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Synthesis, Characterization and Electrochemical Properties of 4,5-Diazafluoren-9-yl or Fluoren-9-yl Terminated Homobimetallic Ruthenium and Osmium Allenylidene, Alkynyl-Allenylidene Complexes

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A variety of rigid ruthenium and osmium allenylidene [$M_1Cl(P\Lambda P)_2=C=C$(4,5-diazafluoren-9-yl)-{$M_2(CHC(PPh_3)CHC(PPh_3)Cl_2(PPh_3)_2$}][$PF_6$]$_3$ (**4a**: M_1=Os, M_2=Os, PΛP=dppm; **4b**: M_1=Os, M_2=Ru, PΛP=dppm; **4c**: M_1=Ru, M_2=Os, PΛP=dppe; **4d**: M_1=Ru, M_2=Ru, PΛP=dppe), ruthenium alkynyl-allenylidene complexes *trans*-[(dppe)$_2$Ru(C≡CPh)Ru=C=C(R)][PF_6] (**6a**: R=fluoren-9-yl; **6b**: R=4,5-diazafluoren-9-yl), *trans*-{(dppe)$_2$[=C=C(fluoren-9-yl)]Ru(C≡C−R−C≡C)Ru[(=C=C(fluoren-9-yl)(dppe)$_2$]} [PF_6]$_2$ (**8a**, R=1,4-phenylene; **8b**, R=1,3-phenylene) terminated by 4,5-diazafluoren-9-yl and fluoren-9-yl group have been prepared. These allenylidene complexes were derived from 9-ethynyl-9-fluorenol and 9-hydroxy-9-ethynyl-4,5-diazafluorene in the presence of *cis*-$OsCl_2$(dppm)$_2$ and *cis*-$RuCl_2$(dppe)$_2$. The respective products have been fully characterized by ^{1}H, ^{13}C, ^{31}P NMR spectrometry, IR spectrometry, elemental analysis, and UV/Vis spectrophotometry. Moreover, electrochemical studies reveal that the dinuclear complexes display a quasi-reversible redox behavior and a moderate electronic communication between the two metal centers in **8a**. UV-Vis studies show a remarkable absorption in the region (λ_{max}=300−700 nm) for these complexes.

Keywords alkynyl-allenylidene complexes, metallacumulene, diazafluorenyl and fluorenyl group, electrochemistry, electronic communication

Introduction

Carbon-rich organometallic complexes with π-conjugated bridges have attracted increasing interests for their versatile structural, electronic, mixed valence or conducting and physicochemical properties[1-3] in fields including liquid crystalline materials,[1h,4] metallomicelles (dye-sensitized photovoltaic cells),[3a,5] nonlinear optical devices,[4e,6] molecular wires/switches,[6b,7] luminescence,[8] and electronic transmission.[8b,9] In particular, metallacumulenes, such as allenylidene, bis(allenylidene), allenylidene-alkynyl and other related highly conjugated complexes play key roles in these fields and have made impressive progress in the chemical community for many years.[6b,10] Highly unsaturated rigid dimetallic complexes offer extended π-conjugated system and have been recognized as being particularly efficient in facilitating electronic transfer.[11,12] More recently, their potential as a model of nano-scale electronics, revealed that the metal atom lies in the same plane as the π-system and can participate in the communication between the metal and the extension of the π-conjugated path.[8b,13]

The diazafluorene and fluorene ligands were preferred to the bipyridyl and biphenyl moiety for its planar rigid configuration,[14] in order to provide increased stability and electronic communication to the reduced form of the allenylidene metals.[14a,14d,15] Those allenylidene complexes modified by fluorene ligands have received much attention due to their facile accessibility, good planarity and remarkable efficiency for electronic delocalization, which have shown promising potential for the development of nanoscopic molecular devices.[10b-10d] In this context, it would be very appealing and crucial to introduce the diazafluorene and fluorene fragments into dinuclear metallacumulene system and understand the factors that control the electron transmission.

As a continuation of our research efforts in the fields of novel dimetallic metallacumulene, we wish to report the synthesis, characterization, and electrochemical properties of the rigid binuclear allenylidene and alky-

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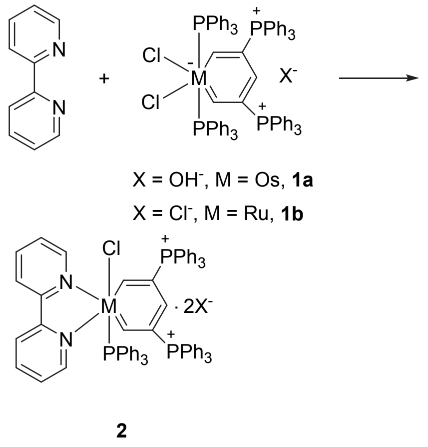
Dedicated to Professor Xi-Kui Jiang on the occasion of his 90th birthday.

nyl-allenylidene complexes modified by the 4,5-diazafluoren-9-yl and fluoren-9-yl group.

Results and Discussion

Synthesis of ruthenium and osmium allenylidene complexes coordinated by metallabenzene

Metallaaromatics are analogues of conventional organic aromatic molecules in which one of the (hydro)carbon segments is formally replaced by an isolobal transition-metal fragment.[16] Metallaaromatics are currently attracting attention not only because of their special structural features but also because they exhibit interesting chemical[17] and physical properties.[18] The combination of metallacumulene with metallaaromatics may creat complexes with novel structures and unique properties as well. In our investigation on the reactivity of metallabenzenes, we have reported that ruthenabenzen and osmabenzene [M(CHC(PPh$_3$)CHC(PPh$_3$)CH)-Cl$_2$•(PPh$_3$)$_2$]X (**1a**:[19] M=Os, X=OH; **1b**:[20] M=Ru, X=Cl) can readily undergo ligand substitution reaction with 2,2'-dipyridine to produce the stable dipyridine-coordinated metallabenzene **2** (Eq. 1).[21] We envisioned complexes [OsCl(dppm)$_2$=C=C=(4,5-diazafluoren-9-yl)][PF$_6$] (**3a**)[22] and [RuCl(dppe)$_2$ = C = C = (4,5-diazafluoren-9-yl)][PF$_6$] (**3b**)[14a] can also undergo ligand substitution reaction with metallabenzenes (**1a** and **1b**). As expected, a series of new complexes coordinated by metallabenzenes have been successfully synthesized and fully characterized via nitrogen coordination to metallabenzenes. The general synthetic route for the allenylidene complexes coordinated by metallabenzenes is outlined in Scheme 1.

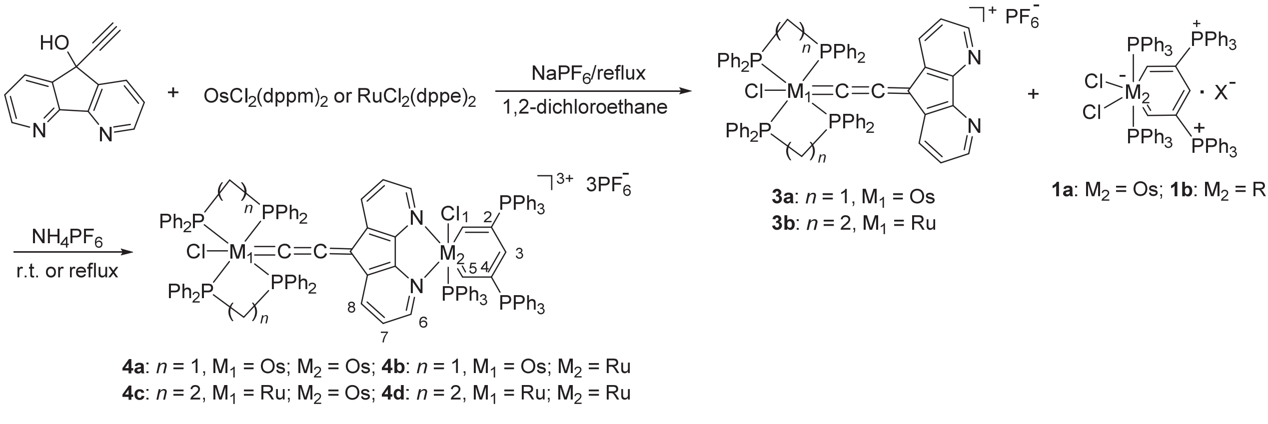


(1)

Following the method first introduced by Selegue in 1982,[23] the allenylidene complexes **3a** and **3b** were readily prepared by reaction of 9-hydroxy-9-ethynyl-4,5-diazafluorene with *cis*-OsCl$_2$(dppm)$_2$ and *cis*-RuCl$_2$-(dppe)$_2$, respectively. Then coordination of **3a**, **3b** was achieved with [Os(CHC(PPh$_3$)CHC(PPh$_3$)CH)Cl$_2$-(PPh$_3$)$_2$]OH (**1a**) in dichloromethane in the presence of 1.5 equivalents of NH$_4$PF$_6$. After reaction for 3 h in refluxing dichloromethane, workup and recrystallization yielded the red-brown bimetallic allenylidene complexes **4a**, **4c** in good yields of 88% and 61%, respectively. Attempts to effect coordination by employing more than two equivalents of CH$_3$OTf per equivalent of **1a**, and refluxing in methanol rather than dichloromethane were also successful. Analogously, the dimetallic allenylidene complexes **4b** and **4d** were obtained at room temperature from the corresponding complexes **3a**, **3b** with [Ru(CHC(PPh$_3$)CHC(PPh$_3$)CH)Cl$_2$(PPh$_3$)$_2$]Cl (**1b**) in 64%, 66% yields. **4a**—**4c** were purified via column chromatography and were found to be bench stable for several days. However, the complex **4d** slowly decomposed in solution under a nitrogen atmosphere at room temperature, forming an unidentified brown oil (Scheme 1).

Many times our attempts to grow quality crystal for **4a**—**4d** are unsuccessful. However, the structures of **4a**—**4d** can be unambiguously assigned on the basis of their elemental analyses and spectroscopic data. Overall, the structures of **4a**—**4d** correspond to the *trans*-chloro-(vinylidene) ruthenium and osmium complexes, as indicated in (^{31}P, ^{13}C) NMR by the equivalence of the four phosphorous nuclei and the low-frequency resonance as a quintet of the (Ru=C, Os=C) carbon nucleus in the range δ: 280—320. In addition, the IR spectra of **4a**—4**d** show characteristic $\nu_{C=C=C}$ vibration stretches in the range ν: 1885—1941 cm^{-1} (Table 1). These re-

Scheme 1 Synthetic pathway for the allenylidene complexes coordinated by metallabenzenes



sults are in line with that reported for the known ruthenium allenylidene complex ([Cl—Ru(dppe)$_2$=C=C=$C_{11}H_6N_2$\{(bpy)$_2$Ru\}][B(C_6F_5)$_4$]$_3$).[14a] As a representative example of these complexes, the ^{31}P NMR spectrum of **4a** shows a singlet at δ –64.87 for the 4 equiv. phosphorus atoms and two other singlets at δ 20.31 [s, CHC(PPh$_3$)], 5.55 [s, Os(PPh$_3$)], respectively. The ^{13}C\{^{1}H\} NMR spectrum of **4a** shows the α and β carbon atoms of the allenylidene unit as a quintet at δ 279.21 ($^2J_{PC}$=13.1 Hz, Cα) and a multiplet at δ 249.94 (m, Cβ), while the Cγ resonance appears at δ 166.02 as a singlet, and the carbon atoms on the metallacycle present at δ 250.01 (C1, C5), 124.32 (C2, C4), 151.6 (C3), respectively.

Synthesis of ruthenium mixed alkynyl allenylidene complexes

The activation of phenylacetylene with *cis*-RuCl$_2$(dppe)$_2$ in dichloromethane and in the presence of NaPF$_6$ has been shown to provide an easy route to vinylidene complex *trans*-[(dppe)$_2$(Cl)Ru=C=CHPh]•[PF$_6$] (**5**)[24] in high yield by Touchard and Lewis, which is very acidic and can be easily deprotonated in base conditions. Therefore, ruthenium mixed alkynyl-allenylidene complexes **6a**, **6b** could be obtained via displacement of the chloride ligand, followed by deprotonation from precursor **5**, and then activation from propargylic alcohols under a weak base condition. The general synthetic route for the preparation of **6a**, **6b** is outlined in Scheme 2.

Treatment of the vinylidene complex **5** with a solution of 9-ethynyl-9-fluorenol in anhydrous dichloromethane, and triethylamine or DBU (1,8-diazabicyclo-[5.4.0]-undec-7-ene) in the presence of NaPF$_6$ led to **6a** in 85% yield as deep violet powder upon precipitation with diethyl ether at room temperature. Under similar reaction condition, **6b** was prepared in 65% yield by following this procedure from precursor **5** and 9-hydroxy-9-ethynyl-4,5-diazafluorene. This reaction was monitored *in situ* by ^{31}P NMR spectroscopy, which was slower than that of **6a**, being completed in about 5 h. Although **6a** and **6b** were air stable in the solid state, it was shown during the preparation of **6b** that this complex slowly decomposed in solution in the presence of an excess of base. Decomposition products were easily removed by filtration through alumina with subsequent recrystallization from CH$_2$Cl$_2$/Et$_2$O.

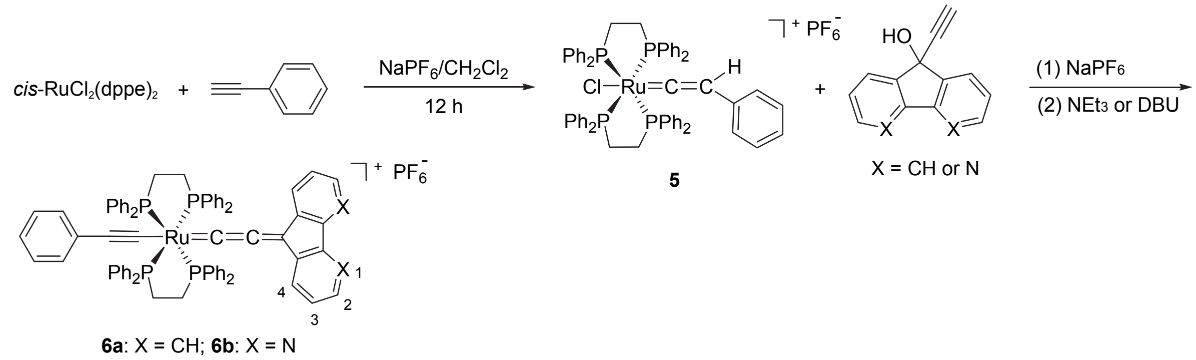
Although an X-ray crystal structure determination for **6a** was performed, the refinement proved unsatisfactory, with poor *R* value, an impossibly irregular geometry, and considerable areas of residual electron density presumably corresponding to disordered solvent. The complexes **6a**, **6b** are characterized in infrared spectra by the presence of two typical absorptions at ν=2075, 2063 cm^{-1} for $\nu_{(C\equiv C)}$ and ν=1920, 1908 cm^{-1} for $\nu_{(C=C=C)}$, consistent with that of analogous complex

Table 1 Selected ^{13}C \{^{1}H\} NMR and IR data for the allenylidene ruthenium and osmium complexes^a

	^{13}C\{^{1}H\} NMR δ					^{31}P\{^{1}H\} NMR δ	IR ν/cm^{-1}	
	α	β	γ	α'	β'		$\nu_{C=C=C}$	$\nu_{C\equiv C}$
4a	279.21	249.94	—	—	—	20.31, 5.55, –64.87	1941	—
4b	261.21	250.84	—	—	—	42.99, 18.59, –63.42	1885	—
4c	320.12	280.30	—	—	—	34.41, 20.44, 5.97	1930	—
4d	319.14	280.60	—	—	—	41.28, 34.46, 18.48	1901	—
6a	319.31	222.98	147.39	120.04	126.52	43.02	1920	2075
6b	316.50	232.75	143.03	123.14	127.17	40.56	1908	2063
8a	319.59	222.08	146.43	121.28	123.72	42.89	1933	2118
8b	319.92	220.63	147.08	120.65	124.13	42.64	1918	2070

^{a} In the IR spectra the $\nu_{(=C=C=C)}$ absorption is observed at ν 1941 cm^{-1}.

Scheme 2 Synthetic pathway for the ruthenium mixed alkynylallenylidene complexes



6a: X = CH; **6b**: X = N

(*trans*-$[Ph_2C{=}C{=}CRu(dppe)_2{-}C{\equiv}C{-}CHPh_2][PF_6]$, 2065 and 1919 cm^{-1}).[25a] In addition, the $^{31}P\{^1H\}$ spectra show a singlet at δ 43.02, 40.56 for the equivalency of the four phosphorus nuclei respectively, suggesting the relatively *trans* position of the alkynyl and allenylidene ligands (Table 1). The low-field $^{13}C\{^1H\}$ signal for the Ru=C carbon nucleus appears as a quintet at δ 319.31, 316.50 with $^2J_{PC}$ of approximately 14 Hz and a broad peak at δ 222.98, 232.75 for the Ru=C=C(β) carbon in agreement with the equivalence of the allenylidene ligands. In particular, in the ^1H NMR spectrum, protons at the 2-position (α to nitrogen) for complex **6b** are marginally deshielded, which can be confirmed by HSQC NMR experiments. Related alkynyl allenylidene complex of formula *trans*-$[(dppe)_2Ru(C{\equiv}CPh)({=}C{=}C{=}CPh_2)][PF_6]$, synthesized by Dixneuf and coworkers,[25b] shows similar spectroscopic data and therefore substantiates our assignment of *trans* geometry for **6a** and **6b**.

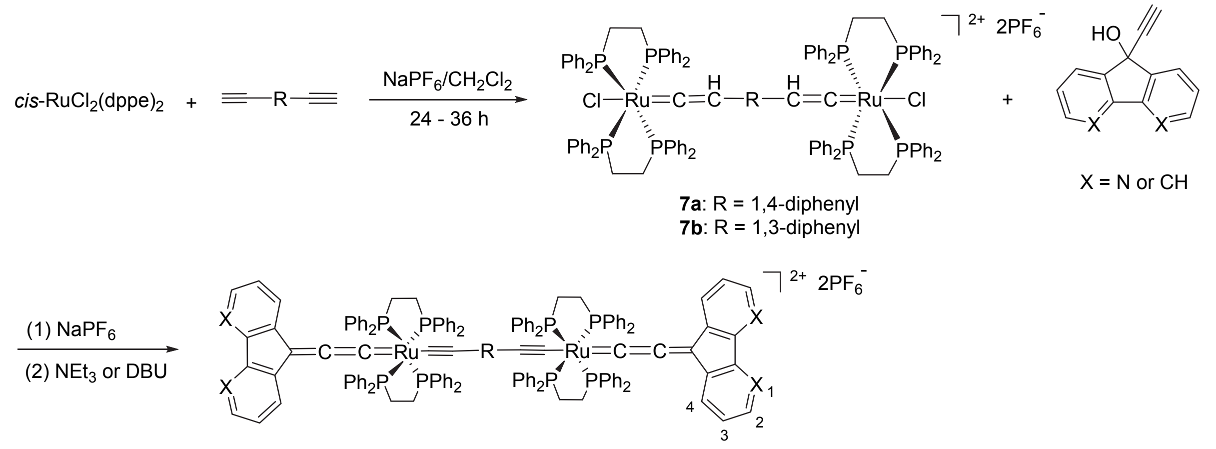
Synthesis of dimetallic ruthenium alkynyl allenylidene complexes

Using the synthetic strategy for the synthesis of the mononuclear ruthenium alkynyl allenylidene complexes **6a** and **6b** above, the vinylidene complexes 1,4-[*trans*-$Cl(dppe)_2Ru{=}C{=}CH]_2C_6H_4$ (**7a**),[13a] 1,3-[*trans*-$Cl(dppe)_2Ru{=}C{=}HC]_2C_6H_4$ (**7b**)[26] were reacted with two equivalents of 9-ethynyl-9-fluorenol, $NaPF_6$ in dichloromethane at room temperature, followed by addition of the base NEt_3 or DBU for about 3 h to give the purple dimetallic alkynyl allenylidene complexes **8a** and **8b** in yields of 53% and 57%, respectively. Similarly, treatment of **7a**, **7b** with 9-hydroxy-9-ethynyl-4,5-diazafluorene led to the desired dimetallic complexes **8c** and **8d** in NMR yields of 24% and 15%, respectively (Scheme 3).

It is worth mentioning that the intermediate vinylidenes **7a** and **7b** were not characterized, but purified by filtration before next step, which had been reported starting from the reaction of two equivalents of *cis*-$RuCl_2(dppe)_2$ with 1,4- or 1.3-diethynylbenzene in high yields by Fillaut in fact.[13c] In a pure form and under an inert atmosphere complexes **8a** and **8b** were stable in solid state at room temperature. However, **8c** and **8d** easily decomposed in solution at ambient temperature under a nitrogen atmosphere. Therefore, the reactions were stopped after 1.5 h to mitigate excessive decomposition of the product, thus explaining the rather low yield. The yields and the reaction time required for a complete conversion of **8a**—**8c** strongly depended on the excess of the base. The reaction rates significantly increased with increasing excess of the base NEt_3 or DBU. On the other hand, aqueous base led to lower yields as a result of decomposition of the product complexes provoked by the nucleophilic attack of water. Note that there have been reported examples for the oxidative cleavage of allenylidene complexes to form coordinated CO and organic alkyne via water-assisted nucleophilic attack at the C_α and C_β carbons.[27]

Unfortunately, the molecular structures of **8a**, **8b** have not been characterized so far by X-ray diffraction, due to lack of X-ray quality single crystals. However, it is believed that all these dimetallic ruthenium alkynyl allenylidene complexes indeed consist of two high symmetry units, which are connected together through 1,4- or 1,3-phenylenediethynyl bridge, as inferred from the NMR data. The $^{31}P\{^1H\}$ NMR analysis shows one singlet at δ 41—43, typical for a symmetrical structure, in agreement with the *trans* geometry of the chain. Additionally, the $^{13}C\{^1H\}$ NMR spectrum displays only three different signals for the cumulenic carbon atoms. The C_α and C_β carbon atoms resonate at δ 310—320 and δ 220—222 as multiplicity, while the C_γ carbon atoms resonate at δ 146—147 as a singlet (Table 1). However, complexes **8c** and **8d** are not stable enough in solution, and the ^{13}C NMR spectrum could not be obtained. In line with the proposed formulation, the FT-IR spectrum presents intense absorption at v 2118, 2070 cm^{-1} and v 1918, 1933 cm^{-1} for complexes **8a** and **8b**, characteristic of the alkynyl and allenylidene substituents, respectively. Further details about the NMR and IR characterization of **8a** and **8b** are summarized in Table 1.

Scheme 3 Synthetic procedure for the dimetallic ruthenium alkynyl-allenylidene complexes



7a: R = 1,4-diphenyl
7b: R = 1,3-diphenyl

8a: X = CH, R = 1,4-diphenyl; **8b**: X = CH, R = 1,3-diphenyl; **8c**: X = N, R = 1,4-diphenyl; **8d**: X = N, R = 1,3-diphenyl

Electrochemical studies

These new rigid mono- and bimetallic complexes are composed of several redox active units and a bridge that allows for electronic communication. To understand the electrochemical properties, the redox behavior of the binuclear complexes **4a**—**4c**, **8a**, **8b** (1 mmol•L^{-1} in CH_2Cl_2) has been investigated by cyclic voltammetry (CV) and differential pulse voltammogram techniques (DPV) with 0.1 mol•L^{-1} n-Bu_4NClO_4 as the supporting electrolyte. The mononuclear ruthenium alkynyl-allenylidene complexes **6a**, **6b** are also tested using electrochemical methods to compare how electronic effects act upon passing from a mononuclear complex to a dinuclear complex. The values of the potentials for some complexes are presented in Table 2, and typical CVs for complex **4a**, **6a**, **8a** are displayed in Figures 1, 2 and 3.

Table 2 Electrochemical data of mono- and binuclear ruthenium and osmium complexes[a]

Complex	Reduction		Oxidation	
	E_{red1}/V	E_{red1}/V	E_{ox1}/V	E_{ox1}/V
4a	−0.17[b]	−0.81[b]	1.39	—
4b	−0.17[b]	−0.82[b]	1.29	0.34[c]
4c	−0.66	−1.11	—	0.20[b]
6a	−0.34[b]	—	1.36[b]	—
6b	−0.08	—	1.47	—
8a	−0.49[b]		0.84[b]	0.45[b]
8b	−0.20[b]	−1.05	—	—

[a] Potential data were determined in CH_2Cl_2 containing 0.1 mol•L^{-1} n-Bu_4NClO_4, potential versus Ag/AgCl, scan rate = 0.10 V/s. [b] Quasi-reversible redox processes. [c] Irreversible redox processes.

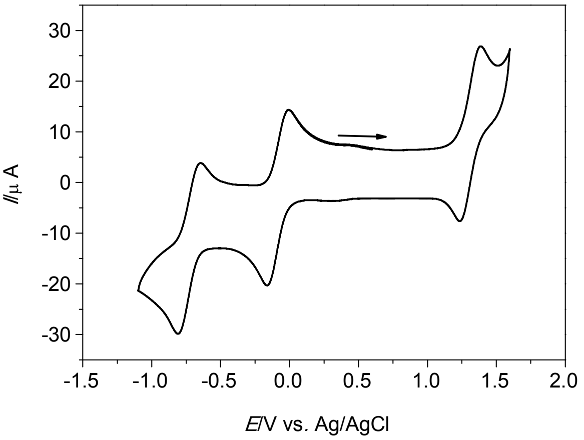


Figure 1 Cyclic voltammograms of complex **4a** in CH_2Cl_2 with 0.1 mol•L^{-1} n-Bu_4NClO_4 at a scan rate of 0.10 V/s.

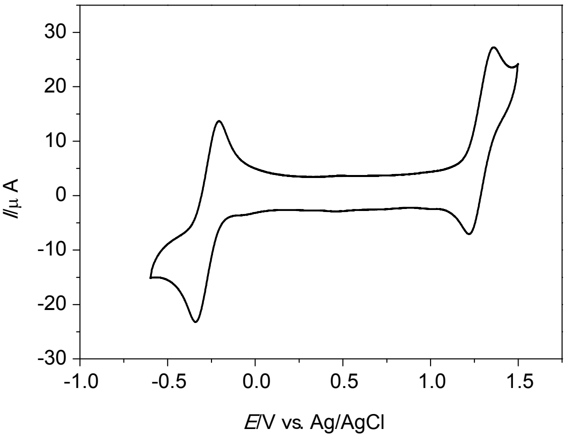


Figure 2 Cyclic voltammograms of complex **6a** in CH_2Cl_2 with 0.1 mol•L^{-1} n-Bu_4NClO_4 at a scan rate of 0.10 V/s.

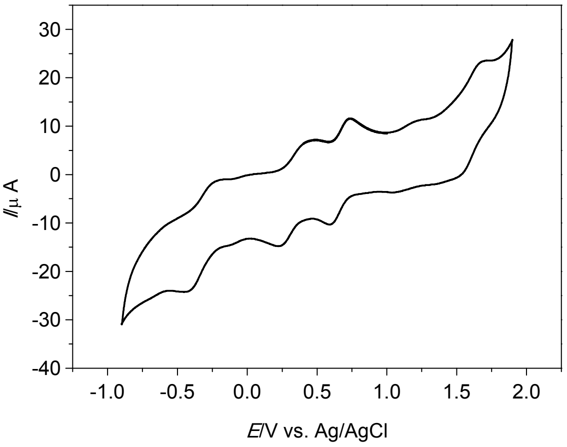


Figure 3 Cyclic voltammograms of complex **8a** in CH_2Cl_2 with mol•L^{-1} n-Bu_4NClO_4 at a scan rate of 0.10 V/s.

For the bimetallic complexes **4a**, **4b**, the first reduction occurs around $E\approx-0.17$ V, and the second around $E\approx-0.82$ V vs. Ag/AgCl, while the reduction of **4c** occurs at $E=-0.66$ V and $E=-1.11$ V (Table 2). In accordance with those of reported allenylidene complexes,[28] the two reversible reductive waves of complexes **4a**—**4c** are attributed to the reduction of cumulenic ligand. Nevertheless, the reduction processes are more favorable than that of the complex [(16-TMC)ClRu = C = C = C(2-Py)$_2$Ru(acac)][PF_6] (TMC = 1,5,9,13-tetraazacyclohexadecane).[14b] It is worth noting that the planarity and rigidity of the diazafluorene obviously enhance stability of the second reduced species. On the other hand, the oxidation processes observed around $E\approx+1.30$ V for **4a**—**4b** are partially chemically reversible, which might be attributed to the Os^{II}/Os^{III} and Ru^{II}/Ru^{III} oxidation of the osmium or ruthenium diimine moieties,[14a] whereas the oxidation of the other metal (Ru or Os) center is likely to be masked by the solvent discharge. Overall, it is difficult to assess the eventual interaction between the two metal centers from the electrochemical data, though DFT studies revealed that in the excited state of these kinds of compounds, there is electronic communication between the two metal centers.[5,22]

For the mononuclear alkynyl-allenylidene complexes **6a**, **6b**, they display a quasi-reversible one-electron reduction at $E\approx-0.34$ and −0.08 V, which could be assigned to the radical reduction of the allenylidene ligands based on the similar phenomenon of CV reported.[25a] Additionally, the quasi-reversible oxidation processes at $E\approx+1.36$ V (Figure 2) and $+1.47$ V are shown at higher potential than those of the neutral metal acetylides, which might be ascribed to the Ru^{II}/Ru^{III} couple with alkynyl-allenylidene ligand participation as well.[29] Such redox shift is also observed in the non-conjugated complex **8b**, in which the allenylidene moieties are in a *meta* orientation on the phenyl linker.

The bimetallic compound **8a** behaves in a manner distinct from that of the mononuclear models. In comparison with **6a** and **8b**, the dinuclear complex **8a** undergoes a well-defined reversible oxidative wave at $E=0.45$ V followed by a partially reversible oxidative peak at $E=0.84$ V (Figure 3). These two oxidations are well separated by 390 mV and should correspond to the formation of the Ru^{III}/Ru^{II} and Ru^{III}/Ru^{III} systems,[25a,29b] which is highly centered on the organic bridge and is stabilized by delocalization along the carbon bridge between the ruthenium centers, indicating moderate electronic communication between the two metal centres through the 1,4-phenylenediethynyl bridges. Interestingly, the neutral dimeric complex containing the same conjugated bridge, $RuCl_2(dppe)_2-C\equiv C-1,4'-C_6H_4-C\equiv C-RuCl_2(dppe)_2$ reported by Dixneuf, showed a smaller difference ($\Delta E=290$ mV) between the oxidation potential of ruthenium-centered redox systems.[30] This phenomenon might be attributed to the admixing of some charge-transfer character of the acetylide to the allenylidene moiety and to the longer conjugated bridge in **8a**.[31] It should be mentioned that the related dirhodium complex $(Ph_2C=C=C=Rh(^iPPr_3)_2-C\equiv C-)_2$ with the same bridge was synthesized by Werner group.[32] However, no electrochemical studies were reported for this complex.

UV-Visible spectra

All the ruthenium and osmium allenylidene complexes, ruthenium alkynyl-allenylidene complexes obtained are deep-colored compounds. Compound **4a** is yellow brown, whereas **4c**, **6a** and **8a** are dark red, deep blue, and deep violet, respectively. Typical UV-Vis absorption spectra are shown in Figure 3 and Figure 4, and the absorption bands of complexes **4a**—**4c**, **6a**, **6b**, **8a**, **8b** are listed in Table 3.

All of these complexes exhibit long-wavelength transitions of strong intensity at about λ_{max} 300—700 nm with high absorbances, which render them red or deep blue. In addition to the intense short-wavelength absorption bands at about λ_{max} 230 nm for transitions involving the dppm, dppe, the metallacycle moiety, the diazafluorene moiety and the carbon-rich bridge (intraligand transitions),[31a,32] the bimetallic complexes **4a**—**4c** show a broad absorption band with a large extinction coefficient at lower energy around λ_{max} 430—450 nm (Figure 4), which are similar in shape to those observed for $M_2{}^{II}(d\pi)\rightarrow\pi^*$(diazafluorene) transition (M_2LCT) in ruthenium complexes coordinated to analogous 4,5-diazafluorene ligands,[34] and the band at λ_{max} 310 — 340 nm attributed to the presence of the $M_1(d\pi)\rightarrow\pi^*$(allenylidene) transition (M_1LCT) involving the allenylidene ligand. As mentioned above, **4b** shows a broad band at λ_{max} 430 nm, which is assigned as the $Ru(d\pi)\rightarrow\pi^*$(diazafluorene) MLCT transition. Moreover, the absorption located at λ_{max} 310 nm is expected to arise from the allowed transition from one of the metal based HOMOs to the allenylidene ligand based LUMO($Os^{II}(d\pi))\rightarrow\pi^*$(allenylidene), MLCT).[31a]

UV-Vis absorption studies were also performed to compare the monometallic system (**6a**, **6b**) with the dimetallic system of ruthenium alkyl-allenylidene complexes (**8a**, **8b**) (Figure 5). Besides the intense short-

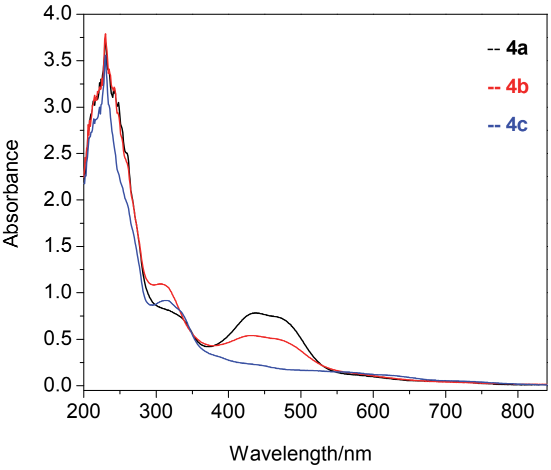


Figure 4 UV-Vis absorption spectra of complexes **4a**—**4c** (5×10^{-5} mol/L) in CH_2Cl_2 at 298 K.

Table 3 UV-vis spectral data for the mono- and binuclear ruthenium and osmium complexes (5.0×10^{-5} mol/L) in methanol at 298 K

Complex	λ_{max}/nm	ε_{max}/(cm^{-1}•mol^{-1}•L)	λ_{max}/nm	ε_{max}/(cm^{-1}•mol^{-1}•L)	λ_{max}/nm	ε_{max}/(cm^{-1}•mol^{-1}•L)
4a	230	74 600	333	14 900	432	15 500
4b	230	75 800	310	21 800	430	10 800
4c	230	71 100	315	18 300	526	3 230
6a	220	51 700	469	6 400	654	8 600
6b	220	>200 000	464	4 660	643	29 400
8a	230	55 600	468	7 970	676	10 900
8b	229	61 200	468	5 140	653	6 880

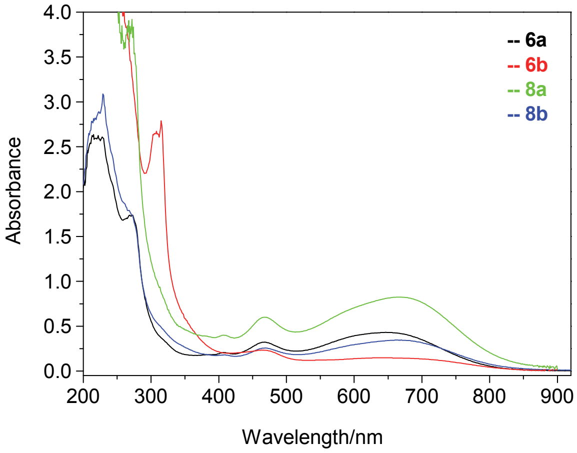


Figure 5 UV-Vis absorption spectra for complexes **6a**, **6b**, **8a**, and **8b** (5×10^{-5} mol/L) in CH_2Cl_2 solution at 298 K: (a) **6a** (black line); (b) **6b** (red line); (c) **8a** (green line); (d) **8b** (blue line).

wavelength absorption band in the ultraviolet region for the n→π^* type transition originating mainly from the dppe ligand, all of these complexes exhibit a broad absorption band extending to the NIR region ($\lambda_{max}>640$ nm), which is regarded to be dominated by the metal-to-ligand charge transfer (MLCT) transition to the allenylidene moiety.[33b,35] Unsurprisingly, **8a** displays an absorption profile similar to that of **6a** yet with higher absorption coefficient due to the seemingly double chromophores. However, because of influence of the variation of the acetylide moiety on the energy of Ru^{II} (dπ), the lowest-energy absorption band of **8a** ($\lambda_{max}=$ 676 nm) is red-shifted compared with that of **6a** ($\lambda_{max}=$ 654 nm). This phenomenon might be attributed to the strong charge transfer effect in **8a**, involving the admixing of some charge-transfer character of the allenylidene to the acetylide moiety and to the conjugated bridge.[31b]

Conclusions

In summary, we have described the synthesis, the spectroscopic, and the voltammetric studies of a series of rigid mono- or dinuclear ruthenium and osmium allenylidene, alkynyl-allenylidene complexes terminated by 4,5-diazafluoren-9-yl or fluoren-9-yl groups. Eletrochemical studies have revealed that these complexes display a quasi-reversible redox behavior and a moderate electronic communication between the two metal centers in **8a**. Moreover, these new structurally rigid complexes show a remarkably broad absorption in the long-wavelength region ($\lambda_{max}=300-700$ nm), which would be excellent candidates for optical materials. Investigations on the NLO properties of these complexes are in progress.

Experimental

Typical procedure for synthesis of dimetallic ruthenium alkynyl allenylidene complexes **8a** and **8b**: In a Schlenk tube, a mixture of *cis*-$RuCl_2(dppe)_2$ (300 mg, 0.312 mmol), 1,4-diethynylbenzene (20 mg, 0.312 mmol), and $NaPF_6$ (150 mg, 0.893 mmol) was stirred in 35 mL CH_2Cl_2 for about 45 h. After filtration the filtrate was concentrated to *ca*. 3 mL and diethyl ether was slowly added to afford 1,4-[*trans*-Cl(dppe)$_2$-Ru=C=CH]$_2$•C_6H_4 (**7a**) as a green powder, which was collected by filtration, washed with diethyl ether (2×10 mL) and dried under vacuum overnight.

To a solution of the complex **7a** (158 mg, 0.0673 mmol) and $NaPF_6$ (45 mg, 0.269 mmol) in CH_2Cl_2 (30 mL) were added dropwise 9-ethynyl-9-fluorenol (28 mg, 0.135 mmol), and triethylamine (28.1 μL, 0.202 mmol) in THF (5 mL). The mixture was stirred for 72 h at room temperature. After filtration and evaporation of solvent a deep violet solid of **8a** (93.8 mg) was obtained in yield of 53%.

The complex **8b** was synthesized in a similar way of **8a**.

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