THF (8 mL) was stirred under N_2 in a sealed tube at 90 °C for 6 h. The reaction mixture was cooled to room temperature, and Na_2SO_4 was added. After 2 h, the solid was removed by filtration, the filtrate was concentrated to approximately 1 mL, and Et_2O (7 mL) 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 complex **18** as a white solid (68%, 68 mg). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, 25 °C): δ 56.8 ppm (s). ^1H NMR (400.1 MHz, $(CD_3)_2CO$, 25 °C): δ 8.82 (d, J = 5.6 Hz, 1H), 8.26 (d, J = 5.2 Hz, 1H), 7.78−7.68 (m, 2H), 7.66−7.46 (m, 9H), 7.38−7.34 (m, 8H), 7.29−7.23 (m, 3H), 7.19−7.14 (m, 4H), 7.06−6.70 (m, 2H), 6.93 (t, J = 7.4 Hz, 8H), 6.78 (t, J = 7.2 Hz, 4H), 5.08 (d, J = 14.5 Hz, 2H; ArCH_2 and PyCH_2), 4.76 (d, J = 17.0 Hz, 1H; PyCH_2), 4.50 (d, J = 16.1 Hz; PyCH_2), 4.35 (dd, J_1 = 14.2 Hz, J_2 = 1.2 Hz, 1H; ArCH_2), 4.27 (d, J = 17.2 Hz; PyCH_2), 0.53 (s, 9H; $CH_2C(CH_3)_3$). ^2D NMR (61.3 MHz, $(CH_3)_2CO$ (set as δ 2.20 ppm), 25 °C): δ 1.66 (1D; RuCD_2); 0.99 ppm (1D; RuCD_2). Anal. Calcd for $C_{61}H_{57}D_2BN_3OPRu$: C, 73.63; H+D, 6.18; N, 4.22. Found: C, 73.75; H, 5.84; N, 4.26. HRMS (MALDI, matrix

CHCA): m/z calcd (%) for $C_{37}H_{39}N_3OPRu^+$ 676.1994, found 676.3060 $[M - BPh_4]^+$.

Complex 17. A mixture of complex **8** (0.050 g, 0.047 mmol) and H_2O (90 μL, 5.0 mmol) in THF (5 mL) was heated under N_2 at 80 °C for 20 h. The mixture was cooled to room temperature. The precipitated solid was collected by filtration, washed with a solvent mixture of THF (0.5 mL) and Et_2O (5 mL), and dried under vacuum to afford complex **17** as a red solid (57%, 0.024 g). Anal. Calcd for $C_{110}H_{98}B_2N_6O_2P_2Ru_2 \cdot 6H_2O$: C, 68.46; H, 5.75; N, 4.35. Found: C, 68.35; H, 5.82; N, 4.30.

X-ray Crystallography Studies of Compounds 4, 8, 13, and 17. The crystals were mounted on glass fibers, and the diffraction intensity data of **4** were collected with a Bruker CCD diffractometer with monochromated Mo Kα radiation (λ = 0.710 73 Å) at 173 K. Lattice determination and data collection were carried out using SMART v.5.625 software. Data reduction and absorption correction were performed using SAINT v 6.26 and SADABS v 2.03. However, the diffraction intensity data of **8**, **13**, and **17** were collected with a Oxford Diffraction GeminiS Ultra with CCD area detector with monochromated Cu Kα radiation (λ = 1.541 78 Å) at 173 K. Lattice determination, data collection, and reduction were carried out using CrysAlisPro 171.32.5. Absorption correction was performed using SADABS built into 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 direct methods and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were introduced at their geometric positions and refined as riding atoms.

■ ASSOCIATED CONTENT

Supporting Information. CIF files giving X-ray structural information for complexes **4**, **8**, **13**, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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