Ruthenium or Ferrocenyl Homobimetallic and RuPdRu and FePdFe Heterotrimetallic Complexes Connected by Unsaturated, Carbon-Rich $-C{\equiv}CC_6H_4C{\equiv}C-$ Bridges

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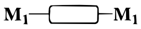
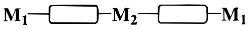
The reaction of 1,4-diethynylbenzene with *cis*-$RuCl_2(dppe)_2$ and iodoferrocene gave the homobimetallic systems $Cl(dppe)_2Ru{-}C{\equiv}CC_6H_4C{\equiv}C{-}Ru(dppe)_2Cl$ (**2**) and $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4){-}C{\equiv}CC_6H_4C{\equiv}C{-}(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$ (**3**), respectively. The organometallic terminal alkynes $Cl(dppe)_2Ru{-}C{\equiv}CC_6H_4C{\equiv}CH$ (**6**) and $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4{-}C{\equiv}CC_6H_4C{\equiv}CH)$ (**8**), obtained by desilylation of the corresponding complexes $Cl(dppe)_2Ru{-}C{\equiv}CC_6H_4C{\equiv}CSi^iPr_3$ (**5**) and $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4{-}C{\equiv}CC_6H_4C{\equiv}CSi^iPr_3)$ (**7**), were used as key starting products for access to the heterotrimetallic systems *trans*-$(P^nBu_3)_2Pd[{-}C{\equiv}CC_6H_4C{\equiv}C{-}Ru(dppe)_2Cl]_2$ (**10**; 53%) and *trans*-$(P^nBu_3)_2Pd[({-}C{\equiv}CC_6H_4C{\equiv}C{-}C_5H_4\text{-}\eta^5)Fe(\eta^5\text{-}C_5H_5)]_2$ (**11**; 73%) by reaction with $PdCl_2(PBu_3)_2$. The cyclic voltammetry studies of the complexes **2** and **3** have shown that the electrochemical response was strongly dependent on the connection type between the two terminal organometallic fragments and the organic bridge and that the insertion of the palladium moiety *trans*-$Pd(PBu_3)_2$ in the trimetallic complexes **10** and **11** induced totally different electrochemical behavior.

Introduction

Conjugated oligomers and polymers[1] have attracted considerable attention due to their application in materials science as conductors[2−5] or liquid crystal[6,7] precursors and light-emitting diodes (LED's).[8−10] The incorporation of transition metals into an oligomer chain is a convenient way to significantly modify the physical properties of the corresponding organic polymers.[11] The large variety of structures and electronic states of organometallic fragments has allowed the generation of new liquid crystal,[12−14] magnetic,[15,16] or nonlinear optical[17−19] properties. The physical properties of the resulting oligomers are expected to be directly related to the extended delocalization along the polymeric chain.[20] This motivates the design of new monomeric models in order to evaluate the capability of communication between two metal centers $\mathbf{M_1}$ made possible by an organic bridge (**A**), according to the nature of the metal-bridge linkage, and the influence of an organometallic fragment "$\mathbf{M_2}$" in a conjugated organic chain (**B**).



A



B

The 1,4-diethynylbenzene unit $-C{\equiv}CC_6H_4C{\equiv}C-$ has already been involved in organic and homometallic polymers (Pd, Pt, or Ni)[21,22] and even recently in heterometallic Ru/Pd, Fe/Pd, or Fe/Ni oligomers.[23] In these oligomers, the bridge is directly connected *via* a metal-carbon bond to metal centers (Ru, Pd, Ni) or indirectly *via* the cyclopentadienyl ligand (ferrocene).

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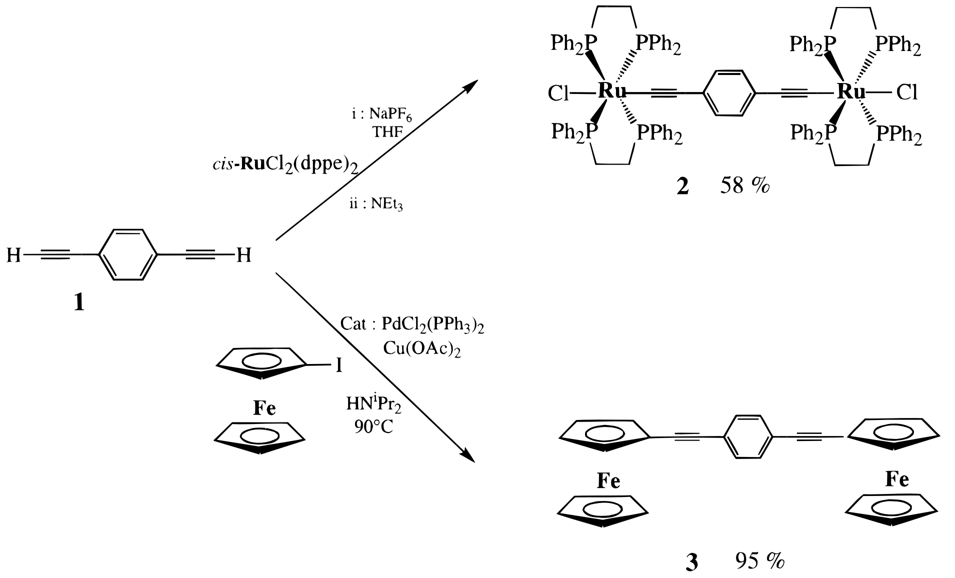
Scheme 1



We wish to report now (i) the synthesis of ruthenium and ferrocenyl homobimetallic complexes connected by 1,4-diethynylbenzene, $-C{\equiv}CC_6H_4C{\equiv}C-$ and by palladium-containing $-C{\equiv}CC_6H_4C{\equiv}C-Pd(L)_2-C{\equiv}CC_6H_4$-$C{\equiv}C-$ bridges and (ii) an electrochemical study of the redox metal sites.

Results and Discussion

Preparation of Complexes. The synthesis of a $Ru-C{\equiv}CC_6H_4C{\equiv}C-Ru$ unit was attempted by the activation of 1,4-diethynylbenzene (**1**) *via* the expected vinylidene intermediate followed by deprotonation, as was shown to occur from $RuCl_2(diphosphine)_2$ complexes and terminal monoalkynes.[24] This approach is in contrast with classical metal–carbon bond formation *via* a metal–halide unit and an organometallic.[25] Thus, the yellow bimetallic ruthenium derivative **2** was made in 58% yield by the reaction of 1,4-diethynylbenzene (**1**) and 2 equiv of *cis*-$RuCl_2(dppe)_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$) in the presence of $NaPF_6$ in THF (Scheme 1). A pale green intermediate formed, likely to be a vinylideneruthenium species, and was deprotonated by NEt_3. The $^{31}P\{^1H\}$ NMR of the yellow complex **2** showed only a singlet at 50.31 ppm (PPh_2) for the eight equivalent ^{31}P nuclei, in accord with a *trans*-chloroalkynylruthenium compound.

The carbon–carbon coupling of the same bridge with two ferrocene groups was attempted by a classical cross-coupling reaction.[26] Two equivalents of the iodoferrocene[27] was reacted with 1 equiv of 1,4-diethynylbenzene (**1**), in the presence of catalytic amounts of $PdCl_2(PPh_3)_2/Cu(OAc)_2$ in HN^iPr_2 at 90 °C, which gave the complex **3** as a brown-red solid (95%) ($^{13}C\{^1H\}$ NMR: δ (ppm) 90.21 and 85.71 (s, $C{\equiv}C$)).

The preparation of a trimetallic system of type **B**, in which two ruthenium moieties ($\mathbf{M_1}$) are connected by a metal-containing bridge, was attempted *via* the initial formation of the organometallic terminal alkyne **6** (Scheme 2), followed by the coupling of the $C{\equiv}CH$ end of **6** to the organometallic fragment $\mathbf{M_2}$. *cis*-$RuCl_2(dppe)_2$ was first reacted with 1-((triisopropylsilyl)ethynyl)-4-ethynylbenzene[28] **4** in the presence of $NaPF_6$ in THF to give a pale green intermediate, likely to be the vinylidene $[Cl(dppe)Ru{=}C{=}CH(C_6H_4C{\equiv}CSi^iPr_3)]^+$-$PF_6^-$ salt. On deprotonation by NEt_3 this intermediate led to the yellow ruthenium complex **5** in good yield (81%; Scheme 2) ($^{31}P\{^1H\}$NMR: δ (ppm) 49.94 (s, PPh_2)). Two $C{\equiv}C$ stretching vibrations were observed in the IR at 2148 cm^{-1} for the silylated $C{\equiv}C$ bond and 2061 cm^{-1} for the ruthenium acetylide moiety. Desilylation of compound **5** by $NBu_4F{\cdot}3H_2O$ in THF led to the ruthenium acetylenic complex **6** as a yellow solid (92%; Scheme 2). Spectroscopic data for **6** were identical with those of the complex **5** except for the acetylenic end group. In the IR the ${\equiv}CH$ and $C{\equiv}CH$ stretching vibrations were observed at 3226 and 2036 cm^{-1}, respectively, and in the $^{13}C\{^1H\}$ NMR signals appeared for the $C{\equiv}CH$ end group (84.99 and 77.19 ppm) and the ruthenium acetylide $Ru-C{\equiv}C$ (δ (ppm) 136.38 (quint, C_α, $^2J_{PC} = 12$ Hz), 130.36 (s, C_β).

The catalytic coupling of iodoferrocene with the silylated diyne **4** in HN^iPr_2 at 90 °C by $PdCl_2(PPh_3)_2/Cu(OAc)_2$ catalysts gave the red ferrocenyl derivative **7** (64%; Scheme 2). The acetylenic moieties were characterized by IR ($\nu_{FcC{\equiv}C}$ 2207 cm^{-1}, $\nu_{SiC{\equiv}C}$ 2151 cm^{-1}) and by $^{13}C\{^1H\}$ NMR (δ 107.2 and 92.9 ppm ($C{\equiv}CSi$), 91.1 and 85.5 ($C{\equiv}C-Cp$)). Desilylation of **7** by treatment with $NBu_4F{\cdot}3H_2O$ in THF gave the orange-red crystalline complex **8** (91%). By using the protection by Si^iPr_3 and the deprotection to give the $C{\equiv}CH$ end, no contamination of **6** and **8** by **2** and **3**, respectively, was observed.

Complexes **6** and **8**, which contain one reactive terminal acetylenic end $C{\equiv}CH$, are key starting materials for access to trimetallic systems. By reaction of 2

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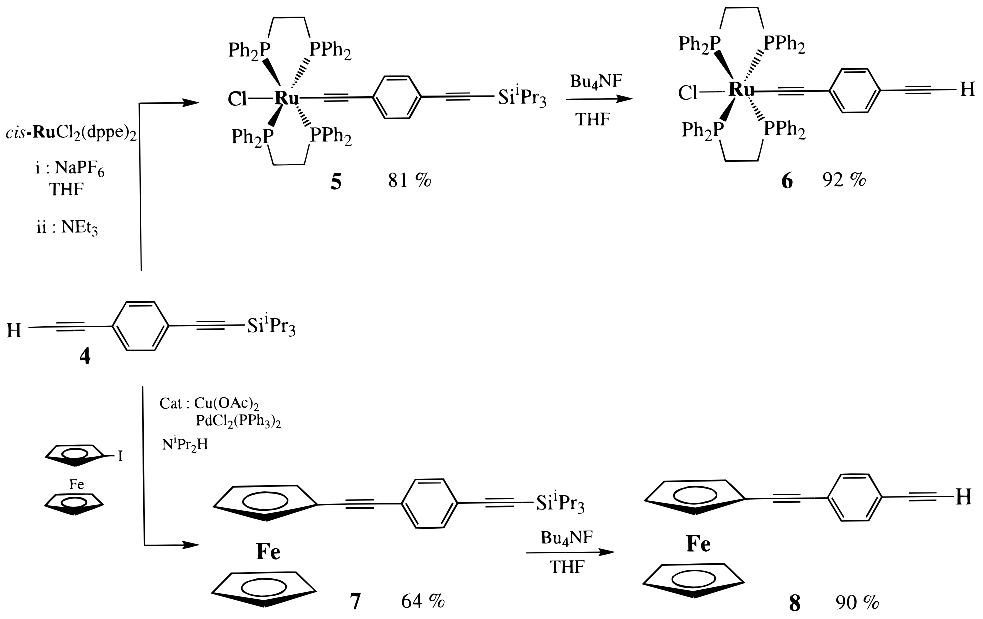
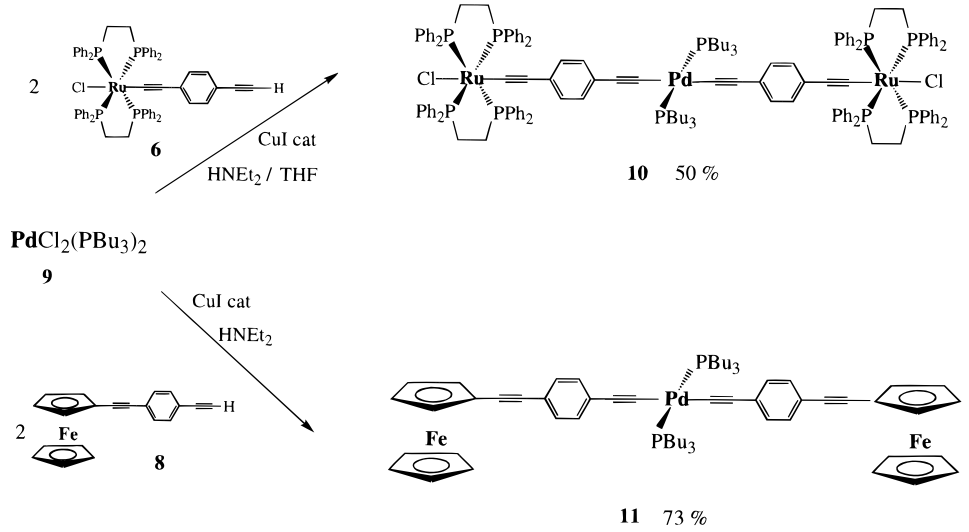
Scheme 2



Scheme 3



equiv of the complex $Cl(dppe)_2Ru\text{-}C{\equiv}CC_6H_4C{\equiv}C\text{-}H$ (**6**) and 1 equiv of $PdCl_2(PBu_3)_2$ (**9**), the yellow compound **10**, containing two ruthenium monoacetylide chains connected *via* a palladium diacetylide moiety, was produced in 50% yield (Scheme 3). The palladium–carbon bonds were formed in $HNEt_2$ in the presence of a catalytic amount of CuI. The $^{31}P\{^1H\}$ NMR showed singlets at 50.82 ppm (PPh_2) and 12.36 ppm (PBu_3) characteristic of a *trans* arrangement for all metal centers. In IR, the ruthenium and palladium acetylide moieties were merged into one vibration band at 2065 cm^{-1} although they are clearly differentiated in $^{13}C\{^1H\}$ NMR (δ (ppm) 137.42 (quintet, $Ru{-}\mathit{C}{\equiv}C$, $^2J_{PC} = 10$ Hz), 111.94 (t, $Pd{-}\mathit{C}{\equiv}C$, $^2J_{PC} = 12$ Hz), 111.91 (t, $Pd{-}C{\equiv}\mathit{C}$, $^3J_{PC} = 3$ Hz).

The similar procedure applied to the ferrocene-containing alkyne **8** gave the trimetallic complex **11** in 73% yield (scheme 3). The ferrocenyl and palladium acetylide fragments were very distinct in the IR ($\nu_{FcC{\equiv}C}$ 2207 cm^{-1}, $\nu_{PdC{\equiv}C}$ 2095 cm^{-1}) and $^{13}C\{^1H\}$ NMR (δ (ppm) 116.0 (t, $Pd{-}\mathit{C}{\equiv}C$, $^2J_{PC} = 17$ Hz), 111.4 (t, $Pd{-}C{\equiv}\mathit{C}$, $^3J_{PC} = 4$ Hz), 89.63 and 87.08 (s, $Fc{-}C{\equiv}C$). A singlet at 11.84 ppm in the $^{31}P\{^1H\}$ NMR was observed, characteristic of a palladium diacetylide complex in a *trans* geometry.

Electrochemical Studies. In order to evaluate the influence of the nature of the terminal organometallic fragment–bridge connection and of the insertion of an organometallic fragment into an conjugated organic chain, the cyclic voltammetry of complexes containing ruthenium (**2**, **5**, **6**, **10**) and ferrocene (**3**, **7**, **8**, **11**) was measured in dichloromethane containing NBu_4PF_6 salt at 100 mV s^{-1} with respect to the saturated calomel electrode (V_{SCE}) (Table 1).

The neutral compound **2** showed two successive reversible oxidation waves ($E° = +0.15$ ($i_{p,a}/i_{p,c} = 1.06$) and +0.55 V_{SCE} ($i_{p,a}/i_{p,c} = 1.03$)) which could be attributed to the formation of the mono- and dications respectively, corresponding to the formation of the Ru^{III}/Ru^{II} and Ru^{III}/Ru^{III} systems. For the two redox systems, the anodic and cathodic peak separation was 80 mV (without correction of the ohmic drop) with a 100 mV s^{-1} scan rate. The first oxidation of compound **2** was much easier ($E_{p,a}$ = 0.19 V_{SCE}) than that of the corresponding

Table 1. Cyclic Voltammetry Data for Complexes 2−11[a]

compd[b]	$E_{p,a}$ (V)	$E_{p,c}$ (V)	$E°$ (V)	ΔE (mV)	$E'_{p,a}$ (V)
$[Ru]{-}C{\equiv}CC_6H_4C{\equiv}C{-}[Ru]$ (**2**)	0.19	0.11	0.15	80	1.6[c]
	0.55	0.47	0.51	80	
$[Ru]{-}C{\equiv}CC_6H_4C{\equiv}C{-}Si^iPr_3$ (**5**)	0.51	0.43	0.47	80	1.36[c]
$[Ru]{-}C{\equiv}CC_6H_4C{\equiv}C{-}H$ (**6**)	0.53	0.44	0.49	90	1.38[c]
$[Pd]{-}(C{\equiv}CC_6H_4C{\equiv}C{-}[Ru])_2$ (**10**)	0.39	0.28	0.33	110	1.14[e]
					1.38[e]
$Fc{-}C{\equiv}CC_6H_4C{\equiv}C{-}[Fc]$ (**3**)	0.64	0.48	0.56	160	
$[Fc]{-}C{\equiv}CC_6H_4C{\equiv}C{-}Si^iPr_3$ (**7**)	0.62	0.54	0.58	80	
$[Fc]{-}C{\equiv}CC_6H_4C{\equiv}CH$ (**8**)	0.64	0.52	0.58	120	
$[Pd]{-}(C{\equiv}CC_6H_4C{\equiv}C{-}[Fc])_2$ (**11**)	0.61	0.50	0.55	110	1.42[d]

[a] Conditions: in CH_2Cl_2, NBu_4PF_6, 100 mV/s scan rate, Pt working and counter electrodes (1 mm diameter), ECS reference electrode, [complex] = $1 \times 10^{-3}-2 \times 10^{-3}$ M. A calibration voltammogram with ferrocene ($E°'$= 0.49 V) was recorded before each measurement. [b] Abbreviations: [Ru] = $ClRu(dppe)_2$; [Pd] = $Pd(P^nBu_3)_2$; [Fc] = $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$. [c] Irreversible oxidation (Ru^{IV}/Ru^{III}). [d] Irreversible oxidation (Pd^{III}/Pd^{II}). [e] Irreversible oxidations ($Ru^{IV}/Ru^{III}$and Pd^{III}/Pd^{II}).

monometallic complexes **5** and **6** ($E_{p,a}$ = 0.51 and 0.53 V_{SCE}, respectively). This difference is due to a greater electron-donating capability, through a $-C{\equiv}CC_6H_4C{\equiv}C-$ bridge, of the ruthenium(II) moiety $ClRu(dppe)_2$ in **2** than the H and Si^iPr_3 groups in **6** and **5**, respectively. The $E°$ values for the two redox processes differed by 360 mV, clearly indicating a communication between the two ruthenium centers through the 1,4-diethynylbenzene bridge. Interestingly, a binuclear compound containing the same conjugated bridge, $(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}dppe)Fe{-}C{\equiv}CC_6H_4C{\equiv}C{-}Fe(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}dppe)$ has just been reported to show a smaller difference (ΔE_0 = 260 mV) between the oxidation potential of iron-centered redox systems.[29] These results indicated that the nature of the terminal metal centers ($ClRu(dppe)_2-$ or $(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}dppe)Fe-$) can influence the electrochemical response of the corresponding bimetallic systems on the basis of the same organic bridge.

This can be seen from the study of the biferrocenyl complex **3** which showed in cyclic voltammetry a single, but large, oxidation wave ($E°$ = + 0.56 V_{SCE} ($i_{p,a}/i_{p,c}$ = 1.03), ΔE = 160 mV). No significant difference was observed with the corresponding monometallic derivatives **7** ($E°$ = + 0.58 V_{SCE} ($i_{p,a}/i_{p,c}$ = 1.01)) and **8** ($E°$ = + 0.58 V_{SCE} ($i_{p,a}/i_{p,c}$ = 0.99)) containing the Si^iPr_3 and H groups. Biferrocenyl derivatives bridged by acetylenic linkages $Fc{-}C{\equiv}C{-}Fc$ and $Fc{-}C{\equiv}CC{\equiv}C{-}Fc$ have already been described and showed similar cyclic voltammograms with quite large waves (ΔE =100−130 mV).[30,31] This observation was analyzed as superimposed one-electron waves rather than two-electron oxidations, where a lower difference ($\Delta E \leq 80$ mV) was expected. Also, it is tempting to explain the small difference between the oxidation potential of the iron redox centers in **3** by the fact that the organic 1,4-diethynylbenzene bridge is connected to the cyclopentadienyl ligands and not directly to the metal centers as in complex **2**. However, this simple hypothesis is not in agreement with the recently reported biferrocenyl derivative $Fc{-}C{\equiv}C{-}Pt{-}C{\equiv}C{-}Fc$,[32] which showed two well-resolved reversible oxidation waves centered on the Fc moieties (ΔE = 260 mV), although the bridge, an organometallic one, was connected to the cyclopentadienyl ligands.

Monometallic ruthenium derivatives **5** and **6** showed similar electrochemical responses with the first reversible oxidation wave (Ru^{III}/Ru^{II}, $E°$ = 0.52 V_{SCE} ($i_{p,a}/i_{p,c}$ = 0.98) followed by a second irreversible oxidation wave attributed to the redox system Ru^{IV}/Ru^{III}. Monoferrocenyl complexes **7** and **8** gave in cyclic voltammetry a single oxidation wave ($E°$ = 0.58 V_{SCE}) in the range 0−1.7 V.

More interesting was the cyclic voltammogram of complex **10**. It showed the first large (ΔE =110 mV) reversible ($i_{p,a}/i_{p,c}$ = 0.99) oxidation wave at $E°$ = 0.33 V_{SCE} (Ru^{III}/Ru^{II}) and two irreversible oxidation waves at more positive potential ($E'_{p,a}$ = 1.14 and 1.38 V_{SCE}) attributed to the Ru^{IV}/Ru^{III} and Pd^{III}/Pd^{II} redox systems. The first wave corresponds to the oxidation of the two ruthenium centers, as was verified by voltammetry with a rotating Pt electrode (2000 rpm). The wave corresponding to the process $Ru^{II} \rightarrow Ru^{III}$ disappeared completely to the benefit of the wave $Ru^{III} \rightarrow Ru^{II}$ after the addition to complex **10** of 2 equiv of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; $E°$ = 0.50 V_{SCE} in CH_2Cl_2).[33] This is in contrast with the result observed for compound **2**. To first approximation the palladium moiety seems to inhibit communication between the two ruthenium centers; this phenomenon has just been observed for the trimetallic complex $L_nRe{-}C{\equiv}C{-}Pd(PBu_3)_2{-}C{\equiv}C\text{-}ReL_n$[34] where the palladium(II) moiety associated with the same two PBu_3 ligands was described as an insulating block for the conjugated chain.

Derivative **11** showed a wave at $E°$ = 0.55 V_{SCE} ($i_{p,a}/i_{p,c}$ = 1.02) corresponding to the two-electron oxidation of the two terminal ferrocenyl moieties, as was confirmed by voltammetry with a rotating Pt electrode (2000 rpm) and 2 equiv of $AgBF_4$ as oxidant.[33a] In addition, **11** showed an irreversible oxidation wave at $E°$ = 1.42 V for the Pd^{III}/Pd^{II} redox system.

Conclusion

In summary, we have reported new bimetallic systems containing an organic or metal-containing conjugated bridge; whereas the ferrocene precursor was made by a classical catalyzed cross-coupling reaction, the ruthenium derivative was produced by activation of terminal diynes by ruthenium(II) moieties and *via* vinylidene intermediates. Electrochemistry studies have shown (i) that the electrochemical behavior of bimetallic complexes was strongly dependent on the nature of the connection between the two terminal organometallic fragments and the 1,4-diethynylbenzene bridge and (ii) that the incorporation of the organometallic fragment *trans*-$Pd(PBu_3)_2$ in the conjugated bridge induced different electrochemical behavior. Studies are currently in progress to apply these results to promote or inhibit electron delocalization in metal-containing conjugated polymers.

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Experimental Section

General Data. Solvents were dried by standard methods, and all reactions involving metal complexes were conducted under nitrogen by standard Schlenk techniques. Elemental analysis were performed by the CNRS analyses laboratory, Villeurbanne, France. NMR spectra were recorded on a Bruker AMWB 300 operating at 300.134 MHz for ^{1}H, 75.469 MHz for ^{13}C, and 121.496 MHz for ^{31}P nuclei or on a Bruker DPX 200 operating at 200.131 MHz for ^{1}H and 81.019 MHz for ^{31}P nuclei; ^{31}P chemical shifts are relative to external H_3PO_4 (85%). Mass spectra were performed at the CRMPO center (university of Rennes) on a Zab Spec TOF mass spectrometer (FAB positive mode). Glycerol was used as the matrix for the FAB spectra. The synthesis of *cis*-$RuCl_2(dppe)_2$,[35] iodoferrocene,[27] 1,4-diethynylbenzene,[28] and 1-((triisopropylsilyl)ethynyl)-4-ethynylbenzene[28] was performed as previously described.

$Cl(dppe)_2Ru{-}C{\equiv}CC_6H_4C{\equiv}C{-}Ru(dppe)_2Cl$ (2). *cis*-$RuCl_2(dppe)_2$ (500 mg, 0.52 mmol), 1,4-diethynylbenzene (**1**; 33 mg, 0.26 mmol), and $NaPF_6$ (173 mg, 1.03 mmol) are stirred in THF (20 mL) for 40 h. After filtration the green solid is washed with pentane. THF (20 mL) and triethylamine (1 mL) were added to the solid. The reaction mixture was stirred for 16 h at room temperature. After filtration and washing with pentane a yellow product was obtained (0.310 g, 58% yield). It was recrystallized in CH_2Cl_2. High-resolution mass spectrometry: M^+ calcd 1991.3232, found: 1991.329. Anal. Calcd for $C_{114}H_{100}Cl_2P_8Ru_2.2CH_2Cl_2$: C, 64.50; H, 4.86. Found: C, 64.20; H, 4.74. IR (cm^{-1}, KBr): 2058 ($\nu_{C\equiv CRu}$). ^{1}H NMR (300.133 MHz, C_6D_6, 297 K): δ (ppm) 7.70−6.92 (m, C_6H_5 and C_6H_4), 2.66 (m, CH_2CH_2). $^{31}P\{^1H\}$ NMR (121.499 MHz, C_6D_6, 297 K): δ (ppm) 50.31 (s, dppe). $^{13}C\{^1H\}$ NMR (75.469 MHz, CD_2Cl_2, 297 K): δ (ppm) 135.19, 134.93, 129.31, 129.03, 127.90, 127.33, 30.59 (m, CH_2).

$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4{-}C{\equiv}CC_6H_4C{\equiv}C{-}C_5H_4\text{-}\eta^5)Fe(\eta^5\text{-}C_5H_5)$ (3). Iodoferrocene (1.0 g, 3.2 mmol), 1,4-diethynylbenzene (**1**; 202 mg, 1.6 mmol), bis(triphenylphosphine)palladium dichloride (91 mg, 0.13 mmol), and copper acetate (24 mg, 0.13 mmol) were dissolved in diisopropylamine (25 mL). The reaction mixture was stirred for 17.5 h at 90 °C. The brown solid obtained by removing the solvent *in vacuo* was dissolved in CH_2Cl_2 (25 mL) and washed with water (3 × 10 mL). Evaporation of the dichloromethane layer and washing with pentane (3 × 15 mL) provided 754 mg (1.53 mmol) of a brown-red solid (96%). High-resolution mass spectrometry: M^+ calcd 494.0421, found 494.042. Anal. Calcd for $C_{30}H_{22}Fe_2$: C, 72.87; H, 4.49. Found: C, 72.55; H, 4.78. IR (cm^{-1}, KBr): 2200 ($\nu_{C\equiv C}$). ^{1}H NMR (300.133 MHz, C_6D_6, 297 K): δ (ppm) 7.36 (s, C_6H_4), 4.46 (m, C_5H_4), 4.07 (s, C_5H_5), 3.94 (m, C_5H_4). $^{13}C\{^1H\}$ NMR (75.469 MHz, $CDCl_3$, 297 K), δ (ppm) 131.2 (s, CH of C_6H_4), 123.1 (s, C_{ipso} of C_6H_4), 90.2 and 85.7 (s, $C\equiv C$), 71.5 and 69.0 (s, CH of C_5H_4), 70.0 (s, C_5H_5), 65.1 (s, C_{ipso} of C_5H_4).

$Cl(dppe)_2Ru{-}C{\equiv}CC_6H_4C{\equiv}CSi^iPr_3$ (5). *cis*-$RuCl_{2(}dppe)_2$ (962 mg, 0.99 mmol), 1-((triisopropylsilyl)ethynyl)-4-ethynylbenzene (**4**; 563 mg, 1.98 mmol), and $NaPF_6$ (169 mg, 1 mmol) were stirred in methylene dichloride (20 mL) for 15 h. After filtration and evaporation of solvent a green solid was obtained and washed with pentane to eliminate excess **4**. The green solid was dissolved in THF (30 mL) to give a red solution. Triethylamine (0.7 mL, 5.22 mmol, 6 equiv) was added, and the reaction mixture was stirred for 4 h at room temperature. The yellow solid obtained by removing the solvent *in vacuo* was dissolved in toluene (20 mL) and filtered. Evaporation of the toluene and washing with pentane yielded 973 mg (0.73 mmol) of a yellow solid (81%). Anal. Calcd for $C_{71}H_{73}ClP_4SiRu$: C, 70.20; H, 6.06. Found: C, 70.64; H, 6.27. IR (cm^{-1}, KBr): 2148 ($\nu_{C\equiv CSi}$), 2061 ($\nu_{C\equiv CRu}$). ^{1}H NMR (300.133 MHz, $CDCl_3$, 297 K): δ (ppm) 7.44−6.91 (m, C_6H_5 and C_6H_4), 6.50 (d, 2H, C_6H_4, $^3J_{HH} = 8$ Hz), 2.66 (m, CH_2CH_2), 1.14 (m, Si^iPr). $^{31}P\{^1H\}$ NMR (121.499 MHz, $CDCl_3$, 297 K): δ (ppm) 49.94 (s, dppe).

$Cl(dppe)_2Ru{-}C{\equiv}CC_6H_4C{\equiv}CH$ (6). To a solution of the silylated product **5** (900 mg, 0.70 mmol) in THF (15 mL) was added a solution of $Bu_4NF{\cdot}3H_2O$ (110 mg, 0.35 mmol) in THF (10 mL) dropwise. The mixture was stirred at room temperature for 30 min. After evaporation of the solvent the crude material was washed with water (4 × 15 mL) and dissolved in methylene dichloride (15 mL). After evaporation of the organic layer the solid was dissolved in toluene (15 mL). Evaporation of the toluene layer and washing with pentane yielded 732 mg of a yellow solid (93%). Anal. Calcd for $C_{62}H_{53}ClP_4Ru$: C, 70.35; H, 5.05. Found: C, 69.61; H, 5.13. IR (cm^{-1}, KBr): 3226 ($\nu_{\equiv CH}$), 2066 ($\nu_{C\equiv CRu}$). ^{1}H NMR (300.133 MHz, $CDCl_3$, 297 K): δ (ppm) 7.45−6.91 (m, C_6H_5 and C_6H_4), 6.51 (d, 2H, C_6H_4, $^3J_{HH} = 8$ Hz), 3.10 (s, $C\equiv CH$), 2.68 (m, CH_2CH_2). $^{31}P\{^1H\}$ NMR (121.499 MHz, $CDCl_3$, 297 K): δ (ppm) 49.83 (s, dppe). $^{13}C\{^1H\}$ NMR (75.469 MHz, CD_2Cl_2, 297 K): δ (ppm) 136.38 (quint, Ru−C, $^2J_{PC} = 12$ Hz), 134.99, 134.37, 131.66, 129.46, 129.19, 127.58, 127.42 (C_6H_5 and C_6H_4), 130.36 (s, Ru-$C\equiv C$), 115.73 and 113.96 (s, C_{ipso} of C_6H_4), 84.99 (s, $C\equiv CH$), 77.19 (s, $C\equiv CH$), 30.99 (CH_2CH_2).

$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4{-}C{\equiv}CC_6H_4C{\equiv}CSi^iPr_3)$ (7). Iodoferrocene (2.0 g, 6.4 mmol), **4** (1.7 g, 6.7 mmol), bis(triphenylphosphine)-palladium dichloride (175 mg, 0.25 mmol), and copper acetate (45 mg, 0.25 mmol) were stirred for 17.5 h at 90 °C in diisopropylamine (40 mL). The brown oil obtained by removing the amine *in vacuo* was extracted with pentane (4 × 30 mL). After filtration and evaporation of the solvent a brown oil was obtained, which was purified via column chromatography (Al_2O_3, CH_2Cl_2/pentane 1:10). Evaporation of the solvents yielded 1.9 g of a red oil (64%). High-resolution mass spectrometry: M^+ calcd 466.1780, found: 466.177. Anal. Calcd for $C_{29}H_{34}FeSi$: C, 74.65; H, 7.35. Found: C, 74.13; H, 7.33. IR (cm^{-1}, KBr): 2207 ($\nu_{C\equiv CFc}$), 2151 ($\nu_{C\equiv CSi}$). ^{1}H NMR (300.133 MHz, $CDCl_3$, 297 K): δ (ppm) 7.40 (s, C_6H_4), 4.49 (m, C_5H_4), 4.24 (m, C_5H_4), 4.15 (s, C_5H_5), 1.12 (m, Si^iPr). $^{13}C\{^1H\}$ NMR (75.469 MHz, CD_2Cl_2, 297 K): δ (ppm) 132.3 and 131.5 (s, CH of C_6H_4), 124.4 and 123.0 (s, C_{ipso} of C_6H_4), 107.2 (s, $C\equiv CSi$), 92.9 (s, $C\equiv CSi$), 91.1 and 85.1 (s, $C\equiv CC_5H_4$), 71.9, 70.4, 69.5, and 68.4 (C_5H_5 and C_5H_4), 18.9 (CH_3), 11.7 (CH).

$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4{-}C{\equiv}CC_6H_4C{\equiv}CH)$ (8). To a solution of the silylated complex **7** (1.0 g, 2.2 mmol) in THF (30 mL) was added dropwise a solution of $Bu_4NF{\cdot}3H_2O$ (694 mg) in THF (15 mL). The mixture was stirred for 10 min at room temperature. After evaporation of the solvent the crude material was dissolved in toluene (25 mL) and washed with water (3 × 15 mL). The dark orange oil obtained by evaporation of the toluene layer was further purified via column chromatography (Al_2O_3, CH_2Cl_2/hexane 1:10), which yielded 620 mg (2.0 mmol) of an orange-red crystalline material (91%). High resolution mass spectrometry: M^+ calcd 310.0445, found 310.045. Anal. Calcd for $C_{20}H_{14}Fe$: C, 77.41; H, 4.65. Found: C, 77.46; H, 5.47. IR (cm^{-1}, KBr): 3269 ($\nu_{\equiv CH}$), 2203 ($\nu_{C\equiv CFc}$), 2103 ($\nu_{C\equiv C}$). ^{1}H NMR (300.133 MHz, $CDCl_3$, 297 K): δ (ppm) 7.45 (s, C_6H_4), 4.50 (m, C_5H_4), 4.27 (m, C_5H_4), 4.24 (s, C_5H_5), 3.16 (s, $C\equiv CH$).

$(P^nBu_3)_2Pd[{-}C{\equiv}CC_6H_4C{\equiv}C{-}Ru(dppe)_2Cl]_2$ (10). The ruthenium complex **6** (600 mg, 0.56 mmol), $PdCl_2(PBu_3)_2$ (**9**; 162 mg, 0.28 mmol), and copper iodide (1 mg, 0.005 mmol) were dissolved in diethylamine (15 mL) and THF (5 mL). The reaction mixture was stirred for 20 h at room temperature. The yellow-ocher solid obtained by removing the solvent in vacuo was dissolved in toluene (30 mL) and washed with water (3 × 20 mL). Evaporation of the toluene layer yielded a yellow-ocher solid. This procedure provided 491 mg (75%) of crude product. Recrystallization in toluene/pentane gave 365 mg of a yellow solid (53%). High-resolution mass spectrometry: M^+ calcd 2624.6249, found 2624.726. Anal. Calcd for $C_{148}H_{158}Cl_2P_{10}PdRu_2$: C, 67.67; H, 6.07. Found: C, 67.48; H, 6.05. IR

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(cm^{-1}, KBr): 2066 ($\nu_{\mathrm{RuC\equiv C}}$ and $\nu_{\mathrm{PdC\equiv C}}$). ^{1}H NMR (200.131 MHz, C_6D_6, 297 K): δ (ppm) 7.81, 7.69, and 7.07 (m, C_6H_5 and C_6H_4), 2.74 (m, PCH_2CH_2P), 2.24, 1.91, and 1.64 (m, CH_2), 1.12 (t, CH_3, $^{3}J_{\mathrm{HH}} = 7$ Hz). $^{31}P\{^{1}H\}$ NMR (81.019 MHz, C_6D_6, 297 K): δ (ppm) 50.83 (s, PPh_2), 12.36 (s, PBu_3). $^{13}C\{^{1}H\}$ NMR (75.469 MHz, C_6D_6, 297 K): δ (ppm) 137.42 (quint, $\mathrm{Ru{-}}\mathit{C}\mathrm{{\equiv}C}$, $^{2}J_{\mathrm{PC}} =$ 10 Hz), 135.63, 135.05, 130.95, 130.84, 129.55, 129.44 and 129.32 (m, C_6H_5, C_6H_4, $\mathrm{Ru{-}C{\equiv}}\mathit{C}$), 124.39 (s, $\mathrm{Pd{-}C{\equiv}C}\mathit{C}$), 114.29 (s, $\mathrm{Ru{-}C{\equiv}C}\mathit{C}$), 111.94 (t, $\mathrm{Pd{-}}\mathit{C}\mathrm{{\equiv}C}$, $^{2}J_{\mathrm{PC}} = 12$ Hz), 111.91 (t, $\mathrm{Pd{-}C{\equiv}}\mathit{C}$, $^{3}J_{\mathrm{PC}} = 3$ Hz), 31.51 (m, dppe CH_2), 27.66, 26.05, and 25.40 (PBu_3 CH_2), 14.59 (CH_3).

$(P^{n}Bu_3)_2Pd[(-C{\equiv}CC_6H_4C{\equiv}C\text{-}C_5H_4\text{-}\eta^{5})Fe(\eta^{5}\text{-}C_5H_5)]_2$ (11). Compound **8** (300 mg, 0,97 mmol), $PdCl_2(PBu_3)_2$ (**9**; 290 mg, 0,49 mmol), and copper iodide (6 mg, 0.032 mmol) were dissolved in diethylamine (20 mL). The reaction mixture was stirred for 20 h at room temperature. The orange oil obtained by removing the amine *in vacuo* was dissolved in toluene (25 mL) and washed with water (4 × 15 mL). Evaporation of the toluenic layer yielded an orange oil, which was washed by pentane. This procedure provided 410 mg (0.36 mmol) of an orange crystalline material (73%). High-resolution mass spectrometry: M^{+} calcd 1128.3490, found 1128.345. Anal. Calcd for $C_{64}H_{80}Fe_2P_2Pd$: C, 68.08; H, 7.14. Found: C, 67.82; H, 7.32. IR (cm^{-1}, KBr): 2207 ($\nu_{\mathrm{FcC\equiv C}}$), 2095 ($\nu_{\mathrm{PdC\equiv C}}$). ^{1}H NMR (200.131 MHz, C_6D_6, 297 K): δ (ppm) 7.53 (s, C_6H_4), 4.45 (m, C_5H_4), 4.06 (s, C_5H_5), 3.92 (m, C_5H_4), 1.98, 1.65, and 1.38 (m, CH_2), 0.89 (t, CH_3, $^{3}J_{\mathrm{HH}} = 6.0$ Hz). $^{31}P\{^{1}H\}$ NMR (121.499 MHz, C_6D_6, 297 K): δ (ppm) 11.84 (s, PBu_3). $^{13}C\{^{1}H\}$ NMR (75.469 MHz, C_6D_6, 297 K): δ (ppm) 132.09 and 131.50 (s, CH of C_6H_4), 121.13 (s, C_{ipso} C_6H_4), 115.98 (t, $\mathrm{C{\equiv}}\mathit{C}\mathrm{Pd}$, $^{3}J_{\mathrm{PC}} = 7.0$ Hz), 111.36 (s, $\mathit{C}\mathrm{{\equiv}CPd}$), 89.63 and 87.08 (s, $\mathit{C}{\equiv}\mathit{C}\mathrm{C_5H_4}$), 72.17 (s, CH C_5H_4), 70.72 (s, C_5H_5), 69.52 (s, CH C_5H_4), 66.36 (s, C_{ipso} C_5H_4), 27.59 (s, $\mathit{C}\mathrm{H_2CH_3}$), 25.99 (m, $\mathrm{P}\mathit{C}\mathrm{H_2CH_2}$), 24.84 (m, $\mathrm{PCH_2}\mathit{C}\mathrm{H_2}$), 14.45 (s, CH_3).

Cyclic Voltammetry. Voltammograms were recorded on an EG&G Princeton Applied Research Model 362 scanning potentiostat. Conditions: CH_2Cl_2 solvent, NBu_4PF_6 (0.1 M) electrolyte, 100 mV/s scan rate, Pt working and counter electrodes (1 mm diameter), ECS reference electrode. Concentrations of organometallic complexes were 1×10^{-3} to 2×10^{-3} M. A calibration voltammogram with ferrocene ($E° = 0.49\mathrm{V}_{\mathrm{SCE}}$) was recorded before each measurement. Potentials have been not corrected for ohmic drop.

Voltammetry with Rotating Electrode. Voltamograms were recorded before and after addition of the chemical redox reagents with a Pt (1 mm diameter) rotating electrode (2000 rpm) with a sweep rate of 100 mV/s in CH_2Cl_2 (30 mL) with NBu_4PF_6 (200 mg) as electrolyte. Voltamograms were recorded 10 min after the addition of 4.3 mg (1.9×10^{-5} mol) of DDQ to 25 mg (9.5×10^{-6} mol) of complex **10** and 30 min after the addition of 12 mg (6×10^{-5} mol) of $AgBF_4$ to 34 mg (3×10^{-5} mol) of complex **11**.

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