

**Novel Structural Rearrangements Induced by
Metal–Metal Interactions in Ruthenium(II)
Ruthenocenyl- and (Pentamethylruthenocenyl)acetylide
Complexes, $\text{RcC}\equiv\text{CRuL}_2(\eta^5\text{-C}_5\text{R}_5)$ and
 $\text{Rc}'\text{C}\equiv\text{CRuL}_2(\eta^5\text{-C}_5\text{R}_5)$ [Rc = Ruthenocenyl, Rc' =
Pentamethylruthenocenyl, L_2 = 2PPh_3 or
 $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dppe), R = H or Me]**

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The reaction of $\text{RcC}\equiv\text{CH}$ [$\text{Rc} = (\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\eta^5\text{-C}_5\text{H}_4)$] with $\text{RuClL}_2(\eta^5\text{-C}_5\text{R}_5)$ [$\text{R} = \text{H}$ or Me; $\text{L}_2 = 2\text{PPh}_3$ or $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dppe)] in the presence of NH_4PF_6 and subsequent treatment with base gave Ru(II) ruthenocenylacetylide complexes $\text{RcC}\equiv\text{CRuL}_2(\eta^5\text{-C}_5\text{R}_5)$ in good yields. In a similar manner, the pentamethylruthenocene analogues, $\text{Rc}'\text{C}\equiv\text{CRuL}_2(\eta^5\text{-C}_5\text{R}_5)$ [$\text{Rc}' = (\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\eta^5\text{-C}_5\text{H}_4)$], were also prepared. Cyclic voltammograms of the complexes showed two reversible one-electron-oxidation processes, consisting of the processes $[\text{Ru}(\text{II})\text{Ru}'(\text{II})]$ to $[\text{Ru}(\text{III})\text{Ru}'(\text{II})]$ and then to $[\text{Ru}(\text{III})\text{Ru}'(\text{III})]$. Chemical oxidation of the complexes induced novel structural rearrangement. The two-electron oxidation of complex $\text{RcC}\equiv\text{CRu}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)$ afforded a kind of allenylidene complex, a cyclopentadienylidenethylydene complex, $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}\{\mu\text{-}\eta^6\text{-}\eta^1\text{-C}_5\text{H}_4\text{C}=\text{C}\}\text{Ru}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]^{2+}$, in 90% yield. The one-electron oxidation of $\text{Rc}'\text{C}\equiv\text{CRu}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)$ gave the vinylidene complex $(\text{Rc}'\text{CH}=\text{C})\text{Ru}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)$ in 62% yield, while the two-electron oxidation led to the fulvene–vinylidene complex $[(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)\text{Ru}\{\mu\text{-}\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{CH}=\text{C}\}\text{Ru}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{R}_5)]^{2+}$ by an intramolecular hydrogen transfer in 59% yield.

Introduction

Both fundamental and applied attention has been attracted to binuclear complexes containing different redox sites in close proximity.¹ These have the potential of possessing unique physical properties which are characteristic of one particular compound, rather than a sum of the properties of the individual redox sites, and of contributing to the understanding of biologically relevant mixed-valence compounds.² Because of the well-defined and stable one-electron redox system, ferrocene has been recognized as a good trigger and terminus for electronically switched phenomena.³ Thus, oxidized species of binuclear ferrocene derivatives have been extensively investigated in relation to the mixed-valence state.^{4–8} However, there have been relatively few reports about the oxidized species of ruthenocene derivatives,^{9–14} because ruthenocene exhibits an ir-

reversible two-electron-oxidation process, and there is difficulty in understanding the process.

We have been intensively attracted to heterobinuclear mixed-valence compounds containing ferrocene as a part of redox centers and have demonstrated new electron delocalization systems and novel reactions of ferrocenylacetylide complexes of various transition metals.¹⁵ In

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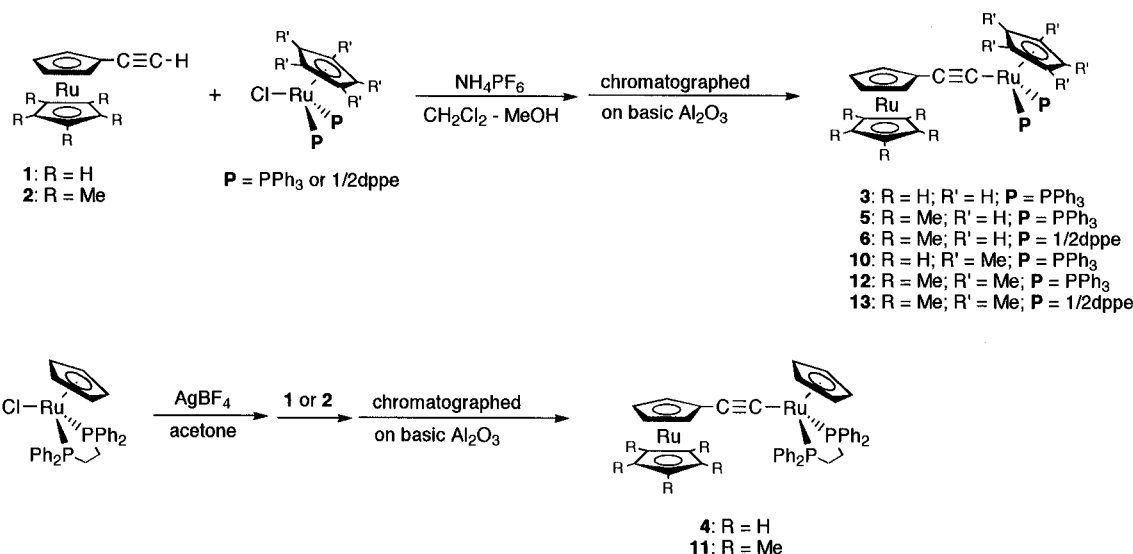
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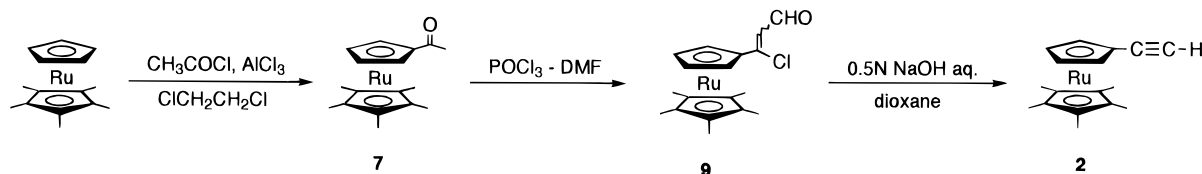
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Scheme 1



Scheme 2



order to extend our previous results concerning ferrocenylacetylide complexes to ruthenocenyl derivatives, we report here syntheses, electrochemistry, and oxidation of ruthenium(II) ruthenocenylacetylides and (pentamethylruthenocenyl)acetylides.

Results and Discussion

Synthesis. Ruthenocenylacetylene, $\text{RcC}\equiv\text{CH}$ (**1**) [$\text{Rc} = (\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\eta^5\text{-C}_5\text{H}_4)$], reacted with $\text{RuCl}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)$ in the presence of NH_4PF_6 in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ at room temperature, and the reaction mixture, after evaporation, was directly chromatographed on basic alumina to give $\text{RcC}\equiv\text{CRu}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)$ (**3**) as yellow crystals in 94% yield. In a similar manner, $\text{RcC}\equiv\text{CRu}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{Me}_5)$ (**5**) and $\text{RcC}\equiv\text{CRu}(\text{dppe})(\eta^5\text{-C}_5\text{Me}_5)$ (**6**) [dppe = 1,2-bis(diphenylphosphino)ethane] were prepared in 40 and 78% yields, respectively. $\text{RcC}\equiv\text{CRu}$ -

(dppe)($\eta^5\text{-C}_5\text{H}_5$) (**4**) could not be obtained under similar conditions, because $\text{RuCl}(\text{dppe})(\eta^5\text{-C}_5\text{H}_5)$ was inert to metathesis with NH_4PF_6 . Therefore, complex **1** was allowed to react with the solution prepared from $\text{RuCl}(\text{dppe})(\eta^5\text{-C}_5\text{H}_5)$ and AgBF_4 in acetone and then the reaction mixture was treated as described above to give **4** in 68% yield (Scheme 1).

Pentamethylruthenocene ($\text{Rc}'\text{H}$) [$\text{Rc}' = (\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\eta^5\text{-C}_5\text{H}_4)$] was reacted with $\text{CH}_3\text{COCl}-\text{AlCl}_3$ in refluxed 1,2-dichloroethane for 3 h to give 1-acetyl-1',2',3',4',5'-pentamethylruthenocene (**7**) and 1,2-diacyl-1',2',3',4',5'-pentamethylruthenocene (**8**) in 68 and 4% yields, respectively, along with the recovery of the starting material (28%). The reaction of **7** with DMF/POCl_3 gave 1-(α -chloro- β -formylvinyl)-1',2',3',4',5'-pentamethylruthenocene (**9**) in 92% yield as orange-red crystals. Complex **9** was refluxed with a mixture of 0.5 N NaOH aqueous solution and dioxane for 1.5 h to give (pentamethylruthenocenyl)acetylene (1-ethynyl-1',2',3',4',5'-pentamethylruthenocene), $\text{Rc}'\text{C}\equiv\text{CH}$ (**2**), in 91% yield as pale yellow crystals (Scheme 2). $\text{Rc}'\text{C}\equiv\text{CRu}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)$ (**10**), $\text{Rc}'\text{C}\equiv\text{CRu}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{Me}_5)$ (**12**), and $\text{Rc}'\text{C}\equiv\text{CRu}(\text{dppe})(\eta^5\text{-C}_5\text{Me}_5)$ (**13**) were prepared from **2** and the corresponding chlororuthenium complexes in 78, 49, and 82% yields, respectively, by following a procedure similar to that for **3**. $\text{Rc}'\text{C}\equiv\text{CRu}(\text{dppe})(\eta^5\text{-C}_5\text{H}_5)$ (**11**) was obtained in 77% yield by the method used in the synthesis of **4** (Scheme 1). For complex **4**, the $\text{C}\equiv\text{C}$ stretching vibration was observed at 2080 cm^{-1} in the IR spectrum, and the ring protons of the ruthenocenyl group were observed at δ 4.02 (2H), 4.11 (5H), and 4.14 (2H), the methylene protons of dppe at δ 2.31 (2H) and 2.67 (2H), the protons of the cyclopentadienyl (Cp) ring of the $\text{Ru}(\text{dppe})(\eta^5\text{-C}_5\text{H}_5)$ part at δ 4.71 (5H), and the phenyl protons of dppe at δ 7.22–7.92 (20H) in the ^1H NMR spectrum. The ^{13}C NMR spectrum of **5**

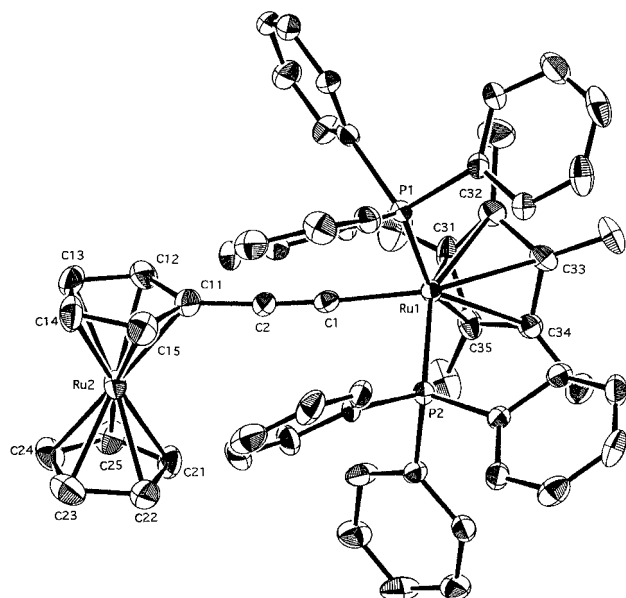
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**Figure 1.** Molecular structure of **5**.**Table 1.** Crystal and Intensity Collection Data for **5**

mol formula	C ₅₈ H ₅₄ P ₂ Ru ₂
mol wt	1015.15
cryst syst	monoclinic
space group	<i>P</i> ₂ / <i>1</i> / <i>n</i> (No. 14)
<i>a</i> , Å	12.872(2)
<i>b</i> , Å	17.614(2)
<i>c</i> , Å	20.590(4)
β , deg	90.23(1)
<i>V</i> , Å ³	4668(1)
<i>Z</i>	4
<i>D</i> _{calc} , g cm ⁻³	1.444
cryst dimens, mm	0.400 × 0.200 × 0.200
linear abs coeff, cm ⁻¹	3.7
radiation (λ , Å)	Mo K α (0.710 73)
2θ range, deg	28.83–29.47
scan type	ω -2 θ
total no. of rflns measd	8926
no. of unique rflns	8521 (<i>R</i> _{int} = 0.061)
no. of rflns used in least squares	3740 [<i>I</i> > 3.00 σ (<i>I</i>)]
no. of variables	613
<i>R</i>	0.046
<i>R</i> _w	0.037
max peak in final Fourier map, e Å ⁻³	0.51
min pea, in final Fourier map, e Å ⁻³	-0.44

exhibited the acetylenic carbons at δ 104.30 and 107.58, the latter signal being assigned to the carbon atom connected directly to the Ru atom of the Ru(dppe)(η^5 -C₅H₅) moiety because it was accompanied by coupling with the phosphorus atoms (²*J*_{PC} = 25.4 Hz).

X-ray Structure of Complex 5. A single-crystal X-ray analysis confirmed the structure of complex **5**. The crystallographic data are listed in Table 1. The ORTEP view of **5** is shown in Figure 1, along with selected numbering of the atoms. Selected bond distances and angles are summarized in Table 2. The geometry around the Ru atom is a typical three-leg piano-stool configuration although with somewhat of a strain. The angle P(1)–Ru(1)–P(2) [99.15(9)°] is larger than P(1)–Ru(1)–C(1) [85.6(2)°] and P(2)–Ru(1)–C(1) [86.2(2)°], probably because of the steric repulsion between the triphenylphosphine ligands. The acetylide ligand is nearly linear [Ru(1)–C(1)–C(2), 176.3(8)°, and C(1)–C(2)–C(11), 170(1)°]. The C–C distances (average 1.40 Å) and the Ru–C distances (average 2.16 Å) of the ruthenocenyl moiety are normal (the C–C distances are

Table 2. Selected Bond Distances and Angles for **5**

Bond Distances (Å)			
Ru(1)–P(1)	2.319(3)	Ru(1)–P(2)	2.309(2)
Ru(1)–C(1)	2.019(9)	C(1)–C(2)	1.21(1)
C(2)–C(11)	1.45(1)	Ru(1)–Cp* (av) ^a	2.27
Ru(2)–Cp (av)	2.16	Cp ring (av)	1.40
Cp* ring (av)	1.42		
Bond Angles (deg)			
P(1)–Ru(1)–P(2)	99.15(9)	P(1)–Ru(1)–C(1)	85.6(2)
P(2)–Ru(1)–C(1)	86.2(2)	Ru(1)–C(1)–C(2)	176.3(8)
C(1)–C(2)–C(11)	170(1)		

^a Cp* = ring carbon.

Table 3. Oxidation Potentials^a of Ru(II) Acetylide Complexes and Related Compounds

complex	<i>E</i> ₁ ^{o'} (<i>E</i> _{1pa} – <i>E</i> _{1pc})	<i>E</i> ₂ ^{o'} (<i>E</i> _{2pa} – <i>E</i> _{2pc})	<i>i</i> _{1pc} / <i>i</i> _{1pa}	<i>i</i> _{2pc} / <i>i</i> _{2pa}
1	+0.58 ^{b,c}			
2	+0.38 ^{b,c}			
3	–0.22 (120 mV)	+0.10 (130 mV)	<i>e</i>	<i>e</i>
4	–0.23 (100)	+0.05 (110)	<i>e</i>	<i>e</i>
5	–0.20 (100)	+0.48 ^b	0.98	
6	–0.39 (110)	–0.01 (120)	1.0	1.0
10	–0.30 (110)	–0.02 (110)	<i>e</i>	<i>e</i>
11	–0.31 (110)	–0.10 (115)	<i>e</i>	<i>e</i>
12	–0.40 (100)	+0.13 ^b	0.72	
13	–0.42 (110)	+0.02 ^b	0.45	
14	+0.05 ^b			
15	–0.26 (110)			
17	+0.26 ^{b,c}			
RC≡C[Ru] ^d				
R = <i>n</i> -Bu	–0.03 ^b			
R = <i>n</i> -Hex	–0.03 ^b			
R = CO ₂ Me	+0.32 ^b			

^a *V* vs FcH^{0/+} and *E*_{pa} – *E*_{pc} = 90 mV. ^b *E*_{pa} due to irreversible oxidation. ^c Two-electron process. ^d [Ru] = Ru(PPh₃)₂(η^5 -C₅H₅). ^e It could not be calculated because *E*₁ and *E*₂ were too close to each other to obtain an accurate base line.

1.43 ± 0.02 Å and the Ru–C distances average 2.21 ± 0.03 Å in ruthenocene).¹⁶ The Ru–C(1) distance [2.019(9) Å] and the C(1)–C(2) distance [1.21(1) Å] are similar to those [2.02(1) and 1.20(1) Å] in (η^5 -C₅H₅)(PPh₃)₂Ru{C≡CC(OCOCF₃)=CMe₂}¹⁷ and those [2.009(3) and 1.204(5) Å] in (η^5 -C₅H₅)(dppe)Ru(C≡CPh),¹⁸ respectively.

Cyclic Voltammetry. The cyclic voltammograms of complexes **3**–**6**, **10**–**13**, and related complexes were measured in a solution of 0.1 M *n*-Bu₄NClO₄ in CH₂Cl₂ at a glassy carbon electrode and a sweep rate of 0.1 V s⁻¹. The redox potentials are summarized in Table 3. The cyclic voltammogram of **10** is shown in Figure 2 as a typical example. In comparison with the reference complexes RcC≡CH or Rc'C≡CH and Ru(C≡CPh)-(PPh₃)₂(η^5 -C₅H₅) (**14**) or Ru(C≡CPh)(PPh₃)₂(η^5 -C₅Me₅) (**15**), the first oxidation wave was assigned to the Ru-(PPh₃)₂(η^5 -C₅H₅) or Ru(PPh₃)₂(η^5 -C₅Me₅) part and the second oxidation wave to the Rc or Rc' part. It was confirmed by thin-layer coulometry that the first and second oxidation waves in **3** consist of one-electron-transfer processes, respectively. That is, the first wave was observed by thin-layer coulometry to be *n* = 0.80 ± 0.03 and the first and second waves amounted to *n* = 1.82 ± 0.08. One of the most characteristic points is

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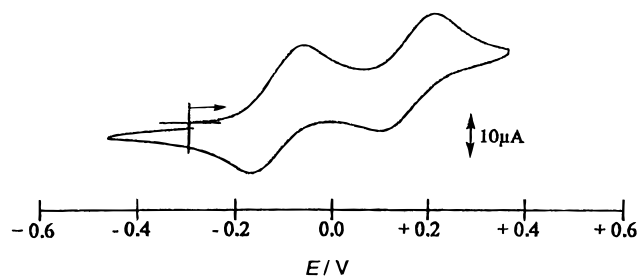


Figure 2. Cyclic voltammogram of **10**.

that the Rc or Rc' moiety in complexes **3–6** and **10–13** displayed a reversible one-electron-oxidation process under conditions using Bu_4NClO_4 as the supporting electrolyte. Generally, ruthenocene derivatives have been known to undergo an irreversible two-electron process when conventional supporting electrolytes such as PF_6^- or ClO_4^- salts have been used^{19–21} and a reversible one-electron-oxidation process only in the case of the particular electrolyte $[\text{Bu}_4\text{N}][\text{B}\{2,5\text{-C}_6\text{H}_3(\text{C-F}_3)_2\}]$.^{22,23} However, decamethylruthenocene²⁴ and octamethyl[3]ruthenocenophane¹⁴ show a reversible one-electron-oxidation wave under usual conditions. The unusual electrochemical properties observed in complexes **3–6** and **10–13** are probably caused by electronically coupled fragments in the molecule.

The oxidation potentials of the first waves in complexes **3–6** and **10–13** decrease in comparison to those of reference complexes **14** and **15**, respectively (e.g., $\Delta E = 0.23$ V in **3**). The second oxidation wave also shifts to a potential lower than that of the reference complex ($\text{RcC}\equiv\text{CH}$ or $\text{Rc}'\text{C}\equiv\text{CH}$) (e.g., $\Delta E = 0.35$ V in **3**). The shift of the first oxidation wave to a lower potential may be explained by the electron-donating effect of ruthenocene. The low-potential shift of the second oxidation wave is very large and is not readily explained by the electrostatic influence of the substituents, because if the electron-attracting effect of the oxidized $\text{Ru}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)$ part is transmitted to the Rc or Rc' part through the $\text{C}\equiv\text{C}$ bond, the second wave should shift to a higher potential. The shift to a lower potential region of the oxidation potential and the one-electron-oxidation process in the Rc part have been similarly observed in [1,1]ruthenocenophane, which is oxidized to the complex containing the Ru–Ru bond,^{12c} and in 1,2-bis(pentamethylruthenoceny)ethylene, which gives a pentafulvalene diruthenium complex on the oxidation.¹³ The observation of these characteristic behaviors suggests that there is a certain strong interaction between the two Ru atoms in complexes **3–6** and **10–13**. That is, the two Ru atoms are oxidized stepwise from Ru(II) to Ru(III), and the unpaired electrons on the two Ru(III) atoms form a pair with spins coupled via the conjugated system connecting the two Ru atoms. Such an interaction may contribute to the lower potential shift of the

oxidation waves and the stabilization of the two-electron-oxidized species of complexes **3–6** and **10–13**. This effect also seems to be responsible for the one-electron oxidation observed in the cyclic voltammogram of the Rc or Rc' part in complexes **3–6** and **10–13**, because the stabilization of two-electron-oxidized species (one-electron oxidation per one Ru atom) makes their further oxidation difficult.

Chemical Oxidation. Complex **3** was oxidized with 1 equiv of AgBF_4 in CH_2Cl_2 at -78°C to give complex **16** as a yellow-brown powder in ca. 50% yield. Complex **16** is considered to be a diamagnetic two-electron-oxidized species, because **16** showed sharp signals in the ^1H NMR spectrum. Actually, **3** was oxidized with 2 equiv of AgBF_4 under similar conditions to give **16** in 90% yield (Scheme 3). The IR spectrum of **16** showed the allenylidene-like stretching absorption at 1980 cm^{-1} . In the ^1H NMR spectrum of **16**, the protons of the two unsubstituted Cp rings resonated at δ 5.47 (5H) and 5.48 (5H) and the substituted Cp ring protons appeared at δ 5.64 (2H) and 6.56 (2H). These signals shift to lower field by more than about 1.0 ppm compared with those of the starting neutral complex, indicating that the positive charge is located on both Ru atoms in **16**. The observation of remarkable splitting between the α - and β -ring protons suggests that a η^6 -fulvene structural description contributes to the bonding in **16**, because such a large splitting is observed in $\text{Cr}(\text{CO})_3(\eta^6\text{-C}_5\text{H}_4\text{-CH}_2)$ (δ 4.52 and 5.32).²⁵ In the ^{31}P NMR spectrum of complex **16**, the signal of the phosphorus nuclei appears at δ 40.57 ppm (cf. δ 50.36 ppm in the neutral complex **3**). The chemical shift observed here is similar to that of the related cationic vinylidene complex $[(\text{PhHC}=\text{C})\text{-Ru}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]\text{BF}_4$ (δ 42.75 ppm) and the neutral acetylide complex $\text{PhC}\equiv\text{CRu}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)$ (δ 50.29 ppm), suggesting that **16** contains a cationic vinylidene structure. Such IR and ^1H NMR spectral data indicate that **16** is a unique complex having an unprecedented cyclopentadienylidenethylydene ligand, although the full characterization of **16** could not be completed because of its extreme instability in solution.

Complex **10**, the pentamethyl analogue of **3**, was oxidized with 1 equiv of ferrocenium tetrafluoroborate ($\text{FcH}^+\text{PF}_6^-$) in CH_2Cl_2 at -78°C to give complex **17** as a brown powder in 62% yield (Scheme 3). The IR spectrum of **17** gave the $\text{C}=\text{C}$ stretching vibration at 1632 cm^{-1} . The ^1H NMR spectrum of **17** showed the olefinic proton accompanied by coupling with the P atoms at δ 4.62 (t, $^4J_{\text{PH}} = 2.3$ Hz). Such long-range coupling is characteristic of vinylidene complexes.²⁶ In coincidence with this suggestion, the ^{13}C NMR spectrum of **17** gave a low-field resonance at δ 355.79 as a triplet ($^2J_{\text{CP}} = 16.6$ Hz), which can be assigned to the α -vinylidene carbon.²⁶ These spectral data indicate that **17** is assigned to a vinylidene complex, $[(\text{Rc}'\text{CH}=\text{C})\text{Ru}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]\text{BF}_4$. The structure was confirmed by regeneration of the starting acetylide complex **10** on treatment of **17** with base. There has so far been no example in which a Ru(II) vinylidene complex is obtained from oxidation of a Ru(II) acetylide complex, to the best of our knowledge. Thus, the one-electron oxidation of the Ru(II) acetylide complexes $\text{Ru}(\text{C}\equiv\text{CR})\text{-}$

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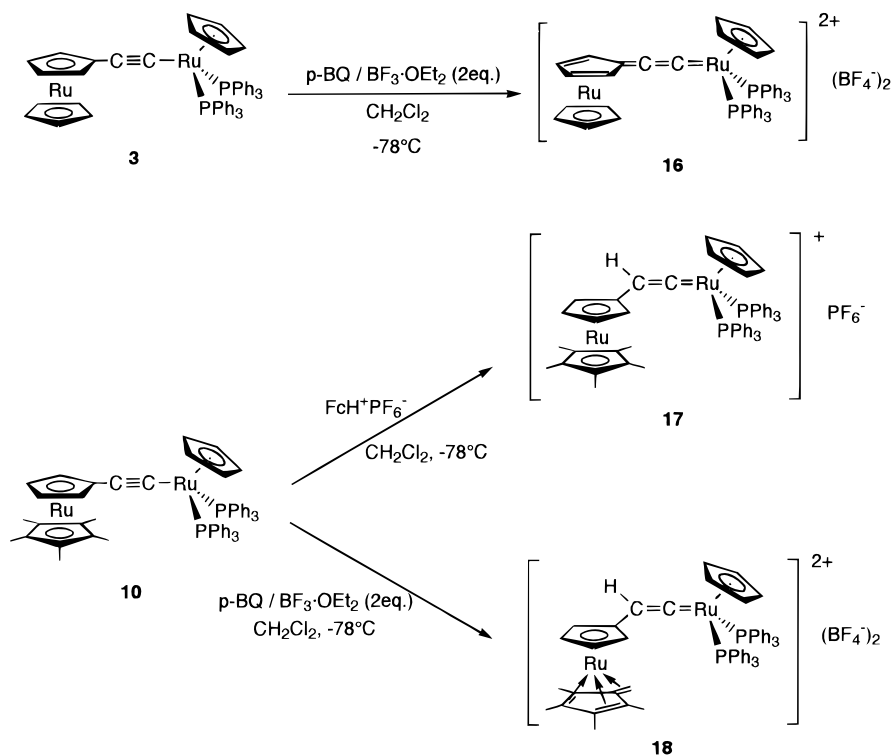
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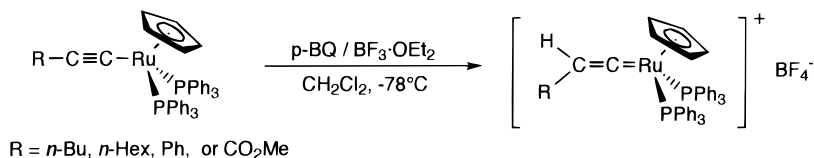
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Scheme 3



Scheme 4



$(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)$ ($\text{R} = n\text{-Bu}, n\text{-Hex}, \text{Ph}, \text{ and } \text{CO}_2\text{Me}$), was examined using *p*-benzoquinone (*p*-BQ)/ $\text{BF}_3 \cdot \text{OEt}_2$ in CH_2Cl_2 at -78°C . The expected vinylidene complexes, $[\text{Ru}(\text{C}=\text{CHR})(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]\text{BF}_4$, were obtained in good yield (Scheme 4). Contrary to our results, the one-electron oxidation of Fe(II) acetylides, which have substituents similar to that in the Ru(II) acetylide complexes described above, gave stable paramagnetic Fe(III) species with no structural change.²⁷ Recently, Lapinte reported that the terminal acetylide complex $\text{Fe}(\text{C}\equiv\text{CH})(\text{dppe})(\eta^5\text{-C}_5\text{Me}_5)$ gave a vinylidene complex, $[\text{Fe}(\text{C}=\text{CH}_2)(\text{dppe})(\eta^5\text{-C}_5\text{Me}_5)]$, on one-electron oxidation.²⁸

Complex **10** was oxidized with 2 equiv of *p*-BQ/ $\text{BF}_3 \cdot \text{OEt}_2$ in CH_2Cl_2 at -78°C to give complex **18** in 84% yield (Scheme 3). Complex **18** was fully characterized by the spectral data and elemental analysis. The $\text{C}=\text{C}$ stretching vibration at 1632 cm^{-1} in the IR spectrum, the signal for the vinylidene proton at $\delta 5.19$ (t, $^4J_{\text{PH}} = 2.3\text{ Hz}$, 1H) accompanied by the long-range coupling with the P nuclei in the ^1H NMR spectrum, and the ^{13}C NMR signal for the vinylidene α -carbon at $\delta 346.75$ as a triplet ($^2J_{\text{CP}} = 15.0\text{ Hz}$) prove that complex **18** contains a vinylidene structure as part of the molecule. In the ^1H NMR spectrum of **18**, the signal

for the *exo*-methylene protons due to the fulvene-like ligand was observed at $\delta 5.24$ (2H) as a singlet, along with the two methyl signals ($2 \times 6\text{H}$) at $\delta 1.81$ and 2.23 , suggesting that the original C_5Me_5 ligand changed to the $\text{C}_5\text{Me}_4\text{CH}_2$ ligand. The ^{13}C NMR spectrum of **18** gave a resonance due to the *exo*-methylene carbon of the fulvene ligand at $\delta 71.69$ ($^1J_{\text{CH}} = 166.0\text{ Hz}$), which was comparable with that in $[\text{Ru}(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)(\eta^5\text{-C}_5\text{Me}_5)]\text{BF}_4$ ($\delta 74.7$, $^1J_{\text{CH}} = 166.0\text{ Hz}$).²⁹ Marks³⁰ and Suzuki³¹ point out that the bonding mode of $\eta^6\text{-C}_5\text{Me}_4\text{CH}_2$ ligands to metal atoms can be expressed as a η^6 -bonded fulvene or a η^5, η^1 -bonded description. According to the classification, η^6 -bonded fulvene complexes show small $^2J_{\text{HH}}$ (0–3 Hz) and large $^1J_{\text{CH}}$ (ca. 150 Hz) coupling constants in the *exo*-methylene group, while η^5, η^1 -bonded fulvene complexes have large geminal coupling ($^2J_{\text{HH}} = 12\text{--}15\text{ Hz}$) and small $^1J_{\text{CH}}$ coupling (ca. 120 Hz). The $^2J_{\text{HH}}$ and $^1J_{\text{CH}}$ values observed in complex **18** are 0 and 166.0 Hz, respectively, supporting the change of the original pentamethylruthenocenyl moiety in **10** to a η^6 -fulvene structure in **18**. The structure of **18** was confirmed by the fact that complex **18** allowed to react with NaOMe in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give the expected $(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{OMe})\text{Ru}\{\mu\text{-}\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{C}\equiv\text{C}\}\text{Ru}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)$ (**19**) in 57% yield (Scheme 5). The structure of **19**

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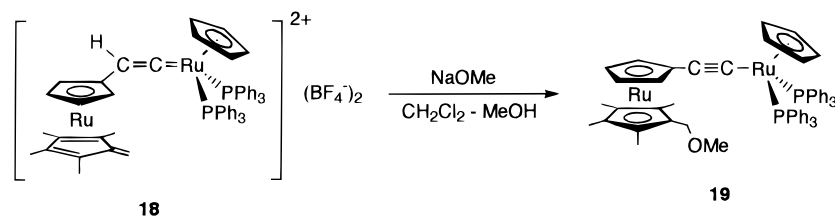
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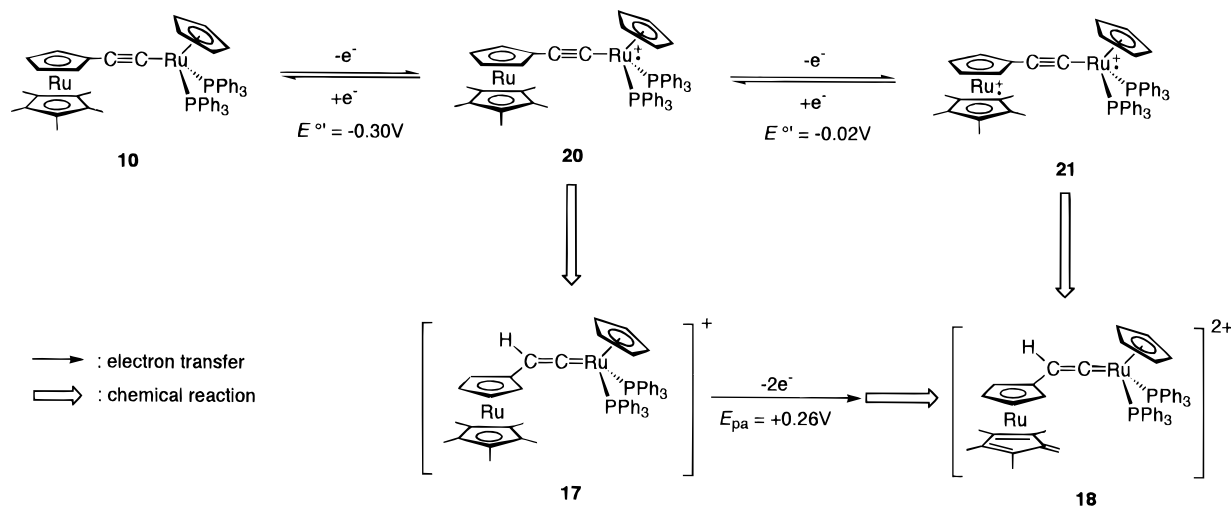
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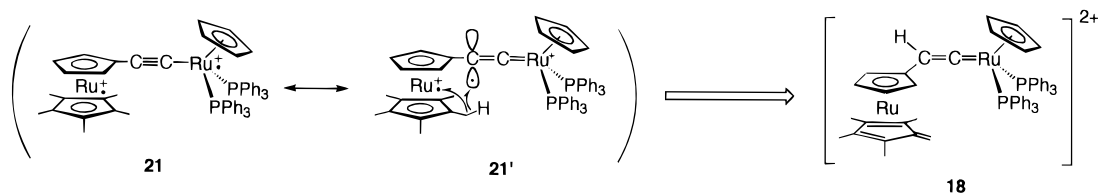
Scheme 5



Scheme 6



Scheme 7



was assigned by IR and ¹H and ¹³C NMR spectra (see Experimental Section).

Plausible Mechanism for the Formation of the Oxidation Products of Complex 10. Ru(II) (pentamethylruthenocenyl)acetylide complex **10** is stepwise oxidized electrochemically to give the one-electron-oxidized intermediate **20** and then the two-electron-oxidized intermediate **21** (Scheme 6). In the one-electron oxidation of complex **10**, the reactive intermediate **20** is converted to the vinylidene complex **17** by the abstraction of hydrogen from the solvent. The formation of **18** on two-electron oxidation of **10** may be explained by two possible mechanisms: In one possible route, complex **18** may be formed by further oxidation of vinylidene complex **17**, resulting from one-electron oxidation of **10**. However, the cyclic voltammogram of complex **17** showed an irreversible two-electron-oxidation process at +0.26 V. In fact, complex **17** could be oxidized with *p*-BQ/BF₃·OEt₂ in CH₂Cl₂ to give **18** in 84% yield, but the oxidation required 2 equiv of the oxidant in order to get a sufficient yield of **18**. In coincidence with this, the oxidation of pentamethylruthenocene [$E_{\text{pa}} = +0.33\text{ V}$ (2e)] with 2 equiv of *p*-BQ/BF₃·OEt₂ in CH₂Cl₂ gave the tetramethylfulvene complex [Ru(η^5 -C₅H₅)(η^6 -C₅Me₄CH₂)]BF₄ in 95% yield. Thus, the overall conversion of **10** into **18** by a stepwise process involving the vinylidene complex **17** requires consumption of 3 equiv of the oxidants. Therefore, the stepwise

route is negligible, because the direct formation of **18** from **10** was accomplished with 2 equiv of oxidant. In the other possible route, intramolecular hydrogen transfer from the methyl group of the η^5 -C₅Me₅ ligand to the β -carbon of the acetylide ligand in the intermediate **21** may yield fulvene-vinylidene complex **18** (Scheme 7). Complex **10** was oxidized with 2 equiv of AgBF₄ in CDCl₃ in which trace H₂O contamination was removed by displacement with D₂O followed by distillation from P₂O₅. Importantly, the product contained no deuterium on the vinylidene β -carbon. This rules out hydrogen abstraction from the solvent by intermediate **21** and seems to support the formation of **18** by intramolecular hydrogen transfer from the methyl group of the Cp* ligand. At the present stage, we have no evidence to decide if the Ru atom in the pentamethylruthenocenyl moiety intervenes in the rearrangement from **21** to **18** by the intramolecular hydrogen transfer.^{9,10} In the two-electron oxidation of complex **3**, an allenylidene type of complex **16** would be formed via structural rearrangement from the two-electron-oxidized species corresponding to the intermediate **21**, because of the absence of the proximate methyl hydrogen atom.

Experimental Section

All reactions were carried out under an atmosphere of N₂, and workups were performed with no precaution to exclude

air. NMR spectra were recorded on Bruker AC200, AM400, or ARX400 spectrometers. IR spectra were recorded on Hitachi 270-50 or Perkin-Elmer System 2000 spectrometers. Cyclic voltammograms were recorded on BAS CV27 in CH_2Cl_2 (freshly distilled from CaH_2 and N_2 purged) solutions of 10^{-1} M $n\text{-Bu}_4\text{NClO}_4$ (polarography grade, Nacalai Tesque, Inc.), and the scan rate was 0.1 V s^{-1} . CV cells were fitted with glassy carbon (GC) working electrodes, Pt wire counter electrodes, and Ag/Ag^+ pseudo reference electrodes. All potentials were represented vs $\text{FcH}^{0/+}$ ($+0.17 \text{ V}$ vs Ag/Ag^+), which were obtained by the subsequent measurement of ferrocene under the same conditions. Thin-layer coulometry was carried out on the apparatus described earlier.³²

Solvents were purified by distillation from a drying agent before use as follows: CH_2Cl_2 (CaCl_2); MeOH (magnesium methoxide); acetone (CaSO_4); CH_3CN (CaH_2); diethyl ether (LiAlH_4). Ruthenocenylacetylene,³³ pentamethylruthenocene [$(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}$],³⁴ $(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{RuCl}$,³⁵ $(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{RuCl}$,³⁶ $(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)_2\text{RuCl}$,³⁷ $(\eta^5\text{-C}_5\text{Me}_5)(\text{dppe})\text{RuCl}$,³⁸ and $(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Ru}(\text{C}\equiv\text{CPh})$ ³⁹ were prepared according to the literature, respectively. Other reagents were used as received from commercial suppliers.

($\text{RcC}\equiv\text{C}$)Ru(PPh_3)₂($\eta^5\text{-C}_5\text{H}_5$) (3). To a solution of $(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{RuCl}$ (72.7 mg, 0.10 mmol) and $\text{RcC}\equiv\text{CH}$ (1) (21.0 mg, 0.10 mmol) in CH_2Cl_2 (5 mL) and MeOH (3 mL) was added NH_4PF_6 (24.5 mg, 0.15 mmol) at room temperature. The solution was stirred for 1 h. After the solvent was removed from the resulting brown solution by rotary evaporator, the residue was chromatographed on basic alumina by elution with $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1:1, v/v). The fraction of a yellow band was collected, and the solvent was removed, giving the title Ru(II) ruthenocenylacetylide complex, $(\text{RcC}\equiv\text{C})\text{Ru}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)$ (3), as a yellow solid. An analytically pure sample was obtained by recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ as yellow needles. Yield: 89 mg (94%). Mp: 215°C . IR (KBr): 2072 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3 , 400 MHz): δ 4.15 (s, 5H, C_5H_5), 4.23 (s, 5H, C_5H_5), 4.38 (s, 2H, $\beta\text{-C}_5\text{H}_4$), 4.82 (s, 2H, $\alpha\text{-C}_5\text{H}_4$), 7.10–7.46 (m, 30H, Ph). ^{13}C NMR (CDCl_3 , 100 MHz): δ 68.00 ($\beta\text{-C}_5\text{H}_4$), 70.43 (C_5H_5), 72.45 ($\alpha\text{-C}_5\text{H}_4$), 85.00 (C_5H_5), 127.15 ($m\text{-Ph}$), 128.34 ($p\text{-Ph}$), 134.00 ($o\text{-Ph}$), 139.05 (t, $^1J_{\text{PC}} = 20.3 \text{ Hz}$, ipso-Ph). ^{31}P NMR (CDCl_3 , 162 MHz, referred to 85% H_3PO_4): 50.36 ppm. Anal. Calcd for $\text{C}_{55}\text{H}_{44}\text{P}_2\text{Ru}_2\cdot\text{CH}_3\text{OH}$: C, 66.38; H, 4.95. Found: C, 66.26; H, 4.65.

($\text{RcC}\equiv\text{C}$)Ru(dppe)($\eta^5\text{-C}_5\text{H}_5$) (4). To a suspension of AgBF_4 (19.5 mg, 0.10 mmol) in acetone (5 mL) was added $(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{RuCl}$ (60.0 mg, 0.10 mmol) in the dark at room temperature. After the mixture was stirred for 1 h, the precipitated AgCl was filtered off and washed with acetone (1 mL \times 2), giving a yellow solution. To the yellow solution was added $\text{RcC}\equiv\text{CH}$ (1) (21.0 mg, 0.10 mmol). The reaction mixture was stirred for 1 h. A brown solution was obtained. After the solvent was removed by rotary evaporator, the residue was chromatographed on basic alumina by eluting with $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1:1, v/v). The yellow fraction was collected, and the solvent was removed, yielding the Ru(II) ruthenocenylacetylide complex $(\text{RcC}\equiv\text{C})\text{Ru}(\text{dppe})(\eta^5\text{-C}_5\text{H}_5)$ (4) as a yellow polycrystalline solid. Yield: 56 mg (68%). Mp: $196\text{--}197^\circ\text{C}$. IR (KBr): 2080 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3 , 400 MHz): δ 2.31 (m, 2H, CH_2), 2.67 (m, 2H, CH_2), 4.02 (t, $J = 1.6 \text{ Hz}$, 2H, $\beta\text{-C}_5\text{H}_4$), 4.11 (s, 5H, C_5H_5), 4.14 (t, $J = 1.6 \text{ Hz}$, 2H, $\alpha\text{-C}_5\text{H}_4$), 4.71 (s, 5H, C_5H_5), 7.22–7.92 (m, 20H, Ph). ^{13}C NMR (CDCl_3 ,

400 MHz): δ 28.04 (t, $^1J_{\text{PC}} = 23.3 \text{ Hz}$, CH_2), 68.00 ($\beta\text{-C}_5\text{H}_4$), 69.95 (C_5H_5), 72.41 ($\alpha\text{-C}_5\text{H}_4$), 78.67 (ipso- C_5H_4), 82.20 (C_5H_5), 104.30 (RcC), 107.58 (t, $^2J_{\text{PC}} = 25.4 \text{ Hz}$, CRu), 127.48 (t, $^3J_{\text{PC}} = 4.6 \text{ Hz}$, $m\text{-Ph}$), 127.78 (t, $^3J_{\text{PC}} = 3.6 \text{ Hz}$, $m\text{-Ph}$), 128.69 ($p\text{-Ph}$), 129.20 ($p\text{-Ph}$), 131.47 (t, $^2J_{\text{PC}} = 5.0 \text{ Hz}$, $o\text{-Ph}$), 134.10 (t, $^2J_{\text{PC}} = 4.8 \text{ Hz}$, $o\text{-Ph}$), 137.03 (m, ipso-Ph), 142.43 (m, ipso-Ph). Anal. Calcd for $\text{C}_{43}\text{H}_{38}\text{P}_2\text{Ru}_2$: C, 63.07; H, 4.68. Found: C, 63.04; H, 4.81.

($\text{RcC}\equiv\text{C}$)Ru(PPh_3)₂($\eta^5\text{-C}_5\text{Me}_5$) (5). Complex 5 was prepared from $\text{RcC}\equiv\text{CH}$ (1) and $(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)_2\text{RuCl}$ by a procedure similar to that for 3 to yield yellow crystals. Yield: 41 mg (40%). Mp: 120°C dec. IR (KBr): 2060 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3 , 400 MHz): δ 1.37 (s, 15H, C_5Me_5), 4.31 (s, 5H, C_5H_5), 4.51 (s, 2H, $\beta\text{-C}_5\text{H}_4$), 4.58 (s, 2H, $\alpha\text{-C}_5\text{H}_4$), 7.06–7.51 (m, 30H, Ph). ^{13}C NMR (CDCl_3 , 100 MHz): δ 9.38 (C_5Me_5), 68.31 ($\beta\text{-C}_5\text{H}_4$), 70.41 (C_5H_5), 72.00 ($\alpha\text{-C}_5\text{H}_4$), 93.36 (C_5Me_5), 126.64 ($m\text{-Ph}$), 128.05 ($p\text{-Ph}$), 134.80 ($o\text{-Ph}$), 137.68 (ipso-Ph). Anal. Calcd for $\text{C}_{58}\text{H}_{54}\text{P}_2\text{Ru}_2$: C, 68.62; H, 5.36. Found: C, 68.20; H, 5.49.

($\text{RcC}\equiv\text{C}$)Ru(dppe)($\eta^5\text{-C}_5\text{Me}_5$) (6). Complex 6 was prepared from $\text{RcC}\equiv\text{CH}$ (1) and $(\eta^5\text{-C}_5\text{Me}_5)(\text{dppe})\text{RuCl}$ by a procedure similar to that for 3 to yield yellow crystals. Yield: 68 mg (77%). Mp: 180°C dec. IR (KBr): 2084 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3 , 400 MHz): δ 1.52 (s, 15H, C_5Me_5), 2.07 (m, 2H, CH_2), 2.15 (m, 2H, CH_2), 4.23 (s, 2H, $\beta\text{-C}_5\text{H}_4$), 4.29 (s, 2H, $\alpha\text{-C}_5\text{H}_4$), 4.30 (s, 5H, C_5H_5), 7.18–7.77 (m, 20H, Ph). ^{13}C NMR (CDCl_3 , 100 MHz): δ 9.99 (C_5Me_5), 29.40 (t, $^1J_{\text{PC}} = 23.0 \text{ Hz}$, CH_2), 67.95 ($\beta\text{-C}_5\text{H}_4$), 70.18 (C_5H_5), 72.11 ($\alpha\text{-C}_5\text{H}_4$), 80.43 (ipso- C_5H_4), 92.33 (C_5Me_5), 101.37 (RcC), 119.32 (t, $^2J_{\text{PC}} = 25.1 \text{ Hz}$, CRu), 127.03 (t, $^3J_{\text{PC}} = 4.4 \text{ Hz}$, $m\text{-Ph}$), 127.32 (t, $^3J_{\text{PC}} = 4.2 \text{ Hz}$, $m\text{-Ph}$), 128.74 ($p\text{-Ph}$), 133.19 (t, $^2J_{\text{PC}} = 5.3 \text{ Hz}$, $o\text{-Ph}$), 133.92 (t, $^2J_{\text{PC}} = 4.8 \text{ Hz}$, $o\text{-Ph}$), 137.03 (m, ipso-Ph), 142.43 (m, ipso-Ph). Anal. Calcd for $\text{C}_{48}\text{H}_{48}\text{P}_2\text{Ru}_2\cdot\text{CH}_2\text{Cl}_2$: C, 60.42; H, 5.17. Found: C, 60.17; H, 5.27.

Two-Electron Chemical Oxidation of 3. To a solution of 3 (9.4 mg, 0.01 mmol) and $p\text{-BQ}$ (2.2 mg, 0.02 mmol) in CH_2Cl_2 was added $\text{BF}_3\cdot\text{OEt}_2$ (0.03 mL, 1.0 mmol) at -78°C . The solution was stirred for 10 min. The initial yellow color of the solution turned rapidly to green, and then yellow-brown solution was obtained. Excess diethyl ether (15 mL) was added. The resulting yellow-brown powder was filtered and washed with ether (2 mL \times 3). Attempts at further purification by recrystallization from any solvent failed. The product was a yellow-brown powder. Yield: 10 mg (90%). Mp: 100°C dec. IR (KBr): 1980 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$), 1080 cm^{-1} (ν_{BF_4}). ^1H NMR (CDCl_3 , 400 MHz): δ 5.47 (s, 5H, C_5H_5), 4.48 (s, 5H, C_5H_5), 5.64 (s, 2H, $\beta\text{-C}_5\text{H}_4$), 6.56 (s, 2H, $\alpha\text{-C}_5\text{H}_4$), 6.99–7.48 (m, 30H, Ph). ^{31}P NMR [$\text{CDCl}_3/(\text{CD}_3)_2\text{CO}$ (1:1 v/v), 162 MHz, referred to 85% H_3PO_4]: 40.57 ppm. Anal. Calcd for $\text{C}_{53}\text{H}_{44}\text{B}_2\text{F}_8\text{P}_2\text{Ru}_2$: C, 56.91; H, 3.96. Found: C, 56.28; H, 3.98.

1-Acetyl-1',2',3',4',5'-pentamethylruthenocene (Acetyl-pentamethylruthenocene) (7). To a mixture of aluminum chloride (1.00 g, 7.5 mmol) and acetyl chloride (0.53 mL, 7.5 mmol) in 1,2-dichloroethane (75 mL) was added dropwise (over a period of 30 min) a solution of pentamethylruthenocene (1.51 g, 5.0 mmol) in 1,2-dichloroethane (75 mL) at room temperature. The resulting orange solution was refluxed for 3 h and poured into ice/water. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (50 mL \times 4). The organic layer and the extracts were collected, dried over MgSO_4 , concentrated by rotary evaporator, and chromatographed on alumina using CH_2Cl_2 as the eluent. The second yellow fraction was collected, and the solvent was removed, giving crude 7 as a yellow solid. An analytically pure sample was obtained by recrystallization from hexane. This sample (yellow crystals) was identical with the authentic sample. Yield: 1.17 g (68%). Mp: $121.5\text{--}122.0^\circ\text{C}$ (lit.³⁸ mp $116\text{--}117^\circ\text{C}$). IR (KBr): 1662 cm^{-1} ($\nu_{\text{C}=\text{O}}$). ^1H NMR (CDCl_3 , 400 MHz): δ 1.85 (s, 15H, C_5Me_5), 2.14 [s, 3H, $\text{C}(\text{O})\text{Me}$], 4.43 (t, $J = 1.8 \text{ Hz}$, 2H, $\beta\text{-C}_5\text{H}_4$), 4.67 (t, $J = 1.8 \text{ Hz}$, 2H, $\alpha\text{-C}_5\text{H}_4$). Anal. Calcd for $\text{C}_{17}\text{H}_{22}\text{ORu}$: C, 59.46; H, 6.46. Found: C, 59.61; H, 6.42.

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The starting material, $\text{Rc}'\text{H}$, was recovered in 28% yield (0.43 g) from the first colorless fraction.

The third fraction of a yellow band gave 1,2-diacetyl-1',2',3',4',5'-pentamethylruthenocene (**8**) in 4% yield (0.08 g) (yellow crystals). Mp: 117.0–117.5 °C. IR (KBr): 1668 ($\nu_{\text{C=O}}$), 1650 cm^{-1} ($\nu_{\text{C=O}}$). ^1H NMR (CDCl_3 , 400 MHz): δ 1.80 (s, 15H, C_5Me_5), 2.31 [s, 6H, $\text{C}(\text{O})\text{Me}$], 4.54 (t, $J = 2.6$ Hz, 1H, $\beta\text{-C}_5\text{H}_4$), 4.67 (d, $J = 2.6$ Hz, 2H, $\alpha\text{-C}_5\text{H}_4$). ^{13}C NMR (100 MHz, CDCl_3): δ 10.71 (C_5Me_5), 29.30 [$\text{C}(\text{O})\text{Me}$], 77.05 ($\beta\text{-C}_5\text{H}_4$), 79.46 ($\alpha\text{-C}_5\text{H}_4$), 85.36 (ipso- C_5H_4), 87.59 (C_5Me_5), 199.24 ($\text{C}(\text{O})\text{Me}$). Anal. Calcd for $\text{C}_{19}\text{H}_{24}\text{O}_2\text{Ru}$: C, 59.20; H, 6.28. Found: C, 59.22; H, 6.21.

1-(α -Chloro- β -formylvinyl)-1',2',3',4',5'-pentamethylruthenocene (9**).** To a solution of 1-acetyl-1',2',3',4',5'-pentamethylruthenocene (**7**) (1.08 g, 3.0 mmol) in DMF was added dropwise Vilsmeier's complex, which was prepared from POCl_3 (4.5 mL) and DMF (45 mL), at 0 °C. The resulting orange-red solution was stirred at 0 °C for 0.5 h and then at room temperature for 2 h. To the solution was slowly added a saturated sodium acetate solution at 0 °C. The solution was stirred at room temperature for 2 h and extracted with CH_2Cl_2 (50 mL \times 4). The extracts were collected, washed with water, dried over MgSO_4 , concentrated by rotary evaporator, and chromatographed on alumina using CH_2Cl_2 as the eluent. The first orange fraction was collected, and the solvent was removed, giving crude **9** as a yellow solid. An analytically pure sample was obtained by recrystallization from CH_2Cl_2 /hexane as Orange-red crystals. Yield: 1.07 g (92%). Mp: 110 °C dec. IR (KBr): 1660 ($\nu_{\text{C=O}}$), 1592 cm^{-1} ($\nu_{\text{C=C}}$). ^1H NMR (CDCl_3 , 400 MHz): δ 1.81 (s, 15H, C_5Me_5), 4.51 (t, $J = 1.7$ Hz, 2H, $\beta\text{-C}_5\text{H}_4$), 4.64 (t, $J = 1.7$ Hz, 2H, $\alpha\text{-C}_5\text{H}_4$), 6.16 (d, $J = 7.2$ Hz, 1H, $=\text{CH}$), 10.06 (d, $J = 7.2$ Hz, 1H, CHO). ^{13}C NMR (100 MHz, CDCl_3): δ 10.93 (C_5Me_5), 72.06 ($\beta\text{-C}_5\text{H}_4$), 76.84 ($\alpha\text{-C}_5\text{H}_4$), 83.73 (ipso- C_5H_4), 86.57 (C_5Me_5), 117.84 ($=\text{CH}$), 153.67 [$\text{C}(\text{Cl})=$], 191.03 (CHO). Anal. Calcd for $\text{C}_{18}\text{H}_{21}\text{OClRu}$: C, 55.45; H, 5.43. Found: C, 55.67; H, 5.45.

1-Ethynyl-1',2',3',4',5'-pentamethylruthenocene [(Pentamethylruthenocenyl)acetylene] (2**).** A mixture of complex **9** (641 mg, 1.64 mmol) in dioxane (100 mL) and 0.5 M NaOH aqueous solution (100 mL) was refluxed vigorously with stirring for 1.5 h. The orange-red color of the solution turned to orange. The solution was concentrated by rotary evaporator and extracted with CH_2Cl_2 (50 mL \times 4). The extracts were collected, dried over MgSO_4 , concentrated, and chromatographed on alumina using hexane as the eluent. The first colorless fraction gave a pale yellow solid of crude **2**. An analytically pure sample (pale yellow crystals) was obtained by recrystallization from CH_2Cl_2 /methanol. Yield: 487 mg (91%). Mp: 64–65 °C. IR (KBr): 2100 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3 , 400 MHz): δ 1.89 (s, 15H, C_5Me_5), 2.74 (s, 1H, CCH), 4.21 (t, $J = 2.0$ Hz, 2H, $\beta\text{-C}_5\text{H}_4$), 4.35 (t, $J = 2.0$ Hz, 2H, $\alpha\text{-C}_5\text{H}_4$). ^{13}C NMR (100 MHz, CDCl_3): δ 11.24 (C_5Me_5), 67.36 ($\text{C}\equiv\text{CH}$), 72.94 ($\text{C}\equiv\text{CH}$), 73.14 ($\beta\text{-C}_5\text{H}_4$), 75.98 ($\alpha\text{-C}_5\text{H}_4$), 81.50 (ipso- C_5H_4), 85.50 (C_5Me_5). Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{Ru}$: C, 62.74; H, 6.19. Found: C, 62.56; H, 6.17.

($\text{Rc}'\text{C}\equiv\text{C}$) $\text{Ru}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)$ (10**).** Complex **10** was prepared from $\text{Rc}'\text{C}\equiv\text{CH}$ and ($\eta^5\text{-C}_5\text{H}_5$)(PPh_3) $_2\text{RuCl}$ by a procedure similar to that for **2**. Yield: 74 mg (78%). Mp: 110 °C dec. IR (KBr): 2074 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3 , 400 MHz): δ 2.05 (s, 15H, C_5Me_5), 4.04 (s, 2H, $\beta\text{-C}_5\text{H}_4$), 4.05 (s, 2H, $\alpha\text{-C}_5\text{H}_4$), 4.25 (s, 5H, C_5H_5), 7.05–7.48 (m, 30H, Ph). ^{13}C NMR (CDCl_3 , 100 MHz): δ 11.76 (C_5Me_5), 70.40 ($\beta\text{-C}_5\text{H}_4$), 74.47 ($\alpha\text{-C}_5\text{H}_4$), 79.47 (ipso- C_5H_4), 84.16 (C_5Me_5), 84.87 (C_5H_5), 103.63 (t, $^2J_{\text{PC}} = 25.5$ Hz, CRu), 106.25 ($\text{Rc}'\text{C}$), 127.02 (t, $^2J_{\text{PC}} = 3.8$ Hz, o-Ph), 128.20 (p-Ph), 133.92 (m-Ph), 139.08 (t, $^1J_{\text{PC}} = 20.6$ Hz, ipso-Ph). Anal. Calcd for $\text{C}_{58}\text{H}_{54}\text{P}_2\text{Ru}_2$: C, 68.42; H, 5.36. Found: C, 66.44; H, 5.39.

($\text{Rc}'\text{C}\equiv\text{C}$) $\text{Ru}(\text{dppe})(\eta^5\text{-C}_5\text{H}_5)$ (11**).** Complex **11** was prepared as yellow crystals from $\text{Rc}'\text{C}\equiv\text{CH}$ and ($\eta^5\text{-C}_5\text{H}_5$)(dppe)- RuCl by a procedure similar to that for **4**. Yield: 63 mg (77%). Mp: 184.0–184.5 °C. IR (KBr): 2084 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3 , 400 MHz): δ 1.78 (s, 15H, C_5Me_5), 2.28 (m, 2H, CH_2),

2.68 (m, 2H, CH_2), 3.50 (s, 2H, $\beta\text{-C}_5\text{H}_4$), 3.81 (s, 2H, $\alpha\text{-C}_5\text{H}_4$), 4.71 (s, 5H, C_5H_5), 7.24–7.89 (m, 20H, Ph). ^{13}C NMR (CDCl_3 , 50 MHz): δ 11.46 (C_5Me_5), 28.27 (t, $^1J_{\text{PC}} = 23.3$ Hz, CH_2), 70.25 ($\beta\text{-C}_5\text{H}_4$), 74.59 ($\alpha\text{-C}_5\text{H}_4$), 79.21 (ipso- C_5H_4), 82.31 (C_5H_5), 83.99 (C_5Me_5), 103.48 (t, $^2J_{\text{PC}} = 26.2$ Hz, CRu), 127.30 (t, $^3J_{\text{PC}} = 5.1$ Hz, m-Ph), 127.73 (t, $^3J_{\text{PC}} = 4.5$ Hz, m-Ph), 128.57 (p-Ph), 129.02 (p-Ph), 131.53 (t, $^2J_{\text{PC}} = 5.3$ Hz, o-Ph), 134.19 (t, $^2J_{\text{PC}} = 5.2$ Hz, o-Ph), 137.43 (t, $^1J_{\text{PC}} = 25.1$ Hz, ipso-Ph), 142.91 (t, $^2J_{\text{PC}} = 18.5$ Hz, ipso-Ph). Anal. Calcd for $\text{C}_{48}\text{H}_{48}\text{P}_2\text{Ru}_2\cdot\text{C}_6\text{H}_6$: C, 67.07; H, 5.63. Found: C, 66.86; H, 5.59.

($\text{Rc}'\text{C}\equiv\text{C}$) $\text{Ru}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{Me}_5)$ (12**).** Complex **12** was prepared as a yellow powder from $\text{Rc}'\text{C}\equiv\text{CH}$ and ($\eta^5\text{-C}_5\text{Me}_5$)(PPh_3) $_2\text{RuCl}$ by a procedure similar to that for **2**. Yield: 50 mg (49%). Mp: 133 °C dec. IR (KBr): 2060 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3 , 400 MHz): δ 1.22 [s, 15H, ($\eta^5\text{-C}_5\text{Me}_5$)Ru], 2.10 [s, 15H, C_5Me_5 (Rc')], 4.05 (s, 2H, $\beta\text{-C}_5\text{H}_4$), 4.15 (s, 2H, $\alpha\text{-C}_5\text{H}_4$), 7.02–7.53 (m, 30H, Ph). ^{13}C NMR (CDCl_3 , 100 MHz): δ 9.53 (C_5Me_5), 12.20 (C_5Me_5), 70.51 ($\beta\text{-C}_5\text{H}_4$), 73.66 ($\alpha\text{-C}_5\text{H}_4$), 81.28 (ipso- C_5H_4), 84.53 (C_5Me_5), 93.14 (C_5Me_5), 126.63 (m-Ph), 127.92 (p-Ph), 134.76 (o-Ph), 137.69 (ipso-Ph). Anal. Calcd for $\text{C}_{63}\text{H}_{64}\text{P}_2\text{Ru}_2\cdot\text{CH}_2\text{Cl}_2$: C, 65.68; H, 5.68. Found: C, 65.96; H, 5.68.

($\text{Rc}'\text{C}\equiv\text{C}$) $\text{Ru}(\text{dppe})(\eta^5\text{-C}_5\text{Me}_5)$ (13**).** Complex **13** was prepared as yellow crystals from $\text{Rc}'\text{C}\equiv\text{CH}$ and ($\eta^5\text{-C}_5\text{Me}_5$)(dppe)- RuCl by a procedure similar to that for **2**. Yield: 79 mg (82%). Mp: >230 °C dec. IR (KBr): 2068 cm^{-1} ($\nu_{\text{C}\equiv\text{C}}$). ^1H NMR (CDCl_3 , 400 MHz): δ 1.52 (s, 15H, C_5Me_5), 1.76 (s, 15H, C_5Me_5), 2.10 (m, 2H, CH_2), 2.70 (m, 2H, CH_2), 3.85 (s, 2H, $\beta\text{-C}_5\text{H}_4$), 3.87 (s, 2H, $\alpha\text{-C}_5\text{H}_4$), 7.17–7.78 (m, 20H, Ph). ^{13}C NMR (CDCl_3 , 100 MHz): δ 10.04 (C_5Me_5), 11.79 (C_5Me_5), 29.69 (t, $^1J_{\text{PC}} = 23.3$ Hz, CH_2), 70.14 ($\beta\text{-C}_5\text{H}_4$), 74.12 ($\alpha\text{-C}_5\text{H}_4$), 81.03 (ipso- C_5H_4), 84.29 (C_5Me_5), 92.33 (C_5Me_5), 100.91 ($\text{Rc}'\text{C}$), 118.19 (t, $^2J_{\text{PC}} = 25.1$ Hz, CRu), 127.02 (t, $^3J_{\text{PC}} = 9.3$ Hz, m-Ph), 127.27 (t, $^3J_{\text{PC}} = 8.5$ Hz, m-Ph), 128.64 (p-Ph), 128.70 (p-Ph) 133.21 (t, $^2J_{\text{PC}} = 10.3$ Hz, o-Ph), 134.13 (t, $^2J_{\text{PC}} = 9.0$ Hz, o-Ph), 137.32 (m, ipso-Ph), 149.49 (m, ipso-Ph). Anal. Calcd for $\text{C}_{53}\text{H}_{58}\text{P}_2\text{Ru}_2$: C, 66.37; H, 6.09. Found: C, 66.36; H, 6.07.

Formation of [$(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}\{\mu\text{-}\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{CH}=\text{C}\}\text{Ru}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)\text{PF}_6$ (17**) by One-Electron Oxidation of Complex **10**.** To a solution of complex **10** (10.2 mg, 0.01 mmol) in CH_2Cl_2 (2 mL) was added FCHPF_6 (3.3 mg, 0.01 mmol) at -78 °C. The solution was stirred for 15 min. The yellow color of the solution turned yellow-brown *via* green. An excess amount of diethyl ether (*ca.* 15 mL) was added. The resulting yellow-brown powder was filtered and washed with diethyl ether (2 mL \times 3). An analytically pure sample was obtained by recrystallization from CH_3CN /ether as brown crystals. Yield: 7 mg (61%). Mp: 152 °C dec. IR (KBr): 1632 ($\nu_{\text{C=C}}$), 836 cm^{-1} (ν_{PF_6}). ^1H NMR (CDCl_3 , 200 MHz): δ 2.00 (s, 15H, C_5Me_5), 4.05 (t, $J = 1.6$ Hz, 2H, $\beta\text{-C}_5\text{H}_4$), 4.26 (t, $J = 1.6$ Hz, 2H, $\alpha\text{-C}_5\text{H}_4$), 4.62 (t, $^4J_{\text{PH}} = 2.3$ Hz, 1H, $\text{Rc}'\text{CH}=\text{C}$), 5.16 (s, 5H, C_5H_5), 7.01–7.39 (m, 30H, Ph). ^{13}C NMR (CDCl_3 , 100 MHz): δ 12.08 (C_5Me_5), 72.21 ($\beta\text{-C}_5\text{H}_4$), 74.14 ($\alpha\text{-C}_5\text{H}_4$), 75.66 (ipso- C_5H_4), 86.12 (C_5Me_5), 95.79 (C_5H_5), 114.74 ($\text{Rc}'\text{CH}=\text{C}$), 129.48 (t, $^2J_{\text{PC}} = 5.1$ Hz, o-Ph), 131.72 (p-Ph), 134.05 (t, $^3J_{\text{PC}} = 5.1$ Hz, m-Ph), 139.08 (m, ipso-Ph), 355.79 (t, $^2J_{\text{PC}} = 16.6$ Hz, CRu). Anal. Calcd for $\text{C}_{58}\text{H}_{55}\text{F}_6\text{P}_3\text{Ru}_2$: C, 60.00; H, 4.77. Found: C, 59.87; H, 4.74.

Formation of [$(\eta^6\text{-C}_5\text{Me}_4\text{CH}_2)\text{Ru}\{\mu\text{-}\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{CH}=\text{C}\}\text{Ru}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)\text{BF}_4$ (18**).** **Path A: By Two-Electron Oxidation of Complex **10**.** To a solution of complex **10** (10.2 mg, 0.01 mmol) and *p*-BQ (2.2 mg, 0.02 mmol) in CH_2Cl_2 was added $\text{BF}_3\cdot\text{OEt}_2$ (0.03 mL, 0.1 mmol) at -78 °C. The solution was stirred for 10 min. The initial yellow color of the solution turned rapidly to green, and then a pale red solution was obtained. Excess diethyl ether (15 mL) was added. The resulting red powder was filtered and washed with ether (2 mL \times 3). Yield: 7 mg (59%).

Path B: By Two-Electron Oxidation of Complex **17.** In a procedure similar to that for path A, complex **17** (11.0 mg, 0.01 mmol) was adopted as the starting material instead of complex **10**. Yield: 10 mg (84%).

An analytically pure sample of **18** was obtained by recrystallization from CH₃CN/diethyl ether as red crystals. Mp: 180 °C dec. IR (KBr): 1616 ($\nu_{C=C}$), 1038 cm⁻¹ (ν_{BF_4}). ¹H NMR (CDCl₃, 200 MHz): δ 1.81 (s, 6H, β -C₅Me₄CH₂), 2.23 (s, 6H, α -C₅Me₄CH₂), 4.98 (t, J = 1.9 Hz, 2H, β -C₅H₄), 5.19 (t, $^4J_{PH}$ = 2.3 Hz, 1H, R_C'CH=), 5.24 (s, 2H, C₅Me₄CH₂), 5.29 (s, 5H, C₅H₅), 5.46 (t, J = 1.9 Hz, 2H, α -C₅H₄), 6.95–7.45 (m, 30H, Ph). ¹³C NMR (CD₃CN, 100 MHz): δ 9.37 (β -C₅Me₄CH₂), 10.74 (α -C₅Me₄CH₂), 71.69 (C₅Me₄CH₂), 82.46 (β -C₅H₄), 85.17 (α -C₅H₄), 93.53 (ipso-C₅H₄), 92.14 (C₅H₅), 101.03 (β -C₅Me₄CH₂), 106.32 (α -C₅Me₄CH₂), 108.22 (ipso-C₅Me₄CH₂), 108.88 (R_C'CH=), 129.31 (t, $^2J_{PC}$ = 5.3 Hz, *o*-Ph), 131.73 (*p*-Ph), 133.72 (t, $^3J_{PC}$ = 5.0 Hz, *m*-Ph), 133.94 (m, ipso-Ph), 346.75 (t, $^2J_{PC}$ = 15.0 Hz, CRu). Anal. Calcd for C₅₈H₅₄B₂F₈P₂Ru₂: C, 58.60; H, 4.58. Found: C, 58.35; H, 4.76.

(η^5 -C₅Me₄CH₂OMe)Ru{ μ - η^5 - η^1 -C₅H₄C \equiv C}Ru(PPh₃)₂(η^5 -C₅H₅) (19**).** To a solution of complex **18** (11.9 mg, 0.01 mmol) in CH₂Cl₂ (2 mL) was added a 10⁻¹ M NaOMe MeOH/diethyl ether solution, prepared from Na and a mixture of MeOH/diethyl ether, at room temperature. The solution was stirred for 10 min. The color of the solution turned from pale red to yellow. After the solvent was removed, the residue was chromatographed on alumina using a mixture of hexane and CH₂Cl₂ as the eluent. The first fraction of yellow band was collected, and the solvent was removed, giving crude **19** as a yellow solid. An analytically pure sample was obtained as yellow crystals by recrystallization from CH₂Cl₂/MeOH. Yield: 6 mg (57%). Mp: 160 °C dec. IR (KBr): 2072 cm⁻¹ ($\nu_{C=C}$). ¹H NMR (CDCl₃, 200 MHz): δ 2.04 (s, 6H, C₅Me₄), 2.07 (s, 6H, C₅Me₄), 3.37 (s, 3H, CH₂OMe), 4.06 (t, J = 1.6 Hz, 2H, β -C₅H₄), 4.09 (t, J = 1.6 Hz, 2H, α -C₅H₄), 4.26 (s, 5H, C₅H₅), 4.29 (s, 2H, CH₂OMe), 7.05–7.52 (m, 30H, Ph). ¹³C NMR (C₆D₆, 100 MHz): δ 11.94 (β -C₅Me₄), 11.99 (α -C₅Me₄), 57.21 (CH₂OMe), 68.42 (CH₂), 71.09 (β -C₅H₄), 74.85 (α -C₅H₄), 80.15, 84.26, 85.39 (C₅H₅), 85.67, 85.81, 105.45 (t, $^2J_{PC}$ = 25.5 Hz, CRu), 106.32 (α -C₅Me₄), 127.42 (t, $^3J_{PC}$ = 4.5 Hz, *m*-Ph), 128.58 (*p*-Ph), 134.36 (t, $^2J_{PC}$ = 4.9 Hz, *o*-Ph), 139.62 (m, ipso-Ph). Anal. Calcd for C₅₉H₅₄OP₂Ru₂: C, 67.93; H, 5.22. Found: C, 67.97; H, 5.37.

[(η^6 -C₅Me₄CH₂)(η^5 -C₅H₅)Ru](BF₄)₂ from Two-Electron Oxidation of Pentamethylruthenocene, (η^5 -C₅Me₅)(η^5 -C₅H₅)Ru. To a solution of pentamethylruthenocene (60.2 mg, 0.2 mmol) and *p*-BQ (43.2 mg, 0.4 mmol) in CH₂Cl₂ was added BF₃·OEt₂ (0.13 mL, 1.0 mmol) at 0 °C. The solution was stirred for 10 min. The resulting pale yellow powder was filtered and washed with diethyl ether (2 mL \times 3). An analytically pure sample (pale yellow crystals) was obtained by recrystallization from CH₃CN/diethyl ether, CH₂Cl₂/diethyl ether, and then CH₃CN/diethyl ether. Yield: 74 mg (95%). Mp: 138 °C dec. IR (KBr): 1040 cm⁻¹ (ν_{BF_4}). ¹H NMR (CD₃CN, 200 MHz): δ 1.74 (s, 6H, β -C₅Me₄), 2.15 (s, 6H, α -C₅Me₄), 5.05 (s, 2H, C₅Me₄CH₂), 5.19 (s, 5H, C₅H₅). ¹³C NMR (CD₃CN, 50 MHz): δ 10.05 (β -C₅Me₄), 11.57 (α -C₅Me₄), 69.40 ($^1J_{CH}$ = 167 Hz, C₅Me₄CH₂), 85.91 (C₅H₅), 101.82 (β -C₅Me₄), 106.74 (α -C₅Me₄), 108.44 (ipso-C₅Me₄). Anal. Calcd for C₁₅H₁₉BF₄Ru: C, 46.53; H, 4.95. Found: C, 46.63; H, 4.94.

Formation of Ru(II) Vinylidene Complexes by One-Electron Oxidation of Ru(II) Acetylide Complexes. Standard Procedure. To a solution of Ru(II) acetylide complex (R_C≡C)Ru(PPh₃)₂(η^5 -C₅H₅) [R = Ph, *n*-Hex, *n*-Bu, or C(O)OMe] (0.02 mmol) and *p*-BQ (2.2 mg, 0.02 mmol) in CH₂Cl₂ was added BF₃·OEt₂ (0.03 mL, 0.1 mmol) at -78 °C. The solution

was stirred for 10 min. The color of the solution turned rapidly from yellow to green, and then to pale red. Excess diethyl ether (15 mL) was added. The resulting red powder was filtered and washed with diethyl ether (2 mL \times 3).

R = Ph. Yield: 13 mg (74%). IR (KBr): 1620 ($\nu_{C=C}$), 1060 cm⁻¹ (ν_{BF_4}). ¹H NMR (200 MHz, CDCl₃): δ 5.31 (s, 5H, C₅H₅), 5.39 (t, $^4J_{PH}$ = 2.4 Hz, 1H, CH=), 7.00–7.43 (m, 35H, Ph). ³¹P NMR [(CD₃)₂CO, 162 MHz, referred to 85% H₃PO₄]: 42.75 ppm.

R = *n*-Hex. Yield: 14 mg (92%). IR (KBr): 1660 ($\nu_{C=C}$), 1038 cm⁻¹ (ν_{BF_4}). ¹H NMR (200 MHz, CDCl₃): δ 0.90 (t, $^3J_{HH}$ = 6.5 Hz, 3H, Me), 1.27 [m, 8H, (CH₂)₄], 2.26 (m, 2H, =CHCH₂), 4.65 (tt, $^3J_{HH}$ = 8.1 Hz, $^4J_{PH}$ = 2.5 Hz, 1H, CH=), 5.11 (s, 5H, C₅H₅), 7.01–7.45 (m, 30H, Ph).

R = *n*-Bu. Yield: 11 mg (64%). IR (KBr): 1658 ($\nu_{C=C}$), 1050 cm⁻¹ (ν_{BF_4}). ¹H NMR (200 MHz, CDCl₃): δ 0.90 (m, 3H, Me), 1.32 [m, 4H, (CH₂)₂], 2.27 (m, 2H, =CHCH₂), 4.66 (tt, $^3J_{HH}$ = 8.2 Hz, $^4J_{PH}$ = 2.5 Hz, 1H, CH=), 5.13 (s, 5H, C₅H₅), 7.03–7.44 (m, 30H, Ph).

R = C(O)OMe. Yield: 12 mg (70%). IR (KBr): 1698 ($\nu_{C=C}$), 1602 ($\nu_{C=O}$), 1048 cm⁻¹ (ν_{BF_4}). ¹H NMR (200 MHz, CDCl₃): δ 3.47 (s, 3H, OMe), 5.03 (s, 1H, CH=), 5.33 (s, 5H, C₅H₅), 7.04–7.47 (m, 30H, Ph).

The spectral data for these samples were identical with those of an authentic sample.³⁷

Structure determination of 5. Crystal data of **5**: C₅₈H₅₄P₂Ru₂, FW = 1015.15, monoclinic, *P*2₁/*n*; *a* = 12.872(2) Å, *b* = 17.614(2) Å, *c* = 20.590(4) Å; β = 90.23(1)°; *V* = 4668(1) Å³; *Z* = 4; *D*_{calc} = 1.444 g cm⁻³; μ (Mo K α) = 7.39 cm⁻¹; *T* = 296 K; crystal size 0.40 \times 0.20 \times 0.20 mm.

Data collection was performed on a Rigaku AFC5R diffractometer with graphite-monochromated Mo K α radiation and a 12 kW rotating anode generator. The data was collected using the ω -2 θ scan technique to a maximum 2 θ value of 50°. Cell constants and the orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range 28.83° < 2 θ < 29.47°. Of the 8926 reflections which were collected, 8521 were unique (*R*_{int} = 0.061). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection, indicating crystal and electronic stability.

The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 3740 observed reflections [*I* > 3.00 σ (*I*)] and 613 variable parameters and converged with unweighted and weighted agreement factors of *R* = $\sum ||F_o| - |F_c|| / \sum |F_o|$ = 0.046 and *R*_w = [$\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2$]^{1/2} = 0.037. The standard deviation of an observation of unit weight was 1.26.

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Supporting Information Available: Single-crystal X-ray diffraction data for complex **5** (45 pages). Ordering information is given on any current masthead page.

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