

Carbon-Rich Ruthenium Complexes Containing Bis(allenylidene) and Mixed Alkynyl–Allenylidene Bridges

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Complexes *cis*-[RuCl(dppe)₂][X] (**2a** X = PF₆, **2b** X = CF₃SO₃) react with a variety of bis(propargylic) alcohols to selectively lead to mono-*trans*-[Cl(dppe)₂Ru=C=C(R)–T–C(R)(OH)–(C≡C–H)][X] (**4**) [R = H, Ph; T = *m,p*-(C₆H₄), 2,5-(thiophene), 5,5'-(2,2'-bithiophene), 5,5'-(2,2':5'2''-terthiophene), –C≡C–] or bis(allenylidene) *trans*-[Cl(dppe)₂Ru=C=C(R)–T–(R)C=C=C–RuCl(dppe)₂][X]₂ (**5**) complexes. New dimetallic and trimetallic complexes containing mixed alkynyl–allenylidene bridges, *trans*-[Cl(dppe)₂Ru–C≡C–*p*-(C₆H₄)–(Ph)C=C=C–

*RuCl(dppe)₂][CF₃SO₃] (**12**) and *trans*-[Cl(dppe)₂Ru–C≡C–*p*-(C₆H₄)₂C=C=C–RuCl(dppe)₂][CF₃SO₃] (**17**)], were prepared by modification of the carbon-rich ligand of acetylide precursors. UV/Vis and cyclic voltammetry studies show the influence of the unsaturated conjugated bridge on the electronic interaction between the redox centers, and the fine tuning of this property.*

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Introduction

Organometallic complexes with π -conjugated bridges are attracting interest for their electronic and structural properties in fields including liquid crystals,^[1] nonlinear optical devices,^[2] luminescence,^[3] and electronic communication.^[4–11] Electronic communication between two functionalities is a fundamental aspect related to a variety of complex systems ranging from life^[12] to photoactive donor/acceptor processes^[13] and electronic devices.^[14] These properties are usually the result of their linear rigid structure and of their π -electron conjugation. Thus, it is crucial to understand the behavior of such systems with multiple redox components, the influence of the linkers, and to develop straightforward methods of access to them.

Dimetallic complexes have been obtained by coupling of organometallic terminal acetylides to bis(vinylidene) and bis(alkynyl) complexes.^[4,5] By contrast, few dimetallic mixed alkynyl–vinylidene or alkynyl–allenylidene complexes have been selectively synthesized by activation of conjugated organic molecules.^[10] For example, the activation of HC≡C–CH(OH)–C≡CH has led to a dimetallic system with a C₅ bridging ligand [CpRu(PPh₃)₂=C=C=

CH–C≡C–Ru(PPh₃)₂Cp]BF₄.^[10a] Highly conjugated molecules resulting from the coupling of an acetylide complex with a vinylidene^[8,9] or an allenylidene^[6] complex are also emerging examples.

Ruthenium systems^[15] present opportunities for the synthesis of novel organometallic compounds as models for electron conduction, and with unusual and stable topologies.^[16,17] The ruthenium [RuCl₂(dppe)₂] (dppe = Ph₂PCH₂CH₂PPh₂) species offers the possibility to easily link two carbon-rich chains to form reversible redox systems^[16,18] with an optical transition highly dependent on the nature of the chain.^[6,19] This fact gave us impetus to build polynuclear systems containing new types of delocalized carbon-rich bridges and linking reversible redox active moieties, especially allenylidenes. We now report the easy synthesis of stable dimetallic complexes containing a variety of new bis(allenylidene) bridges separated by a tunable conjugated linker and the synthesis of novel di- and triruthenium compounds containing mixed allenylidene and alkynyl groups. We further illustrate, in the light of UV/Vis and electrochemical studies, the large influence of the bridge on the electronic interaction between the redox centers.

Results and Discussion

The activation of terminal alkyne functionalities with the sixteen-electron species [ClRu(dppe)₂]⁺ can be potentially employed to access polymetallic systems with carbon-rich unsaturated bridges, as previously shown with the synthesis

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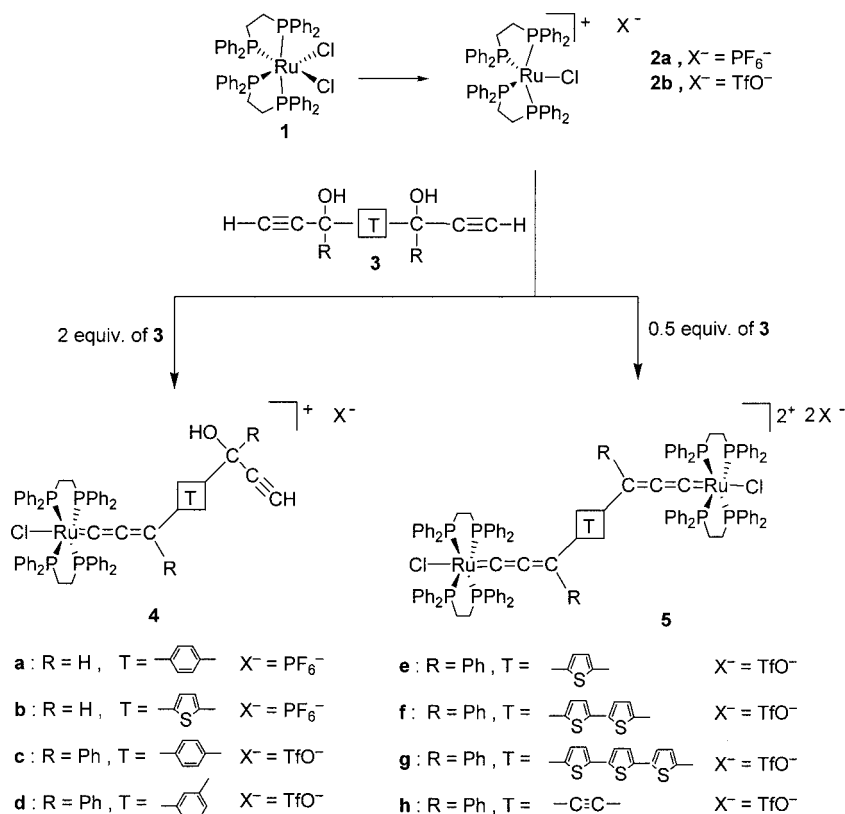
of bis(vinylidene) and bis(acetylide) derivatives.^[20] Herein, we use the selective activation of a variety of functional groups with the intent of forming carbon-rich allenylidene ruthenium derivatives: (i) The simple or double activation of molecules containing two terminal propargylic alcohol functional groups, via the Selegue method,^[21] offers access to mono(allenylidenes) or bis(allenylidenes).^[22] (ii) New mixed terminal alkynyl–allenylidene functionalities separated by a phenyl linker were achieved by using an original step-by-step organometallic synthesis, i.e. by modification and activation of the organic carbon-rich ligand of mono- and dimetallic acetylides to introduce the conjugated allenylidene function.

It has to be noted that we described recently the protonation of a ruthenium bis(allenylidene), obtained by means of the Selegue strategy, into a bis(carbyne).^[19] It is also noteworthy that Werner et al. obtained a similar bis(allenylidene) with rhodium $[\text{Cl}(\text{P}i\text{Pr}_3)_2\text{Rh}=\text{C}=\text{C}=\text{C}(\text{Ph})-m\text{-C}_6\text{H}_4-(\text{Ph})\text{C}=\text{C}=\text{C}=\text{Rh}(\text{P}i\text{Pr}_3)_2\text{Cl}]$ by an identical approach.^[23] A different kind of bis(allenylidene) not connected through the allenylidene functions such as $(\text{Ph}_2\text{C}=\text{C}=\text{C}=\text{Rh}(\text{P}i\text{Pr}_3)_2-\text{C}\equiv\text{C}-)_2$ was also synthesized by the same group.^[24] However, no electrochemical studies were reported for these complexes.

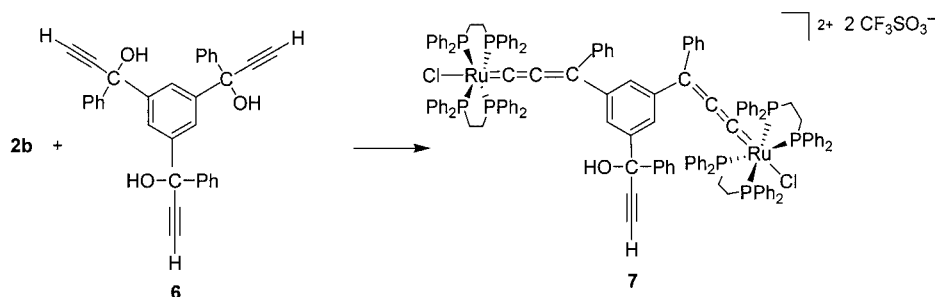
Synthesis of Mono(allenylidene)ruthenium Complexes: The reaction of the 16-electron salts **2a** or **2b** with an excess of bis(propargylic) alcohols^[25] **3a–h** leads to the formation of red monoallenylidene ruthenium complexes **4a–h**

(41–81% yield) bearing a free propargylic alcohol group (Scheme 1). These allenylidenes are stable with respect to the addition of methanol to the C_α carbon.^[26] The FTIR spectra of the allenylidenes **4a–h** show characteristic features for such compounds with $\nu_{\text{C}=\text{C}=\text{C}} = 1921\text{--}1939\text{ cm}^{-1}$ and $\nu_{\text{C}\equiv\text{C}} = 2100\text{--}2200\text{ cm}^{-1}$. The ^{31}P NMR spectra display the equivalence of the four phosphorus nuclei and thus the relative *trans* disposition of the chlorine atom and of the allenylidene ligand. The characteristic allenylidene low-field ^{13}C signal for the C_α carbon nucleus appears as a quintuplet at $\delta = 288\text{--}320\text{ ppm}$ with $^2J_{\text{P,C}} = 15\text{ Hz}$.

Synthesis of Bis(allenylidene)ruthenium Complexes: The free prop-2-yn-1-ol functionality of complexes **4a–h** can be activated with 1 equiv. of **2a** or **2b** in dichloromethane, leading to the slow formation of the bis(allenylidene) complexes **5a–h** (7 d). The same bridged molecules were also readily prepared by the assembly of 2 equiv. of **2a** or **2b** and 1 equiv. of the corresponding bis(propargylic) alcohol and isolated in 42–78% yield after stirring for 7 d (Scheme 1). The tertiary allenylidenes **5c–h** are more stable than the secondary allenylidenes **5a–b** (see Scheme 1). Hence, our studies have been mainly focused on these former complexes. For all complexes, the ^{31}P NMR spectrum demonstrates the high symmetry of the molecule with only one sharp singlet for the eight phosphorus nuclei. The two allenylidene groups are then equivalent, and therefore the ^{13}C NMR spectra show only one set of three different signals for the C_α , C_β and C_γ carbon atoms. However, complex **5h**



Scheme 1

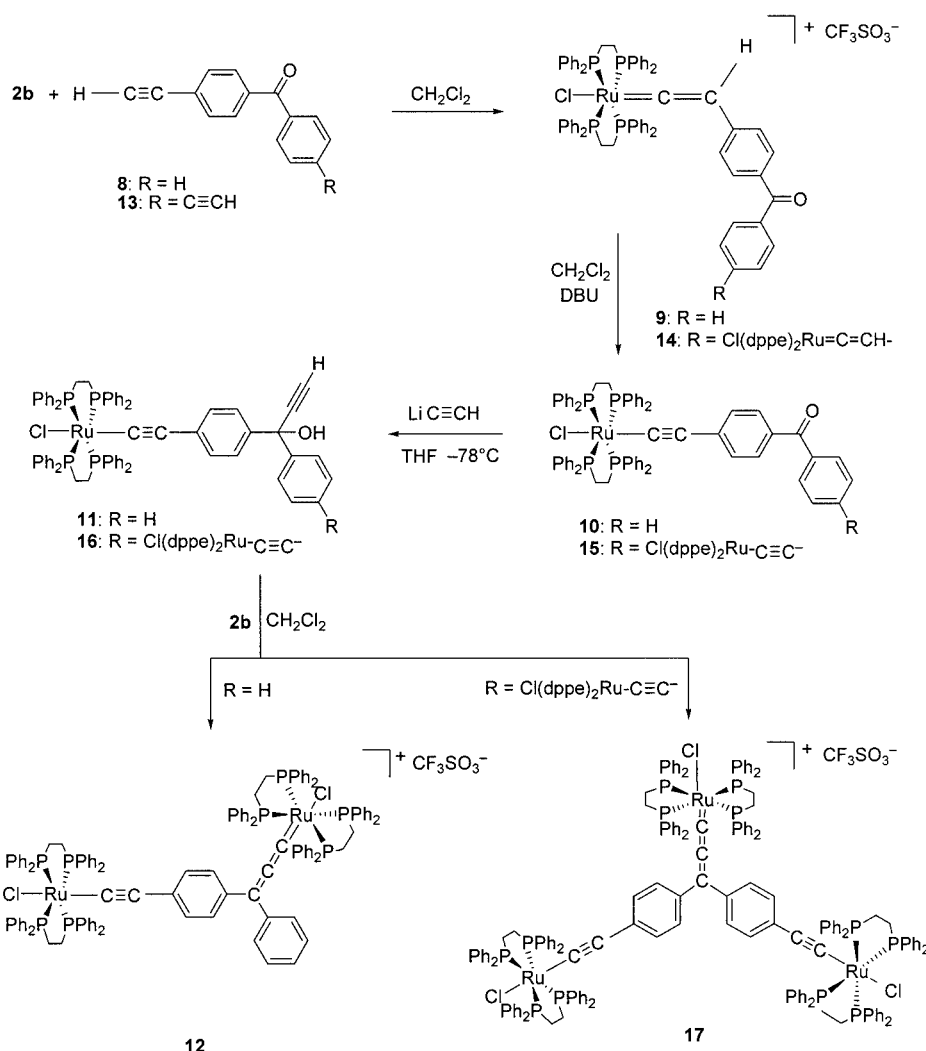


Scheme 2

with the triple bond is not stable enough in solution, and the ^{13}C NMR spectrum could not be obtained. Finally, the attempt to obtain a trisallenylidene complex by triple activation of the propargylic alcohol **6** with **2b** failed. Only the bis(vinylidene) complex **7** was recovered (Scheme 2), probably for steric reasons, as a trisallenylidene ruthenium complex was obtained when the propargylic alcohol functionalities were separated by a larger nonconjugated tripodal core.^[27]

Synthesis of (Alkynyl–Allenylidene)ruthenium Complexes:

The activation of terminal alkyne **8** or **13** bearing a ketone further convertible into a propargylic alcohol function with **2b**, led to the mono- (**9**) and the bis(vinylidene) (**14**) complexes in good yields (Scheme 3). The vinylidenes display characteristic FTIR vibration stretches $\nu_{\text{C}=\text{C}} = 1588 \text{ cm}^{-1}$ and $\nu_{\text{CO}} = 1640 \text{ cm}^{-1}$. The ^1H NMR spectra shows a quintet for the vinylidene proton at $\delta = 4.82 \text{ ppm}$ for **9** and at $\delta = 4.74 \text{ ppm}$ for the two identical vinylidene protons of **14**



Scheme 3

with $^4J_{\text{PH}} = 3$ Hz. The low-field ^{13}C signal for the C_α carbon nucleus appears as a quintet at $\delta = 352$ ppm for **9** and 354 ppm for **14**, and a singlet at $\delta = 195$ ppm for the pendant ketone carbon nucleus is also observed. These vinylidene complexes can be easily deprotonated with a base such as DBU to form the neutral alkynyl–ruthenium derivatives **10** and **15**. The alkynyl–ruthenium complexes show characteristic vibration stretches $\nu_{\text{C}\equiv\text{C}} = 2057$ for **10** and $\nu_{\text{C}\equiv\text{C}} = 2053$ for **15**. The carbonyl group of these complexes is further converted into a propargylic alcohol function by action of lithium acetylide to give **11** and **16**. Characteristic FTIR vibration stretches are observed at $\nu_{\text{C}\equiv\text{H}} = 3050$, $\nu_{\text{C}\equiv\text{CH}} = 2135$, $\nu_{\text{C}\equiv\text{C}} = 2065\text{ cm}^{-1}$ for **11** and $\nu_{\text{C}\equiv\text{H}} = 3052$, $\nu_{\text{C}\equiv\text{CH}} = 2136$, $\nu_{\text{C}\equiv\text{C}} = 2068\text{ cm}^{-1}$ for **16**. Finally, the activation of these propargylic alcohol groups by the active 16-electron species **2b** leads to the isolation of the dimetallic mixed alkynyl–allenylidene **12** or of the trimetallic complex **17** bearing two alkynyl and one allenylidene groups. The overall yields for complexes **12** and **17** are 37 and 50% starting from **2b** after four steps, and they display two typical absorptions at 2040 and 1926 (**12**), 2008 and 1912 (**17**) cm^{-1} . The ^{13}C spectrum shows the presence of the allenylidene group with characteristic resonances for **12** and **17** at $\delta = 345$ and 342 ppm respectively for C_α , and also of the acetylide group with $\delta = 135$ and 134 ppm for C_α' .

Electrochemical and UV/Vis Studies: The bis(allenylidene) complexes are composed of two one-electron redox-active units and of a bridge that allows for electronic communication. To understand the nature of the redox behavior and the role of the linker, the cyclic voltammograms of **4** and **5** were recorded in CH_2Cl_2 solutions (0.1 M Bu_4NPF_6). The reduction potentials and other relevant data for all compounds are reported in Table 1. All complexes exhibit a linear dependence of the peak current on the square root of the sweep rate ($\nu^{1/2}$) from 60 to 600 $\text{mV}\cdot\text{s}^{-1}$, as expected

for a diffusion controlled process, and the ratio of the peak currents ($i_{\text{pa}}/i_{\text{pc}}$) is close to unity. These electrochemical studies show that the cationic monoallenylidenes **4c–h** can undergo a one-electron reduction, and the bis(allenylidenes) **5a–h**, **7**, two consecutive one-electron reductions. The cyclic voltammograms of complexes **4e** and **5e** are presented in Figure 1 for illustration. It is noteworthy that these tertiary monoallenylidenes undergo one reversible process, in contrast to secondary allenylidene complexes, which present an irreversible process.^[22] The electrochemical behavior of the bis(allenylidenes) show several interesting features: (i) the two reversible processes are well separated from each other, and (ii) a significant anodic shift of both reduction potentials indicates that the reductions are thermodynamically favored with respect to the mononuclear analog when the two allenylidene moieties are conjugated in **5a–c**, **e–h**. For example the reduction of **4e** occurs at $E^\circ = -1.000$ V vs. Fc, and reductions of the corresponding dimetallic complex **5e** are observed at less negative potentials, i.e. at $E^\circ_1 = -0.439$ and $E^\circ_2 = -0.749$ V vs. Fc. No such anodic shift is observed in the nonconjugated complexes **5d** or **7**, in which the allenylidene moieties are in a *meta* orientation on the phenyl linker. Indeed, for **5d**, the two reductions occur at $E^\circ_1 = -0.877$ and $E^\circ_2 = -1.056$ V vs. Fc, while **4d** shows a reduction wave at $E^\circ = -0.910$ V vs. Fc. When two different redox processes exist for two otherwise identical redox systems in the same molecule, an important parameter is the comproportionation constant K_c . The large wave separation observed for each dimetallic complex ($\Delta E^\circ > 180$ mV) leads to large comproportionation constants [$K_c > 1.0 \times 10^3$; $-(RT/F) \ln(K_c) = \Delta E^\circ$] and establishes that all the monoreduced species are stable in solution with respect to disproportionation.^[28]

It has already been mentioned that the reduction of allenylidene complexes mainly involves the allenylidene ligands,^[29–32] in contrast to the oxidation of neutral acetyl-

Table 1. Electrochemistry and optical data for complexes **4**, **5** and **7**

	E°_1 [V]	ΔE [mV]	CV ^[a]		$E^\circ_2 - E^\circ_1$ [mV]	K_c	UV/Vis ^[b]	
			E°_2 [V]	ΔE [mV]			$\lambda_{\text{max.}}$ (MLCT) [nm]	ϵ [$\text{mol}^{-1}\cdot\text{L}\cdot\text{cm}^{-1}$]
5a	−0.509	66	−0.711	81	202	2.3×10^3		
5b	−0.335	71	−0.606	80	270	3.2×10^4		
4c	−0.910	60					530	28000
5c	−0.500	60	−0.680	60	180	1.0×10^3	588	54000
4d	−0.910	60					520	28000
5d	−0.877	60	−1.056	60	180	1.0×10^3	522	36000
4e	−1.000	66					560	26400
5e	−0.439	66	−0.749	90	310	1.5×10^5	714	86000
4f	−1.012	60					660	28000
5f	−0.434	66	−0.746	90	320	2.2×10^5	730	48000
4g	−1.027	60					692	25000
5g	−0.427	66	−0.760	69	330	3.2×10^5	752	65000
4h	−0.805	60					512	26000
5h	−0.285	60	−0.645	60	360	1.0×10^6	720	60000
7	−0.890	60	−1.100	60	210	3.2×10^3	520	38000

^[a] Sample 1 mM; Bu_4NPF_6 (0.1 M) in CH_2Cl_2 ; $\nu = 100\text{ mV s}^{-1}$; potentials are reported in V vs. ferrocene as an internal standard. Reversible redox processes. ^[b] In CH_2Cl_2 .

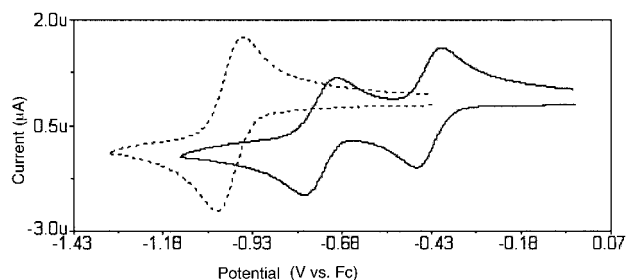


Figure 1. Cyclic voltammetry for **4c** (dashed) and **5c** (solid); Bu₄NPF₆ (0.1 M) in CH₂Cl₂; $\nu = 100 \text{ mV}\cdot\text{s}^{-1}$

ide, which occurs on the metal center.^[33] Thus, the reduction processes of the mono- and the bis(allenylidene) can be attributed to the reduction of the carbon-rich chain in analogy to the mono(allenylidene) species *trans*-[Cl(dppe)₂Ru=C=C=CPh₂]PF₆ (**A1**) and *trans*-[Cl(dppe)₂Ru=C=C=CMe₂]PF₆ (**A2**). Nevertheless, this attribution was verified for **4c** and **5c** with the *p*-phenyl linker. For complex **4c**, the most appropriate reducing agent is the cobaltocene [Cp₂Co] (i) as its reduction potential E° is -1.33 V vs. ferrocene,^[34] and (ii) it is ESR silent down to temperatures considerably below that of liquid nitrogen.^[34b] We generated the reduced form in situ by dropping a crystal of cobaltocene in a THF solution of **4c** in a capped ESR tube. Reduced complex **4c** showed an intense and persistent signal ($g = 2.0048$) similar to that observed for **A1** ($g = 2.0042$), hence centered close to the free electron g value (a in Figure 2). The complex pattern could best be rationalized by the coupling of the unpaired electron with the four phosphorus nuclei and further coupling with the *ortho*, *meta* and *para* hydrogens of the phenyl groups, showing the delocalization of the single electron on the carbon-rich bridge.^[35a] On the other hand, the first reduction of **5c** with decamethylferrocene ($E^\circ = -0.590 \text{ V}$ vs. ferrocene) or with a deficient amount of cobaltocene in the ESR cavity leads to the observation of a broad signal with $g = 2.0244$ (b in Figure 2). The observed shoulders may indicate some transition metal contribution (d-orbitals of the ruthenium atoms) resulting in the coupling of the free electron with the ⁹⁹Ru and ¹⁰¹Ru isotopes (nuclear spin $S = 5/2$, and natural abundances of 12.7 and 17% respectively) with an estimated coupling constant of approximately 5 G.^[35b] It is possible that the large number of magnetically independent nuclei

on the chain together with this metal participation give rise to strongly overlapping resonance lines that cannot be resolved. However, this result suggests that the radical is highly centered on the organic bridge and is stabilized by delocalization along the carbon bridge between the ruthenium centers. Interestingly, further addition of cobaltocene leads to the two-electron reduction and to the disappearance of the signal, which suggest the formation of a diamagnetic doubly reduced species. ³¹P NMR studies of the latter, obtained with 2 equivalents of cobaltocene, show a single signal with $\delta = 49.3 \text{ ppm}$ consistent with a diacetylide species **18** (Scheme 4), that corroborates the communication through the bridge. Unfortunately, the spectra were broad, certainly because of the presence of residual paramagnetic compound (the reductant or first reduced species), and no exploitable proton or carbon spectra could be obtained.

IR studies, recorded in CH₂Cl₂, show the shift of the allenylidene band upon reduction of **4c** from 1925 cm^{-1} to a sharper but more intense band at 1948 cm^{-1} , similar to that observed for **A1** (from 1926 to 1945 cm^{-1}). This new value is somewhat different from that of true acetylide (2000 cm^{-1}) but coherent with the increase of the acetylide character of the reduced complexes, and with the presence of a delocalized electron mainly on the allenylidene carbon atoms of the chain (Scheme 4). Winter's et al. observed similar shifts for other reduced allenylidene complexes.^[31] On the other hand, the first reduction of **5c** leads to a small opposite shift of the allenylidene band from 1912 to 1906 cm^{-1} . This last band is similar to that found for *trans*-[Cl(dppe)₂Ru-C≡C-C(CH₃)=C(H)-C(CH₃)=C=C=Ru(dppe)₂Cl]BF₄ (**C**)^[6] (1898 cm^{-1}) and consistent with the presence of delocalized allenylidene and acetylide moieties on the same bridge; two possible mesomeric forms are represented in Scheme 4. The second reduction leads to the vanishing of the former band, and to the concomitant formation a weak absorption at 1988 cm^{-1} (Figure 3). This corroborates the formation of a diamagnetic bis(acetylide) species such as **18**. It is noteworthy that all these observations are not related to the decomposition of the reduced species. Indeed, all reduced forms were thermally stable and reductions followed by oxidations with ferrocenium salt 30 min later led to the pure starting materials on the basis of ³¹P NMR spectroscopy. Hence, in conclusion to these

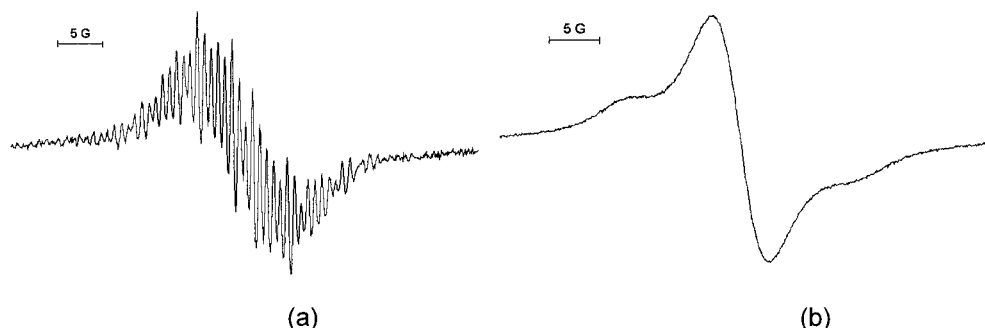
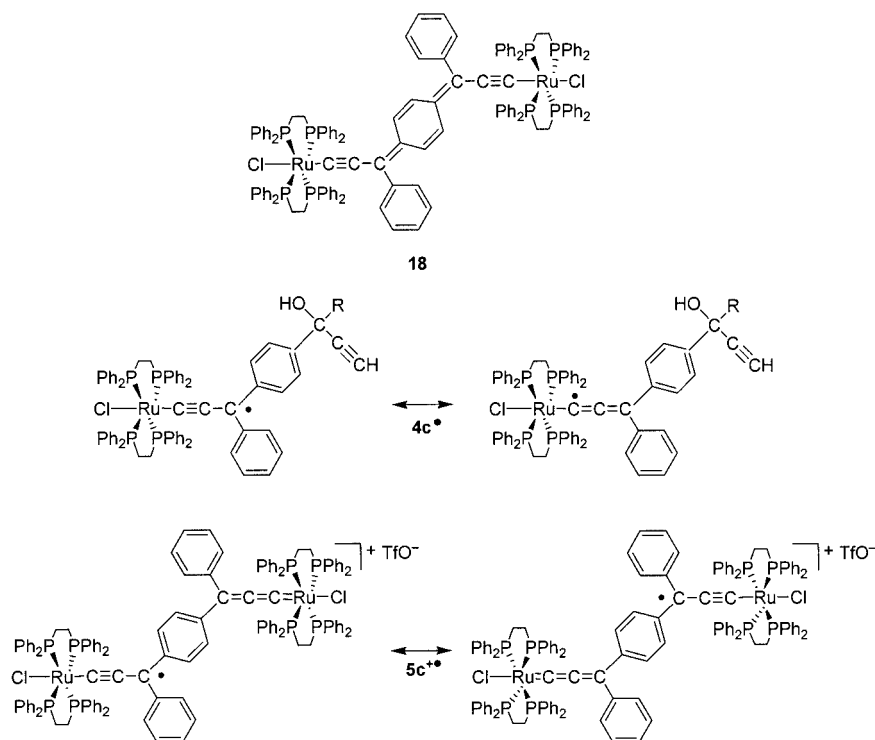


Figure 2. ESR spectra resulting from the reduction of (a) **4c** ($g = 2.0048$), and of (b) **5c** ($g = 2.0244$)



Scheme 4

spectroscopic studies, it is likely that all the electrons issued from reduction processes reside in an orbital with a significant carbon-rich ligand character but also with a non-negligible metal contribution.^[32]

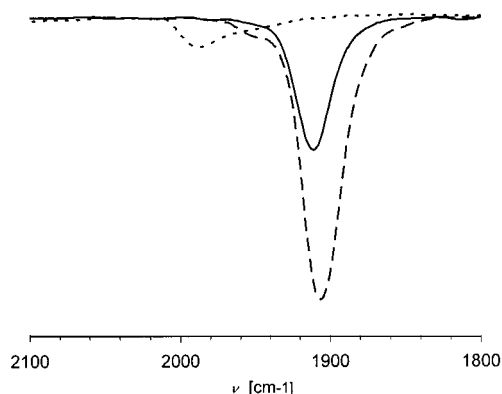


Figure 3. IR spectra of **5c** (—), its first (---), and second (···) reduced species

The dependence of redox potentials on the nature of the carbon-rich-ligand (Table 1) complexes is consistent with the ligand character of the LUMO. The reduction potential within the set of monoallenylidene species is located between 0.805 V and 1.027 V vs. ferrocene. A lower potential, that is, a higher electron stabilization along the chain is observed for **4h** with the triple bond as transmitter with $E^\circ = -0.805$ V vs. Fc. Within the series of bis(allenylidene) species, the variations of E° for both reductions are expected to be much greater. The complexes with the improved conju-

gation will show the stronger variation for both reduction processes in comparison to analogous monometallic species (Figure 1). According to common belief, the difference in electrochemical half-wave potential reflects the strength of interaction between the allenylidene moieties. There are, however, various additional factors that contribute to a stabilization of symmetrical mono- and bireduced complexes and especially electron delocalization. By contrast, when two redox centers are isolated from each other, E_1 and E_2 would be expected to be not only the same or similar but also very close to the potential of the comparable mononuclear analog.^[36] The observed first and second reduction potentials of bis(allenylidene) species such as **5c** are less negative than those of the corresponding mononuclear species; this indicates considerable stabilization of the reduced forms by resonance and allows an analysis of the relative stabilization effects. The variation in potential is greater with less aromatic linkers (thiophene) relative to the phenyl transmitter, and the most efficient group to effect communication is the triple bond (**5h**). For example, this effect was already observed with dimetallic iron acetylides $[\text{Cp}^*(\text{dppe})\text{Fe}-\text{C}\equiv\text{C}-\text{R}-\text{C}\equiv\text{C}-\text{Fe}(\text{dppe})\text{Cp}^*]$ ($\text{R} = -2,5\text{-C}_4\text{H}_2\text{S}-$, $-m\text{-C}_6\text{H}_4-$).^[37] For the nonconjugated complexes **5d** or **7** (with $E^\circ_1 = -0.877$ and -0.890 V vs. Fc respectively) the first reduction potential is very close to that of the monometallic species ($E^\circ = -0.910$ V vs. Fc for **4d**) as the allenylidene centers interact weakly. We also observed that the separation between the two processes (ΔE°) also depends on the nature of the transmitter. The ΔE° value of 180 mV ($K_c = 1.0 \times 10^3$) is observed with the nonconjugated systems **5d** and **7**. Surprisingly, the conjugated *p*-phenyl linker **5c** displays the same value, in contrast

to the acetylide iron systems.^[37] K_c assumes a value of 4 when the two redox sites are completely noninteracting and goes to much higher values as electronic and electrostatic interactions increase. Therefore, the present value is principally attributed to a structural rearrangement, solvation or electrostatic interactions. For the complexes **5a**, **5b**, **5e** and **5h**, this value is noticeably higher, and the greatest difference is observed with **5h** ($\Delta E^\circ = 360$ mV, $K_c = 1.0 \times 10^6$). We then assign this significant increase to an additional contribution from the resonance interaction between the allenylidene moieties through the linkers. Thus, in addition to the largest anodic shift, the less aromatic linkers with the shorter pathways display the greater differences in potential between the reduction processes (**5e–h**) in the following order: Triple bond > thiophene $\approx$ bithiophene $\approx$ terthiophene > phenyl.

UV/Vis studies were performed to compare mono- and dimetallic complexes. Figure 4 shows the absorption spectra obtained for **4c** and **5c**. The intense short-wavelength absorption band for the $n-\pi^*$ type transition originating from the dppe ligand at high energy remains unchanged. By contrast, the lower-energy transition is shifted from $\lambda_{\text{max}} = 530$ nm for **4c** to a broader band at $\lambda_{\text{max}} = 588$ nm for **5c**. This phenomenon is consistent with the observation made for the bis(carbyne) complex $\text{trans}[\text{Cl}(\text{dppe})_2\text{Ru}\equiv\text{C}-\text{HC}=\text{C}(\text{CH}_3)-\text{C}_6\text{H}_4-(\text{CH}_3)\text{C}=\text{CH}-\text{C}\equiv\text{Ru}(\text{dppe})_2\text{Cl}](\text{BF}_4)_2$, which displays a broad band at $\lambda_{\text{max}} = 559$ nm, whereas the monometallic compound, $\text{trans}[\text{Cl}(\text{dppe})_2\text{Ru}\equiv\text{C}-\text{CH}=\text{C}(\text{CH}_3)\text{R}](\text{BF}_4)_2$, absorbs at $\lambda_{\text{max}} = 426$ nm.^[19] For monoallenylidenes, the transition is attributed to the allowed transition from the metal-based HOMO-1 to the LUMO which is delocalized over the allenylidene ligand (the HOMO/LUMO symmetry is forbidden),^[31] and accounts for the strong Metal-to-Ligand Charge Transfer (MLCT). Concerning the new broad band observed for the dimetallic species, an important MLCT character also seems to be present. This large bathochromic shift of the band is observed for all bis(allenylidenes) with respect to monoallenylidenes, except for compounds with nonconjugated linkers (Table 1). The λ_{max} value is almost the same for **4d** and **5d**, $\lambda_{\text{max}} = 520$ and 522 nm respectively, with the *m*-phenyl linker. By contrast, the decrease in the absorption

energy in the bis(allenylidene)s **5c**, **5e**, **5f**, **5g** and **5h** is consistent with a more effective conjugated path between the two organometallic moieties, and with a decreasing energy of the LUMO, as observed in the electrochemical studies. Even though the tendency is the same in the UV/Vis studies, in electrochemistry, some differences are observed. The energy difference between the mono- and the bis(allenylidene) band ($\Delta\lambda$) follows the order: triple bond ($\Delta\lambda = 192$ nm) > thiophene ($\Delta\lambda = 154$ nm) > *p*-phenyl ($\Delta\lambda = 58$ nm), but with bithiophene ($\Delta\lambda = 70$ nm) and terthiophene ($\Delta\lambda = 60$ nm) the difference is barely larger than that for the phenyl group. This observation could be related to the well-known rotational disorder of oligothiophenes in the ground state and to the corresponding reorganization energy necessary in the excited state. In addition, an energy modification of the heavily metal-centered HOMOs arising from a lower metal d-orbital contribution in complexes with more extended π -conjugated ligands cannot be excluded.^[32,38,39] It is noteworthy that the absorption bands are very broad, certainly including several transitions, and these conclusions need to be considered with care, even if similar trends were already observed in acetylide systems.^[5e]

In conclusion, according to both UV/Vis and electrochemical studies, an important contribution from a less aromatic π -conjugated system undoubtedly increases the electronic communication between the allenylidene moieties and stabilizes the LUMO of the bis(allenylidene) complexes, the orbital in which the electrons are injected upon reduction. These results are consistent with the general result that the separation between energy levels continually diminishes in π -conjugated systems with decreasing aromaticity.

The cationic allenylidene complexes with one (**12**) or two (**17**) acetylide moieties were also studied (Figure 5, Table 2). They both show a one-electron reduction wave at $E^\circ_{\text{red}} = -1.170$ and -1.240 V vs. Fc respectively, and **12** displays a one-electron oxidation wave at $E^\circ_{\text{ox}} = 0.140$ V vs. Fc while **17** shows a two-electron oxidation wave at $E^\circ_{\text{ox}} = 0.120$ V vs. Fc. In comparison to the monometallic complexes allenylidene **A1** and the acetylide $\text{trans}[\text{Cl}(\text{dppe})_2\text{Ru}-\text{C}\equiv\text{C}-\text{CHPh}_2]$ (**B**),^[40] we observed that for the bi- or trimetallic species the reduction and the oxidation were more difficult to perform. This difficulty results from electronic communication through the bridge between one metal center and the other, and notably from the donor effect of the neutral acetylide–ruthenium group(s)

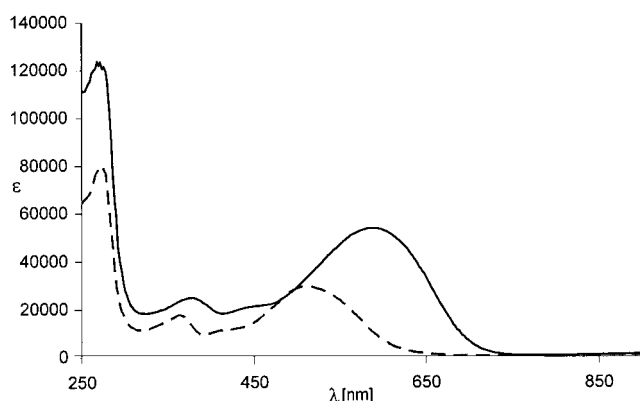


Figure 4. UV/Vis spectra of **4c** (---), and **5c** (—) in CH_2Cl_2

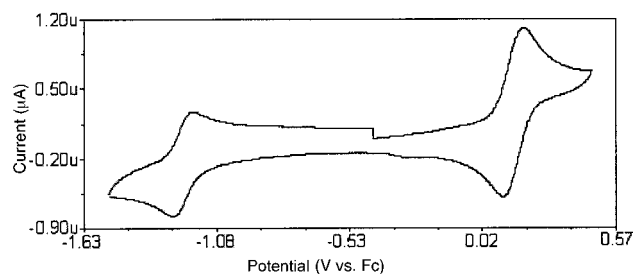


Figure 5. Cyclic voltammetry of **17**; Bu_4NPF_6 (0.1 M) in CH_2Cl_2 ; $\nu = 100 \text{ mV s}^{-1}$

Table 2. Electrochemistry and optical data for complexes **12** and **17**

	E°_{ox} [V]	CV ^[a] ΔE [mV]	E°_{red} [V]	ΔE [mV]	UV/Vis ^[b] λ_{max} (MLCT) [nm]	ϵ [mol ⁻¹ ·L·cm ⁻¹]
12	+0.140	60	-1.170	60	764	63000
17	+0.120	60	-1.240	60	782	84000
A1			-1.030	60	504	18000
B	+0.020	60			360	6000
C	+0.310	60	-1.380	60	763	109000

^[a] Sample 1 mM; Bu₄NPF₆ (0.1 M) in CH₂Cl₂; ν = 100 mV s⁻¹; potentials are reported in V vs. ferrocene as an internal standard. Reversible redox processes. ^[b] In CH₂Cl₂.

and from the withdrawing power of the cationic allenylidene–ruthenium moiety. In analogy to allenylidene and acetylide complexes, the reduction processes are attributed to the reduction of the carbon-rich bridges, and the oxidations are believed to be mainly metal-centered.^[33] Interestingly, in complex **17**, the two acetylide moieties are oxidized at the same potential (two-electron wave). This shows the lack of interaction between these two metal centers in an oxidation process (Figure 5), whereas the variation of the oxidation potential between **17** and **12** is consistent with the presence of an additional electron donor acetylide in **17**. The UV/Vis spectra of **12** and **17** present very high λ_{max} values with a large ϵ for the presumed MLCT at lower energy than for **A1**.^[6a] This phenomenon might be attributed to the admixing of some charge-transfer character of the acetylide to the allenylidene moiety and to the longer conjugated bridge. Finally, the original complex **12** can be considered as a bis(ruthenium) species with a delocalized bridge allowing nine carbon atoms to connect the two ruthenium centers, and it can be compared with the seven-carbon-atom bridge bis(ruthenium) complexes such as *trans*-[Cl(dppe)₂Ru–C≡C–C(CH₃)=C(H)–C(CH₃)=C=C–Ru(dppe)₂Cl]BF₄ (**C**).^[6] The reduction potential is slightly higher and the oxidation potential is slightly lower for **12** than for **C**, both potentials are getting closer to those of the monometallic species. Hence, as observed for bis(allenylidenes), the aromatic cycle in the delocalized pathway and the slightly longer bridge lead to a decrease in the electronic coupling between the redox centers in the mixed complexes.

Conclusion

This work presents the synthesis, the spectroscopic, and the voltammetric studies of a new family of carbon-rich organometallic complexes with novel topologies. First, the formation of stable bis(allenylidene) complexes was reported, and the nature of their reduced species, which are mainly ligand-centered, was studied by means of ESR and IR spectroscopy. The general trends observed with polymetallic acetylides prevail in bis(allenylidene) species: (i) the allenylidene moieties can interact substantially through a linker if the linker is conjugated, and (ii) the UV/Vis and the electrochemical properties significantly depend on the nature of the linker. This opens the door to a potential fine

tuning of their properties. In addition, the original step-by-step synthesis of mixed allenylidene–acetylide di- and trimetallic complexes with nine conjugated atoms were described and the existence of electronic communication between allenylidene and acetylide moieties was demonstrated. As the formation of a nanoscale network is needed for molecular electronic devices, these new long molecules, obtained via controlled preparations, are interesting alternatives to the classical bis(acetylides). Their abilities for *trans* chlorine atom substitution with an acetylide or a cumulenyl chain make them interesting building blocks for the construction of metal-containing unsaturated oligomers and polymers to mediate electron transfer processes.

Experimental Section

General Remarks: All reactions were performed under argon or nitrogen with use of Schlenk techniques. The solvents were deoxygenated and dried by standard methods. Infrared spectra were recorded with a Nicolet 205FTIR spectrometer in solution for oils, and in KBr pellets for solids. The ¹H (300.13 MHz), ³¹P (121.50 MHz) and ¹³C (75.47 MHz) NMR spectra were recorded at 25 °C with a Bruker AV300 spectrometer. Elemental analyses were performed by the “Service Central d’Analyses du CNRS”, Vernaison, France and CRMPO, Rennes, France. The synthesis of *cis*-[(dppe)₂RuCl₂] (**1**),^[41] **2a**, and **2b**,^[42] 1-phenyl-3-trimethylsilylpropyne,^[43] 1,2-dibenzoylacetylene,^[44] and of propargyl alcohols **3a–b**,^[25] were performed by using literature methods. Compounds **3c–d**,^[45] **8**,^[46] and **13**,^[47] reported in this section, were previously described.

HC≡C–(OH)C(Ph)–*p*-(C₆H₄)–(Ph)C(OH)–C≡CH (3c**):** In a Schlenk tube, acetylene (40 mmol) was dissolved in THF (40 mL) at –78 °C. Then, *n*BuLi (18.75 mL, 30 mmol, 1.6 M in hexane) was slowly added. The mixture was stirred at –78 °C for 30 min. In another tube, *p*-dibenzoylbenzene (3.57 g, 12.5 mmol) was dissolved in THF (10 mL) and added to the solution. The mixture was stirred overnight at room temperature before being hydrolyzed with a saturated NH₄Cl solution (10 mL). The crude product was extracted with diethyl ether (4 × 50 mL), washed with water (3 × 20 mL), and dried. Further purification was achieved by chromatography over silica gel (10% diethyl ether in pentane) to afford **3c** (3.29 g) as a white powder in 78% yield. ¹H NMR (CDCl₃): δ = 7.64–7.15 (m, 14 H, Ph), 5.68 (s, 2 H, OH), 3.31 (s, 2 H, C≡CH) ppm. ¹³C{¹H} NMR (CDCl₃): δ = 145.19–125.64 (Ph), 87.08 (C≡CH), 75.53 (C–OH), 73.30 (C≡CH) ppm. IR: $\tilde{\nu}$ = 2146 ($\nu_{\text{C}\equiv\text{C}}$) cm⁻¹. HRMS (EI): m/z = 338.1267; [M]⁺; calcd. 338.1307.

HC≡C–(OH)C(Ph)–*m*-(C₆H₄)–(Ph)C(OH)–C≡CH (3d): By the same procedure, from commercial *m*-dibenzoylbenzene (3.58 g), **3d** (3.04 g) was obtained as a white powder in 72% yield. ¹H NMR (CDCl₃): δ = 7.99–7.21 (m, 14 H, Ph), 3.34 (s, 2 H, OH), 2.83 (s, 2 H, C≡CH) ppm. ¹³C{¹H} NMR (CDCl₃): δ = 144.56–123.44 (Ph), 86.25 (C≡CH), 75.73 (C–OH), 74.37 (C≡CH) ppm. IR: ν̃ = 2113 (ν_{C≡C}) cm^{–1}. HRMS (EI): *m/z* = 338.1270; [M]⁺, calcd. 338.1307.

HC≡C–(OH)C(Ph)–2,5-(thiophene)–(Ph)C(OH)–C≡CH (3e): *n*BuLi (6.74 mL, 10.7 mmol, 1.6 M) was added dropwise to a solution of thiophene (378 mg) in THF (20 mL) at –78 °C. After stirring for 1 h, 1-phenyl-3-trimethylsilylpropyne (2 g, 9.88 mmol) dissolved in THF (10 mL) was also added dropwise. The resulting mixture was stirred for 15 min at –78 °C and for 12 h at room temperature. Then, water (15 mL) and tetrabutylammoniumfluoride solution (18 mL, 1 M in THF) were added slowly, and the resulting mixture was stirred at room temperature for 2 h. The solution was extracted with diethyl ether (3 × 50 mL), and the organic layer was washed with aqueous solution of NH₄Cl. After drying with MgSO₄, the solvents were evaporated to afford a brownish oil. Further purification was achieved by flash chromatography on silica gel with a mixture of diethyl ether/pentane as eluent to give **3e** (1.62 g) as a white solid in 52% yield. ¹H NMR (CDCl₃): δ = 7.71–7.28 (m, 10 H, Ph), 6.88 and 6.82 (2 H, thiophene), 2.92 (s, 2 H, OH), 2.84 (s, 2 H, C≡CH) ppm. ¹³C{¹H} NMR (CDCl₃): δ = 150.07–149.83 (C_{quat}, thiophene), 143.3–125.8 (Ph), 124.96–124.91 (CH, thiophene), 85.56 and 85.51 (C≡CH), 75.17 and 75.14 (C–OH), 71.78 (C≡CH) ppm. IR: ν̃ = 2152 (ν_{C≡C}) cm^{–1}. HRMS (EI): *m/z* = 344.0855 [M]⁺; calcd. 344.0871. C₂₂H₁₆O₂S (344.43): calcd. C 76.72, H 4.68; found C 76.42, H 4.58.

HC≡C–(OH)C(Ph)–5,5'–(2,2'–bithiophene)–(Ph)C(OH)–C≡CH (3f): By the same procedure, from 2,2'–bithiophene (1 g, 6.0 mmol), *n*BuLi (8.25 mL, 13.2 mmol), and 1-phenyl-3-trimethylsilylpropyne (2.67 g, 13.2 mmol), compound **3f** (1.5 g) was obtained in 74% yield as a brownish oil. ¹H NMR (CDCl₃): δ = 7.71–7.21 (m, 10 H, Ph), 6.94 (d, ³J_{H,H} = 4 Hz, 2 H, thiophene), 6.87 (d, ³J_{H,H} = 4 Hz, 2 H, thiophene), 3.31 (s, 2 H, OH), 2.86 (s, 2 H, C≡CH) ppm. ¹³C{¹H} NMR (CDCl₃): δ = 148.63 and 143.39 (s, C_{quat}, thiophene) 137.91–125.77 (Ph), 126.01 and 123.04 (CH, thiophene), 85.45 (C≡CH), 75.28 (C–OH), 71.70 (C≡CH) ppm. IR: ν̃ = 2149 (ν_{C≡C}) cm^{–1}. HR-MS (EI): *m/z* = 426.0730 [M]⁺; calcd. 426.0748. C₂₆H₁₈O₂S₂ (426.56): calcd. C 73.21, H 4.25; found C 73.10, H 4.21.

HC≡C–(OH)C(Ph)–5,5'–(2,2':5',2'–terthiophene)–(Ph)C(OH)–C≡CH (3g): By the same procedure, from 2,2':5',2'–terthiophene (248 mg, 1.0 mmol), *n*BuLi (1.37 mL, 2.2 mmol) and 1-phenyl-3-(trimethylsilyl)propyne (445 mg, 2.2 mmol), compound **3g** (300 mg) was obtained in 59% yield as a brownish oil. ¹H NMR (CDCl₃): δ = 7.71–7.23 (m, 10 H, Ph), 6.98 (m, 4 H, thiophene), 6.91 (d, 2 H, ³J_{H,H} = 4 Hz, thiophene), 3.31 (s, 2 H, OH), 2.86 (s, 2 H, C≡CH) ppm. ¹³C{¹H} NMR (CDCl₃): δ = 148.85 and 143.66 (s, C_{quat}, thiophene) 136.54–126.11 (Ph), 124.87, 123.38 and 110.10 (CH, thiophene), 85.74 (C≡CH), 75.72 (C–OH), 72.16 (C≡CH) ppm. IR: ν̃ = 2146 (ν_{C≡C}) cm^{–1}. HRMS (EI): *m/z* = 508.0633 [M]⁺; calcd. 508.0625. C₃₀H₂₀O₂S₃ (508.68): calcd. C 70.84, H 3.96; found C 70.52, H 3.78.

HC≡C–(OH)C(Ph)–C≡C–(Ph)C(OH)–C≡CH (3h): By the same method as that for the formation of **3c** or **3d**, from 1,2-dibenzoylacetylene (2.93 g, 1.25 mmol), compound **3h** (2.90 g) was obtained as a white solid in 81% yield. ¹H NMR (CDCl₃): δ = 7.80–7.33 (m, 10 H, Ph), 3.61 (s, 2 H, OH), 2.76 (s, 2 H, C≡CH)

ppm. ¹³C{¹H} NMR (CDCl₃): δ = 140.82–125.97 (Ph), 84.87 (C≡C), 83.24 (C≡CH), 74.25 (C≡CH), 64.88 (C–OH) ppm. IR: ν̃ = 2121 (ν_{C≡C}) cm^{–1}. HRMS (EI): *m/z* = 286.0989; [M]⁺; calcd. 286.0994. C₂₀H₁₄O₂ (286.33): calcd. C 83.90, H 4.93; found C 83.99, H 4.98.

1-[3,5-Bis(1-hydroxy-1-phenylprop-2-ynyl)phenyl]-1-phenylpropynol (6): By the same procedure as that for **3h**, from 1,3,5-tribenzoylbenzene (4.88 g, 12.5 mmol), compound **6** (4.09 g) was obtained in 70% yield as a white powder. ¹H NMR (CDCl₃): δ = 7.89–7.12 (m, 18 H, Ph), 5.67 (s, 3 H, OH), 3.24 (s, 3 H, C≡CH) ppm. ¹³C{¹H} NMR (CDCl₃): δ = 145.94–122.91 (Ph), 87.11 (C≡CH), 75.35 (C–OH), 73.55 (C≡CH) ppm. IR: ν̃ = 2113 (ν_{C≡C}) cm^{–1}. HRMS (EI): *m/z* = 468.1744 [M]⁺; calcd. 468.1725. C₃₃H₂₄O₃ (468.55): calcd. C 84.60, H 5.16; found C 84.75, H 5.28.

4-Ethynylbenzophenone (8): In a Schlenk tube, *p*-bromobenzophenone (2.6 g, 9.9 mmol), CuI (180 mg, 0.99 mmol), and [PdCl₂(PPh₃)₂] (690 mg, 0.495 mmol) were dissolved in Et₃N (40 mL) and THF (20 mL). Then, trimethylacetylene (1.81 mL, 1.386 mmol) was added, and the mixture was stirred for 48 h at 50 °C. After cooling, the solvent was removed and the crude product was extracted with diethyl ether and filtered through a celite pad. After evaporation, a yellow solid was obtained. In a flask, 2.4 g of this compound was dissolved in a mixture of THF/MeOH (25 mL) and KOH (12 mL, 1.6 M) was added slowly. The resulting dark mixture was stirred for 1 h at room temperature, and then the solvents were evaporated off. Purification, first by flash chromatography (silica gel, diethyl ether) and then by recrystallization in pentane, afforded **8** (1.51 g) as a pale yellow solid in 85% yield. ¹H NMR (CDCl₃): δ = 7.85–7.38 (m, 9 H, Ph), 3.22 (s, 1 H, C≡CH) ppm. ¹³C{¹H} NMR (CDCl₃): δ = 195.93 (CO) 137.46–126.30 (Ph), 82.87 (C≡CH), 80.21 (C≡CH) ppm. IR: ν̃ = 2150 (ν_{C≡C}), 1647 (ν_{CO}) cm^{–1}. HRMS (EI): *m/z* = 206.0730 [M]⁺; calcd. 206.0732. C₁₅H₁₀O (206.24): calcd. C 87.36, H 4.89; found C 87.15, H 4.87.

4,4'-Bis(ethynyl)benzophenone (13): Starting from 4,4'-dibromobenzophenone (1.69 g) and using the same procedure as that for the formation of **8**, we obtained **13** (0.98 g) as a pale yellow solid in 95% yield. ¹H NMR (CDCl₃): δ = 7.72–7.57 (m, 8 H, Ph), 3.23 (s, 2 H, C≡CH) ppm. ¹³C{¹H} NMR (CDCl₃): δ = 195.06 (CO), 137.10–126.56 (Ph), 82.76 (C≡CH), 80.35 (C≡CH) ppm. IR: ν̃ = 2158 (ν_{C≡C}), 1645 (ν_{CO}) cm^{–1}. HRMS (EI): *m/z* = 230.0730 [M]⁺; calcd. 230.0732. C₁₇H₁₀O (230.27): calcd. C 88.67, H 4.38; found C 88.86, H 4.48.

Synthesis of Monoallenylidene Ruthenium Complexes (4a–b, X = PF₆; 4c–h, X = OTf): Dichloromethane (50 mL) was added to a mixture of [Cl(dppe)₂Ru][X] (**2**) (0.5 mmol) and dipropargylic alcohol (**3**) (1 mmol). The resulting mixture was stirred at room temperature for 24 h, and the solvent was pumped to dryness. The resulting solid was washed with diethyl ether (4 × 25 mL) in order to eliminate the excess of organic reactant. Further purification was achieved by biphasic recrystallization in dichloromethane/pentane (1:2) to afford monoallenylidene complexes (**4a–h**) as powdery solids.

trans-[Cl(dppe)₂Ru=C=C=C(H)–*p*-(C₆H₄)–C(H)(OH)–(C≡C–H)]PF₆ (4a): From **3a** (186 mg), complex **4a** (486 mg) was obtained as a deep red crystalline solid in 71% yield. ¹H NMR (CD₂Cl₂): δ = 9.20 (quint, ⁵J_{PH} = 2.6 Hz, 1 H, Ru=C=C=CH), 7.53–6.88 (m, 44 H, Ph) 5.44 [d broad, ⁴J_{H,H} = 2 Hz, 1 H, HC(OH)], 3.01 (m, 4 H, CH₂ dppe), 2.81 (m, 4 H, CH₂ dppe), 2.72 (d, ⁴J_{H,H} = 2 Hz, 1 H, C≡CH) ppm. ¹³C{¹H} NMR (CD₂Cl₂): δ = 320.76 (quint, ²J_{PC} = 14.4 Hz, Ru=C), 221.91 (quint, ³J_{PC} =

2.2 Hz, Ru=C=C), 151.66 (Ru=C=C=C), 146.57–128.39 (Ph), 83.42 (C≡CH), 74.87 (C≡CH), 63.95 (C–OH), 29.42 (quint, $^1J_{\text{P,C}} + ^3J_{\text{P,C}} = 23$ Hz, PCH₂CH₂P) ppm. ^{31}P NMR (CD₂Cl₂): $\delta = 40.0$ (s, dppe), –143.9 (sept., $^1J_{\text{P,F}} = 713$ Hz, PF₆) ppm. IR: $\tilde{\nu} = 1939$ (s, $\nu_{\text{C}=\text{C}}$), 841 (s, $\nu_{\text{P,F}}$) cm^{–1}. C₆₄H₅₆ClF₆OP₃Ru·CH₂Cl₂ (1246.53): calcd. C 58.64, H 4.39; found C 58.76, H 4.61.

trans-[Cl(dppe)₂Ru=C=C=C(H)–2,5-(thiophene)–C(H)(OH)–(C≡C–H)]PF₆] (4b): From compound **3b** (192 mg), complex **4b** (257 mg) was obtained as a red crystalline solid in 41% yield. ^1H NMR (CD₂Cl₂): $\delta = 8.78$ (quint, $^3J_{\text{P,H}} = 2.6$ Hz, 1 H, Ru=C=C=CH), 7.32–6.85 (m, 42 H, Ph, C₄H₂S) 5.39 (d broad, $^4J_{\text{H,H}} = 2$ Hz, C(OH)H), 2.68 (d, $^4J_{\text{H,H}} = 2$ Hz, ≡CH), 2.99 (m, 4 H, dppe), 2.85 (m, 4 H, dppe) ppm. ^{31}P NMR (CD₂Cl₂): $\delta = 41.8$ (s, dppe), –143.5 (sept., $^1J_{\text{P,F}} = 713$ Hz, PF₆) ppm. IR: $\tilde{\nu} = 1927$ (s, $\nu_{\text{C}=\text{C}}$), 841 (s, $\nu_{\text{P,F}}$) cm^{–1}. C₆₂H₅₄ClF₆OP₃RuS (1252.56): calcd. C 59.45, H 4.35; found C 59.60, H 4.35.

trans-[Cl(dppe)₂Ru=C=C=C(Ph)–p-(C₆H₄)–C(Ph)(OH)–(C≡C–H)]CF₃SO₃] (4c): From compound **3c** (338 mg), complex **4c** (568 mg) was obtained as a deep red crystalline solid in 81% yield. ^1H NMR (CD₂Cl₂): $\delta = 7.75$ –6.68 (m, 54 H, Ph) 4.90 (s broad, 1 H, OH), 3.08 (m, 4 H, dppe), 3.04 (s, ≡CH), 2.92 (m, 4 H, dppe) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂): $\delta = 307.06$ (quint, $^2J_{\text{P,C}} = 14.5$ Hz, Ru=C), 215.14 (Ru=C=C), 160.25 (Ru=C=C=C), 148.97–125.99 (Ph), 121.43 (q, $^1J_{\text{C,F}} = 319$ Hz, CF₃SO₃), 85.17 (C≡CH), 76.43 (C–OH), 74.09 (C≡CH), 27.46 (quint, $^1J_{\text{P,C}} + ^3J_{\text{P,C}} = 23$ Hz, PCH₂CH₂P) ppm. ^{31}P NMR (CD₂Cl₂): $\delta = 38.2$ (s, dppe) ppm. IR: $\tilde{\nu} = 1921$ (s, $\nu_{\text{C}=\text{C}}$) cm^{–1}. HRMS (FAB): $m/z = 1253.2660$ [M]⁺; calcd. 1253.2640. C₇₇H₆₄ClF₃O₄P₄RuS (1402.85): calcd. C 65.93, H 4.60; found C 65.51, H 4.64.

trans-[Cl(dppe)₂Ru=C=C=C(Ph)–m-(C₆H₄)–C(Ph)(OH)–(C≡C–H)]CF₃SO₃] (4d): From compound **3d** (338 mg), complex **4d** (519 mg) was obtained as a deep red crystalline solid in 74% yield. ^1H NMR (CD₂Cl₂): $\delta = 7.78$ –6.58 (m, 54 H, Ph) 4.99 (s broad, 1 H, OH), 3.09 (m, 4 H, dppe), 3.05 (s, ≡CH), 2.94 (m, 4 H, dppe) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂): $\delta = 308.12$ (quint, $^2J_{\text{P,C}} = 14.5$ Hz, Ru=C), 216.17 (Ru=C=C), 161.25 (Ru=C=C=C), 148.98–126.90 (Ph), 121.38 (q, $^1J_{\text{C,F}} = 320$ Hz, CF₃SO₃), 85.18 (C≡CH), 76.48 (C–OH), 74.01 (C≡CH), 27.40 (quint, $^1J_{\text{P,C}} + ^3J_{\text{P,C}} = 23$ Hz, PCH₂CH₂P) ppm. ^{31}P NMR (CD₂Cl₂): $\delta = 38.2$ (s, dppe) ppm. IR: $\tilde{\nu} = 1921$ (s, $\nu_{\text{C}=\text{C}}$) cm^{–1}. HRMS (FAB): $m/z = 1253.2670$ [M]⁺; calcd. 1253.2640. C₇₇H₆₄ClF₃O₄P₄RuS (1402.85): calcd. C 65.93, H 4.60; found C 65.61, H 4.69.

trans-[Cl(dppe)₂Ru=C=C=C(Ph)–2,5-(thiophene)–C(Ph)(OH)–(C≡C–H)]CF₃SO₃] (4e): From compound **3e** (344 mg), complex **4e** (452 mg) was obtained as a deep violet crystalline solid in 64% yield. ^1H NMR (CD₂Cl₂): $\delta = 7.68$ (quint, $^3J_{\text{P,H}} = 4$ Hz, 1 H, thiophene), 7.60–6.78 (m, 51 H, Ph+C₄H₂S) 4.85 (s broad, 1 H, OH), 2.95 (s, ≡CH), 2.94 (m, 4 H, dppe), 2.76 (m, 4 H, dppe) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂): $\delta = 288.47$ (quint, $^2J_{\text{P,C}} = 15$ Hz, Ru=C), 202.24 (Ru=C=C), 164.12 (Ru=C=C=C), 150.86–125.84 (Ph, thiophene) 85.17 (C≡CH), 76.43 (C–OH), 74.09 (C≡CH), 27.46 (quint, $^1J_{\text{P,C}} + ^3J_{\text{P,C}} = 23$ Hz, PCH₂CH₂P) ppm. ^{31}P NMR (CD₂Cl₂): $\delta = 41.0$ (s, dppe) ppm. IR: $\tilde{\nu} = 1928$ (s, $\nu_{\text{C}=\text{C}}$) cm^{–1}. C₇₅H₆₂ClF₃O₄P₄RuS₂ (1408.61): calcd. C 63.94, H 4.44; found C 63.77, H 4.39.

trans-[Cl(dppe)₂Ru=C=C=C(Ph)–5,5'-(2,2'-bithiophene)–C(Ph)(OH)(C≡C–H)]CF₃SO₃] (4f): From compound **3f** (426 mg), complex **4f** (477 mg) was obtained as a dark violet solid in 64% yield. ^1H NMR (CD₂Cl₂): $\delta = 7.69$ –6.78 (m, 54 H, Ph, bithiophene) 4.92 (s broad, 1 H, OH), 3.01 (s, ≡CH), 2.95 (m, 4 H, dppe), 2.79 (m, 4 H, dppe) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂): $\delta = 288.47$ (quint, $^2J_{\text{P,C}} =$

15 Hz, Ru=C), 202.24 (Ru=C=C), 164.12 (Ru=C=C=C), 150.86–125.84 (Ph, thiophene), 85.17 (C≡CH), 76.43 (C–OH), 74.09 (C≡CH), 27.46 (quint, $^1J_{\text{P,C}} + ^3J_{\text{P,C}} = 23$ Hz, PCH₂CH₂P) ppm. ^{31}P NMR (CD₂Cl₂): $\delta = 41.0$ (s, dppe) ppm. IR: $\tilde{\nu} = 1928$ (s, $\nu_{\text{C}=\text{C}}$) cm^{–1}. HRMS (FAB): $m/z = 1341.2076$ [M]⁺; calcd. 1341.2081. C₇₉H₆₄ClF₃O₄P₄RuS₃ (1458.92): calcd. C 63.67, H 4.33; found C 63.25, H 4.19.

trans-[Cl(dppe)₂Ru=C=C=C(Ph)–5,5'-(2,2':5'2''-terthiophene)–C(Ph)(OH)(C≡C–H)]CF₃SO₃] (4g): From compound **3g** (508 mg), complex **4g** (452 mg) was obtained as a deep blue crystalline solid in 58% yield. ^1H NMR (CD₂Cl₂): $\delta = 7.78$ –6.78 (m, 56 H, Ph + terthiophene) 4.95 (s broad, 1 H, OH), 3.05 (s, 1 H, ≡CH), 2.98 (m, 4 H, dppe), 2.79 (m, 4 H, dppe) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂): $\delta = 294.48$ (quint, $^2J_{\text{P,C}} = 15$ Hz, Ru=C), 206.55 (Ru=C=C), 169.52 (Ru=C=C=C), 151.44–126.23 (Ph, thiophene) 85.81 (C≡CH), 76.95 (C–OH), 74.25 (C≡CH), 27.41 (quint, $^1J_{\text{P,C}} + ^3J_{\text{P,C}} = 23$ Hz, PCH₂CH₂P) ppm. ^{31}P NMR (CD₂Cl₂): $\delta = 41.2$ (s, dppe) ppm. IR: $\tilde{\nu} = 1922$ (s, $\nu_{\text{C}=\text{C}}$) cm^{–1}. HRMS (FAB): $m/z = 1423.1970$ [M]⁺; calcd. 1423.1958.

trans-[Cl(dppe)₂Ru=C=C=C(Ph)–(C≡C)–C(Ph)(OH)–(C≡C–H)]CF₃SO₃] (4h): From compound **3h** (286 mg), complex **4h** (506 mg) was obtained as a deep red solid in 75% yield. ^1H NMR (CD₂Cl₂): $\delta = 7.85$ –6.66 (m, 50 H, Ph), 3.08 (m, 8 H, dppe), 3.06 (s, ≡CH) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂): $\delta = 301.20$ (quint, $^2J_{\text{P,C}} = 15$ Hz, Ru=C), 229.68 (Ru=C=C), 142.24 and 141.05 (s, Ph), 134.77 (Ru=C=C=C), 133.92–125.95 (Ph), 120.89 (q, $^1J_{\text{C,F}} = 320$ Hz, CF₃SO₃), 95.60 and 91.04 (C≡C), 82.17 (C≡CH), 75.07 (C≡CH), 65.59 (C–OH), 27.25 (quint, $^1J_{\text{P,C}} + ^3J_{\text{P,C}} = 23$ Hz, PCH₂CH₂P) ppm. ^{31}P NMR (CD₂Cl₂): $\delta = 38.0$ (s, dppe) ppm. IR: $\tilde{\nu} = 1921$ (s, $\nu_{\text{C}=\text{C}}$) cm^{–1}. HRMS (FAB): $m/z = 1201.2336$ [M]⁺; calcd. 1201.2327. C₇₃H₆₀ClF₃O₄P₄RuS (1350.76): calcd. C 64.91, H 4.48; found C 64.97, H 4.47.

Synthesis of Bis(allylenylidene)ruthenium Complexes (5a–b, X=PF₆; 5c–h, X=OTf): To a mixture of [Cl(dppe)₂Ru][X] (0.5 mmol) and dipropargylic alcohol (**3**) (0.2 mmol), dichloromethane (50 mL) was added. The resulting mixture was stirred at room temperature for 7 d, and the solvent was evaporated. The resulting solid was washed with diethyl ether (4 × 25 mL) in order to eliminate the organic reactant excess, and was precipitated three times with 60 mL of pentane after dissolution in dichloromethane (20 mL). Further purification was achieved by biphasic recrystallization in dichloromethane/pentane (1:2) to afford the bis(allylenylidene) complexes **5a–h** as powdery solids.

trans-[Cl(dppe)₂Ru=C=C=C(H)–p-(C₆H₄)–(H)C=C=C–RuCl(dppe)₂]PF₆] (5a): From **3a** (36 mg), complex **5a** (208 mg) was obtained as a blue crystalline solid in 45% yield. ^1H NMR (CD₂Cl₂): $\delta = 9.64$ (quint, $^5J_{\text{P,H}} = 2.8$ Hz, 2 H, Ru=C=C=CH), 7.31–6.46 (m, 84 H, Ph), 2.99 (m, 16 H, dppe) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂): $\delta = 326.28$ (quint, $^2J_{\text{P,C}} = 15$ Hz, Ru=C), 241.33 (Ru=C=C), 152.01 (Ru=C=C=C), 143.24–128.41 (Ph), 29.52 (quint, $^1J_{\text{P,C}} + ^3J_{\text{P,C}} = 23$ Hz, PCH₂CH₂P) ppm. ^{31}P NMR (CD₂Cl₂): $\delta = 39.2$ (s, dppe) ppm. IR: $\tilde{\nu} = 1918$ (s, $\nu_{\text{C}=\text{C}}$) cm^{–1}. C₁₁₆H₁₀₂Cl₂F₁₂P₁₀Ru₂ (2306.85): calcd. C 60.44, H 4.46; found C 59.87, H 4.28.

trans-[Cl(dppe)₂Ru=C=C=C(H)–2,5-(thiophene)–(H)C=C=C–RuCl(dppe)₂]PF₆] (5b): From **3b** (39 mg), complex **5b** (224 mg) was obtained as a deep blue solid in 49% yield. ^1H NMR (CD₂Cl₂): $\delta = 9.36$ (m, 2 H, Ru=C=C=CH), 7.31–6.90 (m, 82 H, Ph, thiophene), 3.06 (m, 16 H, dppe) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₂Cl₂): $\delta = 310.53$ (quint, $^2J_{\text{P,C}} = 17$ Hz, Ru=C), 237.55 (Ru=C=C), 158.33 (Ru=C=C=C), 134.31–128.37 (Ph, thiophene), 29.76 (quint, $^1J_{\text{P,C}} + ^3J_{\text{P,C}} = 23$ Hz, PCH₂CH₂P) ppm. ^{31}P NMR (CD₂Cl₂): $\delta = 39.1$

(s, dppe) ppm. IR: $\tilde{\nu}$ = 1913 (s, $\nu_{C=C}$) cm^{-1} . $\text{C}_{114}\text{H}_{100}\text{Cl}_2\text{F}_{12}\text{P}_{10}\text{Ru}_2\text{S}$ (2312.22): calcd. C 59.20, H 4.36; found C 59.40, H 4.76.

trans-[Cl(dppe)₂Ru=C=C=C(Ph)-p-(C₆H₄)-(Ph)C=C=C=RuCl(dppe)₂][CF₃SO₃]₂ (5c): From **3c** (68 mg), complex **5c** (385 mg) was obtained as a deep blue solid in 78% yield. ¹H NMR (CD₂Cl₂): δ = 7.33–6.56 (m, 94 H, Ph), 3.04 (m, 8 H, dppe), 2.79 (m, 8 H, dppe) ppm. ¹³C{¹H} NMR (CD₂Cl₂): δ = 310.98 (quint, ²J_{PC} = 15 Hz, Ru=C), 228.87 (Ru=C=C), 158.17 (Ru=C=C=C), 145.91–128.41 (s, Ph), 121.51 (q, ¹J_{C,F} = 320 Hz, CF₃SO₃), 27.88 (quint, ¹J_{PC} + ³J_{PC} = 23 Hz, PCH₂CH₂P) ppm. ³¹P NMR (CD₂Cl₂): δ = 38.0 (s, dppe) ppm. IR: $\tilde{\nu}$ = 1912 (s, $\nu_{C=C}$) cm^{-1} . HRMS (FAB): m/z = 2317.3563 [M]⁺⁺; calcd. 2317.3493. $\text{C}_{130}\text{H}_{110}\text{Cl}_2\text{F}_6\text{P}_8\text{O}_6\text{Ru}_2\text{S}_2$ (2467.26): calcd. C 63.29, H 4.49; found C 62.49, H 4.45.

trans-[Cl(dppe)₂Ru=C=C=C(Ph)-m-(C₆H₄)-(Ph)C=C=C=RuCl(dppe)₂][CF₃SO₃]₂ (5d): From **3d** (64 mg), complex **5d** (222 mg) was obtained as a deep red solid in 45% yield. ¹H NMR (CD₂Cl₂): δ = 7.72–6.78 (m, 94 H, Ph), 3.07 (m, 8 H, dppe), 2.97 (m, 8 H, dppe) ppm. ¹³C{¹H} NMR (CD₂Cl₂): δ = 310.01 (quint, ²J_{PC} = 15 Hz, Ru=C), 224.21 (Ru=C=C), 157.47 (s, Ru=C=C=C), 145.84–128.37 (Ph), 121.55 (q, ¹J_{C,F} = 320 Hz, CF₃SO₃), 28.15 (quint, ¹J_{PC} + ³J_{PC} = 23 Hz, PCH₂CH₂P) ppm. ³¹P NMR (CD₂Cl₂): δ = 38.8 (s, dppe) ppm. IR: $\tilde{\nu}$ = 1913 (s, $\nu_{C=C}$) cm^{-1} . HRMS (FAB): m/z = 2317.3507 [M]⁺⁺; calcd. 2317.3493. $\text{C}_{130}\text{H}_{110}\text{Cl}_2\text{F}_6\text{P}_8\text{O}_6\text{Ru}_2\text{S}_2$ (2467.26): calcd. C 63.29, H 4.49; found C 63.11, H 4.51.

trans-[Cl(dppe)₂Ru=C=C=C(Ph)-2,5-(thiophene)-(Ph)C=C=C=RuCl(dppe)₂][CF₃SO₃]₂ (5e): From **3e** (69 mg), complex **5e** (306 mg) was obtained as a deep blue solid in 62% yield. ¹H NMR (CD₂Cl₂): δ = 7.85–6.82 (m, 90 H, Ph), 6.30 (s, 2 H, thiophene), 3.18 (m, 8 H, dppe), 2.85 (m, 8 H, dppe) ppm. ¹³C{¹H} NMR (CD₂Cl₂): δ = 311.53 (quint, ²J_{PC} = 15 Hz, Ru=C), 237.85 (Ru=C=C), 159.33 (Ru=C=C=C), 134.39–128.87 (Ph, thiophene), 121.55 (q, ¹J_{C,F} = 320 Hz, CF₃SO₃), 29.66 (quint, ¹J_{PC} + ³J_{PC} = 23 Hz, PCH₂CH₂P) ppm. ³¹P NMR (CD₂Cl₂): δ = 39.3 (s, dppe) ppm. IR: $\tilde{\nu}$ = 1904 (s, $\nu_{C=C}$) cm^{-1} . HRMS (FAB): m/z = 2173.3587 [M]⁺⁺ – H⁺; calcd. 2173.3459. $\text{C}_{128}\text{H}_{108}\text{Cl}_2\text{F}_6\text{P}_8\text{O}_6\text{Ru}_2\text{S}_3$ (2473.29): calcd. C 62.16, H 4.40; found C 61.97, H 4.37.

trans-[Cl(dppe)₂Ru=C=C=C(Ph)-5,5'-(2,2'-bithiophene)(Ph)C=C=C=RuCl(dppe)₂][CF₃SO₃]₂ (5f): From **3f** (85 mg), complex **5f** (260 mg) was obtained as a deep blue solid in 51% yield. ¹H NMR (CD₂Cl₂): δ = 7.85–6.82 (m, 94 H, Ph, thiophene), 3.04 (m, 16 H, dppe) ppm. ¹³C{¹H} NMR (CD₂Cl₂): δ = 312.24 (quint, ²J_{PC} = 17 Hz, Ru=C), 236.47 (Ru=C=C), 158.99 (Ru=C=C=C), 135.30–128.47 (Ph, thiophene), 121.55 (q, ¹J_{C,F} = 320 Hz, CF₃SO₃), 30.05 (quint, ¹J_{PC} + ³J_{PC} = 23 Hz, PCH₂CH₂P) ppm. ³¹P NMR (CD₂Cl₂): δ = 39.6 (s, dppe) ppm. IR: $\tilde{\nu}$ = 1925 (s, $\nu_{C=C}$) cm^{-1} . $\text{C}_{132}\text{H}_{110}\text{Cl}_2\text{F}_6\text{P}_8\text{O}_6\text{Ru}_2\text{S}_4$ (2555.41): calcd. C 62.07, H 4.30; found C 61.87, H 4.20.

trans-[Cl(dppe)₂Ru=C=C=C(Ph)-5,5'-(2,2':5',2''terthiophene)-(Ph)C=C=C=RuCl(dppe)₂][CF₃SO₃]₂ (5g): From **3g** (102 mg), complex **5g** (232 mg) were obtained as a deep blue solid in 44% yield. ¹H NMR (CD₂Cl₂): δ = 7.85–6.82 (m, 96 H, Ph, thiophene), 2.99 (m, 16 H, dppe) ppm. ¹³C{¹H} NMR (CD₂Cl₂): δ = 313.83 (quint, ²J_{PC} = 17 Hz, Ru=C), 237.85 (Ru=C=C), 159.33 (Ru=C=C=C), 136.30–127.37 (Ph, thiophene), 121.55 (q, ¹J_{C,F} = 320 Hz, CF₃SO₃), 30.96 (quint, ¹J_{PC} + ³J_{PC} = 23 Hz, PCH₂CH₂P) ppm. ³¹P NMR (CD₂Cl₂): δ = 40.3 (s, dppe) ppm. IR: $\tilde{\nu}$ = 1929 (s, $\nu_{C=C}$) cm^{-1} . HRMS (FAB): m/z = 2254.3332 [M]⁺⁺; calcd.

2254.3336. $\text{C}_{136}\text{H}_{112}\text{Cl}_2\text{F}_6\text{P}_8\text{O}_6\text{Ru}_2\text{S}_5$ (2637.54): calcd. C 61.93, H 4.28; found C 62.07, H 4.19.

trans-[Cl(dppe)₂Ru=C=C=C(Ph)-(C≡C)-(Ph)C=C=C=RuCl(dppe)₂][CF₃SO₃]₂ (5h): From **3h** (57 mg), complex **5h** (203 mg) was obtained as a deep blue solid in 42% yield. ¹H NMR (CD₂Cl₂): δ = 7.74–6.67 (m, 90 H, Ph), 2.98 (m, 16 H, dppe) ppm. ³¹P NMR (CD₂Cl₂): δ = 37.8 (s, dppe) ppm. IR: $\tilde{\nu}$ = 1921 (s, $\nu_{C=C}$) cm^{-1} . HRMS (FAB): m/z = 2116.3666 [M]⁺⁺; calcd. 2116.3659.

trans-[3,5-Bis[Cl(dppe)₂Ru=C=C=C(Ph)]₂-(C₆H₃)-C(Ph)-(OH)(C≡C-H)][CF₃SO₃]₂ (7): From **6** (36 mg), complex **7** (208 mg) was obtained as a deep red solid in 63% yield. ¹H NMR (CD₂Cl₂): δ = 7.75–6.48 (m, 98 H, Ph), 4.91 (s broad, 1 H, OH), 3.07 (m, 8 H, dppe), 3.05 (s, 1 H, C≡CH), 2.93 (m, 8 H, dppe) ppm. ¹³C{¹H} NMR (CD₂Cl₂): δ = 311.55 (quint, ²J_{PC} = 15 Hz, Ru=C), 225.52 (Ru=C=C), 156.73 (Ru=C=C=C), 149.38–127.47 (Ph), 121.55 (q, ¹J_{C,F} = 320 Hz, CF₃SO₃), 86.30 (C≡CH), 77.62 (C–OH), 73.09 (s, C≡CH), 28.11 (quint, ¹J_{PC} + ³J_{PC} = 23 Hz, PCH₂CH₂P) ppm. ³¹P NMR (CD₂Cl₂): δ = 38.1 (s, dppe) ppm. IR: $\tilde{\nu}$ = 1921 (s, $\nu_{C=C}$) cm^{-1} . HRMS (FAB): m/z = 2448.3392 ([M]⁺⁺, CF₃SO₃[–]); calcd. 2448.3960. $\text{C}_{139}\text{H}_{116}\text{Cl}_2\text{F}_6\text{P}_8\text{O}_7\text{Ru}_2\text{S}_2$ (2581.41): calcd. C 64.28, H 4.50; found C 65.51, H 4.64.

Synthesis of (Acetylide–allenylidene)ruthenium Complexes

trans-[Cl(dppe)₂Ru=C=CH-p-(C₆H₄)-CO-Ph][CF₃SO₃]₂ (9): In a Schlenk tube, **2b** (1.67 g, 1.55 mmol) and 4-ethynylbenzophenone (**8**) (350 mg, 1.7 mmol) were dissolved in dry dichloromethane (40 mL) and stirred at room temperature for 18 h. Then, the brown solution was filtered, and the solvent was evaporated. The crude product was washed with diethyl ether. Purification was achieved by biphasic recrystallization (CH₂Cl₂/pentane) to afford complex **9** (1.42 g) as orange crystals in 71% yield. ¹H NMR (CD₂Cl₂): δ = 7.82–6.95 (m, 49 H, Ph), 4.82 (quint, ⁴J_{PH} = 3 Hz, 1 H, Ru=C=CH), 2.92 (m, 8 H, dppe) ppm. ¹³C{¹H} NMR (CD₂Cl₂): δ = 352.01 (quint, ²J_{PC} = 14 Hz, Ru=C), 195.41 (CO), 138.01–126.85 (Ph), 123.05 (q, ¹J_{C,F} = 320 Hz, CF₃SO₃), 109.64 (quint, ²J_{PC} = 3 Hz, Ru=C=CH), 29.16 (quint, ¹J_{PC} + ³J_{PC} = 23 Hz, PCH₂CH₂P) ppm. ³¹P NMR (CD₂Cl₂): δ = 36.3 (s, dppe) ppm. IR: $\tilde{\nu}$ = 1588 (s, $\nu_{C=C}$), 1647 (s, ν_{CO}) cm^{-1} . HRMS (FAB): m/z = 1139.2186 [M]⁺; calcd. 1139.2170. $\text{C}_{68}\text{H}_{58}\text{ClF}_3\text{P}_4\text{O}_4\text{RuS}$ (1288.69): calcd. C 63.38, H 4.54; found C 63.40, H 4.53.

trans-[Cl(dppe)₂Ru-C≡C-p-(C₆H₄)-CO-Ph] (10): In a Schlenk tube, complex **9** (625 mg, 0.485 mmol) was dissolved in dry dichloromethane (20 mL) and DBU (0.150 mL, 0.970 mmol) was added. The solution was stirred at room temperature for 2 h and filtered through neutral alumina. The solvent was evaporated to afford **10** (518 mg) as a yellow solid in 92% yield. ¹H NMR (CD₂Cl₂): δ = 7.83–6.64 (m, 49 H, Ph), 2.76 (m, 8 H, dppe) ppm. ¹³C{¹H} NMR (CD₂Cl₂): δ = 195.9 (CO), 139.26–127.49 (Ph), 138.98 (²J_{PC} = 15 Hz, Ru–C≡C), 115.62 (Ru–C≡C), 30.99 (quint, ¹J_{PC} + ³J_{PC} = 23 Hz, PCH₂CH₂P) ppm. ³¹P NMR (CD₂Cl₂): δ = 48.9 (s, dppe) ppm. IR: $\tilde{\nu}$ = 2057 (s, $\nu_{C=C}$), 1584 (s, ν_{CO}) cm^{-1} . HRMS (FAB): m/z = 1138.2076 [M]⁺; calcd. 1138.2092. $\text{C}_{67}\text{H}_{57}\text{ClP}_4\text{ORu}$ (1138.61): calcd. C 70.68, H 5.05; found C 70.08, H 4.92.

trans-[Cl(dppe)₂Ru-C≡C-p-(C₆H₄)-C(OH)(Ph)C≡CH] (11): In a Schlenk tube, acetylene (5 mmol) was dissolved in dry THF (20 mL) cooled to –78 °C. *n*-Butyllithium (1.6 mL, 1 mmol, 1.6 M in hexane) was added slowly under argon and the mixture was stirred at –78 °C for 1 h. Then, **10** (445 mg 0.4 mmol) dissolved in THF (5 mL) was added dropwise. The solution was stirred for 1 h at –78 °C and 1 h at room temperature. After evaporation of the

solvent, the crude product was dissolved in dichloromethane (50 mL), washed with water and dried with magnesium sulfate. Purification by flash chromatography (neutral alumina, dichloromethane) provided **11** (366 mg) as a pale yellow powder in 78% yield. ^1H NMR (CD_2Cl_2): δ = 7.79–6.58 (m, 49 H, Ph), 2.86 (s, 1 H, $\text{C}\equiv\text{CH}$), 2.75 (s, 1 H, OH), 2.64 (m, 8 H, dppe) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ = 144.77–135.46 (Ph), 134.89 (quint, $^2J_{\text{P,C}} = 15$ Hz, $\text{Ru}-\text{C}\equiv\text{C}-$), 134.39–125.35 (Ph), 113.63 ($\text{Ru}-\text{C}\equiv\text{C}$), 30.99 (quint, $^1J_{\text{P,C}} + ^3J_{\text{P,C}} = 23$ Hz, $\text{PCH}_2\text{CH}_2\text{P}$) ppm. ^{31}P NMR (CD_2Cl_2): δ = 50.2 (s, dppe) ppm. IR: $\tilde{\nu}$ = 3050 (s, ν_{CH}), 2135 (s, $\nu_{\text{C}\equiv\text{CH}}$), 2065 (s, $\nu_{\text{C}\equiv\text{C}}$) cm^{-1} . HRMS (FAB): m/z = 1164.2255 [M] $^{+}$; calcd. 1164.2249. $\text{C}_{69}\text{H}_{59}\text{ClP}_4\text{ORu}$ (1164.65): calcd. C 71.16, H 5.11; found C 71.23, H 5.14.

trans-[Cl(dppe) $_2$ Ru-C $\equiv$ C-*p*-(C $_6$ H $_4$)-(Ph)C=C=C-RuCl(dppe) $_2$][CF $_3$ SO $_3$] (12): In a Schlenk tube **11** (300 mg, 0.258 mmol) and **2b** (200 mg, 0.284 mmol) were dissolved in dichloromethane (50 mL), and the resulting mixture was stirred at room temperature for 8 days. After evaporation of the solvent, the crude product was washed with ether (4 $\times$ 25 mL) and precipitated three times with 60 mL of pentane after dissolution in dichloromethane (20 mL). Purification was achieved by biphasic recrystallization (dichloromethane/pentane 1:2) to afford **12** (420 mg) as a deep purple solid in 72% yield. ^1H NMR (CD_2Cl_2): δ = 7.84–6.18 (m, 89 H, Ph), 3.04 (m, 8 H, dppe), 2.77 (m, 8 H, dppe) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ = 345.62 (quint, $^2J_{\text{P,C}} = 15$ Hz, $\text{Ru}=\text{C}$), 192.85 ($\text{Ru}=\text{C}=\text{C}$), 158.32 ($\text{Ru}=\text{C}=\text{C}=\text{C}$), 143.51–123.21 (Ph), 135.45 (quint, $^2J_{\text{P,C}} = 15$ Hz, $\text{Ru}-\text{C}\equiv\text{C}-$), 113.63 ($\text{Ru}-\text{C}\equiv\text{C}$), 30.71 (quint, $^1J_{\text{P,C}} + ^3J_{\text{P,C}} = 23$ Hz, $\text{PCH}_2\text{CH}_2\text{P}$), 27.82 (quint, $^1J_{\text{P,C}} + ^3J_{\text{P,C}} = 23$ Hz, $\text{PCH}_2\text{CH}_2\text{P}$) ppm. ^{31}P NMR (CD_2Cl_2): δ = 49.2 (s, dppe), 40.7 (s, dppe) ppm. IR: $\tilde{\nu}$ = 2040 (s, $\nu_{\text{C}\equiv\text{C}}$), 1926 ($\nu_{\text{C}=\text{C}=\text{C}}$) cm^{-1} . HRMS (FAB): m/z = 2079.3555 [M] $^{+}$; calcd. 2079.3581. $\text{C}_{122}\text{H}_{105}\text{F}_3\text{Cl}_2\text{O}_3\text{P}_8\text{Ru}_2\text{S}$ (2229.08): calcd. C 65.74, H 4.75; found C 65.90, H 4.88.

trans-[Cl(dppe) $_2$ Ru-C $\equiv$ CH-*p*-(C $_6$ H $_4$)-CO-*p*-(C $_6$ H $_4$)-CH=C-RuCl(dppe) $_2$][CF $_3$ SO $_3$] (14): In a Schlenk tube **2b** (1.62 g, 1.5 mmol) and 4,4'-bis(ethynyl)benzophenone (**13**) (154 mg, 0.67 mmol) were dissolved in dry dichloromethane (30 mL), and the mixture was stirred for 18 h at room temperature. After filtration and evaporation of the solvent, the crude product was washed with ether (4 $\times$ 40 mL) and recrystallized by the biphasic method to afford **14** (1.31 g) as orange crystals in 82% yield. ^1H NMR (CD_2Cl_2): δ = 7.67–5.77 (m, 88 H, Ph), 4.74 (quint, $^2H^4J_{\text{PH}} = 3$ Hz, $\text{Ru}=\text{C}=\text{CH}$), 3.01 (m, 16 H, dppe) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ = 354.02 (quint, $^2J_{\text{P,C}} = 14$ Hz, $\text{Ru}=\text{C}$), 196.81 (CO), 138.48–126.95 (Ph), 123.15 (q, $^1J_{\text{C,F}} = 320$ Hz, CF_3SO_3), 109.84 (quint, $^3J_{\text{P,C}} = 3$ Hz, $\text{Ru}=\text{C}=\text{CH}$), 30.16 (quint, $^1J_{\text{P,C}} + ^3J_{\text{P,C}} = 23$ Hz, $\text{PCH}_2\text{CH}_2\text{P}$) ppm. ^{31}P NMR (CD_2Cl_2): δ = 37.3 (s, dppe) ppm. IR: $\tilde{\nu}$ = 1592 (s, $\nu_{\text{C}=\text{C}}$), 1633 (ν_{CO}) cm^{-1} . HRMS (FAB): m/z = 2095.3564 [M] $^{+}$; calcd. 2095.3530. $\text{C}_{123}\text{H}_{106}\text{Cl}_2\text{F}_6\text{O}_7\text{P}_8\text{Ru}_2\text{S}_2$ (2295.15): calcd. C 61.68, H 4.46; found C 61.55, H 4.27.

trans-[Cl(dppe) $_2$ Ru-C $\equiv$ C-*p*-(C $_6$ H $_4$)-CO-*p*-(C $_6$ H $_4$)-C $\equiv$ C-RuCl(dppe) $_2$] (15): In a Schlenk tube **14** (1.31 g, 0.55 mmol) was dissolved in dry dichloromethane (30 mL) and DBU (0.175 mL, 1.10 mmol) was added slowly. The solution was stirred at room temperature for 2 h. After filtration through neutral alumina and evaporation of the solvent, **15** (1.01 g) was obtained as a yellow solid in 87% yield. ^1H NMR (CD_2Cl_2): δ = 7.59–6.64 (m, 88 H, Ph), 2.68 (m, 16 H, dppe) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ = 191.16 (CO), 136.98 (quint, $^2J_{\text{P,C}} = 15$ Hz, $\text{Ru}-\text{C}\equiv\text{C}-$), 135.41–127.45 (Ph), 115.84 ($\text{Ru}-\text{C}\equiv\text{C}$), 31.10 (quint, $^1J_{\text{P,C}} + ^3J_{\text{P,C}} = 23$ Hz, $\text{PCH}_2\text{CH}_2\text{P}$) ppm. ^{31}P NMR (CD_2Cl_2): δ = 50.0 (s,

dppe) ppm. IR: $\tilde{\nu}$ = 2053 (s, $\nu_{\text{C}\equiv\text{C}}$), 1584 (s, ν_{CO}) cm^{-1} . HRMS (FAB): m/z = 2094.3440 [M] $^{+}$; calcd. 2094.3452. $\text{C}_{121}\text{H}_{101}\text{Cl}_2\text{P}_8\text{ORu}_2$ (2091.15): calcd. C 69.37, H 5.00; found C 69.12, H 4.87.

trans-[Cl(dppe) $_2$ Ru-C $\equiv$ C-*p*-(C $_6$ H $_4$)-C(OH)(C $\equiv$ CH)-*p*-(C $_6$ H $_4$)-C $\equiv$ C-RuCl(dppe) $_2$] (16): In a Schlenk tube, acetylene (4 mmol) was dissolved in dry THF (20 mL) cooled to -78°C , *n*-butyllithium (0.8 mL, 0.5 mmol, 1.6 M in hexane) was added slowly, and the mixture was stirred for 1 h at -78°C . Then, **15** (500 mg, 0.238 mmol) was dissolved in dry THF (5 mL) and added dropwise to the mixture. The solution was stirred for 30 min at -78°C and 1 h at room temperature. The solvent was evaporated, the crude product dissolved in dichloromethane (40 mL), washed with water, and dried with MgSO_4 . Purification by flash chromatography (aluminum oxide, dichloromethane) afforded **16** (431 mg) as a yellow solid in 85% yield. ^1H NMR (CD_2Cl_2): δ = 7.66–6.92 (m, 88 H, Ph), 2.95 (s, 1 H, OH), 2.63 (m, 16 H, dppe), 2.58 (s, 1 H, $\text{C}\equiv\text{CH}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ = 138.64–125.42 (Ph), 134.89 (quint, $^2J_{\text{P,C}} = 15$ Hz, $\text{Ru}-\text{C}\equiv\text{C}-$), 113.75 ($\text{Ru}-\text{C}\equiv\text{C}$), 86.28 ($\text{C}\equiv\text{CH}$), 74.91 ($\text{C}\equiv\text{CH}$), 74.54 ($\text{C}-\text{OH}$), 30.77 (quint, $^1J_{\text{P,C}} + ^3J_{\text{P,C}} = 23$ Hz, $\text{PCH}_2\text{CH}_2\text{P}$) ppm. ^{31}P NMR (CD_2Cl_2): δ = 50.1 (s, dppe) ppm. IR: $\tilde{\nu}$ = 3052 (s, ν_{CH}), 2136 (s, $\nu_{\text{C}\equiv\text{CH}}$), 2068 (s, $\nu_{\text{C}\equiv\text{C}}$) cm^{-1} . HRMS (FAB): m/z = 2120.3666 [M] $^{+}$; calcd. 2120.3609. $\text{C}_{123}\text{H}_{106}\text{Cl}_2\text{P}_8\text{ORu}_2$ (2221.4): calcd. C 69.65, H 5.04; found C 69.37, H 5.12.

trans-[Cl(dppe) $_2$ Ru-C $\equiv$ C-*p*-(C $_6$ H $_4$) $_2$ C=C=C-RuCl(dppe) $_2$][CF $_3$ SO $_3$] (17): In a Schlenk tube, **16** (250 mg, 0.118 mmol) and **2b** (139 mg, 0.129 mmol) were dissolved in dichloromethane (50 mL). The mixture was stirred at room temperature for 14 d. The solvent was removed under vacuum, and the crude product was washed with diethyl ether. The product was precipitated three times with 60 mL of pentane after dissolution in dichloromethane (20 mL), and purification was achieved by biphasic recrystallization (dichloromethane/pentane, 1:2) to afford **17** (420 mg) as a deep green solid in 83% yield. ^1H NMR (CD_2Cl_2): δ = 7.57–6.20 (m, 128 H, Ph), 2.94 (m, 8 H, dppe), 2.74 (m, 8 H, dppe), 2.54 (m, 8 H, dppe) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ = 342.32 (quint, $^2J_{\text{P,C}} = 14$ Hz, $\text{Ru}=\text{C}$), 190.85 ($\text{Ru}=\text{C}=\text{C}$), 154.32 ($\text{Ru}=\text{C}=\text{C}=\text{C}$), 138.64–125.42 (Ph), 134.29 (quint, $^2J_{\text{P,C}} = 15$ Hz, $\text{Ru}-\text{C}\equiv\text{C}-$), 116.75 (s, $\text{Ru}-\text{C}\equiv\text{C}$), 30.69 (quint, $^1J_{\text{P,C}} + ^3J_{\text{P,C}} = 23$ Hz, $\text{PCH}_2\text{CH}_2\text{P}$), 28.77 (quint, $^1J_{\text{P,C}} + ^3J_{\text{P,C}} = 23$ Hz, $\text{PCH}_2\text{CH}_2\text{P}$) ppm. ^{31}P NMR (CD_2Cl_2): δ = 49.3 (s, dppe), 40.6 (s, dppe) ppm. IR: $\tilde{\nu}$ = 2008 (s, $\nu_{\text{C}\equiv\text{C}}$), 1912 (s, $\nu_{\text{C}=\text{C}=\text{C}}$) cm^{-1} . HRMS (FAB): m/z = 3035.4966 [M] $^{+}$; calcd. 3035.4941. $\text{C}_{176}\text{H}_{152}\text{Cl}_3\text{F}_3\text{O}_3\text{P}_{12}\text{Ru}_3\text{S}$ (3185.46): calcd. C 66.36, H 4.81; found C 66.65, H 4.90.

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