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1,2-Migration in the reactions of ruthenium vinyl carbene with propargyl alcohols†

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Reactions of the ruthenium vinyl carbene complex [Ru{CHC(PPh$_3$)CH(2-Py)}Cl$_2$PPh$_3$]BF$_4$ (**1**) with five propargyl alcohols HC≡CC(OH)R^{1}R^2, (R^1 = R^2 = Ph; R^1 = Ph, R^2 = CH$_3$; R^1 = H, R^2 = Ph; R^1 = H, R^2 = CH$_3$; R^1 = CH=CH$_2$, R^2 = CH$_3$) have been investigated, which led to the formation of several ten-membered η^2-olefin coordinated ruthenacycles [Ru{O=CR^{2}CHR^1-η^2-CH=CHC(PPh$_3$)=CH(2-Py)}Cl$_2$PPh$_3$]BF$_4$ (R^1 = R^2 = Ph, **2**; R^1 = Ph, R^2 = CH$_3$, **3**; R^1 = H, R^2 = Ph, **4**; R^1 = H, R^2 = CH$_3$, **5**; R^1 = CH=CH$_2$, R^2 = CH$_3$, **6**), respectively. In these reactions, insertion of alkynes and intramolecular 1,2-migration of propargyl alcohols were performed in tandem. The results show that the 1,2-migratory preference of the groups is in the order of H > Ph > CH$_3$. Complexes **2**, **3**, **5**, and **6** were characterized by X-ray diffraction analysis and NMR spectra.

Introduction

Ruthenium vinyl carbenes are widely used as carbene initiators in metathesis reactions.[1,2] They are also extensively reported as crucial intermediates in enyne metathesis.[3] The vinyl substitution has a significant influence on the ruthenium carbene reactivity because the electron-deficient carbene center could be partially stabilized by π–π conjugation.[3d] Investigation into vinyl carbene reactivity would be helpful in understanding the catalytic enyne metathesis. Nevertheless, in sharp contrast to their extensive use, fundamental reactivity studies on such compounds are less explored.[1a,c,4] The first well-defined group 8 vinyl carbene was the neophylidene complex, which was developed by Grubbs' group in 1992.[1a] It was stable towards water, alcohol and the diethyl ether solution of HCl.[1a] However, it could react with strained acyclic olefins and functionalized olefins,[4a] and catalyze the ROMP of norbornene derivatives.[1a,e,f]

Recently, we reported a convenient route to prepare a stable ruthenium vinyl carbene **1**.[5] It was a fused heterocycle different from the reported aromatic metallacycles[6] because of the significant alternation of the bond lengths in the ring. The electron in it was quite localized, so that it was more suitable to be viewed as a 1,3-butadiene moiety.[5] Its C$_\gamma$ was easily attacked by nucleophilic reagents to form a series of ruthenapolycyclic complexes [Ru{CHC(PPh$_3$)CHR(2-Py)}Cl(PPh$_3$)$_2$]BF$_4$ [R = OH, OCH$_3$, NHPh].[4g] It could also react with alkynones and alkynoates in the presence of an acid, leading to the formation of 3-alkenyl-2-phosphonium indolizine salts.[5] For our continuous interest in the reactivity of ruthenium vinyl carbene, we have studied the reactions of **1** with five propargyl alcohols bearing different substituents. The results show that the alkyne groups of propargyl alcohols undergo facile insertion into the ruthenium–carbon double bond of **1**, yielding a series of ten-membered η^2-olefin coordinated ruthenacycles (Chart 1a). The reaction mechanism involves [2 + 2]-cycloaddition and [2 + 2]-cycloreversion reactions, which is related to the typical enyne metathesis steps (Chart 1b).[3] It is also similar to our previous reported work of alkynes' insertion into osmafuran.[7] Interestingly, 1,2-migration of the substituents on propargyl alcohols has been observed in the reactions. The results show that the migratory preference of the substituents is in the order of H > Ph > CH$_3$, which is in accordance with the common phenomenon observed in the singlet carbene and metal carbene species.[8]

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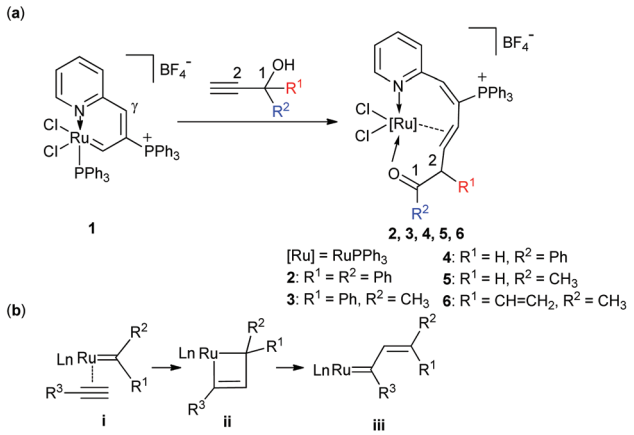


Chart 1 (a) Reactions of **1** with propargyl alcohols; (b) the typical enyne metathesis process.

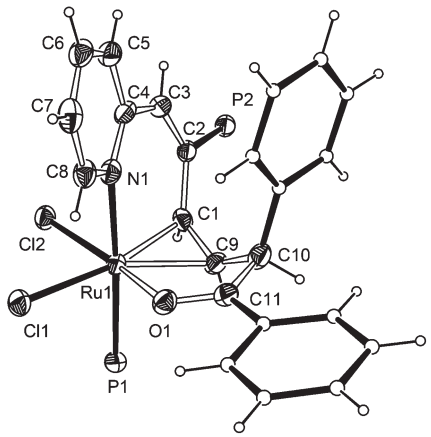


Fig. 1 Molecular structure of complex **2** (ellipsoids at the 50% probability level). The phenyl rings in PPh_3 groups and the counter anion are omitted for clarity. Selected bond distances [Å] and angles [°]: Ru(1)–O(1) 2.085(4), O(1)–C(11) 1.246(6), C(10)–C(11) 1.510(7), C(9)–C(10) 1.526(8), C(1)–C(9) 1.412(7), C(1)–C(2) 1.481(7), C(2)–C(3) 1.348(7), C(3)–C(4) 1.452(7), N(1)–C(4) 1.359(7), Ru(1)–C(1) 2.176(5), Ru(1)–C(9) 2.164(5), Ru(1)–N(1) 2.192(4), O(1)–Ru(1)–C(9) 74.64(17), O(1)–Ru(1)–C(1) 109.99(17), O(1)–C(11)–C(10) 117.7(5), C(9)–C(10)–C(11) 105.2(4), C(10)–C(9)–Ru(1) 110.2(3), C(9)–C(1)–C(2) 130.2(4), C(1)–C(2)–C(3) 129.0(5), C(2)–C(3)–C(4) 129.2(5), N(1)–C(4)–C(3) 122.3(4), O(1)–Ru(1)–N(1) 85.59(15), C(4)–N(1)–Ru(1) 126.6(3), C(9)–Ru(1)–C(1) 37.98(19), N(1)–Ru(1)–P(1) 174.60(12), C(1)–Ru(1)–Cl(1) 167.20(14), O(1)–Ru(1)–Cl(1) 82.35(11), C(9)–Ru(1)–Cl(1) 154.70(14), O(1)–Ru(1)–Cl(2) 166.86(10).

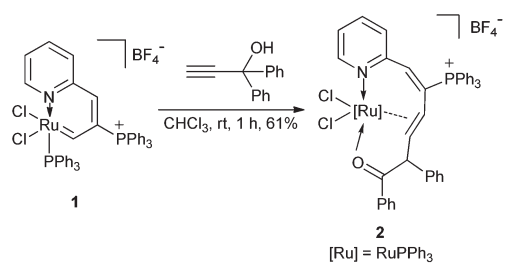
Results and discussion

Reaction of 1 with $HC{\equiv}CC(OH)(Ph)_2$

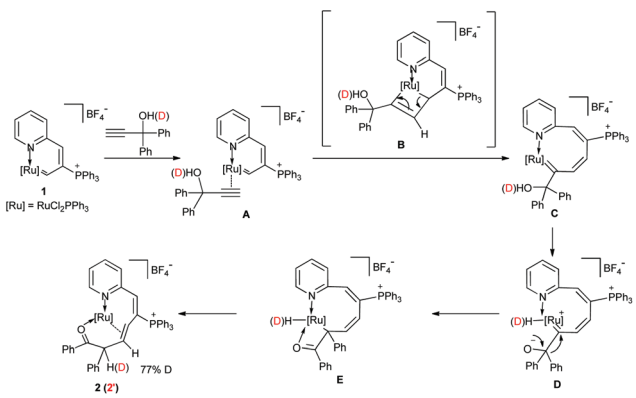
A mixture of ruthenium vinyl carbene **1** with $HC{\equiv}CC(OH)(Ph)_2$ in $CHCl_3$ was stirred at room temperature for 1 h to give a red suspension. The precipitate was collected by filtration in 61% yield and was identified to be a ten-membered η^2-olefin coordinated ruthenacycle **2** [Ru{O=CPhCHPh-η^2-CH=CHC-(PPh_3)=CH(2-Py)}Cl_2PPh_3]BF_4 (Scheme 1). Complex **2** had excellent thermal stability. The solid sample of **2** remains nearly unchanged at 120 °C in air for 5 h.

As shown in Fig. 1, X-ray crystallographic analysis reveals that the atoms O1, C11, C10, C9, C1, C2, C3, C4, N1, together with Ru1, construct the ten-membered distorted metallacycle. The coordination geometry around the Ru atom can be rationalized as a octahedron with the P1 and N1 occupying *trans* positions (P(1)–Ru(1)–N(1) 174.60(12)°), Cl1 *trans* to the η^2-olefin (C(1)–Ru(1)–Cl(1) 167.20(14)°, C(9)–Ru(1)–Cl(1) 154.70(14)°) and Cl2 *trans* to O1 (O(1)–Ru(1)–Cl(2) 166.86(10)°). The NMR spectral data are consistent with the X-ray structure. In particular, the ^{1}H NMR spectrum shows the proton signals of η^2-olefin at 4.53 and 5.46 ppm, respectively. The H10 signal is observed at 5.77 ppm. The signal at 6.44 ppm is attributed to H3. The ^{13}C NMR spectrum shows the characteristic carbon signals of *C*(Ph)=O and η^2-*C*H=*C*H at 218.97, 81.17 and 73.04 ppm, respectively. The signals of the other four carbons C10, C2, C3 and C4 appear at 60.32, 122.14, 147.80 and 151.85 ppm, respectively. The ^{31}P NMR spectrum shows two signals at 23.33 and 37.06 ppm for C*P*Ph_3 and Ru*P*Ph_3, respectively.

A proposed mechanism for the formation of **2** is shown in Scheme 2. Firstly, the alkyne coordinates to the unsaturated Ru center, leading to a π-alkyne intermediate **A**. The addition of $HC{\equiv}CC(OH)(Ph)_2$ into **1** *via* a [2 + 2] cycloaddition process gives metallacyclobutene intermediate **B**, which is a highly regioselective process probably due to the steric hindrance of



Scheme 1 Reaction of **1** with $HC{\equiv}CC(OH)(Ph)_2$.



Scheme 2 Proposed mechanisms for the formation of **2** (**2'**).

the nearby bulky phosphonium substituent. The following cycloreversion generates the carbene intermediate **C**. Then the hydroxyl is activated by the ruthenium center to form the hydride-ruthenacycle **D**, which is followed by 1,2-phenyl migration to generate intermediate **E**. The subsequent reductive elimination, coordination of the carbonyl group and the internal alkene gave the 18-e complex **2**. The deuterium-labeling experiment showed that 77% of hydrogen on C10 was deuterated when HC≡CC(OD)$(Ph)_2$ was used, which suggests that the hydrogen on C10 comes from an active hydrogen.

Investigation of 1,2-migratory preferences

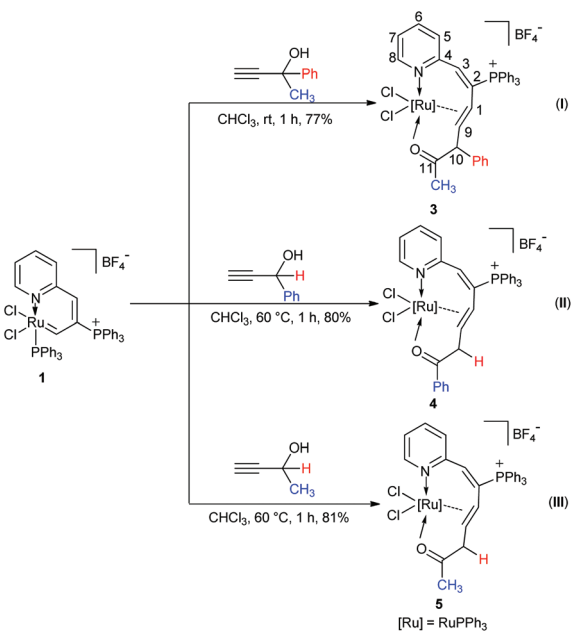
It is worth noting that an intramolecular 1,2-phenyl migration is observed in the formation of **2** (from **D** to **E**). The migration is induced by the electrophilic carbon of the ruthenium carbene intermediate **D**. 1,2-Migration of free carbene or metal carbene has been widely utilized in organic synthesis, especially for catalytic reactions that incorporate rhodium,[8c–h,9] gold,[8i,10] and platinum carbenes.[8i,10d–e,11] The inherent migratory preferences are in the order of H > Ar > alkyl, though the migratory preferences are also affected by nonmigrating factors.[8a,9] However, the 1,2-migratory preferences of Ru carbene are rarely reported,[12] thus propargyl alcohols with different substituents were subjected to the reaction of ruthenium vinyl carbene **1**.

Reactions of **1** with propargyl alcohols HC≡CC(OH)CH_3(Ph) at room temperature readily afforded complex **3** in good isolated yields. Similarly, treatment of **1** with HC≡CCH(OH)Ph and HC≡CCH(OH)CH_3 at room temperature could also generate complexes **4** and **5**, and reacting them at 60 °C could slightly increase the yields (Scheme 3). Complexes **3**, **4**, and **5** were also determined as ten-membered η^2-olefin coordinated ruthenacycles which were similar to complex **2**. The structures of **3** and **5** were also confirmed by X-ray single-crystal structural analysis, in which the Ru atoms are surrounded by a tridentate ligand (N, η^2-CH═CH, O sites) (ESI, Fig. S1-1 and S1-2†).

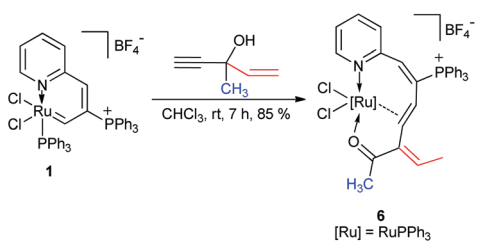
The solution NMR spectra of the three isolated ten-membered η^2-olefin coordinated ruthenacycles show the characteristic ^{1}H NMR signals of the η^2-olefin at around 4.3–5.5 ppm, which is within the typical proton chemical shift range of η^2-olefin.[13] In complex **3**, the ^{1}H NMR spectrum shows the proton signal on C10 at 5.30 ppm, which is significantly lower compared with those of **4** (3.70, 2.92 ppm) and **5** (3.20, 2.71 ppm) respectively, probably due to the deshielding effect by the adjacent Ph group. In the ^{13}C NMR spectra, the carbon signals of the η^2-olefin for these three complexes are in the range of 75.24 to 81.06 ppm. The ^{31}P NMR spectra show similar signals for the three complexes (see the Experimental section), which confirms they are analogous structures as well.

Both the solid and solution states analyses confirmed the well-defined structures of **3**, **4**, and **5**. From the product structures in Scheme 3, migratory aptitudes for H, Ph and CH_3 are evident. As observed in reaction (I), the phenyl group was in preference to migrate compared with the CH_3 group. The hydrogen was more likely to migrate than the phenyl group (reaction (II)). This is consistent with the fact that 1,2-H migration is a highly favorable process. Accordingly, the migration of H was also easier than CH_3 (reaction (III)). Thus, 1,2-migratory preference for the groups is in the order of H > Ph > CH_3, which is consistent with the inherent migratory aptitude of singlet free carbenes and metal carbenes.[8]

In addition, complex **6** was prepared when HC≡CC(OH)CH_3 (CH═CH_2) was subjected to this reaction (Scheme 4). The structure of **6** was also confirmed by X-ray diffraction, and its structure is depicted in Fig. 2. The X-ray diffraction study and solution NMR spectrum confirmed that complex **6** was similar to complexes **2**, **3**, **4**, and **5** (see the Experimental section). It is noted that the vinyl group migrates preferentially as compared to the methyl group and the π-bond isomerization occurs during the migration process.



Scheme 3 Reactions of **1** with propargyl alcohols bearing different migratory groups.



Scheme 4 Reaction of **1** with HC≡CC(OH)CH_3(CH═CH_2).

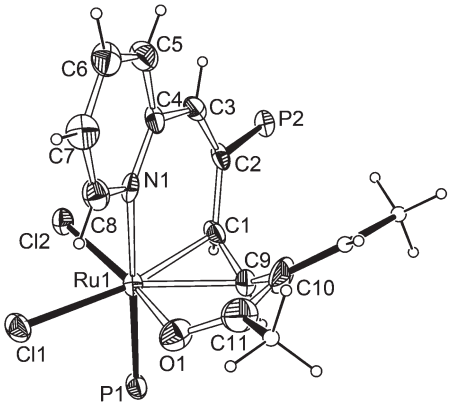


Fig. 2 Molecular structure of complex **6** (ellipsoids at the 50% probability level). The phenyl rings in PPh_3 groups and the counter anion are omitted for clarity. Selected bond distances [Å] and angles [°] of complex **6**: Ru(1)–O(1) 2.092(4), O(1)–C(11) 1.223(8), C(10)–C(11) 1.446(11), C(9)–C(10) 1.506(10), C(1)–C(9) 1.391(9), C(1)–C(2) 1.479(8), C(2)–C(3) 1.337(8), C(3)–C(4) 1.457(8), N(1)–C(4) 1.361(7), Ru(1)–C(1) 2.164(6), Ru(1)–C(9) 2.135(6), Ru(1)–N(1) 2.135(6), O(1)–Ru(1)–C(9) 75.2(2), O(1)–Ru(1)–C(1) 110.9(2), O(1)–C(11)–C(10) 117.4(7), C(9)–C(10)–C(11) 110.8(6), C(10)–C(9)–Ru(1) 105.4(4), C(9)–C(1)–C(2) 128.2(6), C(1)–C(2)–C(3) 129.1(6), C(2)–C(3)–C(4) 129.2(6), N(1)–C(4)–C(3) 121.9(5), O(1)–Ru(1)–N(1) 81.15(17), C(4)–N(1)–Ru(1) 127.1(4), C(9)–Ru(1)–C(1) 37.8(2).

Conclusions

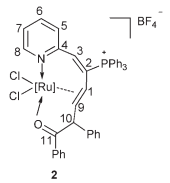
In conclusion, we have investigated the reactions of ruthenium vinyl carbene **1** with five propargyl alcohols, which led to the formation of a series of ten-membered η^2-olefin coordinated ruthenacycles. The proposed mechanisms for the formation of these complexes involve a regioselective [2 + 2] cycloaddition and 1,2-migration process. By introduction of different substituents on propargyl alcohols, we conclude that the intramolecular 1,2-migratory preference of the groups is in the order of H > Ph > CH_3, which is consistent with the inherent migratory aptitude of singlet free carbenes and metal carbenes. Further studies on the reactivities of ruthenium vinyl carbenes are in progress in our laboratory.

Experimental

All syntheses were carried out under an inert atmosphere (N_2) by means of standard Schlenk techniques, unless otherwise stated. Solvents were distilled from sodium/benzophenone (hexane and diethyl ether) or calcium hydride (dichloromethane, chloroform) under N_2 prior to use. Reagents were used as received from commercial sources without further purification. NMR spectroscopic experiments were performed on an AVIII-400 (^{1}H, 400.13 MHz; ^{13}C, 100.63 MHz; ^{31}P, 161.96 MHz) spectrometer at room temperature. ^{1}H and ^{13}C NMR chemical shifts (δ) are relative to tetramethylsilane, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. The absolute values of the coupling constants are given in hertz (Hz). Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), multiplet (m) and broad (br). Elemental analyses were performed on a Vario EL III elemental analyzer.

Compound 2

A mixture of 1,1-diphenyl-2-propyn-1-ol (624 mg, 3.00 mmol) and compound **1** (899 mg, 1.00 mmol) in $CHCl_3$ (30 mL) was stirred at room temperature for 1 h to give a red suspension, which was collected by filtration, washed with Et_2O (3 × 10 mL) and dried under vacuum. Yield: 675 mg, 61%.

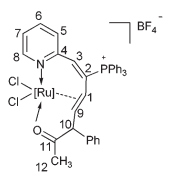


2
[Ru] = $RuPPh_3$

^{1}H NMR (400.13 MHz, CD_2Cl_2): δ = 9.73 (d, J(HH) = 5.3 Hz, 1 H, H8), 6.44 (d, J(PH) = 23.9 Hz, 1 H, H3), 6.22 (t, J(HH) = 7.09 Hz, 1 H, an aromatic proton, confirmed by ^{1}H–^{13}C HSQC), 5.77 (d, J(HH) = 7.8 Hz, 1 H, H10), 5.52 (d, J(HH) = 7.11 Hz, 1 H, an aromatic proton, confirmed by ^{1}H–^{13}C HSQC), 5.46 (m, 1 H, H9), 4.64 (d, J(HH) = 7.28 Hz, 1 H, an aromatic proton, confirmed by ^{1}H–^{13}C HSQC), 4.53 (dd, apparent t, J(PH) = 9.2 Hz, J(HH) = 9.2 Hz, 1 H, H1), 7.90–6.73 ppm (40 H, other aromatic carbon atoms); ^{31}P NMR (161.96 MHz, CD_2Cl_2): 23.33 (s, C*P*Ph_3), 37.06 ppm (s, Ru*P*Ph_3). ^{13}C NMR (100.63 MHz, CD_2Cl_2): δ = 218.97 (s, C11), 157.02 (s, C8), 151.85 (d, J(PC) = 19.3 Hz, C4), 147.80 (d, J(PC) = 19.8 Hz, C3), 122.14 (d, J(PC) = 72.4 Hz, C2), 116.09 (d, J(PC) = 87.23 Hz, carbons on phenyls of PPh_3), 81.11 (d, J(PC) = 4.1 Hz, C9), 73.04 (d, J(PC) = 12.4 Hz, C1), 60.32 (s, C10), 139.00–115.65 ppm (other aromatic carbon atoms); Anal. Calcd for $C_{59}H_{48}Cl_2P_2BF_4NORu$: C, 63.97; H, 4.37; N, 1.26. Found: C, 63.84; H, 4.28; N, 1.14.

Compound 3

2-Phenyl-3-butyn-2-ol (439 mg, 3.00 mmol) was added to a solution of compound **1** (899 mg, 1.00 mmol) in $CHCl_3$ (30 mL) at room temperature. The mixture was stirred for 1 h to give a red solution, and then the same volume of Et_2O was added to obtain a precipitate which was collected by filtration. The precipitate was washed with Et_2O (3 × 10 mL) and dried under vacuum. Yield: 806 mg, 77%.



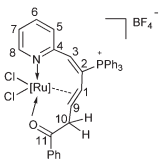
3
[Ru] = $RuPPh_3$

^{1}H NMR (400.13 MHz, CD_2Cl_2): δ = 9.64 (d, J(HH) = 5.3 Hz, 1 H, H8), 6.42 (d, J(PH) = 23.5 Hz, 1 H, H3), 6.42 (1 H, an aromatic proton overlapped with H3, confirmed by ^{1}H–^{13}C HSQC), 5.46 (m, 1 H, H9), 5.46 (1 H, 1 H, an aromatic proton

overlapped with H9, confirmed by ^{1}H–^{13}C HSQC), 5.30 (d, J(HH) = 7.8 Hz, 1 H, H10), 4.61 (d, 1 H, J(HH) = 6.37 Hz, an aromatic proton, confirmed by ^{1}H–^{13}C HSQC), 4.47 (dd, apparent t, J(PH) = 9.8 Hz, J(HH) = 9.8 Hz, 1 H, H1), 1.70 (s, 3 H, H12), 7.87–6.77 ppm (36 H, other aromatic carbon atoms). ^{31}P NMR (161.96 MHz, CD_2Cl_2): 23.26 (s, C*P*Ph_3), 37.82 ppm (s, Ru*P*Ph_3). ^{13}C NMR (100.63 MHz, CD_2Cl_2): δ = 232.93 (s, C11), 157.14 (s, C8), 151.88 (d, J(PC) = 19.7 Hz, C4), 147.78 (d, J(PC) = 15.1 Hz, C3), 122.21 (d, J(PC) = 72.1 Hz, C2), 116.00 (d, J(PC) = 87.9 Hz, carbons on phenyls of PPh_3), 81.06 (d, J(PC) = 4.0 Hz, C9), 73.04 (d, J(PC) = 12.4 Hz, C1), 65.34 (s, C10), 27.7 (s, C12), 139.14–126.00 ppm (other aromatic carbon atoms). Anal. Calcd for $C_{54}H_{46}Cl_2P_2BF_4NORu$: C, 62.02; H, 4.43; N, 1.34. Found: C, 61.90; H, 4.33; N, 1.32.

Compound 4

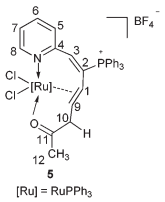
1-Phenyl-2-propyn-1-ol (365 μL, 3.00 mmol) was added to a suspension of complex **1** (899 mg, 1.00 mmol) in $CHCl_3$ (30 mL). The mixture was stirred at 60 °C for 1 h to give a red precipitate. The precipitate was collected by filtration, washed with Et_2O (2 × 5 mL) and dried under vacuum to give **4** (824 mg, 80%) as a red solid.



Complex **4** was separated from the reaction mixture as a precipitate, and the solubility of pure complex **4** was so poor that it prevented NMR characterization. We just characterized complex **4** by *in situ* NMR. *In situ* ^{1}H NMR (400.13 MHz, CD_2Cl_2): δ = 9.41 (d, J(HH) = 3.1 Hz, 1 H, H8), 4.84 (br, 1 H, H9), 4.34 (dd, apparent t, J(PH) = 9.1 Hz, J(HH) = 9.1 Hz, 1 H, H1), 3.70 (br, 1 H, H10), 2.92 (br, 1 H, H10), 7.77–6.98 ppm (39 H, other aromatic carbon atoms and H3); *In situ* ^{31}P NMR (161.96 MHz, CD_2Cl_2): 23.40 (s, C*P*Ph_3), 38.12 ppm (s, Ru*P*Ph_3). *In situ* ^{13}C NMR (100.63 MHz, CD_2Cl_2): δ = 218.79 (s, C11), 156.29 (s, C8), 150.6 (d, J(PC) = 19.7 Hz, C4), 147.80 (d, J(PC) = 15.5 Hz, C3), 122.88 (d, J(PC) = 72.7 Hz, C2), 116.70 (d, J(PC) = 86.7 Hz, carbons on phenyls of PPh_3), 80.80 (d, J(PC) = 3.5 Hz, C9), 77.00 (d, J(PC) = 12.3 Hz, C1), 45.34 (s, C10), 138.78–126.50 ppm (other aromatic carbon atoms); Anal. Calcd for $C_{53}H_{44}BCl_2F_4NOP_2Ru$: C, 61.70; H, 4.30; N, 1.36. Found: C, 61.79; H, 4.66; N, 1.64.

Compound 5

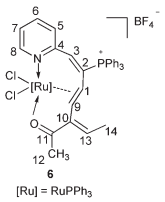
3-Butyn-2-ol (221 μL, 3.00 mmol) was added to a suspension of compound **1** (899 mg, 1.00 mmol) in $CHCl_3$ (30 mL). The mixture was stirred at 60 °C for 1 h to give a brown solution. The solution was concentrated to *ca.* 2 mL, and then Et_2O (20 mL) was added to the solution. The precipitate was collected by filtration, washed with Et_2O (2 × 5 mL) and dried under vacuum to give **5** (780 mg, 81%) as a nacarat solid.



^{1}H NMR (400.13 MHz, CD_2Cl_2–$CDCl_3$ = 3 : 5): δ = 9.54 (d, J(HH) = 4.3 Hz, 1 H, H8), 4.70 (br, 1 H, H9), 4.36 (dd, apparent t, J(PH) = 9.1 Hz, J(HH) = 9.1 Hz, 1 H, H1), 3.20 (br, 1 H, H10), 2.71 (br, 1 H, H10), 1.80 (s, 3 H, H12), 7.78–7.04 ppm (34 H, other aromatic carbon atoms and H3); ^{31}P NMR (161.96 MHz, CD_2Cl_2– $CDCl_3$ = 3 : 5): 23.45 (s, C*P*Ph_3), 38.75 ppm (s, Ru*P*Ph_3). ^{13}C NMR (100.63 MHz, CD_2Cl_2–$CDCl_3$ = 3 : 5): δ = 232.03 (s, C11), 155.29 (s, C8), 149.48 (d, J(PC) = 19.6 Hz, C4), 147.21 (d, J(PC) = 15.6 Hz, C3), 121.16 (d, J(PC) = 71.36 Hz, C2), 115.84 (d, J(PC) = 87.2 Hz, carbons on phenyls of PPh_3), 79.45 (d, J(PC) = 2.7 Hz, C9), 75.24 (d, J(PC) = 12.4 Hz, C1), 48.99 (s, C10), 27.69 (s, C12), 137.83–124.93 ppm (other aromatic carbon atoms). Anal. Calcd for $C_{48}H_{42}BCl_2F_4NOP_2Ru$: C, 59.46; H, 4.37; N, 1.44. Found: C, 59.37; H, 4.18; N, 1.47.

Compound 6

3-Methyl-1-penten-4-yn-3-ol (162 μL, 1.50 mmol) was added to a suspension of complex **1** (449 mg, 0.50 mmol) in $CHCl_3$ (30 mL). The mixture was stirred at room temperature for 8 h to give a red solution. The solution was concentrated to *ca.* 2 mL, and then Et_2O (20 mL) was added to the solution. The precipitate was collected by filtration, washed with Et_2O (2 × 5 mL) and dried under vacuum to give **6** (422 mg, 85%) as a nacarat solid.



^{1}H NMR (400.13 MHz, CD_2Cl_2): δ = 9.63 (d, J(HH) = 5.7 Hz, 1 H, H8), 7.02 (d, J(PH) = 23.1 Hz, 1 H, H3), 6.40 (q, J(HH) = 7.1 Hz, 1 H, H13), 5.59 (dd, apparent t, J(HH) = 8.9 Hz, J(PH) = 8.9 Hz, 1 H, H9), 4.69 (dd, apparent t, J(PH) = 8.9 Hz, J(HH) = 8.9 Hz, 1 H, H1), 1.67 (s, 3 H, H12), 0.86 (d, J(HH) = 7.1 Hz, 3 H, H14), 7.84–7.06 ppm (33 H, other aromatic carbon atoms); ^{31}P NMR (161.96 MHz, CD_2Cl_2): 24.80 (s, C*P*Ph_3), 39.25 ppm (s, Ru*P*Ph_3). ^{13}C NMR (100.63 MHz, CD_2Cl_2): δ = 217.13 (s, C11), 157.40 (s, C8), 150.92 (d, J(PC) = 18.9 Hz, C4), 149.52 (s, C13), 146.79 (d, J(PC) = 15.1 Hz, C3), 142.73 (s, C10), 124.37 (d, J(PC) = 70.22 Hz, C2), 116.45 (d, J(PC) = 87.2 Hz, carbons on phenyls of PPh_3), 73.90 (t, J(PC) = 4.0 Hz, C9), 70.66 (d, J(PC) = 11.1 Hz, C1), 24.15 (s, C12), 15.37 (s, C14), 138.78–125.68 (other aromatic carbon atoms). Anal. Calcd for

$C_{50}H_{44}BCl_2F_4NOP_2Ru$: C, 60.32; H, 4.45; N, 1.41. Found: C, 60.19; H, 4.33; N, 1.68.

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