1',1"'-Bis(ethynyl)biferrocene as a Linking Group for Gold, Ruthenium, and Osmium Fragments: Synthesis, Solid State Structures, and Electrochemical, UV–Vis, and EPR Spectroscopical Studies

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A series of organometallic mono- and disubstituted bis(alkynyl)biferrocenes of type $(L_nMC\equiv C)$ - $(HC\equiv C)bfc (L_nM = (\eta^5-C_5H_5)(Ph_3P)_2Ru (8a), (\eta^5-C_5H_5)(Ph_3P)_2Os (8b), (\eta^5-C_5H_5)(dppf)Ru (8c); bfc = 1',1'''-biferrocenyl, <math>((\eta^5-C_5H_4)_2Fe)_2$; dppf = 1,1'-bis(diphenyl)phosphanyl ferrocene, $(\eta^5-C_5H_4PPh_2)_2Fe)$ and $(L_nMC\equiv C)_2bfc (L_nM = (Ph_3P)Au (6), (\eta^5-C_5H_5)(Ph_3P)_2Ru (9a), (\eta^5-C_5H_5)(Ph_3P)_2Os (9b), (\eta^5-C_5H_5)(dppf)Ru (9c))$ have been synthesized from $(HC\equiv C)_2bfc (4)$ with either $(Ph_3P)AuCl (5)$ in the presence of $HNEt_2/[CuI]$ (synthesis of 6) or $L_nMX (L_nMX = (\eta^5-C_5H_5)(Ph_3P)_2RuCl (7a); (\eta^5-C_5H_5)(Ph_3P)_2Os F (7b); (\eta^5-C_5H_5)(dppf)RuCl (7c))$ together with $[H_4N]PF_6$ and KOtBu (synthesis of 8 and 9), respectively. The structures of 6, 8b, 9a, 9b, and 9c in the solid state were determined by single-crystal X-ray structure analysis, showing unsymmetrical (8) or symmetrical geometries (6, 9), with almost eclipsed conformation of the bfc cyclopentadienyl rings and with *anti* geometry of the linear ethynyl connecting units. UV-vis and NIR spectroscopic measurements suggest a weak interaction between the appropriate metal atoms. The associated radical cations were *in situ* generated by stepwise chemical oxidation and characterized by continuous wave electron paramagnetic resonance (EPR) investigations in X-band performed at low temperature.

Introduction

Biferrocenes (bfc) in which two ferrocenyl units are connected by forming a fulvalenide bridge have attracted much attention because they easily can form mixed-valent Fe(II)–Fe(III) species by electrochemical or chemical oxidation.¹ Molecules of this type are of interest due to their robustness and electronrichness. Those with high conjugation can form multiple electroactive systems joined by a conjugated assembly. Hitherto, electron transfer rates and charge delocalization of alkynyl- and mainly alkyl-functionalized biferrocenium salts have been studied. The structures of these systems in the solid state showed *non*equivalence in the ferrocenyl entities.² As organometallic alkynyl ligands, bis(alkynyl)biferrocenes offer versatile synthetic usability and, due to their structural rigidity, can be considered as bridging and redox-active units between transition metal fragments, allowing communication through the delocalized bonds in the respective array. In contrast to ferrocenes, 1',1'''-functionalized biferrocenyls are less studied due to the lack of straightforward synthesis methodologies.³ Recently, Dong,⁴ Long,^{3a,b} Robinson,^{2a} and our group⁵ reported on the synthesis, reaction chemistry, and electrochemical

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Scheme 1. Modified Synthesis Methodology to Prepare Bis(ethynyl)biferrocene, 4



behavior of alkynyl-containing biferrocenes and polyferrocenes. It was found that ethynyl(poly)ferrocenyl fragments can act as organometallic linking units in molecular switches and arrays; however, the bfc core is incapable of modulating the redox chemistry of cobalt- and platinum-containing terminal groups. To gain a better understanding of the electronic behavior of these molecules, CACAO theoretical studies were carried out on $((Et_3P)_2(Ph)PtC \equiv C)_2bfc$, indicating that the SHOMO is located at the iron atoms and that there is no appropriate route for conjugation between platinum and the central bfc unit.^{2a,3a,6} In contrast, when the end-grafted moieties are manganese-based organometallic fragments, e.g., $Mn(CO)_3(\eta^2-Ph_2PCH_2PPh_2)$, it is observed that the Mn metal atoms donate electron density through the acetylene linkage to the biferrocene spacer.^{3b} In case of the appropriate ruthenium-bfc compounds, for example, $((\eta^2-Ph_2PCH_2PPh_2)(Cl)RuC \equiv C)_2$ bfc, there are different results reported.3b

Based on this contrariety we here report a straightforward method to synthesize gold-, ruthenium-, and osmium-containing bis(ethynyl)biferrocenes. Electrochemical studies together with electron paramagnetic resonance measurements of corresponding radical cations *in situ* prepared by chemical oxidation and UV–vis and NIR spectroscopical studies are also reported.

Results and Discussion

Synthesis. The preparation of bis(ethynyl)biferrocene (**4**) was reported previously by Long and co-workers.^{3a,b} We here describe a new synthesis methodology to prepare **4** with improved yields and ease of purification. The synthesis of **4** was accomplished by the palladium—copper-catalyzed Sonogashira cross-coupling of 2-methyl-3-butyn-2-ol (**2**) with diiodobiferrocene (**1**) in refluxing diisopropylamine to produce (Me₂(OH)C–C≡C)₂bfc (**3**) (bfc = 1',1'''-biferrocenyl, ((η^{5} -C₅H₄)₂Fe)₂). The deprotection of the propargylic groups with powdered KOH in toluene gave orange-red (HC≡C)₂bfc (**4**) (Scheme 1). The advantage of this procedure in comparison to that described earlier^{3a,b} is, in addition to the somewhat higher yield, the more straightforward purification of intermediate **3** (Experimental Section).

The synthesis of $((Ph_3P)AuC \equiv C)_2 bfc$ (6) was accomplished by the [CuI]-catalyzed reaction of 4 with $(Ph_3P)AuCl$ (5) in a 1:1 mixture of diethylamine/tetrahydrofuran with concomitant precipitation of $[Et_2NH_2]Cl$ at ambient temperature (reaction 1). After appropriate workup, complex 6 was obtained as a yellow, fairly stable solid in 55% yield, which dissolves in organic solvents such as tetrahydrofuran and dichloromethane.



The synthesis of mono- and disubstituted ruthenium- and osmium-acetylide biferrocenes can be realized as shown in Scheme 2. Addition of L_nMX ($L_nMX = (\eta^5 - C_5H_5)(Ph_3P)_2RuCl$ (7a), $(\eta^5-C_5H_5)(Ph_3P)_2OsBr$ (7b), $(\eta^5-C_5H_5)(dppf)RuCl$ (7c); dppf = 1,1'-bis(diphenyl)phosphanyl ferrocene, (η^5 -C₅H₄P- $Ph_2)_2Fe$) to 4 in a 1:1 molar ratio in the presence of $[H_4N]PF_6$ and KOtBu resulted in the formation of orange (L_nMC=C)- $(HC \equiv C)bfc (L_nM = (\eta^5 - C_5H_5)(Ph_3P)_2Ru (8a), (\eta^5 - C_5H_5)(Ph_3P)_2 - C_5H_5)(P$ Os (**8b**), and $(\eta^5$ -C₅H₅)(dppf)Ru (**8c**)). Within these reactions metal vinylidene species are ubiquitously formed as intermediates.⁷ Removal of the vinylidene β -hydrogen atom by *tert*butoxide caused the formation of the neutral ruthenium and osmium σ -acetylides 8a-8c (Scheme 2, reaction (i)). It was found that for the synthesis of 8a and 8c a mixture of methanol/ dichloromethane (1:1) was best suited, while under similar reaction conditions compound 8b was not formed. Changing to only methanol as solvent, compound 8b was obtained, after appropriate workup, as an orange solid in moderate yield (Experimental Section).

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Scheme 2. Synthesis of Complexes 8 and 9^a



^{*a*} (i) First: L_nMX ($L_nMX = (\eta^5-C_5H_3)(Ph_3P)_2RuCl$ (**7a**), ($\eta^5-C_5H_5$)(Ph_3P)_2OsBr (**7b**), ($\eta^5-C_5H_5$)(dppf)RuCl (**7c**)), 1 equiv, [NH_4]PF₆, CH₂Cl₂/MeOH (1:1), MeOH (in the case of **7b**), 25 °C, 16 h; second: KOtBu, CH₂Cl₂/MeOH (1:1), MeOH (in the case of **7b**), 25 °C, 5 h. (ii) first: **7a**, **7b**, **7c**, 2 equiv, [NH_4]PF₆, CH₂Cl₂/MeOH (1:1), MeOH (in the case of **7b**), 25 °C, 16 h; second: KOtBu, CH₂Cl₂/MeOH (1:1), MeOH (in the case of **7b**), 25 °C, 5 h. (iii) first: **7a**, **7b**, **7c**, 1 equiv, [NH₄]PF₆, CH₂Cl₂/MeOH (1:1), MeOH (in the case of **7b**), 25 °C, 16 h; second: KOtBu, CH₂Cl₂/MeOH (1:1), MeOH (in the case of **7b**), 25 °C, 16 h; second: KOtBu, CH₂Cl₂/MeOH (1:1), MeOH (in the case of **7b**), 25 °C, 16 h; second: KOtBu, CH₂Cl₂/MeOH (1:1), MeOH (in the case of **7b**), 25 °C, 16 h; second: KOtBu, CH₂Cl₂/MeOH (1:1), MeOH (in the case of **7b**), 25 °C, 16 h; second: KOtBu, CH₂Cl₂/MeOH (1:1), MeOH (in the case of **7b**), 25 °C, 16 h; second: KOtBu, CH₂Cl₂/MeOH (1:1), MeOH (in the case of **7b**), 25 °C, 16 h; second: KOtBu, CH₂Cl₂/MeOH (1:1), MeOH (in the case of **7b**), 25 °C, 16 h; second: KOtBu, CH₂Cl₂/MeOH (1:1), MeOH (in case of **7b**), 25 °C, 16 h; second: KOtBu, CH₂Cl₂/MeOH (1:1), MeOH (in case of **7b**), 25 °C, 5 h.

The synthesis strategy used in the preparation of **8a**–**8c** could successfully be transferred to the organometallic alkynes $(L_nMC=C)_2bfc (L_nM = (\eta^5-C_5H_5)(Ph_3P)_2Ru (9a), (\eta^5-C_5H_5)-(Ph_3P)_2Os (9b), (\eta^5-C_5H_5)(dppf)Ru (9c))$ in which two ruthenium- and osmium-acetylide building blocks are bonded to bfc (Scheme 2, reaction (ii)). Reacting **4** with **7a**–**7c** in a 1:2 stoichiometry produced the tetrametallic M₂Fe₂ complexes **9a**–**9c** (M = Ru, Os) with yields between 60 and 90% (Experimental Section). After column chromatography and crystallization, these compounds could be isolated as orange solid materials (Experimental Section).

It was also possible to synthesize tetranuclear 9a-9c by treatment of 8a-8c with 7a-7c in a 1:1 molar ratio (Scheme 2, reaction (iii)).

Compounds 9a-9c rapidly turn dark after exposure to air and moisture due to oxidation processes, whereby solutions containing these molecules decompose more easily than solid materials. Nevertheless, transition metal compounds 8a-8c are even more reactive than 9a - 9c and, hence, must carefully be handled under an inert gas atmosphere.

Characterization. Complexes **6**, **8**, and **9** were characterized by elemental analysis, IR, NMR (¹H, ¹³C{¹H}, ³¹P{¹H}), UV–vis, and EPR spectroscopy. The identities of **6**, **8b**, and **9a–9c** were further confirmed by single-crystal X-ray diffraction studies. Compounds **6**, **8a–8c**, and **9a–9c** were additionally investigated by cyclic voltammetric measurements. Additionally, spectroelectrochemical studies were carried out.

The progress of the complexation of **4** with ML_n fragments could be monitored by IR spectroscopy since a typical shift of the C=C stretching frequency takes place by changing from **4** ($\nu_{C=C}$ 2109 cm⁻¹) to **6** ($\nu_{C=C}$ 2104 cm⁻¹), **8** ($\nu_{C=C}$ 2074 cm⁻¹ (MC=C), 2100 cm⁻¹ (HC=C)), and **9** ($\nu_{C=C}$ 2075 cm⁻¹ (MC=C)), respectively.^{3a} Conspicuous in the IR spectra of

8a-**8c** is the appearance of two $\nu_{C=C}$ absorptions at 2100 cm⁻¹ for the HC=C unit and at 2074 cm⁻¹ for the MC=C fragment, which is attributed to the monosubstitution of these compounds. A further characteristic vibration is found for **4** at 3302 cm⁻¹ for the H-C= group.

Also the NMR spectroscopic properties of **6**, **8**, and **9** correlate with their formulations as mono- or diacetylide biferrocene complexes (*vide supra*). The cyclopentadienyl protons of the bfc central unit in the symmetric-arranged systems **6** and **9a**–**9c** show, as expected, four signals with an AA'XX' pattern between 3.7 and 4.2 ppm with coupling constants of $J_{\rm HH} = 1.7-1.8$ Hz (for comparison, molecule **4**: 4.00, 4.23, 4.26, and 4.40 ppm^{3a}). For **8a–8c**, with an unsymmetrical geometry, a total of eight signals ranging from 3.8 to 4.4 ppm is typical (Experimental Section). For the ruthenium- and osmium-bonded cyclopentadienyl groups a singlet is found at ca. 4.3 ppm. Due to the different chemical environment, the dppf cyclopentadienyl protons in **8c** and **9c** appear as four separated signals, whereby three of them are found between 4.0 and 4.4 ppm and the other is located at ca. 5.5 ppm.⁸

The ¹³C{¹H} NMR spectra of **6**, **8**, and **9** contain the corresponding carbon signals for bfc, C_5H_5 , and C=C (Experimental Section). Also the carbon signals of the dppf and phenyl groups are found in the expected region.⁸

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Figure 1. ORTEP diagram (50% probability level) of **6** with the atom-numbering scheme (the hydrogen atoms and one disordered CH_2Cl_2 packing solvent molecule are omitted for clarity). Symmetry transformations used to generate equivalent atoms are labeled with "A": -x + 1/2, -y + 5/2, -z + 1 (center of inversion in between C6 and C6A). Selected bond distances (Å) and angles (deg): C1–C11 1.410(11), C11–C12 1.184(11), C12–Au1 1.988(7), Au1–P1 2.257(2), C6–C6A 1.456(16), D1–Fe1 1.628(3), D2–Fe1 1.624(3); C1–C11–C12 176.4(9), C11–C12–Au1 173.9(7), C12–Au1–P1 178.5(2), C13–P1–Au1 113.6(3), C19–P1–Au1 111.1 (3) C25–P1–Au1 113.5(3), D1–Fe1–D2 178.7(1) (D1 = centroid C1 – C5, D2 = centroid of C6–C10). The number in parentheses after each calculated value represents the standard deviation in units of the last significant digits.

The ³¹P{¹H} NMR spectra of all newly synthesized compounds indicate the presence of a single phosphorus environment with resonance signals for the (Ph₃P)Au⁹ and (η^{5} -C₅H₅)ML_n (L_nM = (Ph₃P)₂Ru (**8a**, **9a**), (Ph₃P)₂Os (**8b**, **9b**), (dppf)Ru (**8c**, **9c**)^{8,10}) building blocks at 41.3 (**6**), 49.38 (**8a**), 50.36 (**9a**), 0.15 (**8b**), 0.6 (**9b**), 53.7 (**8c**), and 53.9 (**9c**) ppm (Experimental Section).

Solid State Structures. Single-crystal X-ray structure analysis was performed for 6, 8b, and 9a-9c. A view of the molecules is given in Figure 1 (6), Figure 2 (8b), and Figures 3-5 (9a-9c). Selected bond distances (Å) and angles (deg) are listed in the legend of Figure 1 (6) and Figure 2 (8b) as well as Table 1 (9a-c). The crystal and structure refinement data for all compounds are summarized in Tables 6 and 7 (Experimental Section).

The overall structural features of molecules **6**, **8b**, and **9a**–**9c** are similar to those of related structurally characterized (ethynyl)biferrocene-,^{2a,3a,b,4,5} phosphine-gold(I) acetylide-,⁹ and cyclopentadienyl-phosphine-ruthenium- and cyclopentadienyl-phosphine-osmium-acetylide-containing molecules.¹⁰ They consist of a biferrocene central entity with linear coordinated alkynyl-gold(I) units (**6**) or pseudo-tetrahedral alkynyl-ruthenium or -osmium moieties bonded to the cyclopentadienyl rings (Figures 1–5).

The structures of symmetric **6** and **9a**–**9c** show the molecules to have crystallographic C_i symmetry about the center of the bis(cyclopentadienyl) connectivity. This imposes a *trans*-conformation on the location of the terminal-bonded transition metal fragments with respect to the inversion center with a step-



Figure 2. ORTEP diagram (50% probability level) of **8b** with the atom-numbering scheme (the hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): C43–C44 1.434(5), C42–C43 1.213(5), C42–Os1 2.030(4), Os1–P1 2.2985(9), Os1–P2 2.2920(9), C49–C54 1.470(5), C59–C64 1.413(6), C64–C65 1.193(6), D1–Fe1 1.641(1), D2–Fe1 1.640(1), D3–Fe2 1.646(1), D4–Fe2 1.644(1), D5–Os1 1.887(1); C42–C43–C44 177.5(4), C43–C42–Os1 172.3(3), C42–Os1–P1 95.25(10), C42–Os1–P2 88.50(10), C65–C64–C59 175.8(5), D1–Fe1–D2 178.07(10), D3–Fe2–D4 177.14(9), C12–Os1–D5 122.01(12) (D1 = centroid of C1–C5, D2 = centroid of C6–C10, D3 = centroid of C13–C17, D4 = centroid of C18–C22, D5 = centroid of C25–C29). The number in parentheses after each calculated value represents the standard deviation in units of the last significant digits.

like conformation of the two ferrocenyl rings (Figures 1–5).¹¹ Both organometallic termini of **6** and **9a–9c** point away from the central biferrocenyl connecting unit. The two C₅H₄ rings of this array are coplanar within 0.012 (**6**), 0.003 (**9a**), 0.008 (**9b**), and 0.003 Å (**9c**). Similar observations were made for unsymmetric **8b** (0.039 Å) (Figure 2). The cylopentadienyl rings of individual ferrocenyl building blocks are rotated by 12.92° (**6**), 0.36° (**9a**), 0.53° (**9b**), and 9.47° (**9c**), which verifies a somewhat eclipsed arrangement. In **6** the C₅H₄ rings are approximately

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Figure 3. ORTEP diagram (50% probability level) of **9a** with the atom-numbering scheme (the hydrogen atoms and one disordered CH₂Cl₂ packing solvent molecule are omitted for clarity). Symmetry transformations used to generate equivalent atoms are labeled with "A": -x + 1, -y + 1, -z + 1 (center of inversion in between C6 and C6A). Selected bond distances (Å) and angels (deg) are summarized in Table 1.



Figure 4. ORTEP diagram (50% probability level) of **9b** with the atom-numbering scheme (the hydrogen atoms and one CHCl₃ packing solvent molecule are omitted for clarity). Symmetry transformations used to generate equivalent atoms labeled with "A": -x + 1, -y + 1, -z + 1 (center of inversion in between C6 and C6A). Selected bond distances (Å) and angels (deg) are given in Table 1.

midway between the fully eclipsed (0°) and fully staggered (36°) conformations. The alkynyl ligands and the fulvalenide arrangement are rotated by 157° (**6**), 71° (**9a**), 70° (**9b**), and 80° (**9c**) with respect to each other. The Fe–D distances (D = centroid of the appropriate bfc cyclopentadienyl ligands) (Figures 1–5) are characteristic^{3a,4a} and indicate that the iron atoms are almost equidistant between the cyclopentadienyl and the fulvalenide ligands, corresponding to those bond distances found for other ferrocenes.¹² The bond lengths and bond angles about the cyclopentadienyls, fulvalenides, alkynyls, and phosphino substituents are close to those reported for analogous transition metal fragments.^{8,9}

Compound **8b** does not possess crystallographically imposed inversion symmetry due to its two different substituents, which form a *cis*-conformation (Figure 2). The cylopentadienyl rings of individual ferrocenyl building blocks are rotated by 14.09° (Fe1) and 3.41° (Fe2), which verifies an almost eclipsed conformation and in the case of Fe1 approximately midway between the fully eclipsed and fully staggered conformation. The alkynyl ligand and the fulvalenide arrangement are rotated by 157° (Fe1) with respect to each other, while the free alkyne ligand is rotated by 70° (Fe2).

Cyclic Voltammetry. Cyclovoltammetric measurements have been carried out with compounds 4, 8a-8c, and 9a-9c. The initial scans in the cyclic voltammogram (CV) of these complexes were run from -0.6 to 1.2 V (vs standard calomel electrode (SCE)), and the characteristic data are given in Table 2. The cyclic voltammograms are characterized by several distinct one-electron waves. The bis(alkynyl)biferrocene derivatives 8a-8c, bearing one terminal redox-active building block, display a reversible wave around 0.0 V. This wave can be assigned to the [M(II)]/[M(III)] (M = Ru, Os) redox couples and is fully reversible for 8a and 8b and partially reversible in the case of 8c. Clearly, the dppf ligand destabilizes the [Ru(III)] center. At more positive potentials two other redox events corresponding to the sequential oxidation of the ferrocene units are observed. In the case of the osmium complex 8b, these electron transfers are quasi-reversible at the platinum electrode, but the presence of the [Ru(III)] group in 8a and 8c strongly decreases the chemical stability of the oxidized species. These data suggest that the unpaired electron is probably more delocalized on the alkynyl ligand in the case of the ruthenium complexes $8a^+$ and $8c^+$.

The cyclic voltammograms of complexes 9a-9c, which possess a redox-active metal center at both ends of the bis(alkynyl)biferrocene bridge, show two well-resolved and quasi-reversible (9a) or weakly reversible (9b and 9c) redox events close to 0.0 V, corresponding to the stepwise oxidation of the end groups (Figure 6: 9a, exemplarily). The wave separation close to 0.2 V in the case of the complexes containing ruthenium-based termini and slightly smaller in the case of the bis(osmium) derivative 9b clearly indicates that the electron transfer at one end is sensed by the metal at the opposite site.

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Figure 5. ORTEP diagram (50% probability level) of **9c** with the atom-numbering scheme (the hydrogen atoms and CH₂Cl₂ packing solvent molecules are omitted for clarity). Symmetry transformations used to generate equivalent atoms labeled with "A": -x + 1, -y, -z + 1 (center of inversion in between C6 and C6A). Selected bond distances (Å) and angels (deg) are presented in Table 1.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 9a, 9b, and $9c^{a}$

	9a (M = Ru)	9b ($M = Os$)	9c (M = Ru)
M1-P1	2.2911(9)	2.2808(13)	2.2670(12)
M1-P2	2.2766(9)	2.2915(14)	2.2635(11)
$M1-D1^{b}$	1.8906(16)	1.8887(24)	1.8820(21)
M1-C12	2.022(3)	2.025(5)	2.025(5)
C11-C12	1.209(5)	1.213(8)	1.202(6)
C1-C11	1.429(5)	1.425(7)	1.438(7)
Fe1-D2 ^c	1.6491(15)	1.6472(24)	1.6525(21)
$Fe1-D3^d$	1.6490(15)	1.6487(24)	1.6477(22)
C6-C6A	1.456(6)	1.467(11)	1.477(10)
P1-M1-P2	99.54(3)	99.05(5)	96.13(4)
P1-M1-D1	122.5(1)	125.4(1)	121.8(1)
P1-M1-C12	90.09(9)	87.79(14)	88.86(13)
M1-C12-C11	175.2(3)	174.4(5)	174.8(4)
C1-C11-C12	173.2(3)	172.2(6)	169.9(5)

^{*a*} The number in parentheses after each calculated value represents the standard deviation in units of the best significant digits. ^{*b*} D1 = centroid of C13-C17. ^{*c*} D2 = centroid of C1-C5. ^{*d*} D3 = centroid of C6-C10.

At more positive potentials further irreversible oxidations centered on the biferrocene bridge take place. The presence of a [M(III)] electron-deficient terminus decreases the reversibility of the electron transfers on the biferrocene connectivity. Probably, this behavior is a consequence of a large delocalization of the electronic vacancy on the biferrocene systems as described in Scheme 3. A similar behavior was already observed by Sato and co-workers for related $[(\eta^5-C_5H_5)(PPh_3)_2RuC=CFc][PF_6]^{.7a,b}$

Comparison of the redox potentials found for **9a** with those recently reported for the related compound $[(\eta^5-C_5H_5)(PPh_3)_2-RuC \equiv CFc'C \equiv CRu(PPh_3)_2(\eta^5-C_5H_5)]^{7a}$ (Fc' = $(\eta^5-C_5H_4)_2Fe$) shows that introduction of a second ferrocenyl group in the spacer linking the metal termini favors interactions between the terminal ends. Indeed, for the compound with only one ferrocenyl unit, the cyclic voltammogram does not discriminate the redox potentials of the ruthenium termini, while the potentials of the same termini in **9a** are separated by 0.19 V. No doubt the insertion of an additional ferrocenyl unit between the terminal redox centers increases the thermodynamic stability of the mixed-valence species.

The straightforward determination of the two redox potentials E_0^1 and E_0^2 for the terminal groups for **9a**-**9c** allowed the determination of the comproportionation constants for the equilibrium described by eqs 1 and 2. The potential difference

 (ΔE) between the two redox events and the comproportionation constant K_c are both representative of the thermodynamic stability of the corresponding mixed-valence state relative to other redox states. Their magnitude is determined by the sum of several energetic factors relating to the stability of the reactant and product complexes, and it is important to keep in mind that a single redox event is no evidence for the absence of electronic communication between the redox centers; the presence of two resolved events establishes that through-bridge electron transfer with a significant electronic coupling takes place.^{14,15}

$$\{[M^{\text{red}}]\text{-}B\text{-}[M^{\text{red}}]\}^{n+} + \{[M^{\text{ox}}]\text{-}B\text{-}[M^{\text{ox}}]\}^{(n+2)+} \stackrel{\text{Ac}}{=} 2\{[M^{\text{red}}]\text{-}B\text{-}[M^{\text{ox}}]\}^{(n+1)+} (1)$$

$$\Delta G = \Delta F = F - F = -(RT/F)\log K \qquad (2)$$

UV–Vis Spectroscopy. The UV–vis spectra of **4**, **8a–8c**, and **9a–9c** were recorded in dichloromethane at 293 K, and characteristic data are collected in Table 3. As shown in Figure 7, all the spectra present the same general aspect with, nevertheless, a more intense absorption around 270 nm for **8c** and **9c**, which can be confidently attributed to the contribution of the dppf ligand.⁸ The low-energy bands with maxima below 300 nm can be assigned to $\pi \rightarrow \pi$ intraligand transitions involving the C₃H₅ and phosphine ligands as well as the alkynyl fragments.

With reference to the electronic absorption spectra of ferrocene, which shows low-energy absorptions at 326 and 438 nm, and biferrocene, which presents three maxima at 450, 296, and 269 nm,^{4a} the low-energy absorptions of complex **4** observed at 301 and 450 nm can be assigned to an admixture of the $d\pi$ (Fe) $\rightarrow \pi^*$ (C'C) metal-to-ligand charge transfer (MLCT) transition. Comparison of the data indicates that grafting alkynyl substituents on the biferrocene has only a weak effect on the HOMO-LUMO gap.

The electronic absorption of $(\eta^5-C_5H_5)(PPh_3)_2RuC\equiv CFc$ was characterized by two bands, at 350 and 435 nm, respectively, which are very close to the ferrocene d-d bands.^{7a} Complex **9a**, which can be regarded as a dimer of this complex, presents very similar absorptions. Roughly, the data in Table 3 show that as the number of ferrocenyl and $(\eta^5-C_5H_5)(PPh_3)_2MC\equiv CFc$

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Table 2. Electrochemical Data for 4, 8a–8c, and 9a–9c^a

compd	М	[M(II)]/[M(III)] E (ΔE_{p} , I_{c}/I_{a}) [V]	$[Fe^{2+}]/[Fe^{3+}]$ E (ΔE_p , I_o/I_a) [V]	$\frac{[\text{Fe}_{dppf}^{2+}]/[\text{Fe}_{dppf}^{3+}]}{E (\Delta E_{p}, I_{c}/I_{a}) [V]}$	Kc
4	none		0.47 (0.13, ~1)		
			0.85 (0.13, ~1)		
8a	Ru	0.09 (0.11, 1)	0.65 (0.12, <1)		
			0.89 (0.12, ~0)		
8b	Os	0.04 (0.11, 1)	0.60 (0.11, ~1)		
			$0.82(0.10, \sim 1)$	_	
8c	Ru	0.06 (0.12, <1)	0.57^{b}	0.70^{b}	
			0.98		
9a	Ru	0.03 (0.09, 1)	0.74 (0.12, <1)		1.8×10^{3}
		0.22 (0.10, 1)	0.89^{b}		
9b	Os	-0.03 (0.09, <1)	0.62 (0.10, <1)		0.4×10^{3}
		0.12 (0.05, <1)	0.79 (0.10, <1)		
9c	Ru	0.09 (0.10, <1)	0.64	0.68^{b}	4.0×10^{3}
		0.30 (0.10, <1)	0.99"		

^{*a*} Potentials in dichloromethane (0.1 M [*n*Bu₄N]PF₆; 298 K, platinum electrode, sweep rate 0.100 V s⁻¹) are given in V vs SCE; the ferrocene–ferrocenium couple [Fc]/[Fc⁺] (0.460 V vs SCE) was used as an internal calibrant for the potential measurements.¹³ Redox potentials determined as $(E_a + E_c)/2$ for the reversible or partially reversible couples and as E_a for the nonreversible redox systems. ^{*b*} Irreversible.

Table 3. UV-Vis Absorption Spectral Data of Selected Complexes in Dichloromethane at 298 K

compd	absorption λ/nm (10 ⁻³ ϵ/dm^3 mol ⁻¹ cm ⁻¹)
4	227 (75), 265 (24), 301 (13), 450 (0,8)
8a	227 (105), 270 (3), 346 (14), 430 (4)
8b	228 (11), 274 (3), 346 (12), 445 (3)
8c	227 (101), 263 (54), 344 (12), 440 (3)
9a	227 (135), 345 (22), 440 (5)
9b	227 (161), 272 (46), 350 (22), 440 (4)
9c	270 (147), 347 (10), 438 (2)

Table 4. EPR Data Determined in Glassy Tetrahydrofuran Solution

$compd^a$	$g_{ }$	$g \perp$	Δg^b
4+	3.24	1.91	1.33
4^{2+c}	3.46	1.86	1.60
8a ⁺	4.283	2.005	2.278
$8b^+$	2.810	2.090	0.720
9a ⁺	2.852	1.984	0.868
9a ²⁺	2.885	1.986	0.899
9b ⁺	2.840	2.066	0.774
9 c ⁺	2.828	2.009	0.819

^{*a*} Measured at 66 K. ^{*b*} $\Delta g = g_{\parallel} - g_{\perp}$. ^{*c*} Generated using [AgOTf].

(M = Ru, Os) groups increases, the intensity of the low-energy bands increases, but the maxima remain around 340 and 440 nm. Therefore, the UV-vis analysis does not reveal significant interactions between the metal sites on the neutral compounds.

Electron Paramagnetic Resonance. 1',1"'-Disubstituted biferrocenium salts were subjected to several EPR studies. Important and systematic studies of electron transfer for mixed-valence disubstituted biferrocenium cations have led to a wealth of experimental results. Based on EPR and Mössbauer spectroscopies, works reported by Dong and Hendrickson established a relation between the electron transfer rate in these mixed-valence compounds and the *g*-tensor anisotropy of the EPR spectra. They established that trapped mixed-valence complexes (electron transfer rate <10⁸ s⁻¹) give EPR spectra with a large anisotropy ($\Delta g > 1.5$), while detrapped mixed-valence compounds (electron transfer rate >10⁸ s⁻¹) have EPR spectra with a small anisotropy ($\Delta g < 1.1$).^{16,2b} Systems with intermediate tensors of anisotropy ($1.1 < \Delta g < 1.5$) show Mössbauer behavior changing with the temperature; they are valence localized at

low temperature and become delocalized as the temperature increases (electron transfer rate $\sim 10^8 \text{ s}^{-1}$).¹⁷

The neutral complexes 4 and 8a-8c were reacted with less than 1 (ca. 0.8) equiv of ferrocenium in tetrahydrofuran at -60 °C, while compounds 9a-9c were reacted with both 0.8 and 2.0 equiv of ferrocenium. The obtained solutions were transferred into EPR tubes, and spectra were recorded at 66 K. In most instances, resolved spectra could be obtained, and the *g*-tensor components are summarized in Table 4. All the spectra display the same pattern characteristic of radicals with axialtype symmetry. The g_{\parallel} component ranges between 2.28 and 4.28, and the g_{\perp} tensor varies between 1.86 and 2.09, while the anisotropy of the Δg tensor ranges between 0.77 and 2.60.

It is well-established that piano-stool radicals such as $[(\eta^{5}-C_{5}H_{5})(PPh_{3})_{2}Ru(III)C \equiv CR]^{+}$ are characterized by a rhombic signal with three well-separated *g*-tensor components.^{7c,18,19} In this respect, the EPR data obtained for complexes **8a**–**8c** and **9a**–**9c** clearly establish that the unpaired electrons are not ruthenium or osmium centered, but for all these radicals the axial symmetry of the EPR spectra suggests that the SOMOs possess a significant biferrocenium character in line with the CV data (*vide supra*).

The main feature of the EPR data listed in Table 4 comes from the large variation of the Δg values. The Δg tensor obtained for 4^+ compares well with those obtained for other 1',1"'-disubstituted biferrocenium cations with unsaturated organic moieties.^{16a} The intermediate value found for the tensor of anisotropy of 4^+ suggests that the electron-transfer between the two ferrocene units takes place at a rate close to 10^8 s^{-1} . Connecting a single $(\eta^5-C_5H_5)(PPh_3)_2M$ building block on one of the terminal alkynes produces opposite effects on the electron transfer rate in the monoradicals. Indeed, a very large Δg value is obtained for M = Ru, while small values were found for the related osmium-containing complex. According to these data, complex $8a^+$ should be a trapped mixed-valence complex in contrast with its parent compound $\mathbf{8b}^+$, for which the unpaired electron should be delocalized on the two iron centers. In the case of complex $8c^+$, it was not possible to obtain resolved EPR spectra at liquid nitrogen temperature. In the case of the monoradicals **9a**-c[**PF**₆] featuring two redox-active terminal ends, the axial symmetry of the spectra is maintained, indicating

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compd	transition	$v_{\rm max}~({\rm cm}^{-1})~\epsilon~({\rm M}^{-1}~{\rm cm}^{-1})$	$(\Delta v_{1/2})_{\rm exp} ({\rm cm}^{-1})$	$(\Delta v_{1/2})_{\text{theo}}{}^c (\text{cm}^{-1})$	$H_{\rm ab}~({\rm cm}^{-1})^e$	$H_{\rm ab}~({\rm cm}^{-1})^g$
9a+	LMCT	4500 (6000) ^{<i>a,b,d</i>}	820 ± 20	2900		
	IVCT	$6500 (7200)^a$	2400 ± 50	3600	1098 ± 50	3250
		6600 (7500) ^b	2300 ± 50^{b}	3600 ^b	1105 ± 50	3300 ^b
9a ²⁺	LMCT	4500 (11 400) ^a	800 ± 20	2900		
		4400 (4500) ^b	900 ± 20^{b}	2900 ^b		
	IVCT	$6200 (10\ 200)^a$	2400 ± 50	3500	912 ± 50^{f}	3250
		6400 (8700) ^b	$2400\pm50^{ m b}$	3600 ^b	$855\pm50^{\prime}$	3300 ^b

Table 5. NIR Data for 9a[PF₄] and 9a[PF₄]

^{*a*} In dichloromethane. ^{*b*} In methane/acetone, 1:3. ^{*c*} Calculated using eq 3 for $\Delta G^0 = -800 \text{ cm}^{-1}$. ^{*d*} Masked by a stretching band of the solvent. ^{*e*} Using eq 4 and assuming a through-space Ru–Fe distance of 6.29 Å as determined in the X-ray crystal structure of **9**. ^{*f*} Calculated following eq 5. ^{*s*} Calculated following eq 6.

 Table 6. Crystal and Intensity Collection Data for 6 and 8b

	6	8b
fw	1419.47	1196.91
chemical formula	$C_{60}H_{46}Au_2Fe_2P_2 \cdot 0.5CH_2Cl_2$	C65H52Fe2OsP2
cryst syst	monoclinic	monoclinic
space group	C2/c	$P2_1/n$
a (Å)	30.6325(11)	13.2294(2)
b (Å)	7.5752(2)	20.3860(2)
c (Å)	23.4678(8)	18.4642(3)
β (deg)	110.577(4)	97.5590(10)
$V(Å^3)$	5098.2(3)	4936.42(12)
ρ_{calc} (g cm ⁻³)	1.849	1.610
F(000)	2752	2400
cryst dimens (mm)	$0.6 \times 0.3 \times 0.2$	$0.4 \times 0.2 \times 0.2$
Z	4	4
max. and min. transition	1.00000, 0.46950	1.00000, 0.73240
absorp coeff (λ , mm ⁻¹)	6.503	3.256
scan range (deg)	3.01-26.15	2.85-26.06
index ranges	$-37 \le h \le 37, -9 \le k \le 9,$	$-16 \le h \le 16$,
_	$-29 \le l \le 28$	$-25 \le k \le 24,$
		$-14 \leq l \leq 22$
total refins	23 395	27 526
unique reflns	5060	9705
R _{int}	0.0284	0.0331
data/restraints/params	5060/0/326	9705/0/631
goodness-of-fit on F^2	1.334	1.020
$R_1^a, w R_2^a [I \ge 2\sigma(I)]$	0.0523, 0.1097	0.0260, 0.0536
R_1^a , wR_2^a (all data)	0.0627, 0.1125	0.0464, 0.0624
max. and min. peak (e $Å^{-3}$)	1.621, -1.158	1.555, -0.709

 ${}^{a}R_{1} = [\Sigma(||F_{o}| - |F_{c}|)/\Sigma|F_{o}|); wR_{2} = [\Sigma(w(F_{o}^{2} - F_{c}^{2})^{2})/\Sigma(wF_{o}^{4})]^{1/2}. S = [\Sigma w(F_{o}^{2} - F_{c}^{2})^{2}]/(n - p)^{1/2}. n = \text{number of reflections}, p = \text{parameters used}.$

that the unpaired electrons are not localized on the ruthenium/ osmium termini but on SOMOs with a significant biferrocenium character. Moreover, the Δg parameters are small, and therefore the unpaired electron is expected to be delocalized on the two ferrocenyl units on the EPR time scale. Consequently, the odd electron should be delocalized on the whole molecule and probably exchanges from one redox-active terminus to the other across the biferrocenyl bridge, which acts as a relay in this longdistance electron transfer. A resolved EPR spectrum was also obtained for the dication $9a^{2+}$. However, the lack of data in the literature on EPR spectroscopy of biferrocenium biradicals makes any further interpretation difficult.

Spectro-electrochemistry of 9a. As the tetranuclear complex **9a** presents reversible redox events, the UV–vis–NIR spectra of **9a**[**PF**₆]_n (n = 0, 1, 2) were collected using spectroelectrochemical methods. The UV–vis–NIR spectra were obtained with an optically transparent thin-layer electrosynthetic (OTTLE) cell with a standard design,²⁰ and selected spectra are shown in Figure 8. Measurements were carried out in dichloromethane containing 0.1 M [nBu_4N]PF₆ as supporting electrolyte. The initial spectrum was identical to the spectrum measured for 9a (vide supra). As the oxidation proceeds, a sharp absorption band appears in the visible range at 610 nm, while a very broad absorption increases in the NIR domain with two apparent maxima at 1540 and 2180 nm. The first one-electron oxidation proceeds without shift of these three bands. The molecular extinction coefficients determined for the monocation **9a**[**PF**₆] are 15500, 7200, and 6200 dm³ mol⁻¹ cm⁻¹, respectively. As the second oxidation takes place, small red shifts were observed for the three bands. After completion of the second oxidation, the spectrum of the dication displays three bands with apparent maxima at 632, 1606, and 2180 nm and molecular extinction coefficients of 23 700, 10 200, and 11 400 dm³ mol⁻¹ cm⁻¹, respectively. The two redox events are fully reversible. Indeed, reduction carried out after the two one-electron oxidation processes recovered exactly the initial spectrum of the neutral derivative 9a. One can note that the spectra of the two related complexes $[(\eta^5-C_5H_5)(PPh_3)_2RuC \equiv CFc][PF_6]$ and $[(\eta^5-C_5H_5) (PPh_3)_2RuC \equiv CFc'C \equiv CRu(PPh_3)_2(\eta^5 - C_5H_5)][PF_6]$ are very similar.^{7a,b}

With reference to previous work on Ru(III) and Fe(III) acetylide complexes the band close to 600 nm can be safely attributed to a ligand-to-metal charge transfer (LMCT) band.7c,18 The appearance of two intense absorptions in the NIR range for both the mixed-valence species $9a^{+}[PF_{6}]$ and the dication $9a^{2+}[PF_6]_2$ is puzzling. As the bands in the NIR range were poorly resolved, the deconvolution from the band envelopes was undertaken for the mixed-valence species $9a^{+}[PF_{6}]$ and the dication $9a^{2+}[PF_6]_2$ (Figure 8). Deconvolution in the NIR range of the experimental spectra recorded in dichloromethane and a 1:3 mixture of dichloromethane/acetone was achieved using Gaussian functions and assuming two overlapping transitions. The spectral parameters of the bands obtained for the best fits have been compiled in Table 5. The two bands are of similar intensities, but the band at lower energy is much narrower than the band on the high-energy side of the spectral window.

According to the Hush model applied to class II unsymmetrical mixed-valence complexes, the theoretical half-width $(\Delta v_{1/2})_{\text{theo}}$ of an IVCT transition is related to ΔG^0 , the energy gap between the two potential wells corresponding to the two diabatic redox states, and to v_{max} , the energy on the peak maximum (eq 3). For complex $9a[PF_6] \Delta G^0$ can be estimated from the difference in the oxidation potentials measured by cyclic voltammetry under the same conditions for the closely related model complexes $(\eta^5 - C_5 H_5)(PPh_3)_2 RuC \equiv CPh^{10d} (E_0 =$ 0.535 V) and compound 4. As these values are rather close, the ΔG^0 gap is expected to be not larger than 0.1 V (i.e., 800 cm⁻¹). Comparison of the theoretical and experimental width at half-height for the two bands suggests that probably the band around 4500 cm⁻¹ is too narrow to correspond to an IVCT transition. More likely this band corresponds to a LMCT, its intensity being probably too large for a d-d ligand field transition. Indeed, the intensity of these forbidden transitions are generally close to 100 M⁻¹ cm⁻¹.^{7c} In contrast, the theoretical width at half-

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Table 7. Crystal and Intensity Collection Data for 9a, 9b, and 9c

	9a	9b	9c
fw	1967.32	2214.46	2026.95
chemical formula	C106H86Fe2P4Ru2 2 CH2Cl2	C ₁₀₆ H ₈₆ Fe ₂ Os ₂ P ₄ 2 CHCl ₃	C102H82Fe4P4Ru2 2 CH2Cl2
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a (Å)	11.8236(7)	11.86750(10)	9.98900(10)
b (Å)	16.9641(11)	16.88340(10)	24.0564(2)
<i>c</i> (Å)	22.8373(11)	22.6922(2)	17.26870(10)
β (deg)	95.319(4)	94.9200(10)	94.5000(10)
$V(Å^3)$	4560.9(5)	4529.94(6)	4136.87(6)
$\rho_{\rm calc} \ ({\rm g \ cm^{-3}})$	1.433	1.624	1.627
F(000)	2012	2204	2060
cryst dimens (mm)	$0.6 \times 0.5 \times 0.1$	$0.8 \times 0.2 \times 0.2$	$0.2 \times 0.1 \times 0.1$
Z	2	2	2
max. and min. transition	1.02232, 0.98023	1.00000, 0.59826	1.00000, 0.35330
absorp coeff (λ , mm ⁻¹)	0.873	3.408	10.679
scan range (deg)	2.94-26.09	2.96-26.06	3.67-60.62
index ranges	$-14 \le h \le 14, -20 \le k \le 20,$	$-14 \le h \le 14, -20 \le k \le 20,$	$-11 \le h \le 10, -27 \le k \le 27,$
-	$-28 \leq l \leq 28$	$-28 \leq l \leq 28$	$-19 \leq l \leq 19$
total refins	44 399	44 167	32 181
unique reflns	8999	8934	6185
R _{int}	0.0298	0.0225	0.0518
data/restraints/params	8999/75/569	8934/33/550	6185/0/532
goodness-of-fit on F^2	1.088	1.134	0.971
$\widetilde{R}_1^a, w R_2^a [I \ge 2\sigma(I)]$	0.0427, 0.1207	0.0398, 0.0964	0.0345, 0.0779
R_1^a , wR_2^a (all data)	0.0624, 0.1287	0.0484, 0.1017	0.0546, 0.0878
max. and min. peak (e $Å^{-3}$)	1.859, -1.171	2.336, -2.328	1.095, -0.678

 ${}^{a}R_{1} = [\sum(||F_{o}| - |F_{c}|)/\sum|F_{o}|); wR_{2} = [\sum(w(F_{o}^{2} - F_{c}^{2})^{2})/\sum(wF_{o}^{4})]^{1/2}. S = [\sum w(F_{o}^{2} - F_{c}^{2})^{2}]/(n-p)^{1/2}. n = \text{number of reflections}, p = \text{parameters used}.$



Figure 6. Cyclic voltammogram of **9a** (10^{-3} M solution in dichloromethane at 298 K with [nBu_4N]PF₆ as supporting electrolyte, scan rate = 0.100 V s⁻¹. All potentials are referenced to ferrocene/ferrocenium [Fc/Fc⁺] as an internal reference for potential measurements. E_0 values corrected for [Fc/Fc]⁺ at 0.460 V vs SCE in dichloromethane.¹³

height of the band with a maximum of absorption near 6500 cm⁻¹ is only slightly larger than the experimental half-width, as expected for an IVCT corresponding to an electron transfer occurring at a fast regime on the EPR time scale (*vide supra*).²¹

$$(\Delta v_{1/2})_{\text{theo}} = [2310(v_{\text{max}} - \Delta G^0)]^{1/2}$$
(3)

$$H_{\rm ab} = (2.06 \times 10^{-2} / d_{\rm ab}) (\varepsilon_{\rm max} v_{\rm max} v_{1/2})^{1/2}$$
(4)

$$H_{\rm ab} = (2.06 \times 10^{-2} / d_{\rm ab} 2^{1/2}) (\varepsilon_{\rm max} \nu_{\rm max} \Delta \nu_{1/2})^{1/2}$$
(5)

$$H_{\rm ab} = (v_{\rm max})/2 \tag{6}$$

The influence of the solvent polarity on these bands was also briefly investigated. However, due to low solubility of **9a** in

common polar solvents, the use of such solvents resulted in the rapid precipitation of the complex. Among the polar solvents tested only a 1:3 mixture of dichloromethane/acetone proved to be suitable for a spectro-electrochemical experiment. The data extracted from these measurements reveal that only the Gaussian band at higher energy displayed a solvatochromism consistent with an IVCT transition of a class II mixed-valence complex.²¹ However, one can note that the solvent effect is relatively small, indicating that the electronic coupling between the redox-active centers cannot be regarded as weak.

On the other hand, the similarity between the spectrum obtained for the mixed-valence compound and the dication

⁽²¹⁾ Astruc, D. Electron Transfer and Radical Processes in Transition-Metal Chemistry; VCH: New York, 1995; p 630.



indicates that the IVCT cannot be assigned to a direct Ru-Ru optically induced electron transfer through the bridge. In contrast, the similarity between the NIR spectra obtained for **9a**[**PF**₆] and the complex $[(\eta^5-C_5H_5)(PPh_3)_2RuC \equiv CFc][PF_6]^{7a,b}$ is consistent with an IVCT between the biferrocenyl unit and the Ru(III) termini, in full agreement with the EPR data. During the reviewing process of our manuscript, a study on biferrocenyl triiodide based on MIR and NIR spectroscopy and DFT calculations suggests that the two NIR bands could both be assigned to IVCT transitions.²² It is also noteworthy that the spectral parameters obtained for the mixed-valence complex 9a[PF₆] and the dication 9a[PF₆]₂ are very similar, indicating that the IVCT process occurs through a similar mechanism in both derivatives with comparable reorganization energies. However, the magnetic exchange interaction between the odd electrons through the biferrocene system of the dication remains unclear. Interestingly, the dication behaves as a symmetric molecule constituted by two nonsymmetric mixed-valence units linked by a covalent bond.

Assuming that the Hush theory applies for this IVCT transition between the biferrocene unit and the Ru(III) termini, the electronic coupling (H_{ab}) of the mixed-valence complex **9a[PF_6]** amounts to 1100 \pm 50, according to eq 4, when the Fe–Ru distance is taken as 6.29 Å. In the case of the dication **9a[PF_6]**₂, assuming that two electrons can potentially exchange

between the biferocenyl unit and the two Ru(III) centers and assuming they behave independently, the effective electronic coupling can be determined using the modified Hush equation reported by Bonvoisin and Launay (eq 5) to take into account the double probability that such an event happens (Table 5).²³ Despite the sizable uncertainties associated with the spectroscopic measurements and the sensitivity of the compounds, these values provide support for the proposition that similar electronic couplings are operative in both complexes.

The solvent has only a minor influence on the IVCT bands, and consequently, these compounds cannot be considered as class II mixed-valence complexes in the classification of Robin and Day.²⁴ Consequently, the electronic coupling is underestimated by Hush treatment (eq 4 or 5) and overestimated by class III treatment (eq 6, Table 5). They might be close to borderline class IIA/class IIB according to the subcategorization developed for symmetric mixed-valence complexes by Brunschwig et al.²⁵ In other words, they can be considered as strongly coupled mixed-valence complexes with a localized valency in the ground state.²⁶

Conclusion

A series of bis(ethynyl)biferrocene-based transition metal complexes of structural type $(L_nMC\equiv C)(HC\equiv C)bfc$ $(L_nM = C)(HC\equiv C)bfc$ $(\eta^{5}-C_{5}H_{5})(Ph_{3}P)_{2}Ru, (\eta^{5}-C_{5}H_{5})(Ph_{3}P)_{2}Os, (\eta^{5}-C_{5}H_{5})(dppf)Ru; bfc$ = 1',1"'-biferrocenyl, $((\eta^5-C_5H_4)_2Fe)_2$; dppf = 1,1'-bis(diphenyl)phosphanyl ferrocene, $(\eta^5 - C_5 H_4 PPh_2)_2 Fe)$ and $(L_\eta MC \equiv C)_2 bfc$ $(L_n M = Ph_3 PAu, (\eta^5 - C_5 H_5)(Ph_3 P)_2 Ru, (\eta^5 - C_5 H_5)(Ph_3 P)_2 Os, (\eta^5 - C_5 H_5)(Ph_3 P)_2 Os)$ C₅H₅)(dppf)Ru) have been synthesized in straightforward consecutive synthetic procedures. In these heterobimetallic molecules a biferrocenyl moiety links different organometallic termini including Au-, Ru-, and Os-containing building blocks. The molecule (HC=C)₂bfc is fairly stable toward air and moisture, while the appropriate M_2 bfc compounds (M = Au, Ru, Os) are rapidly oxidized either in solution or in the solid state. The structures of these molecules in the solid state were determined by single-crystal X-ray structure analysis. It was found that symmetric molecules have crystallographic C_i symmetry and show a trans-conformation. Unsymmetric species impose *cis*-conformation. The cyclic voltammetric data established that the 1',1"'-bis(ethynyl)biferrocene acts as a linking group for ruthenium and osmium half-sandwich fragments capable of conveying electronic interaction from one end to the other more efficiently than the 1,1'-(ethynyl)ferrocene, which was recognized to behave as an insulator for a model with the same terminal ends.^{7a,b} The EPR spectroscopy established that the SHOMOs which contain the odd electrons in $9a-c[PF_6]$ possess a significant biferrocene character. Interestingly enough, the small tensors of anisotropy strongly support that the biferrocenyl bridge acts as a relay in this long-distance electron transfer. Analysis of the NIR absorption bands also supports that a direct Ru-Ru electron transfer does not take place in 9a[PF₆], the electron exchange occurring through two successive RuC≡CFc electron transfers favored by a fast exchange between the two ferrocene units. All experimental data support the conclusion that the strongest interaction may occur between one

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Figure 7. UV-vis spectra of complexes 4, 8a-8c, and 9a-9c in dichloromethane at 298 K.



Figure 8. NIR spectra for $9a^+[PF_6]$ (top) and $9a^{2+}[PF_6]_2$ in dichloromethane and proposed deconvolution.

 $(\eta^5-C_5H_5)(PPh_3)_2M$ moiety and the biferrocenyl unit through ethynyl fragments, but while the ferrocene group acts as an insulator, the biferrocene plays the role of a relay, allowing electron transfer from one metal terminus to the other one.

Experimental Section

General Data. All reactions were carried out under an atmosphere of nitrogen or argon using standard Schlenk techniques. Tetrahydrofuran, diethyl ether, and *n*-hexane were purified by distillation from sodium/benzophenone ketyl; dichloromethane was purified by distillation from calcium hydride. Celite (purified and annealed, Erg. B.6, Riedel de Haen) was used for filtrations.

Instruments. Infrared spectra were recorded with a Perkin-Elmer FT-IR Spectrum 1000 spectrometer. NMR spectra were recorded with a Bruker Avance 250 spectrometer (¹H NMR at 250.12 MHz and ¹³C{¹H} NMR at 62.86 MHz) in the Fourier transform mode. Chemical shifts are reported in δ units (parts per million) downfield

from tetramethylsilane with the solvent as reference signal (¹H NMR: CDCl₃ (99.8%), δ 7.26; ¹³C{¹H} NMR: CDCl₃ (99.8%), δ 77.16 ppm). 27 $^{31}P\{^{1}H\}$ NMR spectra were recorded at 101.255 MHz in CDCl₃ with P(OMe)₃ as an external standard ($\delta = 139.0$ ppm, relative to H₃PO₄ (85%) with $\delta = 0.00$ ppm). The abbreviation *pt* in the ¹H NMR spectra corresponds to pseudotriplet. Cyclic voltammograms were recorded in a dried cell purged with purified argon. Platinum wires served as working and counter electrodes. A saturated calomel electrode in a separated compartment served as reference electrode. For ease of comparison, all electrode potentials are converted using the redox potential of the ferroceneferrocenium couple [Fc]/[Fc⁺] (FcH = $(\eta^5 - C_5 H_5)_2$ Fe, $E_0 = 0.46$ V) as reference.¹³ Electrolyte solutions were prepared from tetrahydrofuran and [nBu₄N]PF₆ (Fluka, dried in oil-pump vacuum). The respective organometallic complexes were added at c = 1.0mM. Cyclic voltammograms were recorded in a negative-going direction at the starting potentials using a Voltalab 3.1 potentiostat (Radiometer) equipped with a digital DEA 101 electrochemical analyzer and an IMT 102 electrochemical interface. Melting points were determined using analytically pure samples, sealed off in nitrogen-purged capillaries on a Gallenkamp MFB 595 010 M melting point apparatus. The EPR spectra were recorded in tetrahydrofuran solutions with a concentration of 1 mmol of the complex under investigation and ferrocenium as oxidizing agent with a Bruker EMX-8/2.7 (X-band) spectrometer. UV-visible and NIR spectra were recorded with a Cary 5000. Microanalyses were partly performed by the Institute of Organic Chemistry, Chemnitz, University of Technology.

Reagents. 1',1^{'''}-Bis(ethynyl)biferrocene,^{3a} [(PPh₃)AuCl],^{9e} [(PPh₃)₂-(η^5 -C₅H₅)RuCl],²⁸ [(PPh₃)₂(η^5 -C₅H₅)OsBr],²⁹ and [(dppf)(η^5 -C₅H₅)-RuCl]^{8f} were prepared according to published procedures. All other chemicals were purchased from commercial suppliers and were used without further purification.

Synthesis of 1',1'''-(HC=C)₂bifc (4).^{3a,b} To 1.0 g (1.608 mmol) of 1',1'''-diiodobiferrocene (1) suspended in 60 mL of degassed diisopropylamine were added 0.31 mL (3.21 mmol) of 2-methyl-3-butyn-2-ol followed by 56 mg (5 mol %) of Pd(PPh₃)₂Cl₂ and 32 mg (10 mol%) of Cu(OAc)₂. The resulting reaction mixture was

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heated to 70 °C and stirred for 12 h. After cooling to 25 °C, the reaction mixture was filtered through a pad of Celite and all volatiles were removed under reduced pressure. The remaining material was subjected to column chromatography on silica gel using a mixture of toluene/tetrahydrofuran (8:1, v/v). Thus formed **3** was isolated as a red solid. Yield: 700 mg (1.31 mmol, 81% based on **1**).

IR (KBr, cm⁻¹): 2230 (w, $\nu_{C=C}$), 3429 (s, ν_{O-H}). ¹H NMR (250 MHz, CDCl₃, δ): 1.56 (s, 12 H, CH₃), 2.36 (s, 2 H, OH); 4.03 (pt, $J_{HH} = 1.8$ Hz, 4 H, C_5H_4), 4.16 (pt, $J_{HH} = 1.8$ Hz, 4 H, C_5H_4), 4.24 (pt, $J_{HH} = 1.8$ Hz, 4 H, C_5H_4), 4.41 (pt, $J_{HH} = 1.8$ Hz, 4 H, C_5H_4).

KOH (400 mg, 7.12 mmol) was added to 700 mg (1.31 mmol) of **3**, which was dissolved in 50 mL of toluene. The resulting reaction mixture was heated to 110 °C and stirred 12 h. After cooling to 25 °C, the resulting mixture was filtered through a pad of Celite and all volatiles were removed under reduced pressure. The remaining material was subjected to column chromatography on silica gel using a mixture of toluene/dichloromethane (1:1, v/v). After removal of all solvents compound **4** could be isolated as an orange solid. Yield: 545 mg (1.3 mmol, 99% based on **3**).

IR (KBr, cm⁻¹): 2109 (w, $\nu_{C=C}$), 3305 (w, $\nu_{=CH}$). ¹H NMR (250 MHz, CDCl₃, δ): 2.66 (s, 1 H, ≡CH); 4.02 (pt, J_{HH} = 1.8 Hz, 4 H, C₅H₄), 4.23 (pt, J_{HH} = 1.8 Hz, 4 H, C₅H₄), 4.25 (pt, J_{HH} = 1.8 Hz, 4 H, C₅H₄), 4.4 (pt, J_{HH} = 1.8 Hz, 4 H, C₅H₄).

Synthesis of 1',1'''-((PPh₃)AuC=C)₂bifc (6). To 58 mg (0.138 mmol) of 1',1'''-bis(ethynyl)biferrocene (4) and 137 mg (0.277 mmol) of (Ph₃P)AuCl (5) dissolved in 20 mL of a tetrahydrofuran/ diethylamine mixture of ratio 1:1 was added 5 mg of CuI. The turbid reaction mixture was stirred for 4 h at room temperature, and all volatile materials were removed under reduced pressure. The residue was purified by column chromatography on silica (column dimension: 30×2 cm) using first an *n*-hexane/dichloromethane mixture (ratio 4:1 v/v) to remove unreacted 4. With tetrahydrofuran as eluent the title compound 6 was obtained. Removal of all volatiles in an oil-pump vacuum gave 6 as a yellow solid. Yield: 100 mg (0.074 mmol, 54% based on 4).

Anal. Calcd for C₆₀H₄₆Au₂Fe₂P₂ (1334.5 g/mol): C, 53.99; H, 3.47. Found: C, 54.01; H 3.52. IR (KBr, cm⁻¹): 2104 (w, $\nu_{C \equiv CAU}$). ¹H NMR (250 MHz, CDCl₃, δ): 3.89 (pt, $J_{HH} = 1.8$ Hz, 4 H, C₅H₄), 4.24 (pt, $J_{HH} = 1.8$ Hz, 4 H, C₅H₄), 4.28 (pt, $J_{HH} = 1.8$ Hz, 4 H, C₅H₄), 4.44 (pt, $J_{HH} = 1.8$ Hz, 4 H, C₅H₄), 7.4–7.61 ppm (m, 30 H, Ph). ¹³C{¹H} NMR (62.9 MHz, CDCl₃, δ): 68.1 (*CH*/C₅H₄), 69.9 (*CH*/C₅H₄), 70.8 (*CH*/C₅H₄), 72.6 (*CH*/C₅H₄), 100 (AuC≡C), 104.7 (AuC≡C), 129.3 (d, $J_{CP} = 11.3$ Hz, C^m/C_6H_5), 129.5 (d, $J_{CP} = 55$ Hz, C^i/C_6H_5), 132 (d, $J_{CP} = 2.4$ Hz, C^p/C_6H_5), 134.4 ppm (d, $J_{CP} = 14$ Hz, C^o/C_6H_5). ³¹P{¹H} NMR (101.25 MHz, CDCl₃, δ): 41.39 ppm (s, *P*Ph₃).

Synthesis of 1'-[(PPh₃)₂(η^{5} -C₅H₅)Ru-C=C]-1'''-(HC=C)bifc (8a). To a dark red solution of 100 mg (0.24 mmol) of 4 and 174.2 mg (0.24 mmol) of $(\eta^5-C_5H_5)(PPh_3)_2RuCl$ (7a) in 40 mL of a 1:1 dichloromethane/methanol mixture was added 40.7 mg (0.25 mmol) of $[NH_4]PF_6$ in a single portion. The resulting reaction solution was stirred for 5 h at 25 °C, and then 28 mg (0.25 mmol) of KOtBu was added in a single portion. The thus obtained reaction mixture was stirred for a further 5 h at 25 °C. The complete conversion was monitored by ³¹P{¹H} NMR spectroscopy. Subsequently, all volatiles were removed under reduced pressure. The residue was purified by column chromatography on alumina (column dimension: 30×2 cm) using diethyl ether/*n*-hexane (ratio 1:1, v/v) as eluent. The first band contained unreacted 4 and the second band 8a. By removing all volatiles in an oil-pump vacuum, complex 8a was obtained as a pale orange solid. Yield: 186 mg (0.168 mmol, 70% based on 4).

Anal. Calcd for C₆₅H₅₂Fe₂P₂Ru (1108.12 g/mol): C, 70.38; H, 4.72. Found: C, 70.11; H, 5.06. Mp >125 °C (dec). IR (KBr, cm⁻¹): 2074 (w, $\nu_{C=CRu}$), 2100 (w, $\nu_{C=CH}$), 3284 cm⁻¹ (w, $\nu_{=CH}$). ¹H NMR (250 MHz, CDCl₃, δ): 2.65 (s, 1 H, =CH), 3.79 (pt, J_{HH} = 1.7 Hz,

2 H, C₅H₄), 3.9 (pt, $J_{HH} = 1.9$ Hz, 1.7 Hz, 2 H, C₅H₄), 4.01 (pt, $J_{HH} = 1.9$ Hz 2 H, C₅H₄), 4.02 (pt, $J_{HH} = 1.9$ Hz 2 H, C₅H₄), 4.21 (m, 4 H, C₅H₄), 4.26 (pt, $J_{HH} = 1.9$ Hz, 2 H, C₅H₄), 4.29 (s, 5 H, C₅H₅/Cp), 4.4 (pt, $J_{HH} = 1.9$ Hz, 2 H, C₅H₄), 7.09–7.22 (m, 17 H, Ph),7.48–7.55 ppm (m, 12 H, Ph). ¹³C{¹H} NMR (62.9 MHz, CDCl₃, δ): 64.1 (C=CH), 68.0 (CH/C₅H₄), 68.2 (CH/C₅H₄), 68.8 (CH/C₅H₄), 69.9 (CH/C₅H₄), 70.7 (CH/C₅H₄), 70.3 (CH/C₅H₄), 70.7 (CH/C₅H₄), 73.0 (CH/C₅H₅), 86.7 (C²/C₅H₄), 82.1 (C²/C₅H₄), 82.9 (C=CH), 85.3 (CH/C₅H₅), 86.7 (C²/C₅H₄), 88 (C²/C₅H₄), 107.8 (C=CRu), 109.0 (C=CRu), 127.3 (pt, $J_{CP} = 4.8$ Hz, C^m/C_6 H₅), 128.5 (s, C^p/C_6 H₅), 134.1 (pt, $J_{CP} = 4.8$ Hz, C^o/C_6 H₅), 139.3 ppm (dd, $J_{CP} = 20$ Hz, C^2/C_6 H₅). ³¹P{¹H} NMR (101.25 MHz, CDCl₃, δ): 49.38 ppm (s, *P*Ph₃).

Synthesis of 1',1'''-((PPh₃)₂(η^{5} -C₅H₅)Ru-C=C)₂bifc (9a). To 100 mg (0.24 mmol) of 4 and 363 mg (0.5 mmol) of 7a in 50 mL of a 1:1 dichloromethane/methanol (ratio 1:1, v/v) mixture was added 81.5 mg (0.5 mmol) of [NH₄]PF₆ in a single portion. The reaction mixture was stirred for 5 h at 25 °C, and then 56 mg (0.5 mmol) of KOtBu was added. The resulting reaction mixture was stirred for 6 h at 25 °C. The complete conversion was monitored by ³¹P{¹H} NMR spectroscopy. All volatiles were removed under reduced pressure. The residue was purified by column chromatography on alumina (column dimension: 30 × 2 cm) using a diethyl ether/*n*-hexane mixture (ratio 1:1, v/v) as eluent. After removal of all volatiles in an oil-pump vacuum an orange solid of **9a** was obtained. Yield: 400 mg (0.22 mmol, 92% based on **4**).

Anal. Calcd for $C_{106}H_{86}Fe_2P_4Ru_2$ (1797.54 g/mol): C, 70.84; H, 4.81. Found: C, 70.61; H, 5.08. Mp >154 °C (dec). IR (KBr, cm⁻¹): 2075 cm⁻¹ (m, $\nu_{C=CRu}$). ¹H NMR (250 MHz, CDCl₃, δ): 3.75 (pt, $J_{HH} = 1.58$ Hz, 4 H, C_5H_4), 3.79 (pt, $J_{HH} = 1.58$ Hz, 4 H, C_5H_4) 3.98 (pt, $J_{HH} = 1.6$ Hz, 4 H, C_5H_4), 4.17 (pt, $J_{HH} = 1.6$ Hz, 4 H, C_5H_4), 4.2 (s, 10 H, C_5H_5), 7.01 – 7.16 (m, 39 H, Ph), 7.40–7.47 ppm (m, 21 H, Ph). ¹³C{¹H} NMR (62.9 MHz, CDCl₃, δ): 66.8 (C^i/C_5H_4), 67.0 (CH/C_5H_4), 68.8 (CH/C_5H_4), 69.2 (CH/C_5H_4), 72.2 (CH/C_5H_4), 85.5 (CH/C_5H_5), 106.2 (C=CRu), 109.01 (C=CRu), 127.5 (pt, $J_{CP} = 4.8$ Hz, C^m/C_6H_5), 128.7 (d, $J_{CP} = 1$ Hz, C^p/C_6H_5), 134.3 (pt, $J_{CP} = 21.1$ Hz, C^i/C_6H_5). ³¹P{¹H} NMR (101.25 MHz, CDCl₃, δ): 50.36 ppm (s, PPh_3).

Synthesis of 1'-[(PPh₃)₂(η^{5} -C₅H₅)Os-C=C]-1'''-(HC=C)bifc (8b). To 114 mg (0.27 mmol) of 4 dissolved in 60 mL of methanol was added 232 mg (0.27 mmol) of (PPh₃)₂(η^{5} -C₅H₅)OsBr (7b) followed by addition of 49 mg (0.3 mmol) of [NH₄]PF₆ at 70 °C. The reaction solution was stirred for 3 h at this temperature until all of 7b was dissolved. Then the solution was cooled to 25 °C, and 33.6 mg (0.3 mmol) of KOtBu was added in a single portion. After 3 h of stirring, all volatiles were removed under reduced pressure. The residue was purified by column chromatography on alumina (column dimension: 30 × 3 cm) using a diethyl ether/*n*hexane mixture (ratio 2:1, v/v) as eluent. The first band contained unreacted 4. From the second band 8b could be isolated as an orange powder. Yield: 200 mg (0.16 mmol, 62% based on 4).

Anal. Calcd for $C_{65}H_{52}Fe_2P_2Os$ (1196.98 g/mol): C, 65.22; H, 4.37. Found: C, 65.13; H, 4.42. Mp: 178 °C (dec). IR (KBr, cm⁻¹): 2069 (w, $\nu_{C=COs}$), 2099 (w, $\nu_{C=CH}$), 3226 cm⁻¹ (w, $\nu_{=CH}$). ¹H NMR (250 MHz, CDCl₃, δ): 2.65 (s, 1 H, \equiv CH), 3.79 (pt, $J_{HH} = 1.8$ Hz, 2 H, C_5H_4), 3.87 (pt, $J_{HH} = 1.8$ Hz, 2 H, C_5H_4), 3.98–4.01 (m, J_{HH} = 1.7 Hz, 4 H, C_5H_4), 4.19–4.21 (m, $J_{HH} = 1.7$ Hz, $J_{HH} = 1.8$ Hz, 4 H, C_5H_4), 4.21 (pt, $J_{HH} = 1.8$ Hz, 2 H, C_5H_4), 4.34 (s, 5 H, C_5H_5), 4.38 (pt, $J_{HH} = 1.8$ Hz, 2 H, C_5H_4), 7.09–7.22 (m, 18 H, Ph), 7.41–7.47 ppm (m, 12 H, Ph). ¹³C{¹H} NMR (62.9 MHz, CDCl₃, δ): 64.2 (C \equiv CH), 68.0, (CH/C₅H₄), 68.2 (CH/C₅H₄), 68.8 (CH/ C₅H₄), 69.9 (CH/C₅H₄), 70.1 (CH/C₅H₄), 70.4 (CH/C₅H₄), 70.9 (CH/ C₅H₄), 73.0 (CH/C₅H₄), 73.7 (Cⁱ/C₅H₄), 81.4 (CH/C₅H₅), 82.0 (Cⁱ/ C₅H₄), 82.9 (C \equiv CH), 87 (Cⁱ/C₅H₄), 102.7 (C \equiv COs), 110.1 (C \equiv COs), 127.4 (pt, $J_{CP} = 4.7$ Hz, C^m/C₆H₅), 128.7 (s, C^p/C₆H₅), 134.3 (pt, $J_{CP} = 5.2$ Hz, $C^{\circ}/C_{6}H_{5}$), 139.5 ppm (dd, $J_{CP} = 49.4$ Hz, $J_{CP} = 54.7$ Hz, $C^{\circ}/C_{6}H_{5}$). ³¹P{¹H} NMR (101.25 MHz, CDCl₃, δ): 0.15 ppm (s, *P*Ph₃).

Synthesis of 1',1'''-((PPh₃)₂(η^{5} -C₅H₅)Os-C≡C)₂bifc (9b). To 100 mg (0.24 mmol) of 4 dissolved in 60 mL of methanol were added 413 mg (0.48 mmol) of 7b and then 81.5 mg (0.5 mmol) of [NH₄]PF₆ at 70 °C. The reaction solution was heated to reflux for 3 h at this temperature, whereby the orange suspension turned into a clear red solution. The reaction solution was allowed to cool to 25 °C, and then 56 mg (0.5 mmol) of KOtBu was added in a single portion, causing the precipitation of a yellow solid. After 3 h of stirring, all volatiles were removed under reduced pressure. The residue was subjected to column chromatography on alumina (column dimension: 30 × 3 cm) using a diethyl ether/*n*-hexane mixture (ratio 2:1, v/v) as eluent. After removal of all volatiles under reduced pressure complex **9b** was obtained as an orange solid. Yield: 300 mg (0.15 mmol, 63% based on **4**).

Anal. Calcd for $C_{106}H_{86}Fe_2P_4Os_2$ (1975.86 g/mol): C, 64.43; H, 4.38. Found: C, 64.44; H, 4.46. Mp: 185 °C (dec). IR (KBr, cm⁻¹): 2076 (w, $\nu_{C=COs}$). ¹H NMR (250 MHz, CDCl₃, δ): 3.83 (pt, $J_{HH} =$ 1.8 Hz, 4 H, C_5H_4), 3.86 (pt, $J_{HH} =$ 1.8 Hz, 4 H, C_5H_4), 4.05 (pt, $J_{HH} =$ 1.8 Hz, 4 H, C_5H_4), 3.86 (pt, $J_{HH} =$ 1.8 Hz, 4 H, C_5H_4), 4.05 (pt, $J_{HH} =$ 1.8 Hz, 4 H, C_5H_4), 7.08–7.21 (m, 35 H, Ph), 7.42–7.48 ppm (m, 25 H, Ph). ¹³C{¹H} NMR (62.9 MHz, CDCl₃, δ): 68.4 (*CH*/C₅H₄), 69.6 (*CH*/C₅H₄), 70.7 (*CH*/C₅H₄), 77.5 (*CH*/C₅H₄), 87.2 (*C*/C₅H₄), 81.4 (*CH*/C₅H₅), 109.7 (*C*'COs), 127.1 (pt, $J_{CP} =$ 4.7 Hz, *C*^m/C₆H₅), 128.4 (s, *C*^p/C₆H₅), 134 (pt, $J_{CP} =$ 5.2 Hz, *C*°/C₆H₅), 139.9 ppm (d, $J_{CP} =$ 51.8 Hz, *C*ⁱ/C₆H₅). ³¹P{¹H} NMR (101.25 MHz, CDCl₃, δ): 0.6 ppm (s, *P*Ph₃).

Synthesis of $1' - [(dppf)(\eta^5 - C_5H_5)Ru - C \equiv C] - 1''' - (HC \equiv C)bifc$ (8c). A 100 mg (0.24 mmol) amount of 4 and 173 mg (0.24 mmol) of $(dppf)(\eta^5-C_5H_5)RuCl$ (7c) were dissolved in 40 mL of a dichloromethane/methanol mixture of ratio 1:1 (v/v), and 40.7 mg (0.25 mmol) of [NH₄]PF₆ was added in a single portion. The resulting reaction solution was stirred for 5 h at 25 °C, and then 28 mg (0.25 mmol) of KOtBu was added in a single portion, causing the precipitation of an orange solid. The resulting reaction mixture was stirred for a further 3 h at 25 °C. The complete conversion was monitored by ³¹P{¹H} NMR spectroscopy. Subsequently, all volatiles were removed under reduced pressure. The residue was purified by column chromatography on alumina (column dimension: 30×2 cm) using a diethyl ether/*n*-hexane mixture (ratio 1:1, v/v) as eluent. The first band gave unreacted 4 and the second band 8c. By removing all solvents in an oil-pump vacuum, complex 8a was obtained as a pale orange solid. Yield: 210 mg (0.184 mmol, 77% based on 4).

Anal. Calcd for $C_{63}H_{50}Fe_3P_2Ru$ (1137.62 g/mol): C, 66.51; H, 4.43. Found: C, 66.52; H, 4.65. Mp: 151 °C (dec). IR (KBr, cm⁻¹): 2065 (w, $v_{C \equiv CRu}$), 2108 (w, $v_{C \equiv CH}$), 3290 (w, $v_{\equiv CH}$). ¹H NMR (250 MHz, CDCl₃, δ): 2.67 (s, 1 H, \equiv CH), 3.86 (pt, $J_{HH} = 1.7$ Hz, 2 H, C_5H_4), 3.99–4.02 (m, 2 H, C_5H_4 /dppf), 4.04 (pt, $J_{HH} = 1.7$ Hz, 2 H, C_5H_4), 4.07 (pt, $J_{HH} = 1.7$ Hz, 2 H, C_5H_4), 4.13 (pt, $J_{HH} = 1.7$ Hz, 2 H, C_5H_4), 4.22 (pt, $J_{HH} = 1.7$ Hz, 2 H, C_5H_4), 4.28 (pt, $J_{HH} =$ 1.7 Hz, 2 H, C_5H_4), 4.32 (pt, $J_{HH} = 1.7$ Hz, 2 H, C_5H_4), 4.28 (pt, $J_{HH} =$ 1.7 Hz, 2 H, C_5H_4), 5.5 (pt, $J_{HH} = 1.7$ Hz, 2 H, C_5H_4 /dppf), 7.29–7.4 (m, 10 H, Ph), 7.4–7.5 (m, 5 H, Ph), 7.81–7.89 ppm (m, 5 H, Ph). ¹³C{¹H} NMR (62.9 MHz, CDCl₃, δ): 64.2 (C≡CH), 67.9 (CH/C₅H₄/dpf), 68.2 (CH/C₅H₄/Bfc), 68.3 (CH/C₅H₄/dppf), 68.7 (CH/C₅H₄/Bfc), 69.7 (CH/C₅H₄/Bfc), 69.99 (CH/C₅H₄/Bfc), 70.4 (CH/C₅H₄/Bfc), 70.7 (CH/C₅H₄/Bfc), 71.3 (C²/C₅H₄), 73.0 (CH/ C₅H₄/dppf), 73.1 (*CH*/C₅H₄/Bfc), 73.8 (*CH*/C₅H₄/Bfc), 77.5 (*CH*/C₅H₄/dppf) 82.4 (*C*'CH), 82.9 (*C*'/C₅H₄), 84.7 (*CH*/C₅H₅), 86.6 (*C*'/C₅H₄), 88.9 (*C*'/C₅H₄), 89.1 (Ci), 105.7 (*C*'CRu), 110.04 (*C*≡CRu), 125.4 (s, *CH*/C₆H₅), 127.3−127.6 (m, *CH*/C₆H₅), 128.6 (s, *CH*/C₆H₅), 129.2 (s, *CH*/C₆H₅), 134.1 (pt, $J_{CP} = 5.2$ Hz, *CH*/C₆H₅), 134.5 (pt, $J_{CP} = 4.7$ Hz, *CH*/C₆H₅), 140.7 (*C*'/C₆H₅) 142.7 ppm (*C*'/C₆H₅). ³¹P{¹H} NMR (101.25 MHz, CDCl₃, δ): 53.7 ppm (s, *P*Ph₂, dppf).

Synthesis of 1',1^{'''-((dppf)(η^5 -C₅H₅)Ru-C=C)₂bifc (9c). To 100 mg (0.24 mmol) of **4** and 359 mg (0.5 mmol) of **7c** in 50 mL of a 1:1 dichloromethane/methanol mixture were simultaneously added 81.5 mg (0.5 mmol) of [NH₄]PF₆ and 56 mg (0.5 mmol) of KOtBu. The resulting reaction mixture was stirred for 6 h at room temperature. The complete conversion was monitored by ³¹P{¹H} NMR spectroscopy. All volatiles were removed under reduced pressure. The residue was purified by column chromatography on alumina (column dimension: 30 × 2 cm) using a diethyl ether/*n*-hexane mixture (ratio 1:1, v/v) as eluent. Removal of all volatiles in an oil-pump vacuum gave **9a** as an orange solid. Yield: 420 mg (0.22 mmol, 94% based on **4**).}

Anal. Calcd for $C_{102}H_{82}Fe_4P_4Ru_2$ (1857.16 g/mol): C, 65.96; H, 4.45. Found: C, 66.03; H, 4.49. Mp: 185 °C (dec). IR (KBr, cm⁻¹): 2074 (w, $\nu_{C \equiv CRu}$). ¹H NMR (250 MHz, CDCl₃, δ): 3.8 (pt, $J_{HH} =$ 1.8 Hz, 4 H, C_5H_4), 3.92 (pt, $J_{HH} =$ 1.8 Hz, 4 H, C_5H_4), 3.99 (pt, $J_{HH} =$ 1.8 Hz, 4 H, C_5H_4), 4.05 (pt, $J_{HH} =$ 1.8 Hz, 4 H, C_5H_4), 4.2 (s, 10 H, C_5H_5), 4.21–4.25 (m, 12 H, C_5H_4 /dppf), 5.4 (4H, C_5H_4 / dppf) 7.2–7.36 (m, 25 H, Ph), 7.39–7.46 (m, 10 H, Ph), 7.74–7.82 ppm (m, 5 H, Ph). ¹³C{¹H} NMR (62.9 MHz, CDCl₃, δ): 67.9 (*CH*/ C_5H_4), 68.44 (*CH*/ C_5H_4), 69.54 (*CH*/ C_5H_4), 70.49 (*CH*/ C_5H_4), 71.32 (*CH*/ C_5H_4), 73.1 (*CH*/ C_5H_4), 77.37 (*CH*/ C_5H_4), 84.74 (*CH*/ C_5H_5), 88.7 (*C*ⁱ/ C_5H_4) 89.24 (*C*ⁱ/ C_5H_4), 109.95 (*C*≡CRu), 125.67 (s, *C*/ C_6H_5), 127.3–127.6 (m, *CH*/ C_6H_5), 128.61 (s, *CH*/ C_6H_5), 129.28 (s, *CH*/ C_6H_5), 133.9 (pt, $J_{CP} =$ 5.2 Hz, *CH*/ C_6H_5), 134.77 (pt, $J_{CP} =$ 5.2 Hz, *CH*/ C_6H_5), 140.01 (*C*ⁱ/ C_6H_5), 142.6 ppm (*C*ⁱ/ C_6H_5). ³¹P{¹H</sup> NMR (101.25 MHz, CDCl₃, δ): 53.9 ppm (s, *PPh*₂, dppf).

Crystallography. Crystal data for **6**, **8b**, **9a**, **9b**, and **9c** are presented in Tables 6 (**6**, **8b**) and 7 (**9a**, **9b**, **9c**). All data were collected on a Oxford Gemini S diffractometer with graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) (**6**, **8b**, **9a**, and **9b**) and graphite-monochromatized Cu K α radiation ($\lambda = 1.54184$ Å) (**9c**) at 100 K using oil-coated shock-cooled crystals.³⁰ The structures were solved by direct methods using SHELXS-97³¹ or SIR-92³² and refined by full-matrix least-squares procedures on F^2 using SHELXL-97.³³ All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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