Synthesis, Characterization, and Substituent Effects of Binuclear Ruthenium Vinyl Complexes [RuCl(CO)(PMe$_3$)$_3$]$_2$(μ-CH=CH−Ar−CH=CH)

Xiang Hua Wu, Shan Jin, Jin Hua Liang, Zi Yong Li, Guang-ao Yu, and Sheng Hua Liu*

Key Laboratory of Pesticide and Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, People's Republic of China

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A series of binuclear ruthenium vinyl complexes [RuCl(CO)(PMe$_3$)$_3$]$_2$(μ-CH=CH−Ar−CH=CH) (Ar = C_6H_4 (**6a**), $C_6H_3CH_3$ (**6b**), $C_6H_3OCH_3$ (**6c**), C_6H_3F (**6d**), C_6H_3Cl (**6e**), C_6H_3Br (**6f**), C_6H_3CN (**6g**), $C_6H_3NO_2$ (**6h**), $C_6H_2(CH_3)_2$-2,5 (**6i**), $C_6H_2(OCH_3)_2$-2,5 (**6j**), $C_6H_2(F)_2$-2,5 (**6k**), $C_6H_2(CF_3)_2$-2,5 (**6l**), and $C_6H_3CF_3$ (**6m**)) have been prepared. The respective products have been characterized by elemental analyses, NMR spectrometry, and UV/vis spectrophotometry. The structures of **6h**, **6i**, and **6j** have been established by X-ray crystallography. Electrochemical studies have revealed that intermetallic electron communication between the two Ru centers may be fine-tuned by modification of the bridging spacers, that is, by introducing one or two substituent groups on the 1,4-diethenylphenylene bridge. Electron-releasing substituents have been found to facilitate electron communication between the two metal centers.

Introduction

In the emerging field of molecular electronics, the promise of "tuning" the electronic properties of materials has motivated investigations into the dependence of electronic structure on the functional groups present. For example, electron transfer in organometallic complexes can be perturbed to different extents by electroactive end groups in conjunction with various saturated or conjugated bridges. The effectiveness of this perturbation is highly dependent on the medium, the molecular topology, the nature of the metal complex, and whether the connecting bridge groups are electron-rich or -deficient, bulky or flexible, long- or short-chain, and oxidizable or reducible. By judicious control of these parameters, molecular wires exhibiting quite different electronic properties have been investigated.[1]

Highly unsaturated rigid $-(C\equiv C)_n-$ and $-(C=C)_n-$ bridges offer extended π-systems and have been recognized as being particularly efficient in facilitating electronic transfer.[2−4] In this context, a vast number of mono- and bimetallic complexes with polyynediyl or polyacetylene bridges have been extensively studied.[5−24] For example, as model complexes designed to aid understanding of the influence of substituents on the bonding properties within the metal-acetylide backbone, mononuclear metal (Fe or Ru) σ-arylacetylides [(η^2-dppe)(η^5-C_5Me_5)M(C≡C)-1,4-(C_6H_4)X] have recently been reported by Paul and Bruce et al.[4] Previously, substituent effects in a series of $M_2(DAvF)_4$ (M = Mo, Ni, Ru, Rh; DAvF = diarylformamidinate) and $Ru_2(DMBA)_4$ (DMBA = *N,N′*-dimethylbenzamidinate)bimetallic complexes were studied by Ren et al.[25] Chen et al. have also shown that the electronic properties of binuclear ruthenium polyynediyl complexes largely depend on the ancillary ligands present; intermetallic electronic communication was found to be favored by introducing an electron-donating substituent, but attenuated by an electron-withdrawing substituent.[5a]

In contrast, there have been few studies on the influence of substituents attached to bridging ligands on the electronic communication between the two metal centers. In the work described herein, a series of binuclear ruthenium complexes [RuCl(CO)(PMe$_3$)$_3$]$_2$(μ-CH=CH−Ar−CH=CH), in which the 1,4-diethenylphenylene bridge bears one or two substituent

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* Corresponding author. E-mail: chshliu@mail.ccnu.edu.cn.

(1) See for instance: (a) de Montigny, F.; Argouarch, G.; Roisnel, T.; Toupet, L.; Lapinte, C.; Lam, S. C.-F.; Tao, C.-H.; Yam, V. W.-W. *Organometallics* **2008**, *27*, 1912. (b) Paul, F.; Goeb, S.; Justaud, F.; Argouarch, G.; Toupet, L.; Ziessel, R. F.; Lapinte, C. *Inorg. Chem.* **2007**, *46*, 9036. (c) Samoc, M.; Gauthier, N.; Cifuentes, M. P.; Paul, F.; Lapinte, C.; Humphrey, M. G. *Angew. Chem., Int. Ed.* **2006**, *45*, 7376. (d) Cifuentes, M. P.; Humphrey, M. G.; Morall, J. P.; Samoc, M.; Paul, F.; Roisnel, T.; Lapinte, C. *Organometallics* **2005**, *24*, 4280. (e) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, *178−180*, 431. (f) Bruce, M. I.; Costuas, K.; Ellis, B. G.; Halet, J.-F.; Low, P. J.; Moubaraki, B.; Murray, K. S.; Ouddaï, N.; Perkins, G. J.; Skelton, B. W.; White, A. H. *Organometallics* **2007**, *26*, 3735. (g) Bruce, M. I.; Costuas, K.; Davin, T.; Halet, J.-F.; Kramarczuk, K. A.; Low, P. J.; Nicholson, B. K.; Perkins, G. J.; Roberts, R. L.; Skelton, B. W.; Smithc, M. E.; White, A. H. *Dalton Trans.* **2007**, 5387. (h) Bruce, M. I.; Zaitseva, N. N.; Low, P. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2006**, *691*, 4273. (i) Bruce, M. I.; Costuas, K.; Davin, T.; Ellis, B. G.; Halet, J.-F.; Lapinte, C.; Low, P. J.; Smith, M. E.; Skelton, B. W.; Toupet, L.; White, A. H. *Organometallics* **2005**, *24*, 3864–1. (j) Bruce, M. I.; Low, P. J. *Adv. Organomet. Chem.* **2004**, *50*, 179. (k) Farley, R. T.; Zheng, Q.; Gladysz, J. A.; Schanze, K. S. *Inorg. Chem.* **2008**, *47*, 2955. (l) Stahl, J.; Mohr, W.; de Quadras, L.; Peters, T. B.; Bohling, J. C.; Martín-Alvarez, J. M.; Owen, G. R.; Hampel, F.; Gladysz, J. A. *J. Am. Chem. Soc.* **2007**, *129*, 8282. (m) de Quadras, L.; Bauer, E. B.; Mohr, W.; Bohling, J. C.; Peters, T. B.; Martín-Alvarez, J. M.; Hampel, F.; Gladysz, J. A. *J. Am. Chem. Soc.* **2007**, *129*, 8296. (n) Szafert, S.; Gladysz, J. A. *Chem. Rev.* **2006**, *106*, 1. (o) Szafert, S.; Gladysz, J. A. *Chem. Rev.* **2003**, *103*, 4175. (p) Maurer, J.; Sarkar, B.; Schwederski, B.; Kaim, W.; Winter, R. F.; Záliš, S. *Organometallics* **2006**, *25*, 3701. (q) Winter, R. F.; Záliš, S. *Coord. Chem. Rev.* **2004**, *248*, 1565. (r) Ren, T. *Organometallics* **2005**, *24*, 4854. (s) Fan, Y.; Zhang, L.-Y.; Dai, F.-R.; Shi, L.-X.; Chen, Z.-N. *Inorg. Chem.* **2008**, *47*, 2811. (t) Gao, L.-B.; Liu, S.-H.; Zhang, L.-Y.; Shi, L.-X.; Chen, Z.-N. *Organometallics* **2006**, *25*, 506. (u) Rigaut, S.; Touchard, D.; Dixneuf, P. H. *Coord. Chem. Rev.* **2004**, *248*, 1585. (v) Evans, D. H. *Chem. Rev.* **2008**, *108*, 2113. (w) Schwab, P. F. H.; Smith, J. R.; Michl, J. *Chem. Rev.* **2005**, *105*, 1197. (x) Ceccon, A.; Santi, S.; Orian, L.; Bisello, A. *Coord. Chem. Rev.* **2004**, *248*, 683. (y) Schwab, P. F. H.; Levin, M. D.; Michl, J. *Chem. Rev.* **1999**, *99*, 1863.

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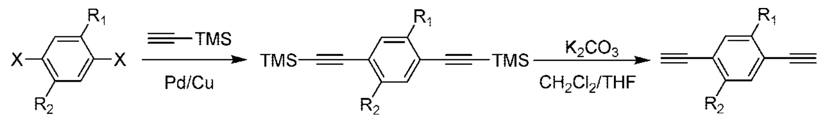
Scheme 1

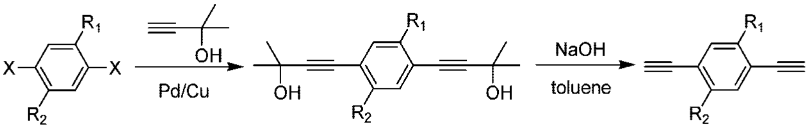


X = I, Br
$R_1 = R_2 = H$, **1a**
$R_1 = H, R_2 = CH_3$, **1b**
$R_1 = H, R_2 = OCH_3$, **1c**
$R_1 = H, R_2 = F$, **1d**
$R_1 = H, R_2 = Cl$, **1e**
$R_1 = H, R_2 = Br$, **1f**
$R_1 = H, R_2 = CN$, **1g**
$R_1 = H, R_2 = NO_2$, **1h**
$R_1 = R_2 = CH_3$, **1i**
$R_1 = R_2 = OCH_3$, **1j**
$R_1 = R_2 = F$, **1k**

$R_1 = R_2 = H$, **2a**
$R_1 = H, R_2 = CH_3$, **2b**
$R_1 = H, R_2 = OCH_3$, **2c**
$R_1 = H, R_2 = F$, **2d**
$R_1 = H, R_2 = Cl$, **2e**
$R_1 = H, R_2 = Br$, **2f**
$R_1 = H, R_2 = CN$, **2g**
$R_1 = H, R_2 = NO_2$, **2h**
$R_1 = R_2 = CH_3$, **2i**
$R_1 = R_2 = OCH_3$, **2j**
$R_1 = R_2 = F$, **2k**

$R_1 = R_2 = H$, **3a**
$R_1 = H, R_2 = CH_3$, **3b**
$R_1 = H, R_2 = OCH_3$, **3c**
$R_1 = H, R_2 = F$, **3d**
$R_1 = H, R_2 = Cl$, **3e**
$R_1 = H, R_2 = Br$, **3f**
$R_1 = H, R_2 = CN$, **3g**
$R_1 = H, R_2 = NO_2$, **3h**
$R_1 = R_2 = CH_3$, **3i**
$R_1 = R_2 = OCH_3$, **3j**
$R_1 = R_2 = F$, **3k**

Scheme 2

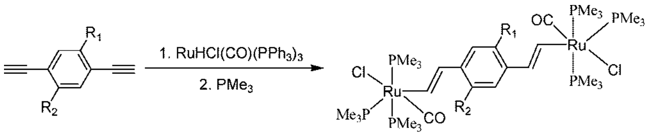


X = I, Br
$R_1 = R_2 = CF_3$, **1l**
$R_1 = H, R_2 = CF_3$, **1m**

$R_1 = R_2 = CF_3$, **4a**
$R_1 = H, R_2 = CF_3$, **4b**

$R_1 = R_2 = CF_3$, **5a**
$R_1 = H, R_2 = CF_3$, **5b**

Scheme 3



$R_1 = R_2 = H$, **3a**
$R_1 = H, R_2 = CH_3$, **3b**
$R_1 = H, R_2 = OCH_3$, **3c**
$R_1 = H, R_2 = F$, **3d**
$R_1 = H, R_2 = Cl$, **3e**
$R_1 = H, R_2 = Br$, **3f**
$R_1 = H, R_2 = CN$, **3g**
$R_1 = H, R_2 = NO_2$, **3h**
$R_1 = R_2 = CH_3$, **3i**
$R_1 = R_2 = OCH_3$, **3j**
$R_1 = R_2 = F$, **3k**
$R_1 = R_2 = CF_3$, **5a**
$R_1 = H, R_2 = CF_3$, **5b**

$R_1 = R_2 = H$, **6a**
$R_1 = H, R_2 = CH_3$, **6b**
$R_1 = H, R_2 = OCH_3$, **6c**
$R_1 = H, R_2 = F$, **6d**
$R_1 = H, R_2 = Cl$, **6e**
$R_1 = H, R_2 = Br$, **6f**
$R_1 = H, R_2 = CN$, **6g**
$R_1 = H, R_2 = NO_2$, **6h**
$R_1 = R_2 = CH_3$, **6i**
$R_1 = R_2 = OCH_3$, **6j**
$R_1 = R_2 = F$, **6k**
$R_1 = R_2 = CF_3$, **6l**
$R_1 = H, R_2 = CF_3$, **6m**

groups, has been synthesized. The variation in the electrochemical properties of these binuclear ruthenium complexes on varying the vinyl bridging ligands has been investigated by voltammetric techniques in order to study the influence of the substituents on the electronic communication between the two Ru centers.

Results and Discussion

Syntheses and Characterization. Substituted 1,4-diethynylbenzene derivatives were synthesized by a sequence of coupling and deprotection reactions. The trimethylsilyl-protected bis(ethynyl) ligand precursors were synthesized by the palladium-catalyzed coupling of trimethylsilylethyne with dibromo/diiodoaryls (Scheme 1).[26] Under these conditions, compounds **2a−k** were obtained in yields ranging from 10 to 85%. In the case of trifluoromethyl substituents, however, this reaction did not proceed satisfactorily. We therefore devised another approach to access the mono- and bis-trifluoromethyl-substituted derivatives and found that the protected diethynylbenzenes **4a** and **4b** could be conveniently obtained by the coupling of **1l** and **1m** with 2-methylbut-3-yn-2-ol (Scheme 2).[27] The ligand precursors were smoothly converted into the corresponding diterminal alkynes **3a−k** by removal of the trimethylsilyl protecting groups with dilute aqueous KOH in MeOH/THF or with K_2CO_3 in MeOH/CH_2Cl_2, while **5a** and **5b** were obtained

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by treating **4a** and **4b** with NaOH in toluene. Diethynylbenzenes **3a**−**k** and **5a**,**b** were characterized by elemental analyses and by ^1H and ^{13}C NMR spectrometry.

The general synthetic route for the preparation of binuclear ruthenium vinyl complexes is outlined in Scheme 3. Diethynylbenzenes **3a**−**k** and **5a**,**b** were reacted with the ruthenium hydride complex $[RuHCl(CO)(PPh_3)_3]$ to give the insertion products $[(PPh_3)_2Cl(CO)Ru]_2(\mu\text{-}CH{=}CH{-}Ar{-}CH{=}CH)$, which were not isolated because they are air-sensitive, especially in solution. PMe_3 was then added to give the corresponding six-coordinated complexes **6**. These complexes were characterized by NMR. The PMe_3 ligands in **6** are meridionally coordinated to ruthenium, as indicated by an AM_2 pattern in the $^{31}P\{^1H\}$ NMR spectrum. The ^1H NMR spectrum (in $CDCl_3$) of **6a** features the two Ru-CH proton signals at $\delta = 7.96$ ppm (**6i**, 7.88; **6j**, 7.88; **6k**, 8.10; **6l**, 8.25), this chemical shift being similar to that found in $[RuCl(CO)(PMe_3)_3]_2(\mu\text{-}(CH{=}CH)_n)$.[5d,g,h] However, two different Ru-CH proton signals are observed in the spectra of the other monosubstituted binuclear complexes. For example, the ^1H NMR spectrum of **6h** displays the Ru-CH signals at $\delta = 8.11$ and 8.26 ppm, respectively, which may be attributed to the asymmetrical structure of this complex. Two different Ru−C═CH proton signals are also observed in the spectra of monosubstituted vinyl complexes. The vinylic proton is in a *trans* geometry and the acetylene is *cis*-inserted into the Ru−H bond, as confirmed by the X-ray structures of **6h**, **6i**, and **6j** (Figures 1−3). Similar ruthenium complexes $[RuCl(CO)(P^iPr_3)_3]_2(\mu\text{-}CH{=}CH\text{-}C_6H_4{-}CH{=}CH)$,[28] $[RuHCl(CO)(PPh_3)_3]_2$ $(\mu\text{-}CH{=}CH\text{-}C_6H_4{-}CH{=}CH)$,[29] $[Fc(CH{=}CH)_3RuCl(CO)(PMe_3)_3]$,[5c] 1,3,5-$[Cl(CO)(PMe_3)_3RuCH{=}CH]_3C_6H_3$,[5f] and $[RuCl(CO)(P^iPr_3)_3]_4(HC{=}CHC_6H_4)(C{=}C)$[30] have recently been reported.

X-ray Structures of 6h, 6i, and 6j. The molecular structures of **6h**, **6i**, and **6j** were determined by X-ray crystallography. The crystallographic details are given in Table 1. Selected bond distances and angles for **6h**, **6i**, and **6j** are presented in Tables S1, S2, and S3, respectively (Supporting Information). The molecular structures of **6h**, **6i**, and **6j** are depicted in Figures 1−3, respectively. The rod-like binuclear ruthenium arrays in **6h**, **6i**, and **6j** consist of two $(PMe_3)_3Cl(CO)Ru$ end groups linked by a diethenylphenylene carbon chain through Ru−C

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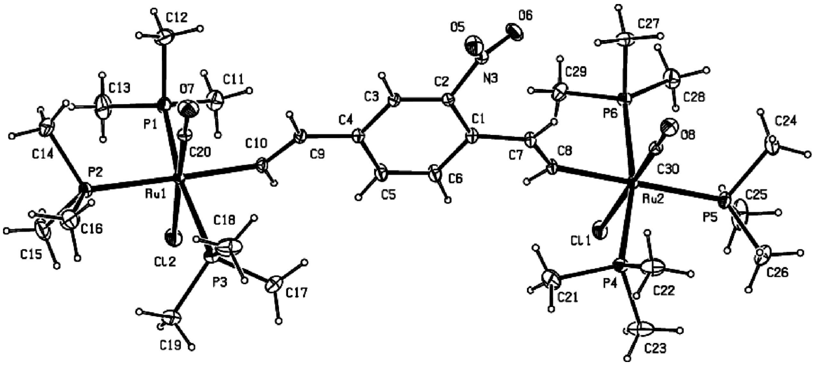

Figure 1. Molecular structure of **6h**.

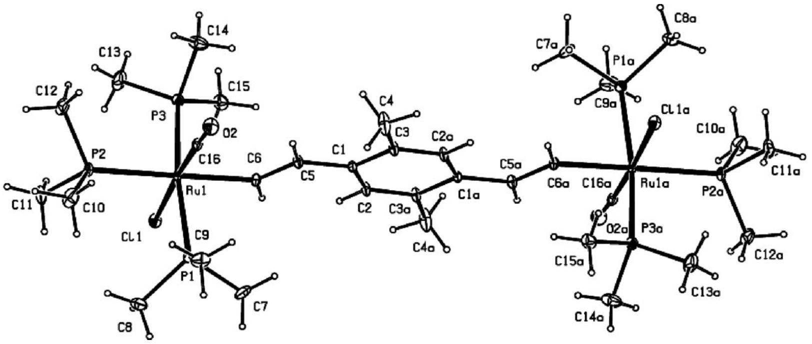

Figure 2. Molecular structure of **6i**.

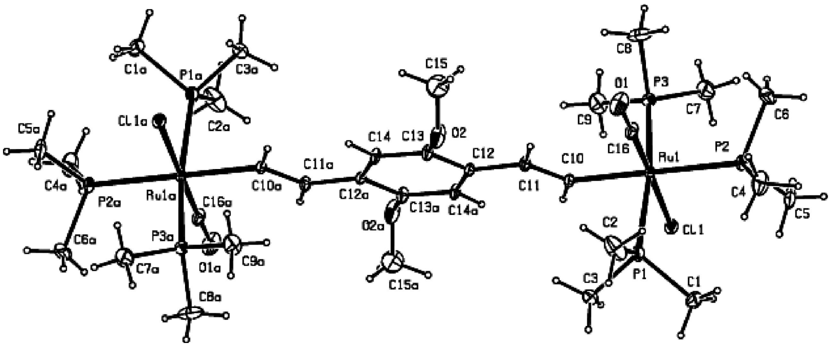

Figure 3. Molecular structure of **6j**.

σ-bonding. The molecular structure of **6h** is asymmetric due to the presence of one NO_2 group on the benzene ring, which prevents coplanarity of the carbon atoms of the μ-CH=CH−Ar−CH=CH unit, as shown in Figure 1. The dihedral angle between the double bond contiguous to the NO_2 group and the benzene ring is 15.73°. The carbon atoms of the benzene ring are nearly coplanar, with a dihedral angle between C(1)/C(2)/C(3) and C(1)/C(4)/C(5)/C(6) of 1.89°. The Ru1···Ru2 distance is 11.497 Å. The molecular structures of **6i** and **6j** are centrosymmetric, as shown in Figures 2 and 3. The compounds contain two Ru centers linked by a μ-CH=CH−Ar−CH=CH bridge (Ar = $C_6H_2(CH_3)_2$-2,5 (**6i**), $C_6H_2(OCH_3)_2$-2,5 (**6j**)). The two Ru centers are related by a pseudo-C_2 rotation axis. The Ru1···Ru1a distances in complexes **6b** and **6c** are 11.922 and 11.919 Å, respectively, which are slightly longer than that in complex **6h**. The carbon atoms of the μ-CH=CH−Ar−CH=CH units are nearly coplanar, with dihedral angles between the core benzene ring and the two vinyl groups of 5.23° (in **6i**) and 3.9° (in **6j**), respectively. The two double bonds are in the *trans* configuration. The Ru−C and C(α)−C(β) bond distances in complexes **6h**, **6i**, and **6j** are within the ranges of those reported for other ruthenium vinyl complexes.[31] The overall geometry about the two ruthenium centers in **6h**, **6i**, and **6j** closely resembles that in the bimetallic ruthenium complexes $[RuCl(CO)(PMe_3)_3]_2$-(μ-(CH=CH)$_n$).[5b,d,g,h] It is worth noting that the vinyl groups are essentially coplanar with Cl−Ru−CO. Such coplanarity of the vinyl group and CO is to be expected, due to the strong π-interaction between these ligands and the metal centers in such a conformation.[5b,d,g,h,32] The three complexes adopt the same crystal system and space group, as can be seen in Table 1.

Electronic Absorption Spectroscopy. The electronic properties of this series of vinyl bimetallic complexes have been investigated by optical absorption spectroscopy. A rather intense

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Table 1. Crystal Data, Date Collection, and Refinement Parameters for 6h, 6i, and 6j

	6h	**6i**	**6j**
formula	$C_{30}H_{61}Cl_2NO_4P_6Ru_2$	$C_{32}H_{66}Cl_2O_2P_6Ru_2$	$C_{32}H_{66}Cl_2O_4P_6Ru_2$
fw	958.66	941.71	973.71
temp (K)	295(2)	295(2)	292(2)
cryst syst	monoclinic	monoclinic	monoclinic
space group	*P*2(1)/*n*	*P*2(1)/*n*	*P*2(1)/*n*
a (Å)	9.9338(5)	9.4873(5)	9.5551(4)
b (Å)	35.9326(17)	11.1223(6)	11.5199(5)
c (Å)	13.3665(12)	21.9002(11)	21.7440(9)
α (deg)	90.00	90	90.00
β (deg)	111.814(10)	97.0950(10)	97.3350(10)
γ (deg)	90.00	90	90.00
V ($Å^{-3}$)	4429.5(5)	2293.2(2)	2373.86(17)
Z	4	2	2
D_{calcd} (g cm^{-3})	1.438	1.364	1.362
cryst size (mm)	0.30 × 0.20 × 0.20	0.40 × 0.03 × 0.01	0.23 × 0.20 × 0.20
F(000)	1968	972	1004
diffractometer	KappaCCD	KappaCCD	KappaCCD
radiation	Mo Kα	Mo Kα	Mo Kα
abs coeff (mm^{-1})	1.050	1.009	0.980
θ range (deg)	1.74−27.00	1.87−27.00	1.89−27.00
hkl range	−11 to 12 −43 to 45 −17 to 17	−11 to 12 −13 to 14 −27 to 27	−12 to 12 −14 to 14 −24 to 27
total no. of rflns	49 729	20 559	18 249
no. of unique rflns	9638	4969	5161
no. of obsd rflns ($I > 2\sigma(I)$)	7398	4051	4429
no. of restraints/params	0/424	0/209	0/218
a, b for W^a	0.0711, 2.0601	0.0624, 2.9242	0.0597, 1.8048
final *R*	0.0556	0.0453	0.0515
R_w	0.1277	0.1074	0.1074
R (all date)	0.0754	0.0615	0.0515
R_w (all date)	0.1382	0.1268	0.1177
goodness of fit/F^2	1.030	1.065	1.079
largest diff peak, hole (e $Å^{-3}$)	0.952, −0.672	0.693, −0.794	0.979, −0.498

[a] $W = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, where $P = (F_o^2 + F_c^2)/3$.

Table 2. UV−vis Data for $[RuCl(CO)(PMe_3)_3]_2$-(μ-CH=CH−Ar−CH=CH) Complexes 6 in CH_2Cl_2

complex	abs, nm ($10^{-3}\epsilon$, M^{-1} cm^{-1})
6a ($R_1 = R_2 = H$)	335 (10.6)
6b ($R_1 = H$, $R_2 = CH_3$)	340 (15.9)
6c ($R_1 = H$, $R_2 = OCH_3$)	345 (15.6)
6d ($R_1 = H$, $R_2 = F$)	344 (15.8)
6e ($R_1 = H$, $R_2 = Cl$)	344 (15.7)
6f ($R_1 = H$, $R_2 = Br$)	343 (15.5)
6g ($R_1 = H$, $R_2 = CN$)	339 (7.6)
6h ($R_1 = H$, $R_2 = NO_2$)	338 (15.3),434 (2.9)
6i ($R_1 = R_2 = CH_3$)	337 (11.7)
6j ($R_1 = R_2 = OCH_3$)	357 (11.5)
6k ($R_1 = R_2 = F$)	349 (13.8)
6l ($R_1 = R_2 = CF_3$)	350 (13.7)
6m ($R_1 = H$, $R_2 = CF_3$)	343 (15.4)

Table 3. Electrochemical Data for Complexes 6a−6m[a]

complex	$E_{1/2}$(A)	ΔE_p	i_b/i_f[b]	$E_{1/2}$(B)	$\Delta E_{1/2}$[c]	K_c[d]
6a ($R_1 = R_2 = H$)	0.30	0.079	0.91	0.59	0.29	8.0×10^4
6b ($R_1 = H$, $R_2 = CH_3$)	0.24	0.086	0.74	0.54	0.30	1.2×10^5
6c ($R_1 = H$, $R_2 = OCH_3$)	0.19	0.075	0.73	0.50	0.31	1.7×10^5
6d ($R_1 = H$, $R_2 = F$)	0.33	0.076	0.74	0.59	0.26	2.5×10^4
6e ($R_1 = H$, $R_2 = Cl$)	0.37	0.090	0.63	0.61	0.24	1.1×10^4
6f ($R_1 = H$, $R_2 = Br$)	0.37	0.077	0.61	0.61	0.24	1.1×10^4
6g ($R_1 = H$, $R_2 = CN$)	0.46	0.068	0.33	0.66	0.20	2.4×10^3
6h ($R_1 = H$, $R_2 = NO_2$)	0.52	0.088	0.36	0.71	0.19	1.6×10^3
6i ($R_1 = R_2 = CH_3$)	0.20	0.078	0.72	0.50	0.30	1.2×10^5
6j ($R_1 = R_2 = OCH_3$)	0.10	0.077	0.72	0.46	0.35	8.2×10^5
6k ($R_1 = R_2 = F$)	0.41	0.071	0.59	0.64	0.23	7.7×10^3
6l ($R_1 = R_2 = CF_3$)	0.57	0.087	0.35	0.75	0.18	1.1×10^3
6m ($R_1 = H$, $R_2 = CF_3$)	0.42	0.075	0.70	0.64	0.22	5.2×10^3

[a] Potential data were determined in CH_2Cl_2 containing 1mmol dm^{-3} compound and 0.1 mol dm^{-3} Bu_4NPF_6. The Ag Ag^+ electrode (internal solution: 0.01 mol dm^{-3} $AgNO_3$ + 0.1 mol dm^{-3} Bu_4NPF_6 in acetonitrile; salt bridge: 0.1 mol dm^{-3} Bu_4NPF_6 in CH_2Cl_2) was used as a reference. [b] $i_b/i_f = i_{backward}/i_{forward}$. [c] $\Delta E_{1/2} = E_{1/2}(B) - E_{1/2}(A)$ denotes the potential difference between redox processes A and B. [d] The comproportionation constants, K_c, were calculated by the formula $K_c = \exp(\Delta E_{1/2}/25.69)$ at 298 K.[33]

electronic transition (except in the case of **6g**) is seen for these vinyl complexes in the region 330−440 nm (Table 2). For all of the complexes, energetic transitions are observed above 350 nm, which can be attributed to $\pi-\pi^*$ ligand-centered transitions. For the nitro complex **6h**, an additional broader and less intense transition is detected near 430 nm. The summarized absorptions account for the yellow colors of **6a−g** and **6i−m** and the unusual purple color of the complex **6h**.

Electrochemistry. The redox behavior of the binuclear complexes **6a−m** (1 mM in CH_2Cl_2) has been investigated by cyclic voltammetry and square-wave voltammetry techniques with 0.1 M *n*-Bu_4NPF_6 as the supporting electrolyte; pertinent data are compiled in Table 3. Plots of the cyclic voltammogram (CV) and the square-wave voltammogram (SWV) for some complexes **6** are depicted in Figures 4 and 5. All of the complexes **6a−m** undergo two consecutive, chemically and electrochemically one-electron oxidation processes, giving rise to redox waves A and B (Table 3) in the potential region from 0.10 to 0.75 V, corresponding to oxidation of $Ru_2^{II,II}$ to $Ru_2^{II,III}$ and then of $Ru_2^{II,III}$ to $Ru_2^{III,III}$. The first redox process of complex **6a** is reversible, with i_b/i_f being 0.91(Table 3). When the substituent group is a strong electron-withdrawing group, the first redox process of complexes **6g**, **6h**, and **6l** are irreversible at high positive potential. However, when the substituent group is a electron-donor group or a weak electron-withdrawing group (F, Cl, and Br), these complexes undergo a quasi-reversible one-eletron oxidation at moderately positive potential during the first redox process. The oxidation and reduction current peaks are typically separated by 80 ± 10 mV (Table 3). The second redox process of these complexes is irreversible.

As shown in Table 3, for complex **6a** with 1,4-diethenylphenylene as the spacer, the $\Delta E_{1/2}$ is 0.29 V with the corresponding K_c being 8.0×10^4. This rather large K_c for **6a** is indicative of

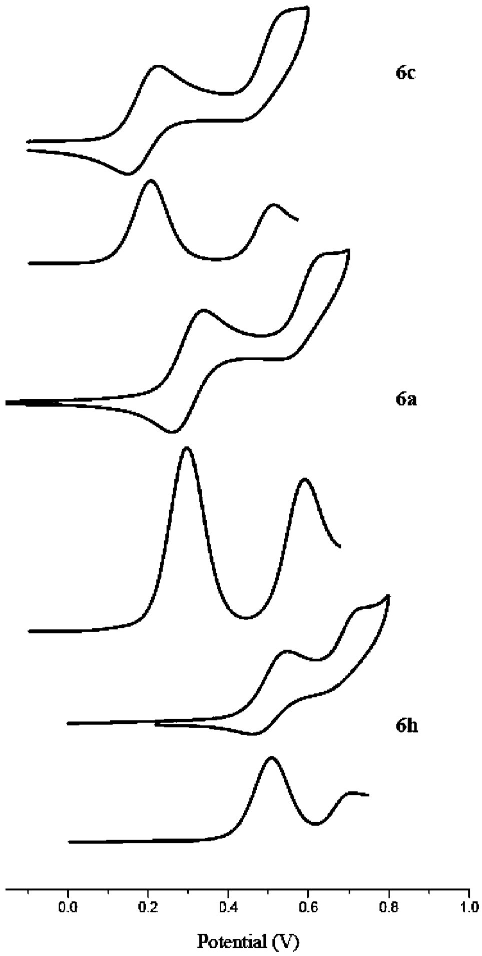

Figure 4. Cyclic voltammograms (CV) of complexes **6c**, **6a**, and **6h** in CH_2Cl_2/Bu_4NPF_6 at $\nu = 0.1$ V s^{-1}. Square-wave voltammograms (SWV) at $f = 10$ Hz. Potentials are given relative to the Ag/Ag^+ standard.

strong electronic communication transmitted through the 1,4-diethenylphenylene bridge. The voltammetric features of the other complexes showed an apparent dependence on the substituents attached to the 1,4-diethenylphenylene unit of the bridging ligands. When the substituent was weakly electron-donating, such as methyl (complex **6b**, with $\Delta E_{1/2}$ being 0.30 V and the corresponding K_c being 1.2×10^5), both the oxidation and reduction couples were cathodically shifted and the electronic interaction was slightly increased (Figure 4). As a strongly electron-donating group, methoxyl proved to be even more favorable for electron communication than methyl (complex **6c**, for which the $\Delta E_{1/2}$ is 0.31 V and the corresponding K_c is 1.7×10^5). By comparison of the $\Delta E_{1/2}$ and K_c values (Table 3), it can be seen that in **6d**, **6g**, **6h**, and **6m**, in which one electron-withdrawing substituent is attached to the 1,4-diethenylphenylene unit, the electronic communication rapidly decreases with increasing electron-withdrawing strength of these substituents ($NO_2 > CF_3 > CN > F$). Interestingly, careful examination of the $\Delta E_{1/2}$ and K_c values for complexes **6d**, **6e**, and **6f** (Table 3) reveals that they show the opposite trend of the above. That is to say, a gradual decrease in $\Delta E_{1/2}$ from 0.26 V (**6d**) to 0.24 V (**6e**) to 0.240 V (**6f**) was observed. The K_c values show a similar downward trend. For the monosubstituted complexes, the maximal $\Delta E_{1/2}$ difference between the complex bearing the most electron-releasing substituent (**6c**) and that bearing the most electron-withdrawing substituent (**6h**) is about 120 mV, and the respective K_c values show a decrease of about 2 orders of magnitude.

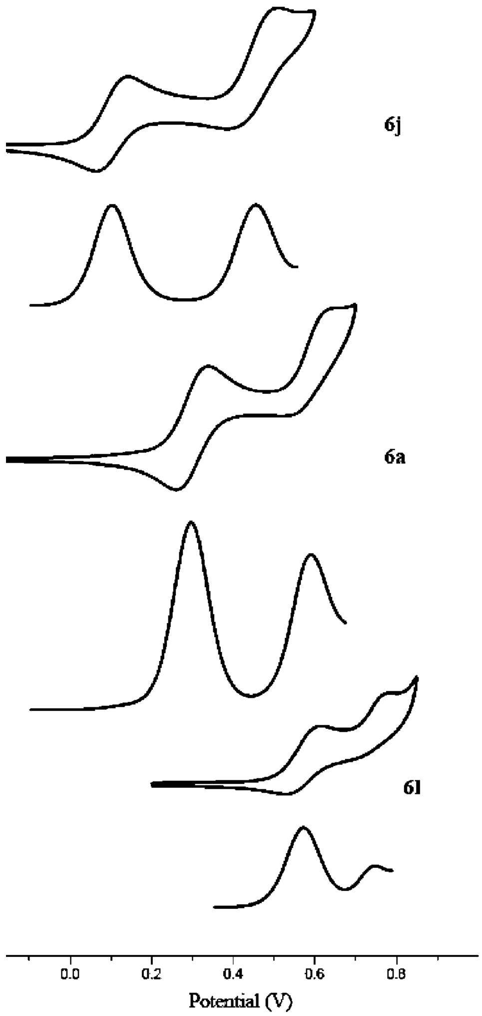

Figure 5. Cyclic voltammograms (CV) of complexes **6j**, **6a**, and **6l** in CH_2Cl_2/Bu_4NPF_6 at $\nu = 0.1$ V s^{-1}. Square-wave voltammograms (SWV) at $f = 10$ Hz. Potentials are given relative to the Ag/Ag^+ standard.

For complexes **6i**−**l**, in which two substituent groups are attached to the 1,4-diethenylphenylene unit, the $\Delta E_{1/2}$ values are 0.30, 0.35, 0.23, and 0.18 V, and the corresponding K_c values are 1.2×10^5, 8.2×10^5, 7.7×10^3, and 1.1×10^3, respectively (Table 3). These data illustrate that the electronic communication is rapidly attenuated with decreasing electron-releasing power of the substituents on the 1,4-diethenylphenylene unit ($OCH_3 > CH_3 > F > CF_3$), which is consistent with the conclusion reached for the monosubstituted complexes mentioned above. For the disubstituted complexes, the maximal $\Delta E_{1/2}$ difference between the complex bearing the most electron-releasing substituents (**6j**) and that bearing the most electron-withdrawing substituents (**6l**) is 0.17 V, and the respective K_c values show a decrease of about 3 orders of magnitude (Figure 5; Table 3).

As shown in Table 3, the $\Delta E_{1/2}$ difference between **6j** and **6a** is 0.06 V, which is larger than the difference of 0.02 V between **6c** and **6a**. The same trend is observed between **6l** and **6a** as well as between **6m** and **6a**, and their $\Delta E_{1/2}$ differences are 0.11 and 0.07 V, respectively. The results indicate the $\Delta E_{1/2}$

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and K_c values of the complexes bearing two strong electron-donating substituents are significantly higher than those of their monosubstituted counterparts, and the $\Delta E_{1/2}$ and K_c values of the complexes bearing two strong electron-withdrawing substituents are significantly lower than those of their monosubstituted counterparts. This explains why disubstitution has a greater effect than monosubstitution.

The result above showed the electronic communication between the metal centers is largely substituent independent. Attaching one or two electron-donating groups to the 1,4-diethenylphenylene unit favors metal−metal communication, whereas electron-withdrawing groups have the opposite effect. The result is in good agreement with the theoretical estimation by Vedova-Brook et al.[33a] and experimental results by Tao et al.[33b] The chemical nature of a substituent can shift the frontier molecular orbital (FMO) and alter the electron transport efficiency through the molecule.[33c] In the presence of an electron-withdrawing substituent, the bridging ligand should be more positive and therefore less favorable for electronic communication between their two metal residues. Conversely, in the presence of an electron-donating substituent, the bridging ligand should be more negatively charged and more favorable for electronic communication. Chen[5a] and Touchard[1u] reported the electrochemical studies of $\{(\mathrm{bph})(\mathrm{PPh_3})_2\mathrm{Ru}\}_2\{\mathrm{C{\equiv}C{-}Ar{-}C{\equiv}C}\}$ (bph = *N*-(benzoyl)-*N*′-(picolinylidene) hydrazine) and *trans*-$[\mathrm{Cl(dppe)_2Ru{=}C{=}C{=}CH{-}Ar{-}CH{=}C{=}C{=}Ru(dppe)_2Cl}](\mathrm{PF_6})_2$ (Ar = $\mathrm{C_4H_2S}$, $\mathrm{C_6H_4}$) and found the electron-richer thiophene ring (pyrrole) can enhance the electron communications.

Conclusions

We have reported here the synthesis, characterization, and electrochemical properties of a series of vinyl binuclear ruthenium complexes. Electrochemical studies have revealed that all of these vinyl complexes display two successive Ru-based one-electron processes and that intermetallic electronic communication between the two Ru centers may be fine-tuned by modification of the 1,4-diethenylphenylene bridging ligand. It has clearly been demonstrated that electron-releasing substituents facilitate electron communication between the two Ru centers.

Experimental Section

General Materials. All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were predried, distilled, and degassed prior to use, except those for spectroscopic measurements, which were of spectroscopic grade. The reagents ethynyltrimethylsilane, 2-methylbut-3-yn-2-ol, 1,4-bis(trifluoromethyl)benzene, 1,4-dibromo-2-methylbenzene (**1b**), 1,4-dibromo-2-fluorobenzene (**1d**), 1,4-dibromo-2-chlorobenzene (**1e**), 1,4-dibromo-2,5-difluorobenzene (**1k**), and 1,4-dibromo-2-(trifluoromethyl)benzene (**1m**) were purchased from Alfa Aesar. Others were commercially available. The starting materials $\mathrm{RuHCl(CO)(PPh_3)_3}$,[34] 1,4-diiodo-2-methoxybenzene (**1c**),[35] 2-bromo-1,4-diiodobenzene (**1f**),[36] 2,5-diiodobenzonitrile (**1g**),[37] 1,4-bis(trifluoromethyl)-2,5-diiodobenzene (**1l**),[38] 2-bromo-1,4-bis(2-(trimethylsilyl)ethynyl)benzene (**2f**),[36] 1,4-diethynylbenzene (**3a**),[39] 1,4-diethynyl-2-fluorobenzene (**3d**),[40] 1,4-diethynyl-2-nitrobenzene (**3h**),[39] 1,4-diethynyl-2,5-dimethylbenzene (**3i**),[41] 1,4-diethynyl-2,5-dimethoxybenzene (**3j**),[40,42] and 1,4-diethynyl-2,5-difluorobenzene (**3k**)[40] were prepared by the procedures described in literature methods.

Synthesis of 1,4-Diethynylbenzene Derivatives. 2-Methyl-1,4-bis(2-(trimethylsilyl)ethynyl)benzene (2b). 1,4-Dibromo-2-methylbenzene (0.5 g, 2.0 mmol), $\mathrm{PdCl_2(PPh_3)_2}$ (0.14 g, 0.2 mmol), and CuI (0.038 g, 0.2 mmol) were dissolved in tetrahydrofuran (30 mL) and diisopropylamine (1 mL). Then (trimethylsily)acetylene (0.43 g, 4.4 mmol) was added to the stirred solution. The reaction mixture was stirred at 40 °C for 24 h. The solvent was then evaporated, and dichloromethane was added to the residue and extracted with brine and water. The organic phases were dried with $\mathrm{Na_2SO_4}$. The crude product was purified by chromatography (Petroleum ether) to give 0.39 g (69% yield) of monoyne and 0.05 g (10% yield) of diyne (**2b**) as a yellow solid.

Diadduct: Anal. Calcd for $\mathrm{C_{17}H_{24}Si_2}$: C, 71.76; H, 8.50. Found: C, 71.64; H, 8.31. ^{1}H NMR (600 MHz, $\mathrm{CDCl_3}$): δ 0.24 (s, 9H, $\mathrm{SiCH_3}$), 0.25 (s, 9H, $\mathrm{SiCH_3}$), 2.39 (s, 3H, $\mathrm{CH_3}$), 7.21 (d, J = 7.8 Hz, 1H, Ph-H), 7.30 (s, 1H, Ph-H), 7.34 (d, J = 8.4 Hz, 1H, Ph-H). ^{13}C{^{1}H} NMR (150 MHz, $\mathrm{CDCl_3}$): δ −0.08, −0.02, 20.37, 95.68, 100.18, 103.51, 104.81, 122.93, 123.12, 128.97, 131.88, 132.73, 140.48.

2-Methoxy-1,4-bis(2-(trimethylsilyl)ethynyl)benzene (2c). To a solution of 1,4-diiodo-2-methoxybenzene[43] (0.736 g, 2.05 mmol), CuI (38 mg, 0.2 mmol), and Pd $\mathrm{(PPh_3)_2Cl_2}$ (140 mg, 0.2 mmol) in 50 mL of triethylamine was added (trimethylsilyl)acetylene (0.603 g, 6.14 mmol). The mixture was stirred at room temperature for 15 h. After removal of the solvent in vacuo, the desired product was separated from the starting material using silica gel with petroleum ether as eluent to yield 0.524 g (85%) of a brown solid. Anal. Calcd for $\mathrm{C_{17}H_{24}OSi_2}$: C, 67.94; H, 8.05. Found: C, 68.23; H, 8.25. ^{1}H NMR (600 MHz, $\mathrm{CDCl_3}$): δ 0.26 (s, 18H, $\mathrm{SiMe_3}$), 3.86 (s, 3H, $\mathrm{OCH_3}$), 6.93 (s, 1H, Ph-H), 7.00 (d, J = 1.2 Hz, 1H, Ph-H), 7.34 (d, J(= 7.8 Hz, 1H, Ph-H). ^{13}C{^{1}H} NMR (150 MHz, $\mathrm{CDCl_3}$): δ −0.14, −0.02, 55.80, 95.92, 100.33, 100.72, 104.62, 112.82, 113.73, 124.16, 124.28, 133.81, 159.77.

2-Chloro-1,4-bis(2-(trimethylsilyl)ethynyl)benzene (2e). Similar coupling procedures to those in **2e** were adopted using 1,4-dibromo-2-chlorobenzene (0.54 g, 2.0 mmol) to obtain a pale yellow solid in 78% yield. Anal. Calcd for $\mathrm{C_{16}H_{21}ClSi_2}$: C, 63.01; H, 6.94. Found: C, 63.46; H, 6.59. ^{1}H NMR (600 MHz, $\mathrm{CDCl_3}$): δ 0.24 (s, 9H, $\mathrm{SiCH_3}$), 0.27 (s, 9H, $\mathrm{SiCH_3}$), 7.25 (dd, J_1 = 1.8 Hz, J_2 = 1.2 Hz, 1H, Ph-H), 7.39 (d, J = 7.8 Hz, 1H, Ph-H), 7.47 (d, J = 1.2 Hz, 1H, Ph-H). ^{13}C{^{1}H} NMR (150 MHz, $\mathrm{CDCl_3}$): δ −0.21, −0.19, 97.60, 100.91, 102.14, 103.08, 123.05, 124.35, 129.69, 132.29, 133.18, 135.92.

2,5-Bis(2-(trimethylsilyl)ethynyl)benzonitrile (2g). Similar coupling procedures as in **2e** were adopted using 2,5-diiodobenzonitrile (0.70 g, 2.0 mmol) to obtain a pale yellow solid in 60% yield. Anal. Calcd for $\mathrm{C_{17}H_{21}NSi_2}$: C, 69.90; H, 7.16; N, 4.74. Found: C, 69.44; H, 7.04; N, 4.49. ^{1}H NMR (600 MHz, $\mathrm{CDCl_3}$): δ 0.25 (s, 9H, $\mathrm{SiCH_3}$), 0.29 (s, 9H, $\mathrm{SiCH_3}$), 7.48 (d, J = 7.8 Hz, 1H, Ph-H), 7.56

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(d, J = 7.8 Hz, 1H, Ph-H), 7.69 (s, 1H, Ph-H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ −0.47, −0.39, 99.09, 100.17, 101.92, 104.12, 115.94, 116.33, 123.80, 126.16, 132.25, 135.15, 135.46.

1,4-Diethynyl-2-methylbenzene (3b). 2-Methyl-1,4-bis(2-(trimethylsilyl)ethynyl)benzene (0.93 g, 3.3 mmol) was dissolved in a mixture of dichloromethane and methanol (40 mL, 1:1, v/v). Powdered potassium carbonate (4.1 g, 30 mmol) was added, and the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was diluted with dichloromethane and washed with brine. The organic layer was dried over $NaSO_4$, and the solvent removed in vacuo. The crude product was purified by chromatography (petroleum ether). Yield: 0.38 g (84%) of pale yellow solid. Anal. Calcd for $C_{11}H_8$: C, 94.25; H, 5.75. Found: C, 94. 52; H, 5.66. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.44 (s, 3H, CH_3), 3.17 (s, 1H, $\equiv$CH), 3.39 (s, 1H, $\equiv$CH), 7.28 (d, J = 8.4 Hz, 1H, Ph-H), 7.36 (s, 1H, Ph-H), 7.42 (d, J = 7.8 Hz, 1H, Ph-H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 20.28, 78.62, 81.89, 83.75, 83.22, 122.25, 122.45, 129.15, 132.29, 132.89, 140.69.

1,4-Diethynyl-2-methoxybenzene (3c). Methanol (20 mL) and aqueous KOH (7 mL, 20%) were added at room temperature to a stirred solution of 2-methoxy-1,4-bis(2-(trimethylsiyl)ethynyl)benzene (0.30 g, 1.0 mmol) in tetrahydrofuran (40 mL), and the reaction mixture was stirred for 2 h. After removal of the solvent in vacuo, the desired product was separated from starting material using silica gel with petroleum ether as eluent to yield 0.119 g (76%) of a brown solid. Anal. Calcd for $C_{11}H_8O$: C, 84.59; H, 5.16. Found: C, 84.36; H, 5.79. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.17 (s, 1H, $\equiv$CH), 3.38 (s, 1H, $\equiv$CH), 3.89 (s, 3H, OCH_3), 6.89 (s, 1H, Ph-H), 7.05 (d, J = 1.2 Hz, 1H, Ph-H), 7.39 (d, J = 7.8 Hz, 1H, Ph-H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 55.87, 78.82, 79.46, 82.78, 83.09, 112.09, 113.98, 123.69, 124.32, 133.89, 160.09.

2-Chloro-1,4-diethynylbenzene (3e). Similar desilylation procedures in **3b** were adopted to obtain an off-white solid in 83% yield. Anal. Calcd for $C_{10}H_5Cl$: C, 74.79; H, 3.14. Found: C, 74.37; H, 3.46. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.21 (s, 1H, $\equiv$CH), 3.46 (s, 1H, $\equiv$CH), 7.32 (dd, J = 1.2 Hz, 1H, Ph-H), 7.46 (d, J = 6.4 Hz, 1H, Ph-H), 7.52 (d, J = 0.6 Hz, 1H, Ph-H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 79.75, 80.21, 81.67, 84.16, 122.51, 123.81, 130.02, 132.56, 133.65, 136.12.

2-Bromo-1,4-diethynylbenzene (3f). Similar desilylation procedures in **3b** were adopted to obtain an off-white solid in 73% yield. Anal. Calcd for $C_{10}H_5Br$: C, 58.57; H, 2.46. Found: C, 58.79; H, 2.64. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.12 (s, 1H, $\equiv$CH), 3.38 (s, 1H, $\equiv$CH), 7.25 (dd, J_1 = 0.6 Hz, J_2 = 1.2 Hz, 1H, Ph-H), 7.34 (d, J = 7.8 Hz, 1H, Ph-H), 7.60 (d, J = 0.6 Hz, 1H, Ph-H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 80.35, 81.43, 81.48, 83.64, 123.80, 124.60, 125.14, 130.48, 133.56, 135.55.

2,5-Diethynylbenzonitrile (3g). Similar desilylation procedures in **3b** were adopted to obtain a white solid in 85% yield. Anal. Calcd for $C_{11}H_5N$: C, 87.40; H, 3.33; N, 9.27. Found: C, 87.76; H, 3.61; N, 9.08. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.31 (s, 1H, $\equiv$CH), 3.60 (s, 1H, $\equiv$CH), 7.56 (d, J = 6.0 Hz, 1H, Ph-H), 7.63 (d, J = 7.8 Hz, 1H, Ph-H), 7.75 (s, 1H, Ph-H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 79.09, 80.67, 81.55, 85.63, 116.11, 116.26, 123.39, 125.66, 132.92, 135.58, 135.77.

1,4-(2,5-Bis(trifluoromethyl)-1,4-phenylene)bis(2-methylbut-3-yn-2ol) (4a). To a solution of 1,4-bis(trifluoromethyl)-2,5-diiodobenzene (0.93 g, 2.0 mmol), CuI (38 mg, 0.2 mmol), and Pd $(PPh_3)_2Cl_2$ (140 mg, 0.2 mmol) in 30 mL of diisopropylamine was added 2-methylbut-3-yn-2-ol (1.0 mL, 10.0 mmol). The mixture was refluxed for 24 h. After removal of the solvent in vacuo, the desired product was separated from starting material using silica gel with petroleum ether/dichloromethane (1:1, v/v) as eluent to give the product as a yellow solid: 0.67 g (88%). Anal. Calcd for $C_{18}H_{16}F_6O_2$: C, 57.15; H, 4.26. Found: C, 57.34; H, 4.58. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.63 (s, 12H, CH_3), 7.81 (s, 2H, Ph-H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 30.85, 65.64, 102.71, 120.95, 123.24, 128.47, 131.25, 134.37.

1,4-(2-Trifluoromethyl-1,4-phenylene)bis(2-methylbut-3-yn-2ol) (4b). Similar coupling procedures as in **4a** were adopted using 1,4-dibromo-2-(trifluoromethyl)benzene (0.6 g, 2.0 mmol) to obtain a brownish-red oil in 85% yield. Anal. Calcd for $C_{17}H_{17}F_3O_2$: C, 65.80; H, 5.52. Found: C, 65.63; H, 5.35. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.61 (s, 6H, CH_3), 1.62 (s, 6H, CH_3), 7.44 (m, 2H, Ph-H), 7.64 (d, J = 1.2 Hz, 1H, Ph-H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 30.79, 31.8, 65.30, 77.68, 80.23, 83.90, 97.03, 101.10, 120.40, 122.77, 128.69, 133.51, 133.93.

1,4-Diethynyl-2,5-bis(trifluoromethyl)benzene (5a). Compound **4a** (0.62 g, 2.0 mmol) and NaOH (1.0 g, excess) were added to toluene (30 mL) in a flask. Then the reaction mixture was refluxed for 24 h. The solvent was evaporated and the residue was purified with flash column chromatography over silica gel, eluted with petroleum ether, to give **5a** as a yellow solid (0.33 g, 63%). Anal. Calcd for $C_{12}H_4F_6$: C, 54.98; H, 1.54. Found: C, 55.30; H, 1.89. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.55 (s, 2H, $\equiv$CH), 7.90 (s, 1H, Ph-H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 77.83, 86.49, 120.99, 121.27, 123.09, 132.22, 135.09.

1,4-Diethynyl-2-(trifluoromethyl)benzene (5b). Similar deprotection procedures in **5a** were adopted to obtain a brownish-red solid in 64% yield. Anal. Calcd for $C_{11}H_5F_3$: C, 68.05; H, 2.60. Found: C, 67.89; H, 2.80. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.24 (s, 1H, $\equiv$CH), 3.46 (s, 1H, $\equiv$CH), 7.57 (m, 2H, Ph-H), 7.76 (d, J = 1.2 Hz, 1H, Ph-H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 78.94, 80.61, 81.65, 84.78, 120.52, 121.93, 122.86, 123.74, 129.49, 132.40, 134.69.

Synthesis of Binuclear Rutheniun Complexes (6). 1,4-[RuCl(CO)$(PMe_3)_3CH{=}CH]_2C_6H_4$ (6a). To a suspension of RuHCl(CO)$(PPh_3)_3$ (0.762 g, 0.80 mmol) in CH_2Cl_2 (30 mL) was slowly added a solution of 1,4-diethynylbenzene (0.063 g, 0.50 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 30 min to give a red solution. Then a 1 M THF solution of PMe_3 (4.0 mL, 4.0 mmol) was added to the red solution. The mixture was stirred for another 15 h. The solution was filtered through a column of Celite. The volume of the filtrate was reduced to ca. 2 mL under vacuum. Addition of hexane (30 mL) to the residue produced a yellow solid, which was collected by filtration, washed with hexane, and dried under vacuum. Yield: 0.26 g, 70%. Anal. Calcd for $C_{30}H_{62}Cl_2O_2P_6Ru_2 \cdot C_6H_{12}$: C, 43.33; H, 7.48. Found: C, 43.04; H, 7.69. $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$): δ −21.01 (t, J = 21.1 Hz), −9.35 (d, J = 21.1 Hz). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.39 (t, J = 3.2, 36H, PMe_3), 1.45 (d, J = 6.8, 18H, PMe_3), 6.54 (m, 2H, Ar-CH=), 7.25 (s, 2H, Ar-H), 7.96 (m, 2H, Ru-CH=). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ 16.56(t, J = 15.2 Hz, PMe_3), 20.13 (d, J = 20.55 Hz, PMe_3), 124.34, 134.86, 137.79, 164.72, 202.48 (CO). IR (KBr, ν in cm^{-1}): 1915 (CO), 1554, 1420 (C=C aryl, vinyl).

1,4-[RuCl(CO)$(PMe_3)_3CH{=}CH]_2C_6H_3CH_3$ (6b). The synthesis is similar to **6a**, with 1,4-diethynylbenzene being replaced by 1,4-diethynyl-2-methylbenzene. Yellow solid, yield: 0.31 g, 83%. Anal. Calcd for $C_{31}H_{64}Cl_2O_2P_6Ru_2$: C, 40.13; H, 6.95. Found: C, 40. 45; H, 7.26. $^{31}P\{^{1}H\}$ NMR (240 MHz, $CDCl_3$): δ −19.14 (t, J = 21.9 Hz, PMe_3), −7.38 (d, J = 21.9 Hz, PMe_3). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.39 (t, J = 3.0 Hz, 36H, PMe_3), 1.47 (d, J = 6.0 Hz, 18H, PMe_3), 2.37 (s, 3H, CH_3), 6.50 (m, 1H, ArCH=), 6.74 (m, 1H, ArCH=), 7.09 (d, J = 7.8 Hz, 2H, Ph-H), 7.44 (d, J = 7.8 Hz, 1H, Ph-H), 7.89−7.97 (m, 2H, RuCH=). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ16.50(t, J = 14.55 Hz, PMe_3), 20.15 (d, J = 20.10 Hz, PMe_3), 53.34, 122.22, 123.91, 125.76, 131.90, 132.10, 134.86, 136.51, 137.49, 162.02, 163.85, 202.37 (CO). IR (KBr, ν in cm^{-1}): 1919 (CO), 1552, 1419 (C=C aryl, vinyl).

1,4-[RuCl(CO)$(PMe_3)_3CH{=}CH]_2C_6H_3OCH_3$ (6c). The synthesis is similar to **6a**, with 1,4-diethynylbenzene being replaced by 1,4-diethynyl-2-methoxybenzene. Yellow solid, yield: 0.33 g, 87%. Anal. Calcd for $C_{31}H_{64}Cl_2O_3P_6Ru_2$: C, 39.45; H, 6.84. Found: C, 39.72; H, 6.52. $^{31}P\{^1H\}$ NMR (160 MHz, CDCl$_3$): δ−19.66 (t, J = 21.9 Hz, PMe$_3$), −7.93 (d, J = 21.9 Hz, PMe$_3$). ^1H NMR (600 MHz, CDCl$_3$): δ 1.38 (t, J = 2.4 Hz, 36H, PMe$_3$), 1.47 (d, J = 6.6 Hz, 18H, PMe$_3$), 3.84 (s, 3H, OCH$_3$), 6.51 (m, 1H, ArCH=), 6.83 (m, 1H, ArCH=), 6.87 (d, J = 6.6 Hz, 1H, Ph-H), 6.90 (d, J = 7.2 Hz, 1H, Ph-H), 7.42 (d, J = 8.4 Hz, 1H, Ph-H), 7.89 (m, 1H, RuCH=), 7.94 (m, 1H, RuCH=). $^{13}C\{^1H\}$ NMR (150 MHz, CDCl$_3$): δ 16.54(t, J = 14.55 Hz, PMe$_3$), 20.09 (d, J = 20.10 Hz, PMe$_3$), 55.84, 106.98, 117.31, 124.44, 127.43, 128.45, 134.98, 138.60, 154.73, 162.30, 202.33 (CO). IR (KBr, ν in cm^{-1}): 1921 (CO), 1549, 1423 (C=C aryl, vinyl).

1,4-[RuCl(CO)(PMe$_3$)$_3$CH=CH]$_2$C$_6$H$_3$F (6d). The synthesis is similar to **6a**, with 1,4-diethynylbenzene being replaced by 1,4-diethynyl-2-fluorobenzene. Yellow solid, yield: 0.28 g, 74%. Anal. Calcd for $C_{30}H_{61}Cl_2FO_2P_6Ru_2$: C, 38.67; H, 6.60. Found: C, 38.59; H, 6.30. $^{31}P\{^1H\}$ NMR (240 MHz, CDCl$_3$): δ −19.04 (t, J = 21.9 Hz, PMe$_3$), −7.42 (d, J = 21.9 Hz, PMe$_3$). ^1H NMR (600 MHz, CDCl$_3$): δ 1.39 (t, J = 3.0 Hz, 36H, PMe$_3$), 1.47 (d, J = 7.2 Hz, 18H, PMe$_3$), 6.50 (m, 1H, ArCH=), 6.73 (m, 1H, ArCH=), 6.97 (t, J = 7.2 Hz, 1H, Ar-H), 7.43 (t, J = 7.2 Hz, 1H, Ar-H), 8.00−8.07 (m, 2H, RuCH=). $^{13}C\{^1H\}$ NMR (150 MHz, CDCl$_3$): δ 16.56(t, J = 14.55 Hz, PMe$_3$), 20.07 (d, J = 20.10 Hz, PMe$_3$), 110.07, 120.11, 124.91, 125.71, 133.81, 139.19, 157.99, 159.60, 165.79, 166.31, 202.23 (CO). IR (KBr, ν in cm^{-1}): 1916 (CO), 1553, 1418 (C=C aryl, vinyl).

1,4-[RuCl(CO)(PMe$_3$)$_3$CH=CH]$_2$C$_6$H$_3$Cl (6e). The synthesis is similar to **6a**, with 1,4-diethynylbenzene being replaced by 2-chloro-1,4-diethynylbenzene. Yellow solid, yield: 0.34 g, 89%. Anal. Calcd for $C_{30}H_{61}Cl_3O_2P_6Ru_2$: C, 38.00; H, 6.48. Found: C, 37.59; H, 6.16. $^{31}P\{^1H\}$ NMR (240 MHz, CDCl$_3$): δ−19.04 (t, J = 21.9 Hz, PMe$_3$), −7.45 (d, J = 21.9 Hz, PMe$_3$). ^1H NMR (600 MHz, CDCl$_3$): δ 1.38 (t, J = 3.0 Hz, 36H, PMe$_3$), 1.47 (d, J = 6.6 Hz, 18H, PMe$_3$), 6.47 (m, 1H, ArCH=), 6.92 (m, 1H, ArCH=), 7.12 (d, J = 1.2 Hz, 1H, Ar-H), 7.24 (d, J = 1.8 Hz, 1H, Ar-H), 7.45 (d, J = 7.8 Hz, 1H, Ar-H), 8.02−8.11 (m, 2H, RuCH=). $^{13}C\{^1H\}$ NMR (150 MHz, CDCl$_3$): δ 16.60(t, J = 14.55 Hz, PMe$_3$), 20.07 (d, J = 20.10 Hz, PMe$_3$), 122.75, 124.62, 124.80, 130.47, 133.46, 134.62, 138.84, 153.80, 165.31, 167.66, 202.22 (CO). IR (KBr, ν in cm^{-1}): 1922 (CO), 1545, 1421 (C=C aryl, vinyl).

1,4-[RuCl(CO)(PMe$_3$)$_3$CH=CH]$_2$C$_6$H$_3$Br (6f). The synthesis is similar to **6a**, with 1,4-diethynylbenzene being replaced by 2-bromo-1,4-diethynylbenzene. Yellow solid, yield: 0.28 g, 71%. Anal. Calcd for $C_{30}H_{61}BrCl_2O_2P_6Ru_2$: C, 36.30; H, 6.19. Found: C, 35.95; H, 5.73. $^{31}P\{^1H\}$ NMR (240 MHz, CDCl$_3$): δ −19.11 (t, J = 21.9 Hz, PMe$_3$), −7.48 (d, J = 21.9 Hz, PMe$_3$). ^1H NMR (600 MHz, CDCl$_3$): δ 1.38 (t, J = 3.0 Hz, 36H, PMe$_3$), 1.47 (d, J = 3.6 Hz, 18H, PMe$_3$), 6.46 (m, 1H, ArCH=), 6.87 (m, 1H, ArCH=), 7.16 (d, J = 7.8 Hz, 1H, Ar-H), 7.42 (s, 1H, Ar-H), 7.44 (s, 1H, Ar-H), 7.99−8.06 (m, 2H, RuCH=). $^{13}C\{^1H\}$ NMR (150 MHz, CDCl$_3$): δ 16.50(t, J = 14.55 Hz, PMe$_3$), 19.93 (d, J = 20.10 Hz, PMe$_3$), 121.69, 123.09, 123.34, 125.70, 127.83, 133.20, 136.07, 139.09, 165.63, 168.05, 202.09 (CO). IR (KBr, ν in cm^{-1}): 1921 (CO), 1541, 1420 (C=C aryl, vinyl).

1,4-[RuCl(CO)(PMe$_3$)$_3$CH=CH]$_2$C$_6$H$_3$CN (6g). The synthesis is similar to **6a**, with 1,4-diethynylbenzene being replaced by 2,5-diethynylbenzonitrile. Yellow solid, yield: 0.28 g, 74%. Anal. Calcd for $C_{31}H_{61}NCl_2O_2P_6Ru_2$: C, 39.66; H, 6.55; N, 1.49. Found: C, 39.93; H, 6.37; N, 1.14. $^{31}P\{^1H\}$ NMR (240 MHz, CDCl$_3$): δ−19.01 (t, J = 21.9 Hz, PMe$_3$), −7.38 (d, J = 21.9 Hz, PMe$_3$). ^1H NMR (600 MHz, CDCl$_3$): δ 1.38 (t, J = 3.0 Hz, 36H, PMe$_3$), 1.47 (d, J = 5.4 Hz, 18H, PMe$_3$), 6.49 (m, 1H, ArCH=), 6.97 (m, 1H, ArCH=), 7.39 (s, 1H, Ar-H), 7.41 (d, J = 6.4 Hz, 1H, Ar-H), 7.53 (d, J = 6.4 Hz, 1H, Ar-H), 8.13 (m, 1H, RuCH=), 8.41 (m, 1H, RuCH=). $^{13}C\{^1H\}$ NMR (150 MHz, CDCl$_3$): δ 16.55 (t, J = 14.55 Hz, PMe$_3$), 19.93 (d, J = 20.10 Hz, PMe$_3$), 107.26, 119.52, 123.97, 127.42, 128.35, 132.60, 135.07, 137.51, 139.77, 168.43, 173.93, 201.85 (CO). IR (KBr, ν in cm^{-1}): 1920 (CO), 1552, 1420 (C=C aryl, vinyl).

1,4-[RuCl(CO)(PMe$_3$)$_3$CH=CH]$_2$C$_6$H$_3$NO$_2$ (6h). The synthesis is similar to **6a**, with 1,4-diethynylbenzene being replaced by 1,4-diethynyl-2-nitrobenzene. Purple solid, yield: 0.28 g, 74%. Anal. Calcd for $C_{30}H_{61}Cl_2NO_4P_6Ru_2$: C, 37.50; H, 6.61; N, 1.46. Found: C, 37.71; H, 6.58; N, 1.38. $^{31}P\{^1H\}$ NMR (160 MHz, CDCl$_3$): δ −21.82 (t, J = 22.7 Hz, PMe$_3$), −10.37 (d, J = 22.7 Hz, PMe$_3$). ^1H NMR (400 MHz, CDCl$_3$): δ 1.41 (t, J = 3.2 Hz, 36H, PMe$_3$), 1.47 (d, J = 6.8 Hz, 18H, PMe$_3$), 6.53 (m, 1H, Ar-CH=), 6.84 (m, 1H, Ar-CH=), 7.43−7.56 (m, 3H, Ar-H), 8.21 (m, 1H, Ru-CH=), 8.29 (m, 1H, Ru-CH=). $^{13}C\{^1H\}$ NMR (150 MHz, CDCl$_3$): δ 16.71(t, J = 14.55 Hz, PMe$_3$), 20.02 (d, J = 20.15 Hz, PMe$_3$), 119.06, 126.99, 127.71, 128.64, 131.32, 132.68, 138.06, 146.48, 170.58, 202.04 (CO). IR (KBr, ν in cm^{-1}): 1919 (CO), 1515, 1419 (C=C aryl, vinyl).

1,4-[RuCl(CO)(PMe$_3$)$_3$CH=CH]$_2$C$_6$H$_2$-2,5-(CH$_3$)$_2$ (6i). The synthesis is similar to **6a**, with 1,4-diethynylbenzene being replaced by 1,4-diethynyl-2,5-dimethylbenzene. Yellow solid, yield: 0.17 g, 46%. Anal. Calcd for $C_{32}H_{66}Cl_2O_2P_6Ru_2$: C, 40.81; H, 7.06. Found: C, 40.23; H, 7.01. $^{31}P\{^1H\}$ NMR (160 MHz, CDCl$_3$): δ −22.12 (t, J = 21.1 Hz, PMe$_3$), −10.43 (d, J = 21.1 Hz, PMe$_3$). ^1H NMR (400 MHz, CDCl$_3$): δ 1.40 (t, J = 3.2 Hz, 36H, PMe$_3$), 1.47 (d, J = 6.8 Hz, 18H, PMe$_3$), 2.34 (s, 6H, CH$_3$), 6.74 (m, 2H, Ar-CH=), 7.25−7.52 (m, 2H, Ar-H), 7.88 (m, 2H, Ru-CH=). $^{13}C\{^1H\}$ NMR (100 MHz, CDCl$_3$): δ 16.69 (t, J = 15.3 Hz, PMe$_3$), 19.69, 20.26 (d, J = 20.6 Hz, PMe$_3$), 125.54, 129.83, 132.45, 136.32, 162.91, 202.58 (CO). IR (KBr, ν in cm^{-1}): 1919 (CO), 1550, 1421 (C=C aryl, vinyl).

1,4-[RuCl(CO)(PMe$_3$)$_3$CH=CH]$_2$C$_6$H$_2$-2,5-(OCH$_3$)$_2$ (6j). The synthesis is similar to **6a**, with 1,4-diethynylbenzene being replaced by 1,4-diethynyl-2,5-dimethoxybenzene. Yellow solid, yield: 0.27 g, 68%. Anal. Calcd for $C_{32}H_{66}Cl_2O_4P_6Ru_2$: C, 39.47; H, 6.83. Found: C, 39.43; H, 7.21. $^{31}P\{^1H\}$ NMR (160 MHz, CDCl$_3$): δ −22.05 (t, J = 21.1 Hz, PMe$_3$), −10.22 (d, J = 21.1 Hz, PMe$_3$). ^1H NMR (400 MHz, CDCl$_3$): δ 1.40 (t, J = 3.2 Hz, 36H, PMe$_3$), 1.47 (d, J = 6.8 Hz, 18H, PMe$_3$), 3.89 (s, 6H, OCH$_3$), 6.88 (m, 2H, Ar-CH=), 7.04 (s, 2H, Ar-H), 7.88 (m, 2H, Ru-CH=). $^{13}C\{^1H\}$ NMR (150 MHz, CDCl$_3$): δ 16.61(t, J = 15.0 Hz, PMe$_3$), 20.17 (d, J = 20.10 Hz, PMe$_3$), 57.46, 109.24, 128.58, 128.58, 149.82, 164.59, 202.29 (CO). IR (KBr, ν in cm^{-1}): 1918 (CO), 1548, 1421 (C=C aryl, vinyl).

1,4-[RuCl(CO)(PMe$_3$)$_3$CH=CH]$_2$C$_6$H$_2$-2,5-F$_2$ (6k). The synthesis is similar to **6a**, with 1,4-diethynylbenzene being replaced by 1,4-diethynyl-2,5-difluorobenzene. Yellow solid, yield: 0.32 g, 85%. Anal. Calcd for $C_{30}H_{60}F_2Cl_2O_2P_6Ru_2$: C, 37.97; H, 6.37. Found: C, 38.10; H, 5.97. $^{31}P\{^1H\}$ NMR (240 MHz, CDCl$_3$): δ−19.01 (t, J = 21.9 Hz, PMe$_3$), −7.51 (d, J = 21.9 Hz, PMe$_3$). ^1H NMR (600 MHz, CDCl$_3$): δ 1.39 (t, J = 3.0 Hz, 36H, PMe$_3$), 1.47 (d, J = 6.0 Hz, 18H, PMe$_3$), 6.71 (m, 2H, ArCH=), 7.13 (t, J = 8.0 Hz, 2H, Ph-H), 8.10 (m, 2H, RuCH=). $^{13}C\{^1H\}$ NMR (150 MHz, CDCl$_3$): δ 16.59(t, J = 15.0 Hz, PMe$_3$), 20.05 (d, J = 20.10 Hz, PMe$_3$), 111.28, 124.73, 125.56, 153.20, 167.80, 201.91 (CO). IR (KBr, ν in cm^{-1}): 1917 (CO), 1550, 1415 (C=C aryl, vinyl).

1,4-[RuCl(CO)(PMe$_3$)$_3$CH=CH]$_2$C$_6$H$_2$-2,5-(CF$_3$)$_2$ (6l). The synthesis is similar to **6a**, with 1,4-diethynylbenzene being replaced by 1,4-diethynyl-2,5-bis(trifluoromethyl)benzene. Yellow solid, yield: 0.32 g, 77%. Anal. Calcd for $C_{32}H_{60}Cl_2F_6O_2P_6Ru_2$: C, 36.61; H, 5.76. Found: C, 36.91; H, 5.52. $^{31}P\{^1H\}$ NMR (240 MHz, CDCl$_3$): δ−18.82 (t, J = 21.9 Hz, PMe$_3$), −7.26 (d, J = 21.9 Hz, PMe$_3$). ^1H NMR (600 MHz, CDCl$_3$): δ 1.40 (t, J = 3.0 Hz, 36H, PMe$_3$), 1.48 (d, J = 7.2 Hz, 18H, PMe$_3$), 6.90 (m, 2H, ArCH=), 7.79 (s, 1H, Ar-H), 8.25 (m, 1H, RuCH=). $^{13}C\{^1H\}$ NMR (150

MHz, $CDCl_3$): δ 16.51(t, $J = 15.0$ Hz, PMe_3), 20.01 (d, $J = 20.10$ Hz, PMe_3), 123.71, 126.48, 135.52, 136.83, 168.35, 172.97, 202.05 (CO). IR (KBr, ν in cm^{-1}): 1926 (CO), 1541, 1414 (C═C aryl, vinyl).

1,4-[RuCl(CO)(PMe_3)$_3$CH═CH]$_2$$C_6H_3CF_3$ (6m). The synthesis is similar to **6a**, with 1,4-diethynylbenzene being replaced by 1,4-diethynyl-2-(trifluoromethyl)benzene. Yellow solid, yield: 0.32 g, 82%. Anal. Calcd for $C_{31}H_{61}Cl_2F_3O_2P_6Ru_2$: C, 37.93; H, 6.26. Found: C, 37.57; H, 6.08. $^{31}P\{^1H\}$ NMR (240 MHz, $CDCl_3$): δ −19.07 (t, $J = 21.9$ Hz, PMe_3), −7.35 (d, $J = 21.9$ Hz, PMe_3). ^1H NMR (600 MHz, $CDCl_3$): δ 1.39 (t, $J = 3.0$ Hz, 36H, PMe_3), 1.48 (d, $J = 6.0$ Hz, 18H, PMe_3), 6.54 (m, 1H, ArCH═), 6.89 (m, 1H, ArCH═), 7.41 (s, 2H, Ar-H), 7.60 (d, $J = 7.8$ Hz, 1H, Ar-H), 8.09−8.17 (m, 1H, RuCH═). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 16.50 (t, $J = 15.0$ Hz, PMe_3), 19.93 (d, $J = 20.10$ Hz, PMe_3), 121.34, 123.52, 124.34, 125.71, 126.15, 129.92, 133.60, 135.81, 137.07, 165.61, 170.29, 201.89 (CO). IR (KBr, ν in cm^{-1}): 1922 (CO), 1546, 1416 (C═C aryl, vinyl).

Crystallographic Details. Crystals suitable for X-ray diffraction were grown from a dichloromethane of solution **6h**, **6i**, and **6j** layered with hexane. A crystal with approximate dimensions of 0.30 × 0.20 × 0.20 mm^3 for **6h**, 0.40 × 0.03 × 0.01 mm^3 for **6i**, and 0.23 × 0.20 × 0.20 mm^3 for **6j** was mounted on a glass fiber for diffraction experiment. Intensity data were collected on a Nonius Kappa CCD diffractometer with Mo Kα radiation (0.71073 Å) at room temperature. The structures were solved by a combination of direct methods (SHELXS-97[44]) and Fourier difference techniques and refined by full-matrix least-squares (SHELXL-97[45]). All non-H atoms were refined anisotropically. The hydrogen atoms were placed in the ideal positions and refined as riding atoms. Further crystal data and details of the data collection are summarized in Table 1. Selected bond distances and angles are given in Tables 2, 3, and 4, respectively.

Physical Measurements. Elemental analyses (C, H, N) were performed by Vario ElIII Chnso. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were collected on a Varian Mercury Plus 400 spectrometer (400 MHz) or on a Varian Mercury Plus 600 spectrometer (600 MHz). ^1H, ^{13}C NMR chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. IR spectra were recorded on a Nicolet Avatar 360 FT-IR spectrophotometer using KBr disks. UV−vis spectra were recorded on a PDA spectrophotometer by quartz cells with a path length of 1.0 cm. The electrochemical measurements were performed on a CHI 660C potentiostat (CHI USA). A three-electrode one-compartment cell was used to contain the solution of the compound and supporting electrolyte in dry CH_2Cl_2. Deaeration of the solution was achieved by argon bubbling through the solution for about 10 min before measurement. The ligand and electrolyte (Bu_4NPF_6) concentrations were typically 0.001 and 0.1 mol dm^{-3}, respectively. A 500 μm diameter platinum disk working electrode, a platinum wire counter electrode, and an Ag/Ag^+ reference electrode were used. The Ag/Ag^+ reference electrode contained an internal solution of 0.01 mol dm^{-3} $AgNO_3$ in acetonitrile and was incorporated into the cell with a salt bridge containing 0.1 mol dm^{-3} Bu_4NPF_6 in CH_2Cl_2. All electrochemical experiments were carried out under ambient conditions.

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Supporting Information Available: Tables of bond distances and angles, and X-ray crystallographic files (CIF) for 1,4-[RuCl(CO)(PMe_3)$_3$CH═CH]$_2$$C_6H_3NO_2$ (**6h**), 1,4-[RuCl(CO)(PMe_3)$_3$-CH═CH]$_2$$C_6H_2$-2,5-($CH_3$)$_2$ (**6i**), and 1,4-[RuCl(CO)(PMe_3)$_3$-CH═CH]$_2$$C_6H_2$-2,5-($OCH_3$)$_2$ (**6j**). The materials are available free of charge via the Internet at http://pubs.acs.org.

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