Synthesis and Redox Behavior of Ruthenium(II) 2,3,4,5-Tetramethylruthenocenylacetylide and Related Complexes. Formation of μ-η^6:η^1-[(Cyclopentadienylidene)ethylidene]diruthenium Complexes Containing a Strong Metal−Metal Interaction

Masaru Sato,* Ayako Iwai, and Masanobu Watanabe

Chemical Analysis Center, Saitama University, Urawa, Saitama 338-8570, Japan

Received February 26, 1999

1-Ethynyl-2,3,4,5-tetramethylruthenocene was prepared by the reaction of 1-formyl-2,3,4,5-tetramethylruthenocene with trimethylsilyldiazomethyllithium and also by the reaction of 1-(2′,2′-dichlorovinyl)-2,3,4,5-tetramethylruthenocene, which was obtained from the reaction of 1-formyl-2,3,4,5-tetramethylruthenocene with lithium dichloromethyldiethylphosphonate and *tert*-butyllithium in good yield. 1-Ethynyl-2,3,4,5-tetramethylruthenocene reacted with $RuCl\mathbf{P}_2L$ ($\mathbf{P}_2$ = 2 PPh_3 or dppe; L = η-C_5H_5, η-C_5Me_5, or η^5-C_9H_7) in the presence of NH_4PF_6 or $AgBF_4$, followed by the column chromatography on deactivated Al_2O_3, to give Ru(C≡CRc′)$\mathbf{P}_2$L in moderate or good yield. Ru(C≡CRc)$\mathbf{P}_2$(η^5-C_9H_7) and Ru(C≡CRc*)$\mathbf{P}_2$(η^5-C_9H_7) were similarly prepared (Rc, Rc′, and Rc* are ruthenocenyl, 2,3,4,5-tetramethylruthenocenyl, and 1′,2′,3′,4′,5′-pentamethylruthenocenyl, respectively). The structures of Ru(C≡CRc′)(dppe)-(PPh_3)$_2$(η-C_5H_5), Ru(C≡CRc)(dppe)(η^5-C_9H_7), and Ru(C≡CRc′)(dppe)(η^5-C_9H_7) were determined by X-ray analysis. Cyclic voltammetry of the acetylide complexes showed two well-separated quasi-reversible waves. Chemical oxidation of ruthenium(II) 2,3,4,5-tetramethylruthenocenylacetylide complexes gave products whose stability was dependent on the ligand on the Ru(II) moiety. The ^{13}C NMR spectrum of the oxidized species isolated as stable crystals confirmed the structural rearrangement of the bridging acetylide ligand to a μ-η^6:η^1-[(cyclopentadienylidene)ethylidene] ligand. The structure of [(η-C_5H_5)Ru(μ-η^6:η^1-C_5Me_4═C═C)Ru-(dppe)(η^5-C_5Me_5)]$(BF_4)_2$ was determined by X-ray analysis.

Introduction

Investigation of binuclear complexes bridged by an unsaturated hydrocarbon is a burgeoning field of organometallic chemistry, and complexes with two different redox sites in close proximity or at a moderate distance are of current interest to basic and applied study.[1] These complexes potentially possess unique physical properties as one particular compound rather than as the sum of the properties of the individual redox sites. Binuclear complexes with metallocene termini have been extensively investigated because of their great stability. In particular, ferrocene derivatives[2−6] have been studied intensively as mixed-valence complexes,[7] since ferrocene is stable in both the neutral and oxidized forms.[8] However, there have been relatively few reports about the oxidation of ruthenocene derivatives,[9−14] because ruthenocene shows an irreversible two-electron oxidation process which hinders understanding.

(1) (a) Beck, W.; Niemer, B.; Wieser, M. *Angew. Chem., Int. Ed. Engl.* **1993**, 32. 923. (b) Ward, M. D. *Chem. Soc. Rev.* **1995**, 121. (c) Astruc, D. *Electron Transfer and Radical Processes in Transition-metal Chemistry*; VCH Publishers: New York, 1995.

(2) (a) Cowan, D. O.; Kaufman, F. *J. Am. Chem. Soc.* **1970**, *92*, 219. (b) Kaufman, F.; Cowan, D. O. *J. Am. Chem. Soc.* **1970**, *92*, 6198. (c) Cowan, D. O.; LeVanda, C.; Park, J.; Kaufman, F. *Acc. Chem. Res.* **1973**, *6*, 1.

(3) (a) Cowan, D. O.; LeVanda, C. *J. Am. Chem. Soc.* **1972**, *94*, 9271. (b) Mueller-Westerhoff, U. T.; Eilbracht, P. *J. Am. Chem. Soc.* **1972**, *94*, 9272. (c) LeVanda, C.; Bechgaard, K.; Cowan, D. O.; Mueller-Westerhoff, U. T.; Eilbracht, P.; Candela, G. A.; Collins, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 3181. (d) Morrison, W. H., Jr.; Krogsrud, S.; Hendrickson, D. N. *Inorg. Chem.* **1973**, *12*, 1998.

(4) (a) LeVanda, C.; Bechgaard, K.; Cowan, D. O. *J. Org. Chem.* **1976**, *41*, 2700. (b) Motoyama, I.; Watanabe, M.; Sano, H. *Chem. Lett.* **1978**, 513. (c) Kramer, J. A.; Hendrickson, D. N. *Inorg. Chem.* **1980**, *19*, 3330. (d) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 4393.

(5) Amer, S. I.; Sadler, G.; Henry, P. M.; Ferguson, G.; Ruhl, B. L. *Inorg. Chem.* **1985**, *24*, 1517.

(6) Lee, M.-T.; Foxman, B. M.; Rosenblum, M. *Organometallics* **1985**, *4*, 539.

(7) Brown, D. B., ed. *Mixed-Valence Compounds*; D. Reidel Publishing Company: Dordrecht, The Netherlands, 1980.

(8) Togni, A.; Hayashi, T. *Ferrocenes*; VCH Publishers: New York, 1995.

(9) Kölle, U.; Grub, J. *J. Organomet. Chem.* **1985**, *289*, 133.

(10) Rybinskaya, M. I.; Kreindlin, A. Z.; Fadeeva, S. S. *J. Organomet. Chem.* **1988**, *358*, 363.

(11) (a) Watanabe, M.; Sano, H. *Chem. Lett.* **1991**, 555. (b) Watanabe, M.; Iwamoto, T.; Kawata, S.; Kubo, A.; Sano, H.; Motoyama, I. *Inorg. Chem.* **1992**, *31*, 177. (c) Watanabe, M.; Iwamoto, T.; Sano, H.; Motoyama, I. *J. Coord. Chem.* **1992**, *26*, 223. (d) Watanabe, M.; Iwamoto, T.; Sano, H.; Motoyama, I. *Inorg. Chem.* **1993**, *32*, 5223. (e) Watanabe, M.; Motoyama, I.; Shimoi, M.; Iwamoto, T. *Inorg. Chem.* **1994**, *33*, 2518. (f) Watanabe, M.; Motoyama, I.; Sano, H. *Inorg. Chim. Acta* **1994**, 225, 103.

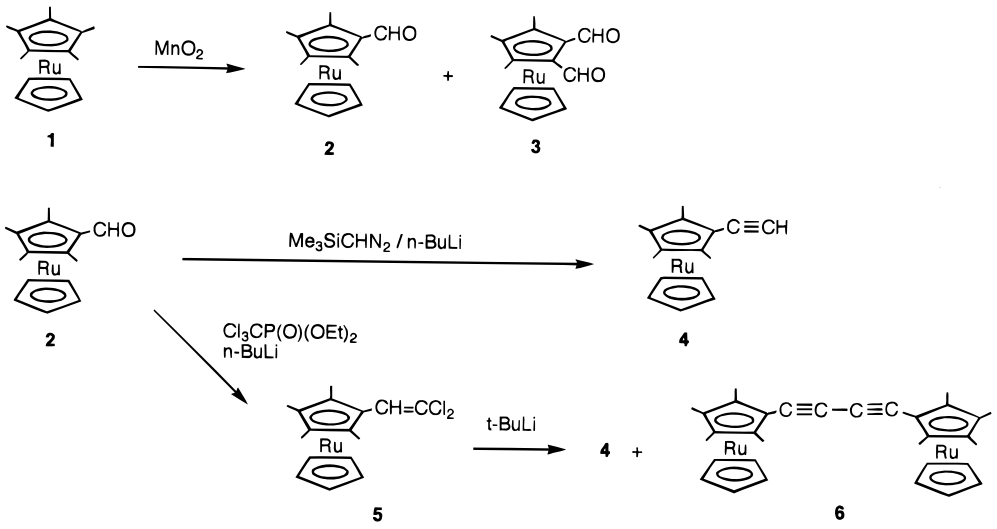
(12) (a) Mueller-Westerhoff, U. T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 711. (b) Diaz, A. F.; Mueller-Westerhoff, U. T.; Nazzal, A.; Tanner, M. *J. Organomet. Chem.* **1982**, *236*, C45. (c) Mueller-Westerhoff, U. T.; Rheingold, A. L.; Swiegers, G. F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1352.

(13) (a) Sato, M.; Kudo, A.; Kawata, Y.; Saitoh, H. *J. Chem. Soc., Chem. Commun.* **1996**, 25. (b) Sato, M.; Kawata, Y.; Kudo, A.; Iwai, A.; Saitoh, H.; Ochiai, S. *J. Chem. Soc., Dalton Trans.* **1998**, 2215.

(14) Hashidzume, K.; Tobita, H.; Ogino, H. *Organometallics* **1995**, *14*, 1187.

10.1021/om990138u CCC: $18.00
Publication on Web 07/17/1999

Scheme 1



We have been interested in heterobinuclear mixed-valence compounds containing ferrocene as part of a redox center and have demonstrated new electron delocalization systems[15] and novel reactions of ferrocenylacetylide complexes of various transition metals.[16] In these investigations, it was shown that the main product of one-electron oxidation of ruthenium(II) ruthenocenyl- and 1′,2′,3′,4′,5′-pentamethylruthenocenylacetylide complexes is the vinylidene analogues.[17] Two-electron (2 e) oxidation of ruthenium(II) 1′,2′,3′,4′,5′-pentamethylruthenocenylacetylide gave the fulvene−vinylidene complex, and that of ruthenium(II) ruthenocenylacetylide complex led to μ-η^6:η^1-[(cyclopentadienylidene)ethylidene]diruthenium, which is sufficiently interesting to warrant attempts at isolation. Stabilization by means of steric protection was considered, namely the introduction of methyl groups in the substituted cyclopentadienyl ring of ruthenocenylacetylene or the use of an indenyl ligand. It has been recently shown that the preferred conformation of the indenyl ligand in allenylidene complexes is such that the benzo ring is oriented cis to the allenylidene group,[18] while the preferred conformation is trans in acetylide complexes.[19] We now report the synthesis, redox behavior, and chemical oxidation of the acetylide complexes Ru(C≡CRc′)-$\mathbf{P}_2$L, Ru(C≡CRc)$\mathbf{P}_2$(η^5−C_9H_7), and Ru(C≡CRc*)$\mathbf{P}_2$(η^5−C_9H_7) (Rc, Rc′, and Rc* are the abbreviations for ruthenocenyl, 2,3,4,5-tetramethylruthenocenyl, and 1′,2′,3′,4′,5′-pentamethylruthenocenyl groups, respectively; $\mathbf{P}_2$ = 2 PPh_3 or dppe; L = η-C_5H_5, η-C_5Me_5, or η^5−C_9H_7).

Results and Discussion

Synthesis of 1-Ethynyl-2,3,4,5-tetramethylruthenocene. Pentamethylruthenocene (**1**) was oxidized with activated manganese oxide (available from Aldrich, Inc.) in refluxing 1,2-dichloroethane for 4 h to give 1-formyl-2,3,4,5-tetramethylruthenocene (**2**) and 1,2-diformyl-3,4,5-trimethylruthenocene (**3**) in 42% and 8% yields, respectively, with the recovery of the starting material (40%). The use of activated manganese oxide, which was prepared according to Attenburrow's procedure,[20] gave a rather low yield of the desired product. A similar oxidative approach was reported in the conversion of decamethylruthenocene to the corresponding mono- and diformyl derivatives.[21] The application of the modified procedure[22] of the Colvin rearrangement[23] to the aldehyde (**2**) afforded an excellent result. Thus, the addition of **2** to a solution prepared from trimethylsilyldiazomethane and LDA in THF at −78 °C, with subsequent heating under reflux for 3 h, gave 1-ethynyl-2,3,4,5-tetra-methylruthenocene (Rc′C≡CH, **4**) in 71% yield. 1-Ethynyl-1′,2′,3′,4′,5′-pentamethylruthenocene (Rc*C≡CH) was similarly obtained in moderate yield from 1-formyl-1′,2′,3′,4′,5′-pentamethylruthenocene. As another route to the acetylene **4**, the aldehyde **2** was allowed to react with the solution prepared from diethyl(trichloromethyl)phosphonate[24] and *n*-BuLi in THF at −90 °C to give 1-(2′,2′-dichlorovinyl)-2,3,4,5-tetramethylruthenocene (**5**) in 85% yield. The reaction of dichloro derivative **5** with *t*-BuLi in THF at −78 °C led to the mixture of acetylene **4** (70% yield) and 1,4-(2′,3′,4′,5′-tetramethylruthenocenyl)-1,3-butadiyne (**6**) (19% yield), which were separated by SiO_2 chromatography (Scheme 1).

Synthesis of Acetylide Complexes. Acetylene **4** reacted with $RuCl(PPh_3)_2(\eta$-$C_5H_5)$ in the presence of NH_4PF_6 in CH_2Cl_2/MeOH, with subsequent column

(15) (a) Sato, M.; Hayashi, Y.; Shintate, H.; Katada, M.; Kawata, S. *J. Organomet. Chem.* **1994**, *471*, 179. (b) Sato, M.; Shintate, H.; Kawata, Y.; Sekino, M.; Katada, M.; Kawata, S. *Organometallics* **1994**, *13*, 1956. (c) Sato, M.; Mogi, E. *Organometallics* **1995**, *14*, 4837. (d) Sato, M.; Hayashi, Y.; Kumakura, S.; Shimizu, N.; Katada, M.; Kawata, S. *Organometallics* **1996**, *15*, 721. (e) Sato, M.; Mogi, E. *J. Organomet. Chem.* **1996**, *517*, 1.

(16) Sato, M.; Mogi, E.; Kumakura, S. *Organometallics* **1995**, *14*, 3157.

(17) Sato, M.; Kawata, Y.; Shintate, H.; Habata, Y.; Akabori, S.; Unoura. K. *Organometallics* **1997**, *16*, 1693.

(18) (a) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; García-Granda, S.; Pérez-Carreñ, O, E. *Organometallics* **1996**, *15*, 2137. (b) Gamasa, M. P.; Gimeno, J.; Gonzalez-Bernardo, C.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 2483.

(19) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; López-González, M. C.; Borge, J.; García-Granda, S. *Organometallics* **1997**, *16*, 4453.

(20) Attenburrow, J.; Cameron, A. F. B.; Chapman, J. H.; Evans, R. M.; Hems, B. A.; Jansen, A. B. A.; Walker, T. *J. Chem. Soc.* **1952**, 1094.

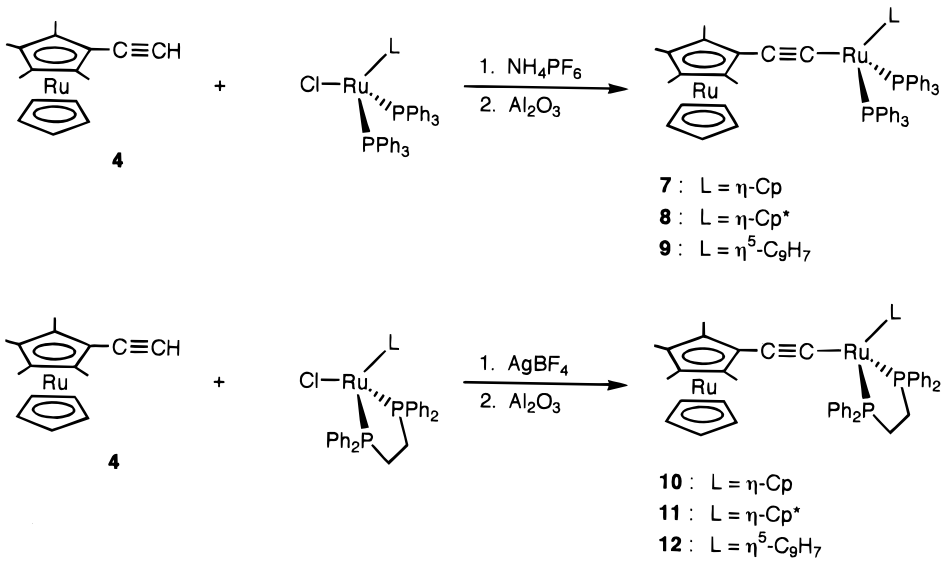
(21) Kreindlin, A. Z.; Petrovskii, P. V.; Rybinskaya, M. I. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1987**, 1620.

(22) Miwa, K.; Aoyama, T.; Shioiri, T. *Synlett* **1994**, 107.

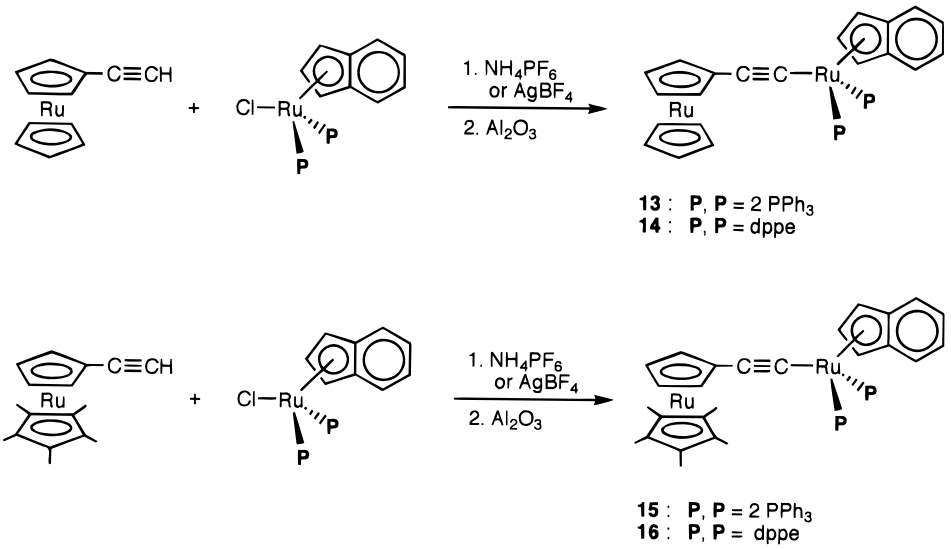
(23) Colvin, E. W.; Hamill, B. J. *J. Chem. Soc. Chem. Commun.* 1973, 151. Colvin, E. W.; Hamill, B. J. *J. Chem. Soc., Perkin Trans 1* **1977**, 869.

(24) Kosolapoff, G. M. *J. Am. Chem. Soc.* **1947**, *69*, 1002.

Scheme 2



Scheme 3



chromatography on deactivated alumina, to give the acetylide complex, Ru(C≡CRc′)(PPh_3)$_2$(η-C_5H_5) (**7**) in 97% yield (Scheme 2). In a similar manner, the acetylide complexes Ru(C≡CRc′)(PPh_3)$_2$(η-C_5Me_5) (**8**), Ru(C≡CRc′)(PPh_3)$_2$(η^5−C_9H_7) (**9**), and Ru(C≡CRc′)(dppe)(η-C_5Me_5) (**11**) were obtained in good yields. The acetylide complexes Ru(C≡CRc′)(dppe)(η-C_5H_5) (**10**) and Ru(C≡CRc′)(dppe)(η^5−C_9H_7) (**12**) were prepared by using $AgBF_4$ in acetone instead of NH_4PF_6. To examine the effect of an indenyl ligand, Ru(C≡CRc)(PPh_3)$_2$(η^5−C_9H_7) (**13**), Ru(C≡CRc*)(PPh_3)$_2$(η^5−C_9H_7) (**15**), Ru(C≡CRc)(dppe)(η^5−C_9H_7) (**14**), and Ru(C≡CRc*)(dppe)(η^5−C_9H_7) (**16**) were prepared (Scheme 3). The structure of these acetylide complexes was determined on the base of spectral data, some of which are summarized in Table 1. The formation of the acetylide chain is clearly confirmed by the IR C≡C stretching vibration in the range 2062−2089 cm^{-1}, which is somewhat lower in wavelength than that of Rc′C≡CH (2103 cm^{-1}). The ^{1}H NMR spectra exhibited signals in accordance with the proposed structures. In the ^{13}C NMR spectra, the signals of the acetylene carbons were observed in the range 100−120 ppm. The β-carbon signal of the acetylide bridge was observed in the narrow range (104−106 ppm), while the α-carbon signal attached directly to the Ru(II) atom is influenced by the ligands on the Ru(II) atom, especially the η-C_5Me_5 ligand, which caused a considerably large high-field shift.

X-ray Analysis of the Acetylide Complexes. The structure of complex **10** was determined by X-ray diffraction. The crystallographical data are collected in Table 2 , and the selected bond distances and angles are summarized in Table 3. The ORTEP view of **10** is shown in Figure 1. The Ru(II) center clearly adopts a pseudooctahedral geometry, as generally observed for the piano-stool complexes, with the η-C_5H_5 ring occupying three coordination sites and the carbon atom of the acetylide ligand and the two P atoms of triphenylphosphines occupying the other three sites. The Ru−C(1) distance is 2.018(4) Å, which is similar to those in Ru(C≡CPh){$Ph_2PCH(CH_3)CH(CH_3)PPh_2$}($\eta$-$C_5H_5$) (2.038(7) Å),[25] [Ru(C≡CPh)(NH_3)(dppe)$_2$]PF_6 (2.014(5) Å),[26]

(25) Consiglio, G.; Morandini, F.; Sironi, A. *J. Organomet. Chem.* **1986**, *306*, C45.
(26) Touchard, D.; Haquette, P.; Guesmi, S.; Pichon, L. L.; Daridor, A.; Toupet, L.; Dixnerf, P. H. *Organometallics* **1997**, *16*, 3640.

Table 1. IR and ^{13}C and ^{31}P NMR Data for the Acetylide Complexes 7−16[a]

complex			^{13}C NMR		
no.	formula	IR ν(C≡C)	Ru−*C*≡C	RuC≡*C*	^{31}P NMR
7	Rc′C≡CRu(PPh$_3$)$_2$(η-Cp)	2081	105.90 (25.1)	107.58	50.74
8	Rc′C≡CRu(PPh$_3$)$_2$(η-Cp*)	2062	117.81 (24.3)	106.26	52.72
9	Rc′C≡CRu(PPh$_3$)$_2$(η^5-Ind)	2075	104.01 (28.3)	107.22	53.36
10	Rc′C≡CRu(dppe)(η-Cp)	2088	106.45 (24.4)	105.48	87.35
11	Rc′C≡CRu(dppe)(η-Cp*)	2073	119.92 (25.9)	102.78	81.61
12	Rc′C≡CRu(dppe)(η^5-Ind)	2089	107.23 (25.0)	105.21	89.08
13	RcC≡CRu(PPh$_3$)$_2$(η^5-Ind)	2086	102.80 (25.6)	106.55	51.34
14	RcC≡CRu(dppe)(η^5-Ind)	2070	106.65 (26.0)	104.64	86.48
15	Rc*C≡CRu(PPh$_3$)$_2$(η^5-Ind)	2088	101.31 (25.7)	106.54	50.49
16	Rc*C≡CRu(dppe)(η^5-Ind)	2079	103.83 (25.5)	104.16	87.52

[a] η-Cp = η^5-cyclopentadienyl, η-Cp* = η^5-pentamethylcyclopentadienyl, and η^5-Ind = η^5-indenyl.

Table 2. Crystal and Intensity Collection Data for 9, 10, 14, and 19

compound	**9**	**10**	**14**	**19**
chem formula	$C_{70}H_{63}P_2Ru_2$	$C_{47}H_{46}P_2Ru_2$	$C_{48}H_{44}OP_2Ru_2$	$C_{52}H_{56}B_2F_8Ru_2$
fw	1168.37	874.97	900.97	1118.72
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/a$	$P2_1/n$	$P2_1/n$	$P1$
a, Å	24.489(6)	13.138(4)	10.5230(5)	12.556(2)
b, Å	23.689(5)	15.190(3)	25.456(1)	12.192(1)
c, Å	9.751(3)	20.45(1)	14.6560(8)	18.405(2)
α, deg				82.461(7)
β, deg	94.63(2)	104.99(2)	91.574(3)	93.184(3)
γ, deg				70.405(6)
V, Å^3	5638.2(3)	1073.7	3924.5(2)	2534.4(5)
Z	4	4	4	2
D_{calcd}, g cm^{-3}	1.376	1.47	1.525	1.466
cryst dimens, mm	0.35 × 0.3 × 0.2	0.26 × 0.16 × 0.15	0.25 × 0.10 × 0.10	0.24 × 0.06 × 0.04
linear abs coeff, cm^{-1}	6.141	8.624	8.622	7.082
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
rfln (hkl) limits	$-31 \le h \le 31$	$0 \le h \le 16$	$0 \le h \le 14$	$0 \le h \le 17$
	$-30 \le k \le 0$	$0 \le k \le 21$	$0 \le k \le 34$	$-15 \le k \le 17$
	$-1 \le l \le 12$	$-29 \le l \le 28$	$-20 \le l \le 20$	$-24 \le l \le 25$
total no. of rflns measd	15216	9937	10928	12326
no. of unique rflns	8471	9636	8415	10991
no. of rflns used in L.S.	7782	6870	8415	5840
L.S. params	766	640	626	604
R	0.073	0.034	0.048	0.078
R_w	0.082	0.036	0.050	0.098
max peak in final Fourier map, e Å^{-3}	0.96	0.55	1.86	1.41
min peak in final Fourier map, e Å^{-3}	−0.96	−1.05	−0.65	−1.51

Table 3. Selected Bond Distances and Angles for 10, 14, and 9

10		**14**		**9**	
		Bond Distances (Å)			
Ru(1)−C(1)	2.018(4)	Ru(1)−C(1)	2.022(5)	Ru(1)−C(1)	1.988(10)
Ru(1)−P(1)	2.247(2)	Ru(1)−P(1)	2.268(2)	Ru(1)−P(1)	2.314(3)
Ru(1)−P(2)	2.243(2)	Ru(1)−P(2)	2.230(2)	Ru(1)−P(2)	2.309(3)
				Ru(1)−C(17)	2.238(12)
				Ru(1)−C(18)	2.207(12)
				Ru(1)−C(19)	2.241(11)
				Ru(1)−C(20)	2.400(00)
				Ru(1)−C(21)	2.398(11)
C(1)−C(2)	1.208(6)	C(1)−C(2)	1.210(7)	C(1)−C(2)	1.216(14)
C(2)−C(3)	1.425(6)	C(2)−C(3)	1.432(7)	C(2)−C(3)	1.426(14)
Ru(2)−C(Cp-ring)	2.182(av)	Ru(2)−C(Cp ring)	2.170(av)	Ru(2)−C(Cp ring)	2.166(av)
C−C(Rc′ ring)	1.416(av)	C−C(Rc ring)	1.421(av)	C−C(Rc′ ring)	1.424(av)
		Bond Angles (deg)			
C(1)−C(2)−C(3)	175.1(4)	C(1)−C(2)−C(3)	174.2(5)	C(1)−C(2)−C(3)	176.7(11)
Ru(1)−C(1)−C(2)	179.2(4)	Ru(1)−C(1)−C(2)	174.0(4)	Ru(1)−C(1)−C(2)	172.9(9)
C(1)−Ru(1)−P(1)	86.7(2)	C(1)−Ru(1)−P(1)	80.1(2)	C(1)−Ru(1)−P(1)	89.3(3)
C(1)−Ru(1)−P(2)	82.7(2)	C(1)−Ru(1)−P(2)	87.8(2)	C(1)−Ru(1)−P(2)	90.2(3)
P(1)−Ru(1)−P(2)	84.6(1)	P(1)−Ru(1)−P(2)	84.9(1)	P(1)−Ru(1)−P(2)	101.4(1)

and Ru{C≡C(η^1-C$_7$H$_7$)}(PPh$_3$)$_2$(η-C$_5$H$_5$) (2.03(1) Å).[27] The structural features of the Rc′C≡C− part in complex **10** [C(1)−C(2) 1.208(6) Å, Ru(1)−C(1)−C(2) 179.2(4)°, C(1)−C(2)−C(3) 175.1(4)°] is very similar to those in Ru(C≡CRc)(PPh$_3$)$_2$(η-C$_5$Me$_5$), [C(1)−C(2) 1.21(1) Å, Ru(1)−C(1)−C(2) 176.3(8)°, C(1)−C(2)−C(11) 170(1)°].[17] The plane of the η-C$_5$Me$_4$ ring in the Rc′ group is inclined by 50.3(2)° from the plane consisting of the Ru(1) atom, the center of the η-C$_5$H$_5$ ring, and the C(1) atom. In

(27) Tamm, M.; Jentzsch, T.; Werncke, W. *Organometallics* **1997**, *16*, 1418.

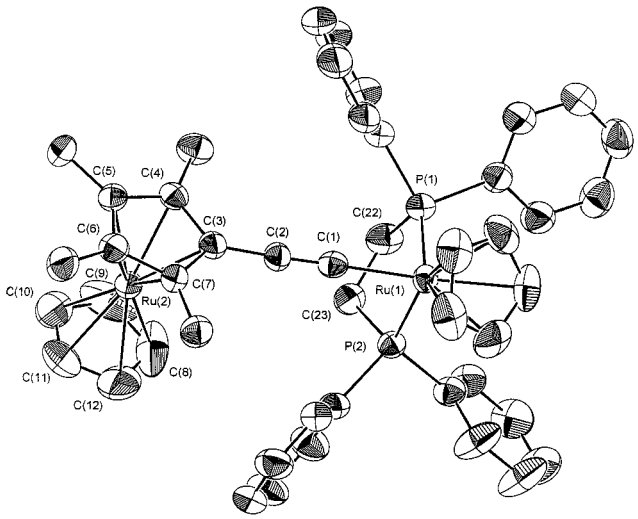


Figure 1. ORTEP view of complex **10**.

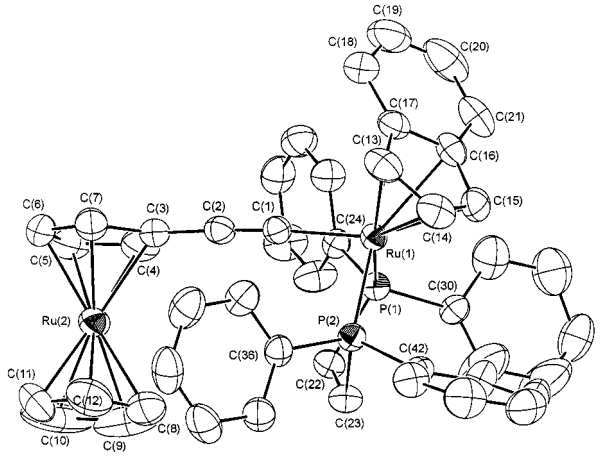


Figure 2. ORTEP view of complex **14**.

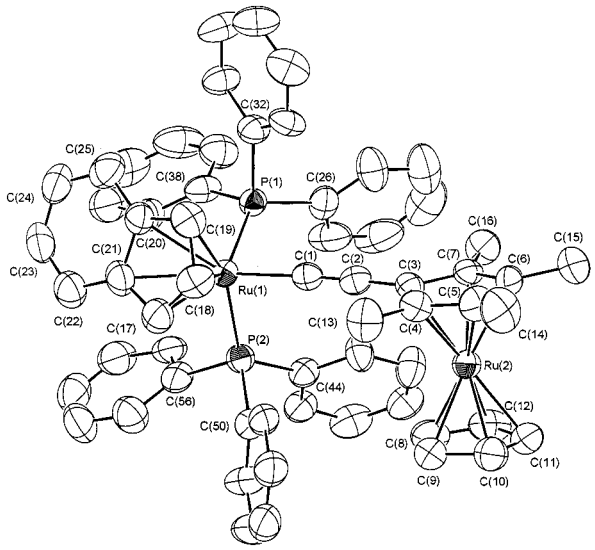


Figure 3. ORTEP view of complex **9**. (The solvent molecule is removed for clarity.)

contrast to this, the plane of η-C_5H_4 ring of the Rc group in $Ru(C{\equiv}CRc)(PPh_3)_2(\eta\text{-}C_5Me_5)$ is inclined to less extent (26.4°) from the plane described above. As the result, the bridging acetylide moiety in **10** is protected by the methyl substituents in 2,5-positions of the Rc′-group and each phenyl group on the P atoms of the dppe ligand. On the other hand, in the complex, $Ru(C{\equiv}CRc)(PPh_3)_2(\eta\text{-}C_5Me_5)$, only two phenyl groups of the triphenylphosphine ligands take part in the protection of the bridging acetylide moiety and therefore do not hinder attack of a reagent. This may account for the increased stability of the oxidized product of **10** (vide infra).

Crystallographic data for **14** are collected in Table 2, and selected bond distances and angles are summarized in Table 3. The ORTEP view of **14** is shown in Figure 2. The geometry around the Ru(II) atom in **14** is a typical three-legged piano-stool, as seen in **10**. The Ru−C(1) and the C(1)−C(2) distances are nearly the same with those in complex **10**. The plane of the η-C_5H_4 ring in the Rc group is inclined by 55.3(2)° from the plane consisting of the Ru(1) atom, the center of the five-membered ring of the indenyl ligand, and the C(1) atom. The angle is similar to that (50.3°) in complex **10**, rather than that of $Ru(C{\equiv}CRc)(PPh_3)_2(\eta\text{-}C_5Me_5)$, suggesting that the magnitude of the inclination may be due to the common dppe ligand. The plane consisting of the Ru(1) atom, the center of the 5-membered ring of the indenyl ligand, and the center of the six-membered ring of the indenyl ligand is inclined away from the Rc group by 61.6(11)° from the plane containing the Ru(1) atom, the center of the five-membered ring of the indenyl ligand, and the C(1) atom. That is, the benzo ring of the indenyl ligand takes an orientation cis to the Rc part, contrary to the trans orientation in $Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}C_9H_7)$ (161.9(1)°).[19] In the allenylidene complex, the benzo ring of the indenyl ligand was reported to have a cis orientation for the phenylacetylide part (9.6(3)°).[18] Such a change in the indenyl ligand may allow for an increased protecting effect around the ruthenocenylacetylide moiety in the oxidized complex of **14** and related complexes; a similar steric protection effect by the indenyl ligand is indicated in the nucleophilic attack to the allenylidene chain.[19,28]

The molecular geometry of **9**, which is the most congested ruthenium(II) ruthenocenylacetylide complexes reported herein, was determined by X-ray diffraction. The unit cell contains 3/2 benzene molecules with the center of one benzene molecule situated at a center of symmetry. The crystallographic data are collected in Table 2, and the selected bond distances and angles are summarized in Table 3. An ORTEP view of **9** is shown in Figure 3. The stereochemistry of the η-C_9H_7 and the acetylide ligands and two triphenylphosphines around the Ru(II) atom keeps a three-legged piano-stool configuration, similar to **10** and **14**. The plane of η-C_5H_4 ring in the Rc group is inclined by 26.2(1)° from the plane consisting of the Ru(1) atom, the center of the five-membered ring of the indenyl ligand, and the C(1) atom. The angle is similar to that (26.4°) of $Ru(C{\equiv}CRc)(PPh_3)_2(\eta\text{-}C_5Me_5)$[17] and is different from those of **10** and **14** and seems to support the suggestion that the magnitude of the inclination may be dependent on the kind of phosphine ligand coordinated to the Ru(II) atom. The orientation of the benzo ring of the indenyl ligand is nearly trans to the Rc′ group (161.2(5)°), which resembles with that observed in $Ru(C{\equiv}CCPh_2C{\equiv}CH)(PPh_3)_2(\eta^5\text{-}C_9H_7)$ (161.9(1)°).[19]

(28) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Lastra, E. *J. Organomet. Chem.* **1994**, *474*, C27.

Table 4. Redox Potentials of the Acetylide Complexes

complex	$E_{1/2}(1)$	$E_{1/2}(2)$	$\Delta E_{1/2}$
RcC≡CRu(PPh_3)$_2$(η-Cp)[a]	−0.22	+0.10	0.32
RcC≡CRu(PPh_3)$_2$(η-Cp*)[a]	−0.34	+0.16[b]	0.46[c]
RcC≡CRu(PPh_3)$_2$(η^5-C_9H_7) (**13**)	−0.24	+0.09	0.33
Rc′C≡CRu(PPh_3)$_2$(η-Cp) (**7**)	−0.32	−0.09	0.23
Rc′C≡CRu(PPh_3)$_2$(η-Cp*) (**8**)	−0.41	+0.06	0.47
Rc′C≡CRu(PPh_3)$_2$(η^5-C_9H_7) (**9**)	−0.32	−0.05	0.27
Rc*C≡CRu(PPh_3)$_2$(η-Cp)[a]	−0.30	−0.02	0.28
Rc*C≡CRu(PPh_3)$_2$(η-Cp*)[a]	−0.40	+0.13[b]	0.48[c]
Rc*C≡CRu(PPh_3)$_2$(η^5-C_9H_7) (**14**)	−0.31	−0.01	0.30
RcC≡CRu(dppe)(η-Cp)[a]	−0.23	+0.05	0.28
RcC≡CRu(dppe)(η-Cp*)[a]	−0.39	−0.01	0.38
RcC≡CRu(dppe)(η^5-C_9H_7) (**15**)	−0.11	+0.10	0.20
Rc′C≡CRu(dppe)(η-Cp*) (**11**)	−0.47	−0.11	0.36
Rc′C≡CRu(dppe)(η-Cp) (**10**)	−0.39	−0.18	0.21
Rc′C≡CRu(dppe)(η^5-C_9H_7) (**12**)	−0.24	−0.04	0.20
Rc*C≡CRu(dppe)(η-Cp)[a]	−0.31	−0.10	0.21
Rc*C≡CRu(dppe)(η-Cp*)[a]	−0.42	+0.02[b]	0.38[c]
Rc*C≡CRu(dppe)(η^5-C_9H_7) (**16**)	−0.33	−0.08	0.25

[a] Reference 17. [b] Irreversible, E_{pa} value. [c] $E_{pa}(2) - E_{pa}(1)$. Cf. PhC≡CRu(PPh_3)$_2$(η-Cp), $E_{1/2} = +0.05$ V; Rc′C≡CH, $E_{1/2} = 0.59$ V.

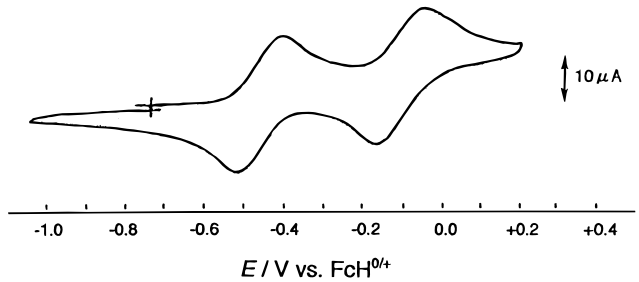


Figure 4. Cyclic voltammogram of complex **11** measured at a scan rate of 0.10 V/s in the 10^{-3} M solution in CH_2Cl_2.

Redox Properties. The electrochemical properties of the acetylide complexes prepared were measured by cyclic voltammetry at the scan rates of 0.025−0.50 V/s. The data obtained are summarized in Table 4, along with those from previous work.[17] The cyclic voltammogram of complex **11** is given in Figure 4 as a typical example. As seen clearly in Figure 4 and Table 4, the Ru(II) ruthenocenylacetylide complexes show two 1 e quasi-reversible waves, except for a few exceptions. Each wave was confirmed to be a 1 e process by using the Randles−Sevcik equation for complex **7** [$n = 0.74$ for $E_{pa}(1)$ and $n = 0.71$ for $E_{pc}(2)$ when the diffusion coefficient of **7** was assumed to be similar to that in ferrocene]. Ruthenocene itself shows a 2 e irreversible wave at +0.55 V (vs FcH/FcH$^+$) under ordinary conditions,[29] although a reversible 1 e redox wave was observed for decamethylruthenocene[30] and octamethyl-[3]ruthenocenophane[14] or when a large counteranion was used.[31] The first and second redox waves are assigned to the Ru(II) and the ruthenocenyl moieties by comparison with the redox potentials of Ru(C≡CPh)-(PPh_3)$_2$(η-C_5H_5) ($E_{pa} = +0.05$ V) and RcC≡CH ($E_{pa} = +0.58$ V), respectively. Both the first and second waves are shifted to lower potential compared with those of corresponding reference compounds. In complex **7**, for example, the first ($E_{pa} = -0.01$ V) and second oxidation potentials ($E_{pa} = +0.22$ V) are lower by 0.37 and 0.47 V (ΔE_{pa} values) than those of the reference complexes, Ru-(C≡CPh)(PPh_3)$_2$(η-C_5H_5) ($E_{pa} = +0.05$ V) and Rc′C≡CH ($E_{pa} = +0.69$ V), respectively. The lower potential shift of the first redox wave is probably due to the raised HOMO level of the complexes by the electron-donating effect of the ruthenocenyl group or more reasonably by the filled/filled interaction between the nonbonding d orbital of the Ru atoms and the bonding p orbital (HOMO) of the bridging acetylide function. The latter interaction was confirmed by photoelectron spectroscopy in some transition-metal acetylide complexes.[32] The lower potential shift of the second redox wave is unexpected, because the oxidized Ru(II) moiety in the acetylide complexes should act as an electron-attracting group and decrease the electron density of the ruthenocenyl moiety through the C≡C bond electrostatically and cause the second redox wave to shift to a higher potential region, as seen in the case of biferrocene derivatives.[33] The similar large shift of the oxidation potential to a lower potential region was also observed in [1.1]ruthenocenophane, which led to the complex containing a Ru−Ru bond on the oxidation,[12c] and 1,2-bis(ruthenocenyl)ethylenes, which are oxidized to pentafulvadiene diruthenium complexes.[13] This characteristic low-potential shift of the second redox wave observed here suggests that the strong interaction acts between the two metal sites in the 2 e oxidized species. Thus, both Ru atoms in the Ru(II) ruthenocenylacetylide complexes **7**−**16** are oxidized stepwise by a 1 e process from Ru(II) to Ru(III) states and then the unpaired electrons on the two Ru(III) atoms form a pair with spins coupled through the C≡C bond connecting the two Ru atoms. Such interaction seems to be responsible for the stabilization of the 2 e oxidized species and may also cause the reversible 1 e oxidation of the ruthenocenyl moiety observed in the cyclic voltammograms of the Ru(II) acetylide complexes **7**−**16**, owing to the difficulty of further oxidation of the stabilized 2 e oxidized species. From Table 4, the following features are also found: (i) The η-C_5Me_5 ligand makes the first redox wave shift to a lower potential region and the second one to a higher potential region compared with the η-C_5H_5 ligand, so that the $\Delta E_{1/2}$ value is increased. (ii) The effect of the η^5-C_9H_7 ligand is similar to that of the η-C_5H_5 ligand. (iii) The methyl substituent in the Rc moiety causes a shift ($\Delta \sim 0.08$ V) of the first wave to lower potential. (iv) The displacement of the PPh_3 ligand by the dppe ligand results in only a slight effect.

Chemical Oxidation. Chemical oxidation of the ruthenium(II) 2,3,4,5-tetramethylruthenocenylacetylide complexes **7**−**12** was carried out. In the oxidation of **7** and **11** with excess *p*-benzoquinone and BF_3·OEt_2 in CH_2Cl_2 below −80 °C, a deep green solution was obtained, which changed immediately to a red brown solution on standing or on warming to −70 °C. Com-

(29) (a) Kuwana, T.; Bublitz, D. E.; Hoh, G. *J. Am. Chem. Soc.* **1960**, *82*, 5811. (b) Kukharenko, S. V.; Bezrkova, A. A.; Rubezhov, A. Z.; Strelets, A. *Metalloorg. Khim.* **1990**, *3*, 634. (c) Denisovich, L. I.; Zakurin, N. V.; Bazurukova, A. A.; Gubin, S. P. *J. Organomet. Chem.* **1974**, *81*, 207. (d) Gubin, S. P.; Smirnova, L. I.; Denisovich, L. I.; Lubovich, A. A. *J. Organomet. Chem.* **1971**, *30*, 243.
(30) Kölle, U.; Salzer, A. *J. Organomet. Chem.* **1983**, *243*, C27.
(31) Gale, R.; Job, R. *Inorg. Chem.* **1981**, *20*, 42. (b) Hill, M. G.; Lamanna, W. M.; Mann, K. R. *Inorg. Chem.* **1991**, *30*, 4688.
(32) (a) Louwen, J. N.; Hengelmolen, R.; Grove, D. M.; Oskam, A. *Organometallics* **1984**, *3*, 908. (b) Lichtenberger, D. L.; Renshaw, S. K.; Bullock, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 3276.
(33) (a) Levanda, C.; Bechgaard, K.; Cowan, D. O. *J. Org. Chem.* **1976**, *41*, 2700. (b) Levanda, C.; Bechgaard, K.; Cowan, D. O.; Rausch, M. D. *J. Am. Chem. Soc.* **1977**, *99*, 2964.

Scheme 4

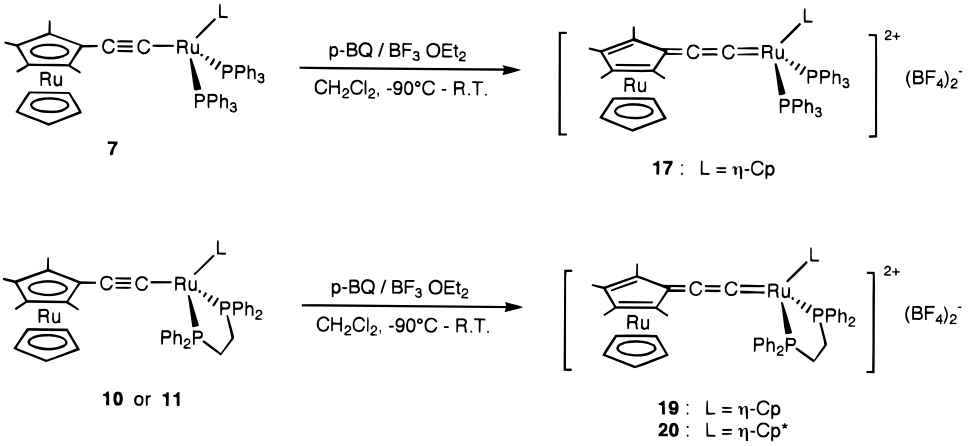


Table 5. ^{13}C NMR Spectral Data for the 2 e Oxidized Complexes 17, 19, and 20

complex	C_5Me_5	C_5Me_4	CH_2	C_5H_5	C_5Me_4	C_5Me_5	RuCC***C***	Ru***C***CC	Ru***C***CC	others
17	- - -	11.58	- - -	90.32	103.53	- - -	129.99	172.67	315.41	129.71, 132.24
		97.95	112.08					134.17,	135.04	
19	- - -	11.19	28.27	89.50	103.43	- - -	116.55	167.01	313.45	130.16, 130.25
	11.31		94.89	110.98					132.21,	132.68
								132.16,	133.71	
20	10.96	11.32	28.88	88.75	102.73	106.54	116.48	169.57	311.58	129.92, 130.34
			111.97					132.58,	132.84	
								133.32,	133.36	
								134.33,	134.90	

plexes **7**, **10**, and **11** gave the 2 e oxidized complexes **17**, **19**, and **20** as stable crystalline compounds (Scheme 4) after workup (see Experimental Section). Complexes containing the indenyl ligand (**9**) gave a stable but inseparable mixture. No stable 2 e oxidized complex could be isolated from the chemical oxidation of complexes **8** and **12**. In the ^{1}H NMR spectra of complexes **17**, **19**, and **20**, the protons of the η-C_5H_5 ring of the ruthenocenyl moiety appeared at δ 5.61, 4.90, and 4.92 as singlets, respectively, which are shifted by 1.2−1.5 ppm to lower field than those of the neutral complexes (**7**, δ 4.42; **10**, δ 3.70; **11**, δ 4.40). Also, the proton signals for the η-C_5H_5 ligand coordinated to the Ru atom in complexes **17** and **19** were observed at δ 5.70 and 6.04, respectively, which showed a low-field shift by ca. 1.3 ppm compared with those of the starting acetylide complexes (**7**, δ 4.44; **10**, δ 4.75). These results suggest that the positive charge is localized in both Ru atoms in these oxidized species. The C═C stretching vibration in the IR spectra of the oxidized species was observed at 1816, 1825, and 1803 cm^{-1} for **17**, **19**, and **20**, respectively, whose frequencies were intermediate between that of the vinylidene complexes (ca. 1650 cm^{-1})[34b] and that of the allenylidene complexes (1908−1952 cm^{-1}).[18] The ^{13}C NMR data of **17**, **19**, and **20** are summarized in Table 5. The most noticeable points are the chemical shift of the bridging unsaturated carbons. The resonance of the C(α) atom is observed at 311.6−315.4 ppm, which is in an intermediate region between that (325.9−364.5 ppm) of the cationic vinylidene complexes,[34a] and that (235.4−296.7 ppm) of the cationic allenylidene complexes.[18,27] The resonance of the phosphine ligand in the ^{31}P NMR spectra of **17**, **19**, and **20** occurs at 42.34, 76.98, and 72.50 ppm, respectively. The chemical shift in **17** is close to that (40.57 ppm) of [(η^5-C_5H_5)Ru(μ-η^6:η^1-C_5H_4C═C═)Ru(PPh_3)$_2$(η^5-C_5H_5)]-(BF_4)$_2$[17] and resembles that (42.75 ppm) of the vinylidene complex [Ru(═C═CHPh)(PPh_3)$_2$(η-C_5H_5)](BF_4)$_2$.[17] The chemical shifts of **19** and **20** are similar to those in the cationic vinylidene complex [Ru(═C═CHPh)(dppe)-(η-C_5H_5)]PF_6 (76.4 ppm)[35] and the related cationic allenylidene complex [Ru(═C═C═CPh_2)(dppe)(η^5-C_9H_7)]-PF_6 (81.73 ppm).[18a] These IR and ^{13}C and ^{31}P NMR data suggest that the vinylidene- or allenylidene-like structure occurs in the bridging unsaturated chain of the 2 e oxidized species **17**, **19**, and **20**. In the ^{13}C NMR spectra of **17**, **19**, and **20**, the signal of the C(γ) atom appeared at 116.5−130.0 ppm, whose chemical shift is similar to that of the corresponding C atom of the fulvene complexes [Ru(η^6-$C_5Me_4CH_2$)(η^5-C_5Me_5)]PF_6 (107.2 ppm)[36] and [Ru(η^6-$C_5Me_4CH_2$)(η^5-C_5H_5)]BF_4 (108.44 ppm)[17] but is much different from that of the cationic allenylidene complex [Ru(═C═C═CPh_2)(PPh_3)$_2$(η^5-C_9H_7)]-PF_6 (156.59 ppm).[18a] The signal of the C(β) atom was observed at 167.0−172.7 ppm, whose values are in much higher field than that of the corresponding carbon of the fulvene complexes [Ru(η^6-$C_5Me_4CH_2$)(η^5-C_5Me_5)]PF_6 (77.8 ppm)[36] and [Ru(η^6-$C_5Me_4CH_2$)(η^5-C_5H_5)]BF_4 (69.4 ppm)[17] and in much lower field than that of the cationic allenylidene complex [Ru(═C═C═CPh_2)(PPh_3)$_2$(η^5-C_9H_7)]-PF_6 (208.44 ppm)[18a] and similar to that of the corre-

(34) (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Bruce, M. I.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1471. (c) Lomprey, J. P.; Selegue, J. P. *J. Am. Chem. Soc.* **1992**, *114*, 5518. (d) Touchard, D.; Haquette, P.; Pilio, N., Toupet, L.; Dixneuf, P. L. *Organometallics* **1993**, *12*, 3132. (e) Le Lagadec, R.; Roman, E.; Toupet, L.; Müller, U.; Dixneuf, P. H. *Organometallics* **1994**, *13*, *3*, 5030. (f) Delos Pios, I.; Tenorio, M. J.; Ruerta, M. C.; Valerga, P, *J. Am. Chem. Soc.* **1997**, *119*, 6529. (g) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Borge, J.; Garcia-Granda, S., *Organometallics* **1997**, *16*, 3178. (h) Chang, C.-W.; Lin, Y.-C.; Lee, G.-H.; Huang, S.-L.; Wang, Y. *Organometallics* **1998**, *17*, 2534.

(35) Consiglio, G.; Morandini, F. *Inorg. Chimica Acta* **1987**, *127*, 79.

(36) Kreindlin, A. Z.; Petrovskii, M. I.; Rybinskaya, M. I.; Yanovskii, A. I.; Struchkov, Yu. T. *J. Organomet. Chem.* **1987**, *319*, 229.

Table 6. Selected Bond Distances and Angles for 19

Bond Distances (Å)			
Ru(1)−P(1)	2.317(2)	Ru(1)−P(2)	2.343(2)
Ru(1)−C(1)	1.886(8)	Ru(2)−C(2)	2.281(9)
Ru(2)−C(3)	2.081(10)	Ru(2)−C(4)	2.195(13)
Ru(2)−C(5)	2.240(12)	Ru(2)−C(6)	2.246(10)
C(2)−C(3)	1.409(14)	C(3)−C(4)	1.468(16)
Ru(2)−C(7)	2.179(10)	C(1)−C(2)	1.246(12)
C(3)−C(7)	1.448(18)	C(4)−C(5)	1.412(19)
C(5)−C(6)	1.38(2)	C(6)−C(7)	1.401(17)
Ru(2)−C(Cp-ring)	2.188(av)		
Bond Angles (deg)			
C(1)−C(2)−C(3)	154.0(9)	Ru(1)−C(1)−C(2)	173.8(7)
C(1)−Ru(1)−P(1)	86.4(3)	C(1)−Ru(1)−P(2)	87.5(3)
P(1)−Ru(1)−P(2)	82.9(1)		

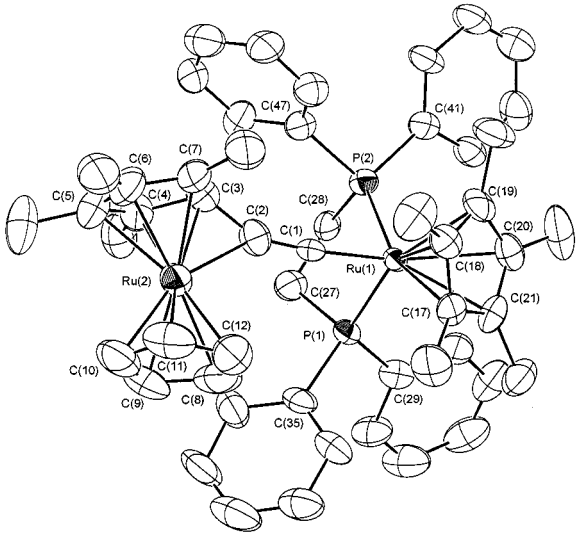


Figure 5. ORTEP view of the cationic part in complex **19**.

sponding carbon in the recently reported (cycloheptatrienylidene)ethenylidene complex [Ru(=C=C=C_7H_6)−(PPh_3)$_2$(η-C_5H_5)]PF_6 (168.2 ppm).[27] The chemical shift of the η^6-C_5Me_4 ring carbon (102.8−103.5 ppm in the 3,4-positions and 110.0−112.1 ppm in the 2,5-positions) in the 2 e oxidized species **17**, **19**, and **20** closely resembles those of the fulvene complexes [Ru(η^6-C_5Me_4-CH_2)(η^5-C_5H_5)]BF_4 (101.82 and 106.74 ppm).[17] It is evident from these spectral data that the 2 e oxidized complexes **17**, **19**, and **20** are the complexes containing a (cyclopentadienylidene)ethenylidene structure in the bridging chain, that is, [(η^5-C_5H_5)Ru(μ^2-η^6:η^1-C_5Me_4C=C=)Ru$\mathbf{P}_2$L](BF$_4$)$_2$ ($\mathbf{P}_2$ = 2 PPh_3 or dppe; L = η-C_5H_5 or η-C_5Me_5). A similar structure was also proposed for the 2 e oxidized product of RcC≡CRu(PPh_3)$_2$(η-C_5H_5), but it was assigned on the basis of only IR and ^{1}H NMR spectral data.[17]

Crystallographic data for **19** are collected in Table 2, and selected bond distances and angles are summarized in Table 6. The ORTEP view of the cationic part of **19** is shown in Figure 5. The geometry around the Ru(II) atom in **19** is a typical three-legged piano-stool configuration, as seen in the neutral complex **10**. The most remarkable feature in **19** is the presence of a (tetramethylcyclopentadienylidene)ethylidene structure in the bridging ligand. The Ru(1)−C(1) distance is 1.886(8) Å, which is in the region of the double bond distance between the Ru and C atoms, and a similar bond distance has been observed in the various vinylidene (1.76−1.882 Å)[33] and allenylidene complexes (1.878−1.94 Å).[18,27] The C(1)−C(2) distance [1.246(12) Å] is somewhat longer than that [1.208(6) Å] in the neutral acetylide complex **10**, suggesting somewhat loss of the triple bond character. A similar elongation of the C−C bond was also reported in the various vinylidene (1.22−1.34 Å)[33] and allenylidene complexes (1.23−1.267 Å).[18,27] In the oxidation, the ruthenocenyl part in **10** is transformed to the structure of the ruthenium(II) fulvene complex in **19**. That is, the η^6-C_5Me_4C moiety of **19** has a similar bond alternation as can be seen in the cationic fulvene complex [Ru(η^5-C_5Me_5)(η^6-$C_5Me_4CH_2$)]BPh_4[37] and the fulvene complexes Ru(η^6-$C_5Me_4CH_2$)(η^4-C_8H_{12}),[38] [$RuCl_2$(η^6-$C_5Me_4CH_2$)]$_2$,[39] RuCl(η^2-ButNSPh)(η^6-$C_5Me_4CH_2$),[40] and Cr(η^6-C_5H_4-CH_2)$(CO)_3$.[41] Thus, the C(2)−C(3) distance [1.409(14) Å] in **19** is shorter than the corresponding distances in **10** [1.425(6) Å]. The C(3)−C(4) [1.468(16) Å] and C(3)−C(7) distances [1.448(18) Å] are long and the C(4)−C(5) [1.412(19) Å] and C(6)−C(7) distances [1.401(17) Å] are short. The Ru(2)−C(3) distance [2.081(10) Å] proves the presence of the Ru−C bond, being rather shorter than that in [Ru(η^5-C_5Me_5)(η^6-$C_5Me_4CH_2$)]BPh_4 [2.270(3) Å],[37] [$RuCl_2$(η^6-$C_5Me_4CH_2$)]$_2$ [2.268(4) and 2.271(4) Å],[39] and [Ru_2(η^5-C_5Me_5)$_2$(μ-η^6:η^6-$C_5H_4CHCHC_5H_4$)](BF$_4$)$_2$ [average 2.410 Å].[13] The C(1)−C(2)−C(3) angle is no longer linear [154.0(9)°] because of the Ru(2)−C(3) bond. Moreover, only a slight distortion of the planarity of the C_5-Me_4 ring is observed in **19** (the displacement of the C(3) atom from the C(4)−C(7) plane is not greater than 0.066 Å, the dihedral angle between this and the C(4)C(3)-C(7) plane being 4.4°), while the C(2)−C(3) bond is bent by 40.4(10)° from the plane of the η-C_5Me_4 ring toward the Ru(1) atom, whose angle is near that in the related fulvene complexes (35−40°). The tilting angle between the η-C_5Me_4 and η-C_5H_5 rings in the fulvene complex part of **19** is 13.53(3)°, which is much larger than that in **10** (1.54°). A similar large tilting angle was also observed in [Ru_2(η^5-C_5Me_5)$_2$(μ-η^6:η^6-$C_5H_4CHCHC_5H_4$)]-(BF$_4$)$_2$ (11.29°)[13] and the isomorphous Os analog (14°)[42] of [Ru(η^5-C_5Me_5)(η^6-$C_5Me_4CH_2$)]BPh_4. The η-C_5Me_4 ring plane in the fulvene complex part of **19** is inclined by 71.0(2)° from the plane consisting of the Ru(1) atom, the center of the η-C_5H_5 ring, and the C(1) atom. This is considerably larger than that in **10** [50.3(2)°], being probably because of the steric hindrance due to the increased tilting in the fulvene complex part.

The formation of **17**, **19**, and **20**, having a μ-η^6:η^1-[(cyclopentadienylidene)ethylidene]diruthenium structure, in the 2 e oxidation of the corresponding acetylide derivatives may be elucidated as follows: In the oxidation process, one electron is first removed from the Ru(II) atom of the Ru$\mathbf{P}_2$L moiety because of the higher electron density and then the second electron is removed from the Ru atom of the ruthenocene moiety. As a result, a transient Ru(III)/Ru(III) species, which may

(37) Yanovskii, A. I.; Struchkov, Yu. T.; Kreindlin, A. Z.; Rybinskaya, M. I. *J. Organomet. Chem.* **1989**, *369*, 125.
(38) Koelle, U.; Kang, B. S.; Thewalt, U. *J. Organomet. Chem.* **1990**, *386*, 267.
(39) Fan, L.; Wei, C.; Aigbirhio, F. I.; Turner, M. L, Gusev, O. V.; Morozova, L. N.; Knowles, D. R. T.; Maitlis, P. M. *Organometallics* **1996**, *15*, 98.
(40) Hankin, D. M.; Danopoulos, A. A.; Wilkinson, G.; Sweet, T. K. N.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1996**, 4063.
(41) Koch O.; Erdmann, F.; Behrens, U. *Chem. Ber.* **1982**, *115*, 1313.
(42) Rybinskaya, M. I.; Kreindlin, A. Z.; Struchkov, Yu. T.; Yanovsky, A. I. *J. Organomet. Chem.* **1989**, *359*, 233.

be responsible for the deep green solution observed in the oxidation at low temperature, results, and the electronic communication between the two metal sites accompanied by a chemical process immediately causes structural rearrangement to the μ-η^6:η^1-[(cyclopentadienylidene)ethylidene]diruthenium complex. On the other hand, in the case of the 1′,2′,3′,4′,5′-pentamethylruthenocenyl derivative,[17] the intramolecular hydrogen transfer takes place in the transient Ru(III)/Ru(III) species at first and then the rearrangement to the fulvene−vinylidene complex follows. The difference between the two processes seems to depend on the stability of the μ-η^6:η^1-[(cyclopentadienylidene)ethylidene]-diruthenium system. In the 2,3,4,5-tetramethylruthenocenyl series, the two methyl groups next to the cumulative bond of the five-membered ring would act as a steric protection toward the cumulative bond of the system. A similar stabilization effect due to the electronic interaction between two metal sites was observed in the 2 e oxidation of bis(ruthenocenyl)ethylenes, which gave (μ-η^6:η^6-pentafulvadiene)diruthenium complexes,[13b] and [1.1]ruthenocenophane, which led to the dicationic complex containing a Ru−Ru bond.[12a] Such an interaction is very similar to that in the conversion of butadienediyldiiron complex into a bis(carbene)-type complex upon 2 e oxidation.[43,44] A similar oxidative transformation accompanied by a structural rearrangement was also reported in sp-carbon-bridged dirhenium complexes[45] and fulvalene-[46] and cyclooctatetraene-bridged dinuclear complexes.[47]

Experimental Section

All reactions were carried out under an atmosphere of N_2 and/or Ar, and workups were performed without precaution to exclude air. NMR spectra were recorded on a Bruker AM400 or ARX400 spectrometer. IR (KBr disk) spectra were recorded on a Perkin-Elmer System 2000 spectrometer. Cyclic voltammetry was carried out by using BAS CV27 in a 10^{-1} M solution of *n*-Bu_4NClO_4 (polarography grade, Nacalai tesque) in CH_2Cl_2. CV cells were fitted with a glassy carbon (GC) working electrode, a Pt wire counter electrode and a Ag/Ag^+ pseudo reference electrode. The cyclic voltammograms were obtained at a scan rate of 0.1 V s^{-1} in a 10^{-3} M solution of complexes. All potentials were represented vs FcH/FcH^+, which were obtained by the subsequent measurement of ferrocene at the same conditions. Solvents were purified by distillation from the drying agent prior to use as follows: CH_2Cl_2 ($CaCl_2$); $ClCH_2CH_2Cl$ ($CaCl_2$); CH_3CN (CaH_2); acetone ($CaSO_4$); THF (Na−benzophenone); ether ($LiAlH_4$). 1,2,3,4,5-Pentamethylruthenocene (**1**),[48] ethynylruthenocene,[49] 1-ethynyl-1′,2′,3′,4′,5′-pentamethylruthenocene,[17] $RuCl(PPh_3)_2(\eta$-$C_5H_5)$,[50] $RuCl(PPh_3)_2(\eta$-$C_5Me_5)$,[51] $RuCl(PPh_3)_2(\eta^5$−$C_9H_7)$,[52] $RuCl(dppe)(\eta$-$C_5H_5)$,[53] $RuCl(dppe)(\eta$-$C_5Me_5)$,[54] and $RuCl(dppe)(\eta^5$−$C_9H_7)$[52] were prepared according to the literature. 1-Ethynyl-1′,2′,3′,4′,5′-pentamethylruthenocene was also prepared by the Colvin rearrangement[23] modified by Shioiri[22] (vide infra). Other reagents were used as received from commercial suppliers.

1-Formyl-2,3,4,5-tetramethylruthenocene (2). Activated MnO_2 (Aldrich Inc., 3 g) was added to a solution of 1,2,3,4,5-pentamethylruthenocene (**1**) (0.60 g, 2 mmol) in $ClCH_2CH_2Cl$ (60 mL). The mixture was refluxed for 2 h. After cooling, the mixture was filtered and the residue was washed with CH_2Cl_2. The filtrate and the washing were combined and condensed under reduced pressure. The residue was chromatographed on alumina with hexane giving the recovered starting material (**1**) (0.24 g, 40%). Elution with CH_2Cl_2 afforded the title compound (**2**) which was recrystallized from hexane giving yellow crystals (0.23 g, 37%). Mp: 151−152 °C. IR (KBr): 1673 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.01 (s, 6H, β-CH_3), 2.18 (s, 6H, α-CH_3), 4.35 (s, 5H, Cp), and 10.11 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 11.6 (α-CH_3), 12.1 (β-CH_3), 73.5 (Cp), 80.0 (ipso-C), 87.3 (α-C), 90.3 (β-C), and 191.7 (CO). Anal. Calcd for $C_{15}H_{18}ORu$: C, 57.13; H, 5.75. Found: C, 57.22; H, 5.79.

Elution with CH_2Cl_2−ethyl acetate (5%) gave 1,2-diformyl-3,4,5-trimethylruthenocene (**3**) (23 mg, 7%) as yellow crystals after recrystallization from CH_2Cl_2-hexane. Mp: 178.5−179.5 °C. IR (KBr): 1679 and 1730 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.08 (s, 3H, β-CH_3), 2.28 (s, 6H, α-CH_3), 4.55 (s, 5H, Cp), and 10.30 (s, 2H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 11.1 (α-CH_3), 12.4 (β-CH_3), 74.9 (Cp), 82.0 (ipso-C), 92.3 (α-C), 94.5 (β-C), and 191.3 (CO). Anal. Calcd for $C_{15}H_{16}O_2Ru$: C, 54.70; H, 4.90. Found: C, 54.81; H, 4.88.

1-Ethynyl-2,3,4,5-tetramethylruthenocene (4) (Procedure A). To a solution of LDA, prepared from diisopropylamine (0.2 mL, 1.3 mmol) and *n*-BuLi (0.75 mL of 1.5 M solution in hexane, 1.2 mmol) in THF (8 mL) at 0 °C, was added trimethylsilyldiazomethane (0.65 mL of 1.9 M solution, 1.2 mmol) at −78 °C under Ar. After the reaction mixture was stirred for 10 min, a solution of **1** (0.32 g, 1.0 mmol) in THF (2 mL) was added. The solution was sirred for 1 h at the same temperature and then gently refluxed for 3 h. The solution was poured into a saturated aqueous solution of NH_4Cl (30 mL). The mixture was extracted with diethyl ether. The extract was washed with water and dried over $MgSO_4$. After evaporation, the residue was chromatographed on SiO_2 with elution of hexane−benzene (2:1) to give 1-ethynyl-2,3,4,5-tetramethylruthenocene (**4**) (0.22 g, 71%) as pale yellow crystals. Mp: 77.5−78.5 °C. IR (KBr): 2103 cm^{-1} (ν(C≡C)). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.95, (s, 6H, CH_3), 2.06, (s, 6H, CH_3), 2.87 (s, 1H, ≡CH), and 4.28 (s, 5H, Cp). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 12.2 (α-CH_3), 12.8 (β-CH_3), 68.4 (C≡) 73.3 (Cp), 76.4 (d, ≡CH, $^1J_{CH}$ = 247 Hz), 81.9 (ipso-C), 86.3 (α-C), and 87.2 (β-C). Anal. Calcd for $C_{16}H_{18}Ru$: C, 61.72; H, 5.83. Found: C, 61.84; H, 5.83.

Similarly, 1-ethynyl-1′,2′,3′,4′,5′-pentamethylruthenocene[17] was also prepared using the procedure described above. Yield: 70%.

1-Ethynyl-2,3,4,5-tetramethylruthenocene (4) (Procedure B). A 1.5 M solution of *t*-BuLi in pentane (1.7 mL, 1.3

(43) (a) Le Narvor, N.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1993**, 357. (b) Le Narvor, N.; Toupet, L.; Lapinte, C. *J. Am. Chem. Soc.* **1995**, *117*, *7*, 7129. (c) Le Narvor, N.; Lapinte, C. *Organometallics* **1995**, *14*, 634. (d) Coat, F.; Lapinte, C. *Organometallics* **1996**, *15*, 477. (e) Weyland, T.; Lapinte C.; Frapper, G.; Calhorda, M. J.; Halet, J.-F.; Toupet, L. *Organometallics* **1997**, *16*, 2024.

(44) (a) Etzenhouser, B. A.; Cavanaugh, M. D.; Spurgeon, H. N.; Sponsler, M. B. *J. Am. Chem. Soc.* **1994**, *116*, 2221. (b) Etzenhouser, B. A.; Chen, Q.; Sponsler, M. B. *Organometallics* **1995**, *14*, 1920.

(45) (a) Seyler, J. W.; Weng, E.; Zhou, Y.; Gladysz, J. A. *Organometallics* **1993**, *12*, 3802. (b) Zhou, Y.; Seyler, J. W.; Weng, E.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 8509. (c) Brady, M.; Weng, E.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1994**, 2655. (d) Bartik, T.; Bartik, B.; Brady, M.; Dembinski, R.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 414.

(46) Delville, M.-H.; Lacoste, M.; Astruc, D. *J. Am. Chem. Soc.* **1992**, *114*, 8310.

(47) (a) Edwin, J.; Geiger, W. E. *J. Am. Chem. Soc.* **1990**, *112*, 7104. (b) Geiger, W. E.; Salzer, A.; Edwin, J.; von Pillipsborn, W.; Pinatini, U.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 7113. (c) Chin, T. T.; Geiger, W. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 5002.

(48) Kudinov, A. R.; Rybinskaya, M. I.; Struchkov, Yu. T.; Yanovskii, A. I.; Petrovskii, P. V. *J. Organomet. Chem.* **1987**, *336*, 187.

(49) Hofer, O.; Schlögl, K. *J. Organomet. Chem.* **1968**, *13*, 443.

(50) Bruce, M. I.; Windsor, N. J. *Aust. J. Chem.* **1977**, *30*, 1601.

(51) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166.

(52) Oro, L. A.; Ciriano, M. A.; Campo, M.; Foces-Foces, C.; Cano, F. H. *J. Organomet. Chem.* **1985**, *289*, 117.

(53) Ashby, G. S.; Bruce, M. I.; Tomkins, I. B.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1003.

(54) Oshima M.; Suzuki, H.; Moro-oka, Y. *Chem. Lett.* **1984**, 1161.

mmol) was added dropwise under Ar to a solution of 1,1-dichloro-2-(2′,3′,4′,5′-tetramethylruthenocenyl)ethylene (**5**) (0.50 g, 1.3 mmol) cooled below −80 °C. The solution was stirred for 10 min at that temperature and then warmed to ca. 5 °C for a period of 1 h. After hydrolysis with a saturated aqueous solution of NH_4Cl, the solution was extracted with ether. The extract was dried over $MgSO_4$ and then evaporated under reduced pressure. The residue was chromatographed on SiO_2 by elution with hexane−benzene (10:1) to give the title compound (**4**) (282 mg, 70%) and 1,4-bis(2′,3′,4′,5′-tetramethylruthenocenyl)-1,3-butadiyne (**6**) (86 mg, 19%). Mp: 253−254 °C. IR (KBr): 2137 cm^{-1} (ν(C≡C)). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.94, (s, 6H, CH_3), 2.03, (s, 6H, CH_3), and 4.29 (s, 5H, Cp). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 12.20 (CH_3), 12.88 (CH_3), 65.26, 67.4, 68.79 (ipso-C, Rc′ *C*≡C, or Rc′ C≡*C*), 73.2 (Cp), 86.24 (α-C), and 87.25 (β-C). Anal. Calcd for $C_{32}H_{34}Ru_2$: C, 61.92; H, 5.52. Found: C, 61.80; H, 5.80.

Sometimes, 1-acetyl-2,3,4,5-tetramethylruthenocene was isolated from the reaction mixture, although in a tiny yield. Mp: 122−122.5 °C. IR (KBr): 1656 cm^{-1} (ν C═O). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.99, (s, 6H, CH_3), 2.18, (s, 6H, CH_3), 2.48 (s, 3H, $COCH_3$), and 4.29 (s, 5H, Cp). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 11.3 (CH_3), 13.2 (CH_3), 73.0 (Cp), 83.2 (ipso-C), 85.4 (α-C), 88.8 (β-C), and 202.7 (CO). Anal.Calcd for $C_{16}H_{20}ORu$: C, 58.34; H, 6.12. Found: C, 58.43; H, 6.07.

1,1-Dichloro-2-(2′,3′,4′,5′-tetramethylruthenocenyl)ethylene (5). A solution of diethyl(trichloromethyl)phosphonate (0.24 mL, 1.3 mmol) in anhydrous diethyl ether (1.2 mL) and THF (1 mL) was chilled below −100 °C. To the solution was added a solution of *n*-BuLi (0.45 mL of 1.5 M solution in hexane, 0.72 mmol), and the resulting solution was stirred for 5 min. A solution of **2** (132 mg, 0.42 mmol) in THF (1 mL) was added dropwise to the solution. After warming slowly to room temperature, the solution was refluxed for 1 h and then chilled at −50 °C, followed by hydrolysis with 2 N H_2SO_4. The solution was extracted with diethyl ether. The extract was dried over $MgSO_4$ and evaporated under reduced pressure. The residue was chromatographed on SiO_2 by elution of hexane to give pale yellow crystals which were recrystallized from hot hexane (136 mg, 85%). Mp: 68−69 °C. IR (KBr): 1634 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.97, 1.98, (2 × s, 12H, CH_3), 4.24 (s, 5H, Cp), and 6.74 (s, 1H, CH═). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 12.2 (α-CH_3), 13.5 (β-CH_3), 72.8 (Cp), 82.9 (ipso-C), 84.7 (α-C), 86.5 (β-C), 127.1 (CH═), and 83.4 (═CCl_2). Anal. Calcd for $C_{16}H_{18}Cl_2Ru$: C, 50.27; H, 4.75. Found: C, 50.39; H, 4.72.

(η-C_5H_5)Ru(μ-η^5:η^1-C_5Me_4C≡C)Ru(PPh_3)$_2$(η-C_5H_5) (7). To a solution of 1-ethynyl-2,3,4,5-tetramethylruthenocene (**4**) (23.3 mg, 0.07 mmol) and RuCl(PPh_3)$_2$(η-C_5H_5) (49.6 mg, 0.07 mmol) in CH_2Cl_2 (3 mL) and MeOH (1.8 mL) was added NH_4PF_6 (20 mg, 1.6 mmol) under an atmosphere of Ar at room temperature. The solution was stirred for 1 h. After evaporation of the solvent under reduced pressure, the resulting deep brown residue was chromatographed on alumina deactivated with 5% H_2O by elution with hexane. The title complex was obtained as yellow-orange crystals (68 mg, 97%). Mp: 135 °C. IR (KBr): 2081 cm^{-1} (ν(C≡C)). ^1H NMR (C_6D_6, 400 MHz): δ 2.06 (s, 6H, CH_3), 2.37 (s, 6H, CH_3), 4.21 (s, 5H, η-C_5H_5 in Rc′), 4.44 (s, 5H, η-C_5H_5), and 6.93−7.76 (m, 30H, Ph). ^{13}C NMR (C_6D_6, 100 MHz): δ 12.92 (CH_3), 14.29 (CH_3), 72.60 (η-C_5H_5 in Rc), 80.67 (ipso-C_5Me_4), 84.07 (C_5Me_4), 86.02 (η-C_5H_5), 86.20 (C_5Me_4), 105.90 (t, $^2J_{CP}$ = 25.1 Hz, RuC≡), 107.59 (C≡), 127.47 (t, $^3J_{CP}$ = 4.4 Hz, *m*-Ph), 128.60 (*p*-Ph), 134.42 (t, $^2J_{CP}$ = 5.1 Hz), and 139.81 (m, ipso-Ph). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 50.74. Anal. Calcd for $C_{57}H_{52}P_2Ru_2{\cdot}CH_2Cl_2$: C, 64.14; H, 5.01. Found: C, 64.29; H, 5.02.

(η-C_5H_5)Ru(μ-η^5:η^1-C_5Me_4C≡C)Ru(PPh_3)$_2$(η-C_5Me_5) (8). To a solution of **4** (28 mg, 0.09 mmol) and RuCl(PPh_3)$_2$(η^5-C_5Me_5) (71.7 mg, 0.09 mmol) in CH_2Cl_2 (4 mL) and MeOH (2.5 mL) was added NH_4PF_6 (18 mg, 1.1 mmol) under bubbling of nitrogen at room temperature. After the solution had been stirred for 30 min, a 0.1 M solution of KOH in MeOH (1.2 mL) was added. After evaporation under reduced pressure, the residue was chromatographed on Al_2O_3 deactivated with 5% H_2O by elution with CH_2Cl_2. The title complex was obtained as yellow crystals (38 mg, 39%). The product was purified by SiO_2 column chromatography (eluate: benzene) and then recrystallization from benzene−MeOH to give orange crystals, mp 141 °C. IR (KBr): 2062 cm^{-1} (ν(C≡C)). ^1H NMR (C_6D_6, 400 MHz): δ 1.40 (s, 15H, CH_3), 2.15 (s, 6H, CH_3), 2.52 (s, 6H, CH_3), 4.60 (s, 5H, Rc), and 6.9−8.1 (bm, 30H, Ph). ^{13}C NMR (C_6D_6, 100 MHz): δ 10.00 (CH_3 in Cp*), 12.93 (CH_3), 14.70 (CH_3), 72.61 (η-C_5H_5 in Rc), 81.48 (ipso-C_5Me_4), 84.26 (η-C_5Me_4), 86.46 (η-C_5Me_4), 93.67 (η-C_5Me_5), 106.26 (C≡), 117.81 (t, $^2J_{CP}$ = 24.3 Hz, RuC≡), 127.01 (*p*-Ph), 128.48 (bs, *m*-Ph), 135.38 (bs, *o*-Ph), and 138.31 (bs, ipso-Ph). ^{31}P NMR (162 MHz, C_6D_6): δ 52.72. Anal. Calcd for $C_{62}H_{62}P_2Ru_2{\cdot}C_6H_6$: C, 71.06; H, 5.96. Found: C, 70.89; H, 5.96.

(η-C_5H_5)Ru(μ-η^5,η^1-C_5Me_4C≡C)Ru(PPh_3)$_2$(η^5-C_9H_7) (9). To a solution of **4** (28 mg, 0.09 mmol) and RuCl(PPh_3)$_2$(η^5-C_9H_7) (67.5 mg, 0.09 mmol) in CH_2Cl_2 (4 mL) and anhydrous MeOH (2.5 mL) was added NH_4PF_6 (18 mg, 0.11 mmol) under an atmosphere of Ar at room temperature. The solution was stirred for 1 h. After evaporation of the solvent under reduced pressure, the resulting deep brown residue was chromatographed on Al_2O_3 deactivated with 5% H_2O by elution with hexane. The title complex was obtained as red crystals (76 mg, 80%), which are recrystallized from CH_2Cl_2−MeOH. Mp: ∼165 °C dec. IR (KBr): 2075 cm^{-1} (ν(C≡C). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.99 (s, 6H, CH_3), 2.11 (s, 6H, CH_3), 4.00 (s, 5H, η-C_5H_5), 4.45 (d, J = 2.5 Hz, 2H, 1-C_9H_7), 5.12 (t, J = 2.5 Hz, 1H, 2-C_9H_7), 6.44 (dd, J = 3.0 and 6.3 Hz, 2H, 5-C_9H_7), 6.74 (dd, J = 3.0 and 6.3 Hz, 2H, 4-C_9H_7), and 7.03−7.41 (m, 30H, Ph). ^{13}C NMR (C_6D_6, 100 MHz): δ 12.89 (CH_3), 14.38 (CH_3), 72.69 (η-C_5H_5), 74.90 (1-C_9H_7), 80.36 (ipso-C_5Me_4), 84.11 (C_5Me_4), 86.28 (C_5Me_4), 95.47 (2-C_9H_7), 104.01 (t, $^2J_{CP}$ = 28.3 Hz, RuC≡), 107.22 (C≡), 109.88 (ipso-C_9H_7), 123.45 (4 or 5-C_9H_7), 126.13 (4 or 5-C_9H_7), 127.38 (t, $^3J_{CP}$ = 4.6 Hz, *m*-Ph), 128.61 (*p*-Ph), 134.60 (t, $^2J_{CP}$ = 4.6 Hz, *o*-Ph), and 138.83 (m, ipso-Ph). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 53.36. Anal. Calcd for $C_{61}H_{54}P_2Ru_2{\cdot}CH_3OH$: C, 68.75; H, 5.40. Found: C, 68.86; H, 5.19.

(η-C_5H_5)Ru(μ-η^5:η^1-C_5Me_4C≡C)Ru(dppe)(η-C_5H_5) (10). To a solution of $AgBF_4$ (44 mg, 0.23 mmol) in anhydrous acetone (10 mL) was added RuCl(dppe)(η-C_5H_5) (118 mg, 0.20 mmol) under nitrogen bubbling, and then the solution was stirred for 1 h at room temperature. The resulting precipitate of AgCl was removed by filtration. To the filtrate was added **4** (59.3 mg, 0.19 mmol) under an atmosphere of nitrogen at room temperature. The solution was stirred for 1 h. After evaporation of the solvent under reduced pressure, the resulting deep brown residue was chromatographed on Al_2O_3 deactivated with 5% H_2O by elution with hexane. The title complex was obtained as deep yellow crystals (80 mg, 48%). Mp: 175 °C dec. IR (KBr): 2088 cm^{-1} (ν(C≡C)). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.44 (s, 6H, CH_3), 1.74 (s, 6H, CH_3), 2.60 (m, 2H, CH_2), 2.86 (m, 2H, CH_2), 3.70 (s, 5H, Rc), 4.75 (s, 5H, η-C_5H_5) and 7.07−8.01 (m, 20H, Ph). ^{13}C NMR (C_6D_6, 100 MHz): δ 12.74 (CH_3), 13.19 (CH_3), 28.64 (t, J = 22.6 Hz), 72.29 (Cp in Rc), 80.27 (ipso-C), 82.98 (Cp), 83.76 (α-C), 85.99 (β-C), 105.48 (C≡), 106.45 (t, $^2J_{CP}$ = 24.4 Hz, RuC≡), 127.92 (t, $^3J_{CP}$ = 3.9 Hz, *m*-Ph), 128.44 (*p*-Ph), 129.73 (*p*-Ph), 131.39 (t, $^2J_{CP}$ = 5.2 Hz, *o*-Ph), 135.46 (t, $^2J_{CP}$ = 5.4 Hz, *o*-Ph), 137.70 (m, ipso-Ph), and 134.23 (m, ipso-Ph). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 87.35. Anal. Calcd for $C_{47}H_{46}P_2Ru_2{\cdot}CH_3OH$: C, 63.56; H, 5.56. Found: C, 63.29; H, 5.26.

(η-C_5H_5)Ru(μ-η^5:η^1-C_5Me_4C≡C)Ru(dppe)(η-C_5Me_5) (11). This complex was prepared according with the procedure used in the preparation of **7**, to give yellow crystals (86%). Mp: 195 °C. IR (KBr): 2073 cm^{-1} (ν(C≡C)). ^1H NMR (C_6D_6, 400 MHz): δ 1.68 (s, 15H, η-C_5Me_5), 1.91 (s, 6H, Me), 1.95 (s, 6H, Me), 2.15 (m, 2H, CH_2), 2.94 (m, 2H, CH_2), 4.40 (s, 5H, Rc), and 6.98−7.96 (m, 20H, Ph). ^{13}C NMR (C_6D_6, 100 MHz): δ 10.44

(η-C_5Me_5), 12.79 (Me), 13.25 (Me), 29.64 (m, CH_2), 72.41 (η-C_5H_5 in Rc), 81.03 (ipso-C), 83.90 (α-C), 86.15 (β-C), 92.60 (η-C_5Me_5), 102.78 (C≡), 119.92 (t, $^2J_{CP}$ = 25.9 Hz, RuC≡), 127.48 (t, $^3J_{CP}$ = 4.5 Hz, *m*-Ph), 128.67 (*p*-Ph), 129.21 (*p*-Ph), 133.53 (t, $^2J_{CP}$ = 5.1 Hz), 134.73 (t, $^2J_{CP}$ = 4.6 Hz), 138.15 (dd, J = 44.0 and 3.0 Hz, ipso-Ph) and 139.75 (dd, J = 36.4 and 3.0 Hz, ipso-Ph). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 81.61. Anal.Calcd for $C_{52}H_{56}P_2Ru_2$: C, 66.09; H, 5.97. Found: C, 66.05; H, 5.97.

(η-C_5H_5)Ru(μ-η^5:η^1-C_5Me_4C≡C)Ru(dppe)(η^5-C_9H_7) (12). To a solution of $AgBF_4$ (21 mg, 0.11 mmol) in anhydrous acetone (10 mL) was added RuCl(dppe)(η^5-C_9H_7) (59 mg, 0.09 mmol) under nitrogen bubbling, and then the solution was stirred for 3 min at room temperature. To the resulting deep green mixture was added **4** (28 mg, 0.09 mmol) under an atmosphere of nitrogen at room temperature. The solution was stirred for 10 min. After evaporation of the solvent under reduced pressure, the resulting brown residue was chromatographed on Al_2O_3 deactivated with 5% H_2O by elution with CH_2Cl_2. The title complex was obtained as orange-yellow crystals (56 mg, 67%). Mp: 222 °C dec. IR (KBr): 2089 cm^{-1} (ν(C≡C)). ^{1}H NMR (C_6D_6, 400 MHz): δ 1.79,(s, 6H, CH_3), 1.91 (s, 6H, CH_3), 2.12 (m, 2H, CH_2), 2.64 (m, 2H, CH_2), 4.03 (s, 5H, η-C_5H_5), 4.88 (t, J = 2.5 Hz, 1H, 2-C_9H_7), 4.88 (d, J = 2.5 Hz, 1H, 1-C_9H_7), and 6.96−7.64 (m, 24H, Ph + 4,5-C_9H_7). ^{13}C NMR (C_6D_6, 100 MHz): δ 12.72 (CH_3), 13.12 (CH_3), 28.58 (t, J = 23.1 Hz, CH_2), 70.18 (1-C_9H_7), 72.42 (Cp), 79.87 (ipso-C_5-Me_4), 83.80 (C_5Me_4), 86.01 (C_5Me_4), 92.62 (2-C_9H_7), 105.21 (C≡), 107.23 (t, $^2J_{CP}$ = 25.0 Hz, RuC≡), 108.48 (ipso-C_9H_7), 123.91 (4 or 5-C_9H_7), 124.67 (4 or 5-C_9H_7), 127.90 (t, $^3J_{CP}$ = 3.7 Hz, *m*-Ph), 128.71 (*p*-Ph), 129.71 (*p*-Ph), 131.75 (t, $^2J_{CP}$ = 5.0 Hz, *o*-Ph), 135.18 (t, $^2J_{CP}$ = 5.2 Hz, *o*-Ph), 136.33 (m, ipso-Ph), and 143.04 (m, ipso-Ph). ^{31}P NMR (162 MHz, $CDCl_3$): δ 89.08. Anal. Calcd for $C_{51}H_{48}P_2Ru_2$·CH_3OH: C, 65.26; H, 5.48. Found: C, 65.45; H, 5.18.

(η-C_5H_5)Ru(μ-η^5,η^1-C_5H_4C≡C)Ru(PPh_3)$_2$(η^5-C_9H_7) (13). This complex was prepared from ethynylruthenocene and RuCl(PPh_3)$_2$(η^5-C_9H_7) according to the procedure described for complex **7** and purified by recrystallization from benzene−pentane, to give red crystals (82%). Mp; 165 °C dec. IR (KBr): 2086 cm^{-1} (ν(C≡C)). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.16 (s, 5H, Cp), 4.38 (t, J = 1.6 Hz, 2H, C_5H_4), 4.49 (d, J = 2.5 Hz, 2H, 1-C_9H_7), 4.57 (t, J = 1.6 Hz, 2H, C_5H_4), 5.35 (t, J = 2.5 Hz, 1H, 2-C_9H_7), 6.10 (dd, J = 3.0 and 6.3 Hz, 2H, 5-C_9H_7), 6.68 (dd, J = 3.0 and 6.3 Hz, 2H, 4-C_9H_7), and 7.00−7.35 (m, 30H, Ph). ^{13}C NMR (C_6D_6, 100 MHz): δ 68.74 (C_5H_4), 71.02 (Cp), 73.10 (C_5H_4), 74.80 (1-C_9H_7), 80.7 (ipso-C_5H_4), 95.49 (2-C_9H_7), 102.80 (t, $^2J_{CP}$ = 25.6 Hz, RuC≡), 106.55 (C≡), 109.34 (ipso-C_9H_7), 122.99 (4 or 5-C_9H_7), 125.90 (4 or 5-C_9H_7), 127.36 (t, $^3J_{CP}$ = 4.5 Hz, *m*-Ph), 128.60 (*p*-Ph), 134.61 (t, $^2J_{CP}$ = 4.8 Hz, *o*-Ph), and 138.74 (m, ipso-Ph). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 51.34. Anal. Calcd for $C_{57}H_{46}P_2Ru_2$·$2C_6H_6$: C, 71.98; H, 5.08. Found: C, 71.64; H, 5.05.

(η-C_5H_5)Ru(μ-η^5:η^1-C_5H_4C≡C)Ru(dppe)(η^5-C_9H_7) (14). This complex was prepared from ethynylruthenocene and RuCl(dppe)(η^5-C_9H_7) according to the procedure described for complex **12** and purified by recrystallization from CH_2Cl_2−MeOH. The title complex was obtained as red-orange crystals (52 mg, 66%). Mp 232 °C. IR (KBr): 2070 cm^{-1} (ν(C≡C)). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.09 (m, 2H, CH_2), 2.48 (m, 2H, CH_2), 3.99 (t, J = 1.6 Hz, β-C_5H_4), 4.11 (s, 5H, η-C_5H_5), 4.14 (t, J = 1.6 Hz, α-C_5H_4), 4.99 (d, J = 2.6 Hz, 1H, 1-C_9H_7), 5.18 (t, J = 2.6 Hz, 1H, 2-C_9H_7), 6.89 (A_2B_2 type, 2H, 4-or 5-C_9H_7), 6.98 (A_2B_2 type, 2H, 4-or 5-C_9H_7), and 7.07−7.52 (m, 20H, Ph). ^{13}C NMR (C_6D_6, 100 MHz): δ 28.30 (t, J = 23.4 Hz, CH_2), 68.69 (η-C_5H_4), 69.64 (1-C_9H_7), 70.71 (η-C_5H_5), 73.00 (η-C_5H_4), 79.65 (ipso-C_5H_4), 92.43 (2-C_9H_7), 104.64 (C≡), 106.65 (t, $^2J_{CP}$ = 26.0 Hz, RuC≡), 107.91 (ipso-C_9H_7), 123.76 (4 or 5-C_9H_7), 124.31 (4 or 5-C_9H_7), 127.60 (t, $^3J_{CP}$ = 5.0 Hz, *m*-Ph), 127.84 (t, $^3J_{CP}$ = 4.3 Hz, *m*-Ph), 128.99 (*p*-Ph), 129.48 (*p*-Ph), 132.30 (t, $^2J_{CP}$ = 5.2 Hz, *o*-Ph), 134.45 (t, $^2J_{CP}$ = 5.0 Hz, *o*-Ph), 136.91 (m, ipso-Ph) and 141.68 (m, ipso-Ph). ^{31}P NMR (162 MHz, $CDCl_3$): δ 86.48. Anal. Calcd for $C_{47}H_{40}P_2Ru_2$·1/2CH_3OH: C, 64.47; H, 4.78. Found: C, 64.32; H, 4.83.

(η-C_5Me_5)Ru(μ-η^5,η^1-C_5H_4C≡C)Ru(PPh_3)$_2$(η^5-C_9H_7) (15). This complex was prepared from 1-ethynyl-1′,2′,3′,4′,5′-pentamethylruthenocene and RuCl(PPh_3)$_2$(η^5-C_9H_7) according to the procedure used in preparing **9** and purified by recrystallization from CH_2Cl_2−MeOH, to give red-orange crystals (60%). Mp ∼195 °C dec. IR (KBr): 2088 cm^{-1} (ν(C≡C)). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.08 (s, 15H, CH_3), 4.02 (s, 4H, η-C_5H_4), 4.51 (d, J = 2.7 Hz, 2H, 1-C_9H_7), 5.41 (t, J = 2.7 Hz, 1H, 2-C_9H_7), 6.67 (A_2B_2 type, 2H, 5-C_9H_7), 6.74 (A_2B_2 type, 2H, 4-C_9H_7), and 7.03−7.26 (m, 30H, Ph). ^{13}C NMR (C_6D_6, 100 MHz): δ 12.30 (C_5Me_5), 71.12 (η-C_5H_4), 74.86 (η-C_5H_4), 74.78 (1-C_9H_7), 79.82 (ipso-C_5H_4), 84.53 (C_5Me_5), 95.40 (2-C_9H_7), 101.31 (t, $^2J_{CP}$ = 25.7 Hz, RuC≡), 106.54 (C≡), 109.33 (ipso-C_9H_7), 123.16 (4 or 5-C_9H_7), 125.69 (4 or 5-C_9H_7), 127.25 (t, $^3J_{CP}$ = 4.5 Hz, *m*-Ph), 128.54 (*p*-Ph), 134.60 (t, $^2J_{CP}$ = 4.9 Hz, *o*-Ph), and 138.72 (m, ipso-Ph). ^{31}P NMR (162 MHz, $CDCl_3$): δ 50.49. Anal. Calcd for $C_{62}H_{56}P_2Ru_2$: C, 69.91; H, 5.30. Found: C, 69.84; H, 5.26.

(η-C_5Me_5)Ru(μ-η^5:η^1-C_5H_4C≡C)Ru(dppe)(η^5-C_9H_7) (16). This complex was prepared from 1-ethynyl-1′,2′,3′,4′,5′-pentamethylruthenocene and RuCl(dppe)(η^5-C_9H_7) according to the procedure described for **12** and purified by recrystallization from CH_2Cl_2−MeOH. The title complex was obtained as red-orange crystals (48%). Mp: ∼170 °C dec. IR (KBr): 2079 cm^{-1} (ν(C≡C)). ^{1}H NMR (C_6D_6, 400 MHz): δ 1.82 (m, 2H, CH_2), 2.00 (s, 15H, η-C_5Me_5), 2.40 (m, 2H, CH_2), 3.82 (t, J = 1.6 Hz, β-C_5H_4), 4.02 (t, J = 1.6 Hz, α-C_5H_4), 5.08 (d, J = 2.6 Hz, 2H, 1-C_9H_7), 5.25 (t, J = 2.6 Hz, 1H, 2-C_9H_7), 6.87 (A_2B_2 type, 2H, 4- or 5-C_9H_7), 7.10 (A_2B_2 type, 2H, 4- or 5-C_9H_7), and 7.00−7.62 (m, 20H, Ph). ^{13}C NMR (C_6D_6, 100 MHz): δ 12.08 (η-C_5Me_5), 28.21 (t, J = 23.3 Hz, CH_2), 70.16 (1-C_9H_7), 70.75 (η-C_5H_4), 75.10 (η-C_5H_4), 79.70 (ipso-C_5H_4), 84.30 (η-C_5Me_5), 92.62 (2-C_9H_7), 104.16 (C≡), 103.83 (t, $^2J_{CP}$ = 25.5 Hz, RuC≡), 107.89 (ipso-C_9H_7), 123.74 (4 or 5-C_9H_7), 124.24 (4 or 5-C_9H_7), 127.52 (t, $^3J_{CP}$ = 5.0 Hz, *m*-Ph), 128.88 (*p*-Ph), 129.36 (*p*-Ph), 132.26 (t, $^2J_{CP}$ = 5.0 Hz, *o*-Ph), 134.48 (t, $^2J_{CP}$ = 5.0 Hz, *o*-Ph), 137.11 (m, ipso-Ph), and 141.85 (m, ipso-Ph). ^{31}P NMR (162 MHz, $CDCl_3$): δ 87.52. Anal. Calcd for $C_{52}H_{50}P_2Ru_2$: C, 66.51; H, 5.37. Found: C, 66.12; H, 5.31.

[(η-C_5H_5)Ru(μ-η^6:η^1-C_5Me_4C=C=)Ru(PPh_3)$_2$(η-C_5H_5)](BF$_4$)$_2$ (17). A solution of complex **7** (30 mg, 0.03 mmol) and *p*-benzoquinone (5.5 mg, 0.05 mmol) in CH_2Cl_2 (3 mL) was chilled below −80 °C. To the solution was added BF_3·OEt_2 (0.1 mL). The color of the solution turned orange to deep green and then to reddish brown as the reaction temperature rose. At −40 °C, anhydrous diethyl ether (4 mL) was added, and then the mixture was allowed to warm to room temperature. The upper solution was removed by syringe, and the oily crystals remaining were washed with diethyl ether. The residues were dissolved in dry CH_2Cl_2 (8 mL). The solution was diluted with diethyl ether (8 mL) and then kept in a freezer. The title complex was obtained as dark brown needles (28 mg, 79%). Mp: 169 °C dec. IR (KBr): 1816 cm^{-1}. ^{1}H NMR (400 MHz, acetone-d_6): δ 2.10 (s, 6H, CH_3), 2.28 (s, 6H, CH_3), 5.61 (s, 5H, η-C_5H_5 in Rc), 5.70 (s, 5H, η-C_5H_5), and 7.18−7.52 (m, 30H, Ph). ^{13}C NMR (100 MHz, acetone-d_6): δ 11.58 (CH_3), 90.32 (η-C_5H_5), 97.95 (η-C_5H_5), 103.53 (η-C_5Me_4), 112.08 (η-C_5Me_4), 129.71 (t, J = 5.1 Hz, *m*-Ph), 129.99 (ipso-C_5Me_4), 132.24 (*p*-Ph), 134.17 (t, J = 5.4 Hz, *o*-Ph), 135.04 (m, ipso-Ph), 172.67 (RuCCC), and 315.41 (t, J = 15.2 Hz, RuCCC). ^{31}P NMR (162 MHz, acetone-d_6): δ 42.34. Anal. Calcd for $C_{57}H_{52}B_2F_8P_2Ru_2$·1/2$CH_2Cl_2$: C, 56.74; H, 4.39. Found: C, 56.53; H, 4.51.

[(η-C_5H_5)Ru(μ-η^6:η^1-C_5Me_4C=C=)Ru(dppe)(η-C_5H_5)](BF$_4$)$_2$ (19). This complex was prepared from **10** according to the above procedure, yielding dark brown needles (81%). Mp: 180 °C dec. IR (KBr): 1825 cm^{-1}. ^{1}H NMR (400 MHz, acetone-d_6): δ 1.71 (s, 6H, CH_3), 2.07 (s, 6H, CH_3), 3.31 (m, 4H, PCH_2), 4.90 (s, 5H, η-C_5H_5 in Rc), 6.04 (s, 5H, η-C_5H_5), and 7.39−7.87 (m, 20H, Ph). ^{13}C NMR (100 MHz, acetone-d_6): δ 11.19 (CH_3),

11.31 (CH_3), 28.07 (m, PCH_2), 89.50 (η-C_5H_5), 94.89 (η-C_5H_5), 103.43 (η-C_5Me_4), 110.98 (η-C_5Me_4), 116.55 (ipso-C_5Me_4), 130.16 (d, J = 5.1 Hz, *m*-Ph), 130.25 (d, J = 4.9 Hz, *m*-Ph), 132.21 (*p*-Ph), 132.16 (d, J = 5.7 Hz, *o*-Ph), 132.68 (*p*-Ph), 133.71 (d, J = 5.4 Hz, *o*-Ph), 167.01 (Ru*C*C), and 313.45 (t, J = 16.7 Hz, Ru*C*C). No signal was observed for ipso-Ph. ^{31}P NMR (162 MHz, acetone-d_6): δ 76.98. Anal. Calcd for $C_{47}H_{46}B_2F_8P_2Ru_2$: C, 53.84; H, 4.42. Found: C, 53.63; H, 4.41.

[(η-C_5H_5)Ru(μ-η^6:η^1-$C_5Me_4C{=}C{=}$)Ru(dppe)(η-C_5Me_5)](BF_4)$_2$ (20). This complex was prepared from **11** according to the procedure described for complex **17**. The complex was recrystallized from acetone/diethyl ether, to give dark brown needles (70%). Mp: 207 °C dec. IR (KBr): 1803 cm^{-1}. ^{1}H NMR (400 MHz, acetone-d_6): δ 1.76 (s, 6H, CH_3), 1.84 (s, 15H, η-C_5Me_5), 2.07 (s, 6H, CH_3), 3.00 (m, 2H, PCH_2), 3.22 (s, 2H, PCH_2), 4.92 (s, 5H, η-C_5H_5 in Rc), and 7.19−7.72 (m, 20H, Ph). ^{13}C NMR (100 MHz, acetone-d_6): δ 10.96 (CH_3), 11.32 (CH_3), 28.88 (m, PCH_2), 88.75 (η-C_5H_5), 102.73 (η-C_5Me_4), 106.54 (η-C_5Me_5), 111.97 (η-C_5Me_4), 116.48 (ipso-C_5Me_4), 129.92 (d, J = 10.0 Hz, *m*-Ph), 130.34 (d, J = 10.0 Hz, *m*-Ph), 132.58 (*p*-Ph), 132.84 (*p*-Ph), 133.32 (d, J = 10.0 Hz, *o*-Ph), 133.36 (d, J = 10.0 Hz, *o*-Ph), 134.33 (m, ipso-Ph), 134.90 (m, ipso-Ph), 169.57 (Ru*C*C), and 311.58 (t, J = 16.0 Hz, Ru*C*C). ^{31}P NMR (162 MHz, acetone-d_6): δ 72.50. Anal. Calcd for $C_{52}H_{56}B_2F_8P_2Ru_2$: C, 55.82; H, 5.05. Found: C, 56.10; H, 5.18.

Structure Determination. The crystallographic data are listed in Table 1 for **9**, **10**, **14**, and **19**. Data collection for **9** was performed at room temperature on a Mac Science MXC18K diffractometer with graphite-monochromated Mo Kα radiation and an 18-kW rotating anode generator. The structure was solved with the SIR method in CRYSTAN-G (software package for structure determination) and refined by a full-matrix least-squares procedure. Absorption correction with the ψ-scan method and anisotropic refinement for non-hydrogen atoms were carried out. Data collections of crystal data for **10**, **14**, and **19** were performed at room temperature by the Weissenberg method on a Mac Science DIP3000 image processor with graphite-monochromated Mo Kα radiation and an 18-kW rotating anode generator. The structures were solved with the Dirdif-Patty or SIR method in Crystan-G (software-package for structure determination) and refined finally by a full-matrix least-squares procedure. Absorption correction with the Difab method and anisotropic refinement for non-hydrogen atoms were carried out. The hydrogen atoms, located from difference Fourier maps or calculation, were isotopically refined.

Acknowledgment. The present work was supported by a Grant-in Aid for Science Research (No. 10640538) from the Ministry of Education, Science, and Culture of Japan. We thank Dr. Akiko Nakano at Mac Science Co., Ltd. for some valuable advice in the structural analysis of complex **19**.

Supporting Information Available: Tables of crystallographic data, fractional atomic coordinates, anisotropic thermal parameters, interatomic distances, bond angles, and least-squares planes and ORTEP drwawings showing the complete numbering system for complexes **9**, **10**, **14**, and **19**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990138U