

Intermetallic communication through a 1,3,5-triethynylbenzene connector

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ABSTRACT

The electrochemical behavior of two series of homo- and heterometallic 1,3,5-triethynylbenzene-based transition metal complexes containing $[(\eta^2\text{-dppf})(\eta^5\text{-C}_5\text{H}_5)\text{Ru}]$, $[(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)\text{Os}]$, $[(^t\text{Bu}_2\text{bpy})\text{-(CO)}_3\text{Re}]$, and $[(\text{bpy})(\text{CO})_3\text{ClRe}]$ (dppf = 1,1'-bis(diphenylphosphino)ferrocene; ^tBu₂bpy = 4,4'-di-*tert*-butyl-2,2'-bipyridyl; bpy = 2,2'-bipyridyl-5-yl) building blocks have been studied, showing that there is electronic interaction between the appropriate metal atoms. The electronic absorption spectra reveal high energy bands corresponding to intraligand $\pi \rightarrow \pi^*$ transitions (bpy, alkynyl) and low energy absorptions which are attributed to MLCT transitions; replacement of ruthenium by osmium results in a blue-shift of the MLCT bands. The associated radical cations of three complexes were in situ generated by chemical oxidation and characterized by continuous wave electron paramagnetic resonance (EPR) investigations in X-band performed at low temperatures.

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1. Introduction

Organometallic compounds in which different early and late transition metal atoms are connected by carbon-rich π -conjugated organic bridging units are of increasing interest due to, for example, their reversible redox chemistry, luminescence, and nonlinear optical properties [1–3]. One possibility to connect metal fragments is given by using 1,3,5-triethynylbenzene as core because this building block is of interest due to its geometry and active-coordination sites [4]. This unit allows to incorporate different transition metal fragments around the periphery of the organic benzene ligand, in order to study the ability of the metals to participate in π -delocalization or the ability for interaction of the metal d-orbitals with the conjugated π -orbitals of the organic central entity.

In this report we describe the use of 1,3,5-triethynylbenzene as bridging ligand for different transition metal building blocks including $[(\eta^2\text{-dppf})(\eta^5\text{-C}_5\text{H}_5)\text{Ru}]$, $[(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)\text{Os}]$, $[(^t\text{Bu}_2\text{bpy})\text{-(CO)}_3\text{Re}]$, and $[(\text{bpy})(\text{CO})_3\text{ClRe}]$, respectively, (dppf = 1,1'-bis(diphenyl-phosphino)ferrocene; ^tBu₂bpy = 4,4'-di-*tert*-butyl-2,2'-bipyridyl; bpy = 2,2'-bipyridyl-5-yl) [5]. The electrochemical behavior and spectroscopic characterization of these heterometallic complexes to investigate electronic communication between the metal centers is discussed.

2. Results and discussion

2.1. Cyclic voltammetry

The structural formula of the investigated 1,3,5-triethynylbenzene-based transition metal complexes with the molecule numbering are shown in Fig. 1.

The cyclic voltammogram of **1** is displayed in Fig. 2. For a better comparison with previously published data compound **1** was measured once again in dichloromethane taking the potential of the ferrocene–ferrocenium couple as the reference [4].

Molecule **1** shows an irreversible oxidation wave at $E_{p,ox} = 0.665$ V and a quasi-reversible reduction couple at $E_0 = -2.070$ V ($\Delta E_p = 0.18$ V) (Fig. 2, Table 1).

The introduction of one terminal $[(\eta^2\text{-dppf})(\eta^5\text{-C}_5\text{H}_5)\text{Ru}]$ unit, as given in **2** (Fig. 3, top), does slightly influence the potential of the $[\text{Re(I)}]/[\text{Re(II)}]$ oxidation (Fig. 3, Table 1). The $[\text{Ru(II)}]/[\text{Ru(III)}]$ oxidation in the ruthenium σ -acetylide complex **2** is found at $E_0 = -0.015$ V with $\Delta E_p = 0.10$ V, whereas the oxidation of iron(II) occurs at $E_0 = 0.530$ V ($\Delta E_p = 0.12$ V). While the free dppf ligand reveals a reversible oxidation wave at $E_0 = 0.190$ V, its $[\text{Fe(II)}]/[\text{Fe(III)}]$ oxidation is positive shifted to 0.490 V in $[(\eta^5\text{-C}_5\text{H}_5)(\text{dppf})\text{RuCl}]$ in which the oxidation of $[\text{Ru(II)}]$ to $[\text{Ru(III)}]$ takes place at 0.077 V [8]. Compared to that, the redox potentials of $[\text{Ru(II)}]$ and $[\text{Fe(II)}]$ in **2** show small cathodic and anodic shifts, respectively. The additionally observed oxidation processes in complex **2** may originate from further oxidation at the ruthenium center, which can be verified by

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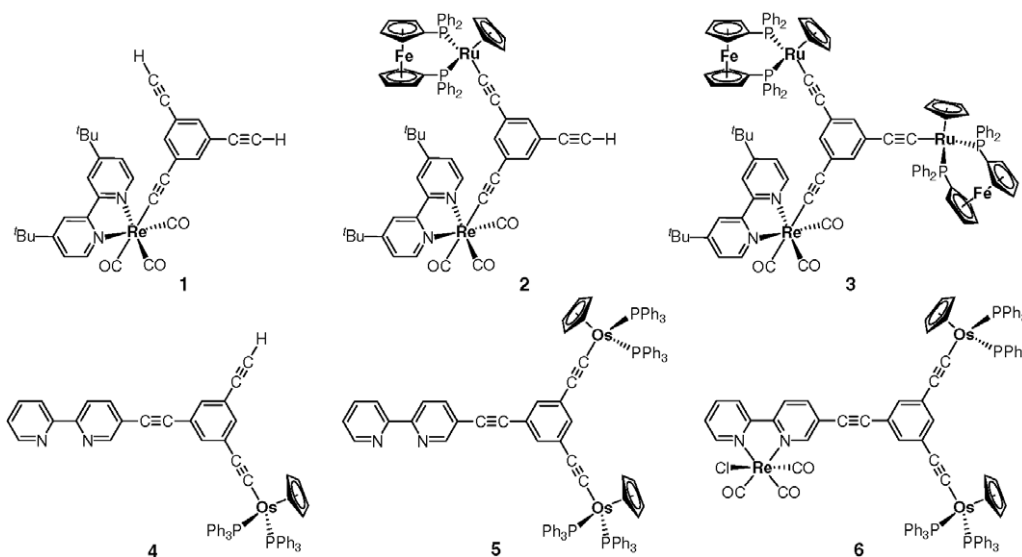


Fig. 1. Structural formula of the heterometallic compounds 1–6 containing the 1,3,5-triethynylbenzene core as the bridging unit [5].

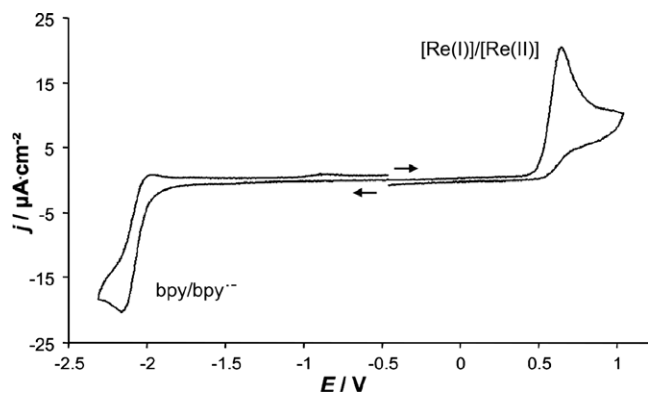


Fig. 2. Cyclic voltammogram of a platinum electrode in a solution of dichloromethane, 0.1 M $[\text{tBu}_4\text{N}]\text{PF}_6$ and 1.0 mmol of **1**, $dE/dt = 0.10 \text{ V s}^{-1}$, argon saturated solution [6,7].

Table 1

Data from cyclic voltammograms (all values in V vs. E_0 of the ferrocene/ferrocenium redox couple [6,7], $dE/dt = 0.10 \text{ V s}^{-1}$)

Compound	bpy/bpy ⁻ (ΔE_p)	E_0	[Ru(II)]/ [Ru(III)] (ΔE_p)	E_0	[Fe(II)]/ [Fe(III)] (ΔE_p)	E_0	[Re(I)]/ [Re(II)] (ΔE_p) ^a	$E_{p,ox}/E_0$ (ΔE_p) ^a
1	-2.070 (0.18)						0.665	
2	-2.080 (0.13)		-0.015 (0.10)		0.530 (0.12)		0.730	0.495 0.895 (0.115)
3	-2.110 (0.175)		-0.130 (0.105) 0.065 (0.13)		0.505 (0.12)		0.695	0.475 0.935

^a Irreversible or quasi-reversible redox processes that may result from oxidation of the ruthenium center [8,9].

comparison to other complexes containing $[(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)\text{Ru}]$ or $[(\eta^2\text{-dppf})(\eta^5\text{-C}_5\text{H}_5)\text{Ru}]$ termini [8,9].

The introduction of a second $[(\eta^2\text{-dppf})(\eta^5\text{-C}_5\text{H}_5)\text{Ru}]$ unit as given in 1- $[(\text{tBu}_2\text{bpy})(\text{CO})_3\text{Re-C}\equiv\text{C}]-3,5-[(\eta^2\text{-dppf})(\eta^5\text{-C}_5\text{H}_5)\text{Ru-C}\equiv\text{C}]_2\text{C}_6\text{H}_3$ (**3**) leads to two clearly separated reversible oxidations at $E_0 = -0.130 \text{ V}$ ($\Delta E_p = 0.105 \text{ V}$) and $E_0 = 0.065 \text{ V}$ ($\Delta E_p = 0.13 \text{ V}$), respectively, which are ascribable to the step-wise one-electron oxidation of $[\text{Ru}_2(\text{II},\text{II})]$ into $[\text{Ru}_2(\text{II},\text{III})]$ and $[\text{Ru}_2(\text{III},\text{III})]$ systems

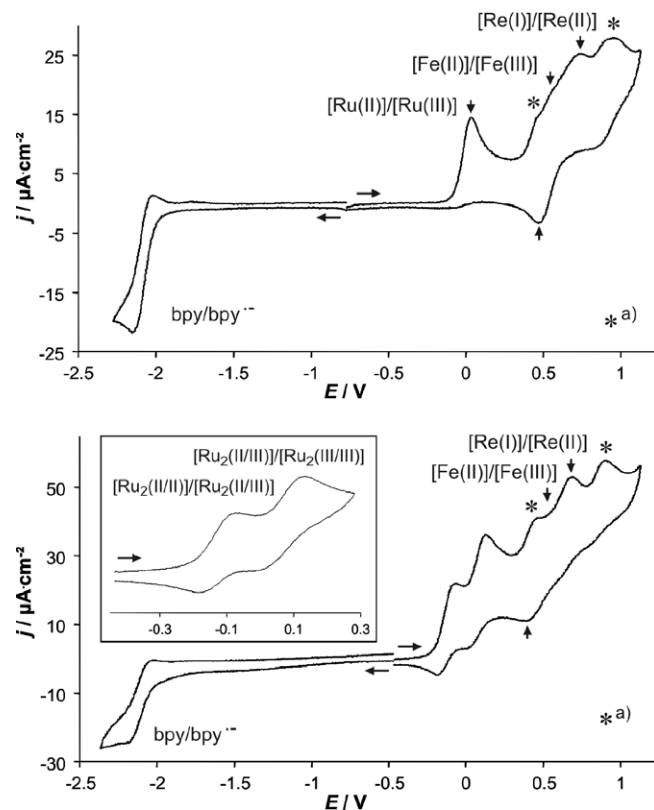


Fig. 3. Cyclic voltammograms of a platinum electrode in a solution of dichloromethane, 0.1 M $[\text{tBu}_4\text{N}]\text{PF}_6$ and 1.0 mmol of **2** (top) or **3** (bottom), $dE/dt = 0.10 \text{ V s}^{-1}$, argon saturated solution [6,7]. (a) Irreversible or quasi-reversible redox processes that may result from oxidation of the ruthenium center [8,9].

as shown in Fig. 3 (bottom). The potential separation between the two oxidation processes ($\Delta E_0 = 0.195 \text{ V}$) allows a K_c of 2×10^3 to be calculated, which confirms that the mixed valence $[\text{Ru}_2(\text{II},\text{III})]$ monocation belongs to the slightly delocalized Robin-Day's Class II. The comproportionation constant is similar to that found in 1,3,5-triethynylbenzene-based 1,3- $[(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)\text{Ru-C}\equiv\text{C}]_2\text{-5-(HC}\equiv\text{C)}\text{C}_6\text{H}_3$ ($K_c = 2.4 \times 10^3$) [4n].

Table 2

Data from cyclic voltammograms (all values in V vs. E_0 of the ferrocene/ferrocenium redox couple [6,7], $dE/dt = 0.10 \text{ V s}^{-1}$)

Compound	bpy/bpy ⁻ E_0 (ΔE_p)	[Os(II)]/[Os(III)] E_0 (ΔE_p)	[Re(I)]/[Re(II)] $E_{p,ox}$	$E_{p,ox}/E_0$ (ΔE_p)
(Ph ₃ P) ₂ (η^5 -C ₅ H ₅)OsBr		0.00 (0.12)		0.945 (0.135)
4		-0.065 (0.09)		1.180 (0.16)
				0.805 (0.195)
				1.095 (0.13)
5		-0.175 (0.10)		0.915
		-0.015 (0.11)		1.250
6	-1.685 (0.12)	-0.155 (0.085)	0.565	0.950
		-0.010 (0.095)		1.225

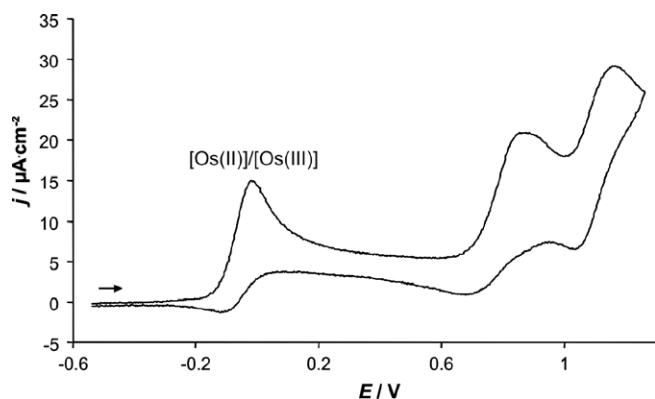


Fig. 4. Cyclic voltammogram of a platinum electrode in a solution of dichloromethane, 0.1 M [Bu₄N]PF₆ and 1.0 mmol of **4**, $dE/dt = 0.10 \text{ V s}^{-1}$, argon saturated solution [6,7].

As it can be seen from Fig. 3 (bottom), the oxidation wave of the dpfp-Fe(II) center is somewhat covered by the oxidation at 0.475 V. In contrast, the corresponding reduction wave occurs at 0.445 V; by using the ΔE_p value of complex **2** an $E_0 = 0.505 \text{ V}$ is calculated.

For the [(^tBu₂bpy)Re(CO)₃] moiety an oxidation peak appears at $E_{p,ox} = 0.695 \text{ V}$ which is similar to that found for complex **2**. The additionally observed irreversible oxidation processes at $E_{p,ox} = 0.475$ and 0.935 V are comparable to **2** and may originate from oxidation at the ruthenium centers as typical for ruthenium complexes containing, for example, [(Ph₃P)₂(η^5 -C₅H₅)Ru] and [(η^2 -dppf)(η^5 -C₅H₅)Ru] termini, respectively [8,9].

Another series of mono- to trinuclear complexes based on the 1,3,5-triethynylbenzene core are **4–6** (Fig. 1, Table 2). The cyclic voltammogram of **4** with one [(Ph₃P)₂(η^5 -C₅H₅)Os] entity displays for the [Os(II)]/[Os(III)] oxidation process in dichloromethane solution a wave at $E_0 = -0.065 \text{ V}$ ($\Delta E_p = 0.09 \text{ V}$) (Fig. 4) which is characteristic for osmium(II) organometallic complex fragments [10]. Measuring into more positive region the cyclic voltammogram reveals two quasi-reversible peaks at $E_0 = 0.805 \text{ V}$ ($\Delta E_p = 0.195 \text{ V}$) and $E_0 = 1.095 \text{ V}$ ($\Delta E_p = 0.13 \text{ V}$), respectively, which most likely are associated to [Os(III)]/[Os(IV)] and [Os(IV)]/[Os(V)] oxidations since these redox processes are also observed in the precursor molecule [(Ph₃P)₂(η^5 -C₅H₅)OsBr] (Table 2). However, the expected reduction of the bipyridyl group [11] is not observed in the electrochemical window of dichloromethane.

Fig. 5 (top) illustrates the cyclic voltammetric response given by the diosmium complex 1,3-[(Ph₃P)₂(η^5 -C₅H₅)Os-C≡C]₂-5-[bpy-C≡C]₂C₆H₃ (**5**) in dichloromethane solution. The two osmium(II) units result in two separated one-electron oxidation processes and therefore due interact with each other. The comproportionation constant K_c for **5** is with 510 smaller than that found for polynuclear 1-[Fc-C≡C]-3,5-[(dppm)₂(Cl)Os-C≡C]₂C₆H₃ [**4m**]. As in **4**

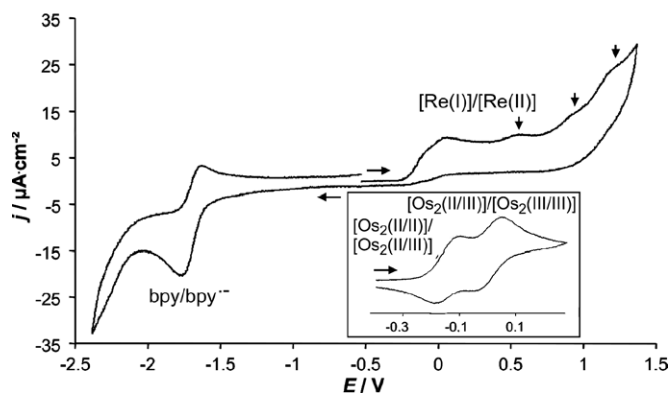
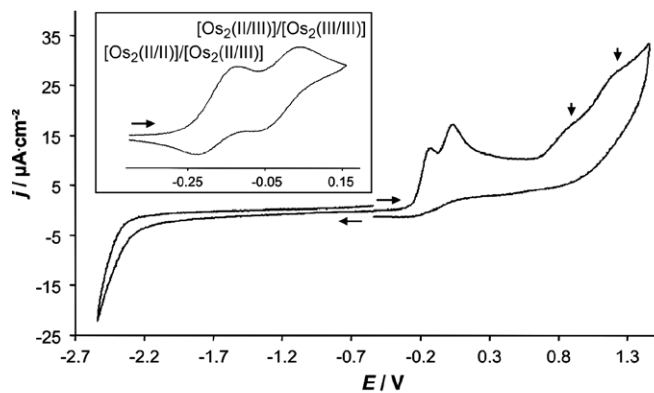


Fig. 5. Cyclic voltammograms of a platinum electrode in a solution of dichloromethane, 0.1 M [Bu₄N]PF₆ and 1.0 mmol of **5** (top) or **6** (bottom), $dE/dt = 0.10 \text{ V s}^{-1}$, argon saturated solution [6,7].

Table 3

Electronic absorption data for **1–6** in CH₂Cl₂ at 298 K

Compound	Absorption λ/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)
1	290 (42 000), 326 (17 200), 395 (4400)
2	286 (55 500), 323 (36 000), 410 (5100)
3	297 (82 600), 316 (73 000, sh), 406 (6900)
4	319 (53 300), 339 (41 000, sh)
5	303, (75 000), 328 (67 000), 345 (50 000)
6	345 (48 100), 380 (35 100)

two oxidation peaks are found at 0.915 V and 1.250 V somewhat shifted to higher potentials.

As Fig. 5 (bottom) shows, the trimetallic ReOs₂ complex affords a similar cyclic voltammetric response concerning the [Os(II)]/[Os(III)] redox couples (Table 2) which are not significantly influenced by the introduction of a [Re(CO)₃Cl] moiety at the 2,2'-bipyridyl group. However, compared to **5** the comproportionation constant ($K_c = 285$) somewhat decreases upon introduction of the [Re(CO)₃Cl] building block (Table 2).

In addition to these two reversible one-electron oxidations, a irreversible oxidation which can be assigned to the change of [Re(I)] to [Re(II)] at $E_{p,ox} = 0.565 \text{ V}$ is found (Fig. 5, bottom). At 0.950 and 1.225 V, respectively, the further oxidation of the osmium centers takes place comparable to **5** (vide supra). In the anodic region a reversible reduction is observed at $E_0 = -1.685 \text{ V}$ ($\Delta E_p = 0.12 \text{ V}$) for the bpy/bpy⁻ couple, which differs from **4** and **5**. The appearance of this wave is explainable by the formation of a [(bpy)Re(CO)₃Cl] building block resulting in a more electron-deficient diimine ligand. This makes this moiety easier to reduce, which is typical for this type of molecules [12].

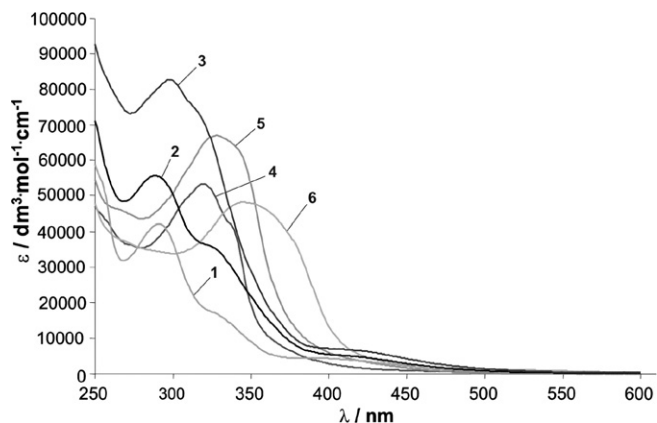


Fig. 6. UV-Vis spectra of the complexes **1–6** in dichloromethane at 298 K.

Summarizing, one can say that in accordance with previous findings the two-dimensional 1,3,5-triethynylbenzene organic unit acts as a connector between the organometallic building blocks to mediate significant electronic interactions from one metal to the other [4b,4m,4n]. The wave separations are not as large as that determined for comparable 1,4-diethynylbenzene derivatives [1a,1b,1d,1e,3c,13], but nevertheless, it constitutes a significant interaction between the two ruthenium or osmium centres, respectively, as evidenced by these observations. Despite the 1,3,5-substitution of the phenyl ring, which excludes a delocalization occurring through the participation of a quinoidal resonance structure, one can suppose that there is a continuous overlap between the d-orbitals of the metal centers and the π -orbitals of the polyethynylbenzene ligands.

2.2. UV-Vis-spectroscopy

The electronic absorption spectra of complexes **1–6** were run in dichloromethane at 298 K (Table 3 and Fig. 6). All these compounds display intense bands in the UV-Vis range. The spectrum of the mononuclear complex **1** shows two high energy bands (290, 326 nm) and one low energy band (395 nm). The high energy bands correspond to intraligand $\pi \rightarrow \pi^*$ transitions and can also be observed in the free bpy and alkynyl ligands [2d]. The band observed on the low energy side of the spectrum can be mainly attributed to metal-to-ligand charge transfer with residual ligand-to-ligand character. Introduction of one or two ruthenium atoms (compounds **2** and **3**) produces a very small red shift (ca. 10 nm) of this band and an increase of its intensity. For the rhenium containing compounds **1–3** the low energy bands can tentatively be assigned to $d\pi(\text{Re}) \rightarrow \pi^*(\text{C}\equiv\text{C})$ transitions with a weak $d\pi(\text{Ru}) \rightarrow \pi^*(\text{C}\equiv\text{C})$ character in the case of **2** and **3**. Analysis of the spectra of the osmium complexes **4** and **5** shows dominant intraligand charge transfer.

Substitution of ruthenium by osmium building blocks should probably be associated with a weaker overlap between the π -orbitals of the alkynyl ligand and the d-orbitals of the metal center as recently reported [14]. Consequently, the MLCT transition observed in the spectrum of **6** should be blue-shifted with respect to the MLCT transition present in the spectrum of **3**. In this respect, the intense shoulder observed at 380 nm which is specific of the complex **6**, probably originates from an admixture of the $d\pi(\text{Os}) \rightarrow \pi^*(\text{C}\equiv\text{C})$ and $d\pi(\text{Re}) \rightarrow \pi^*(\text{C}\equiv\text{C})$ transitions.

2.3. EPR-spectroscopy

Complexes **2**, **3** and **6** were reacted with a large excess of silver triflate (4–5 equiv.) at -60°C in tetrahydrofuran and EPR spectra

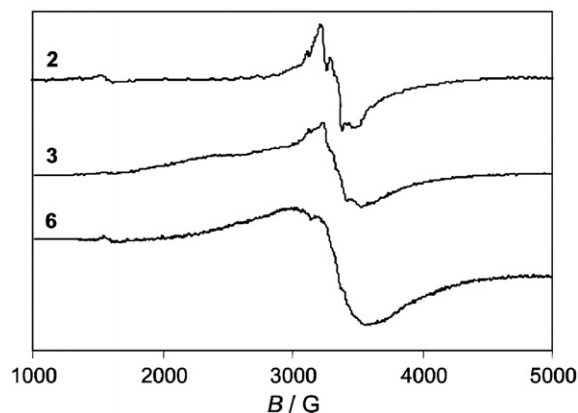


Fig. 7. EPR spectra of the oxidized complexes **2**, **3** and **6** in tetrahydrofuran at 77 K.

were run at 77 K with the resulting solutions. The spectrum obtained for **2** displays a complex pattern in accord with the oxidation of the three metal groups ([Re(II)], [Ru(III)], [Fe(III)]) (Fig. 7).

The complex feature centered at $g = 2.065$ is in accord with the presence of the [Ru(III)] and [Fe(III)] and [Re(II)] centers. The characteristic signature of the ferrocenium center is observed at $g = 4.266$ and corresponds to the parallel component of the g tensor. Moreover, in the low-field component, one can clearly observe a part of the sextet which results from the hyperfine coupling of an unpaired electron with the nuclear spin of rhenium ($I, {}^{185,187}\text{Re} = 5/2$, $a_{\text{Re}} = 124 \text{ G}$) probing the presence of the [Re(II)] center. The spectrum of **3** shows a similar pattern with two features centered at 2.011 and 4.265, respectively, but the line broadening did not allow the observation of the hyperfine coupling with rhenium. The presence of the oxidized dppe unit precludes the observation of the forbidden $\Delta M_s = \pm 2$ transition characteristic of the triplet state. Indeed, this so-called half field transition, if present, overlaps with the intense low-field signature of ferrocenium so that no conclusion can be drawn [15]. More conclusive is the spectrum obtained for **6** which displays two features centered at $g = 2.105$ and 4.289, respectively. The latter signal can conclusively be regarded as the signature of the triplet state indicating that two spin carriers are magnetically coupled. The $\Delta M_s = \pm 3$ transition corresponding to the quartet state can never be observed suggesting that the rhenium center does not magnetically interact with the two equivalent osmium centers. A similar finding was previously observed in a closely related system, where two or three $[(\eta^5\text{-C}_5\text{Me}_5)(\eta^2\text{-dppe})\text{Fe(III)-C}\equiv\text{C}]^+$ units are linked to a connecting arene in *meta* positions [4b]. According to the Ovchinnikov rule, a ferromagnetic metal-metal exchange takes place [16].

3. Conclusion

In summary, we have reported on the electrochemical, electron paramagnetic resonance and UV-Vis spectroscopic properties of two new series of homo- and heterometallic transition metal complexes in which different organometallic building blocks such as $[(\eta^2\text{-dppe})(\eta^5\text{-C}_5\text{H}_5)\text{Ru}]$, $[(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)\text{Os}]$, $[(\text{Bu}_2\text{bpy})(\text{CO})_3\text{Re}]$, and $[(\text{bpy})(\text{CO})_3\text{ClRe}]$ are connected by the conjugated organic spacer 1,3,5-triethynylbenzene. In accordance with previous findings, this two-dimensional organic unit acts as a connector between the organometallic building blocks to mediate significant electronic interactions between the two ruthenium or osmium centres, respectively, as evidenced by cyclic voltammetry. Furthermore, it could be demonstrated by UV-Vis-spectroscopy that also Re/Ru and Re/Os interactions occur across the bonding of the connector. The observation of the triplet state of $[\mathbf{6}]^{2+}$ or $[\mathbf{6}]^{3+}$ by EPR

spectroscopy clearly establishes that magnetic coupling takes place between the Os centres.

4. Experimental

Compounds **1–6** (see Fig. 1) were prepared as described elsewhere under an atmosphere of purified nitrogen using standard Schlenk techniques [5].

Cyclic voltammograms were recorded with $dE/dt = 0.10 \text{ V s}^{-1}$ in a glass cell (Radiometer) equipped with a platinum wire electrode (WE), a platinum wire counter electrode (CE) and a saturated calomel electrode (SCE) with dichloromethane as solvent serving as a reference electrode (RE). A potentiostat Voltalab PGZ 100 (Radiometer) was used. For ease of comparison with previously published data electrode potentials are converted taking the rest potential of the ferrocene–ferrocenium couple as the reference [6,7]. This was also desirable because the RE employed showed some drift as is frequently encountered with this type of electrode when filled with organic solvent based electrolyte solutions [17]. Electrolyte solutions were prepared from dichloromethane (dried and freshly distilled from calcium hydride) and $[\text{Bu}_4\text{N}]\text{PF}_6$ (0.1 M, Fluka). The respective organometallic complexes were added at $c = 1 \text{ mM}$. All experiments were performed at 25°C under an inert argon atmosphere. UV–Vis spectra were obtained on a Cary 5 spectrometer. The EPR spectra were recorded on frozen tetrahydrofuran solutions at 77 K with a Bruker EMX-8/2.7 (X-band) spectrometer. Tetrahydrofuran solutions of the diamagnetic neutral complexes ($5 \times 10^{-3} \text{ M}$) were reacted with a large excess of silver triflate (4–5 equiv.) at -60°C . After 15 min of stirring, the solutions were transferred at this temperature in quartz EPR tubes and were immediately frozen with liquid nitrogen and EPR spectra were run at 77 K.

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References

- [1] (a) N. Chawdhury, N.J. Long, M.F. Mahon, L. Ooi, P.R. Raithby, S. Rooke, A.J.P. White, D.J. Williams, M. Younus, *J. Organomet. Chem.* 689 (2004) 840; (b) F. de Montigny, G. Argouarch, K. Costuas, J.F. Halet, T. Roisnel, L. Toupet, C. Lapinte, *Organometallics* 24 (2005) 4558; (c) M. Younus, N.J. Long, P.R. Raithby, J. Lewis, *J. Organomet. Chem.* 570 (1998) 55; (d) O. Lavastre, J. Plass, P. Bachmann, S. Guesmi, C. Moinet, P.H. Dixneuf, *Organometallics* 16 (1997) 184; (e) S.I. Ghazala, F. Paul, L. Toupet, T. Roisnel, P. Hapiot, C. Lapinte, *J. Am. Chem. Soc.* 128 (2006) 2463; (f) T. Weyland, C. Lapinte, G. Frapper, M.J. Calhorda, J.F. Halet, L. Toupet, *Organometallics* 16 (1997) 2024.
- [2] (a) N.J. Long, C.K. Williams, *Angew. Chem., Int. Ed.* 42 (2003) 2586; (b) V.W.W. Yam, K.K.W. Lo, K.M.C. Wong, *J. Organomet. Chem.* 578 (1999) 3; (c) S.C.F. Lam, V.W.W. Yam, K.M.C. Wong, E.C.C. Cheng, *N. Zh. Organomet.* 24 (2005) 4298; (d) K.M.C. Wong, S.C.F. Lam, C.C. Ko, N. Zhu, V.W.W. Yam, S. Roué, C. Lapinte, S. Fathallah, K. Costuas, S. Kahlal, J.F. Halet, *Inorg. Chem.* 42 (2003) 7086.
- [3] (a) C.E. Powell, M.G. Humphrey, *Coord. Chem. Rev.* 248 (2004) 725; (b) M.P. Cifuentes, M.G. Humphrey, *J. Organomet. Chem.* 689 (2004) 3968;
- [4] (c) S.K. Hurst, M.P. Cifuentes, A.M. McDonagh, M.G. Humphrey, M. Samoc, B. Luther-Davies, I. Asselberghs, A. Persoons, *J. Organomet. Chem.* 642 (2002) 259; (d) T. Weyland, I. Ledoux, S. Brasselet, J. Zyss, C. Lapinte, *Organometallics* 19 (2000) 5235.
- [5] (a) H. Fink, N.J. Long, A.J. Martin, G. Opromolla, A.J.P. White, D.J. Williams, P. Zanello, *Organometallics* 16 (1997) 2646; (b) T. Weyland, K. Costuas, A. Mari, J.F. Halet, C. Lapinte, *Organometallics* 17 (1998) 5569; (c) R.R. Tykwinski, P.J. Stang, *Organometallics* 13 (1994) 3203; (d) T.J.J. Müller, H.J. Lindner, *Chem. Ber.* 129 (1996) 607; (e) M.J. Irwin, L. Manojlovic-Muir, K.W. Muir, R.J. Puddephatt, D.S. Yufit, *Chem. Commun.* (1997) 219; (f) S. Leininger, P.J. Stang, S. Huang, *Organometallics* 17 (1998) 3981; (g) M.P. Cifuentes, C.E. Powell, J.P. Morrall, A.M. McDonagh, N.T. Lucas, M.G. Humphrey, M. Samoc, S. Houbrechts, I. Asselberghs, K. Clays, A. Persoons, T. Isoshima, *J. Am. Chem. Soc.* 128 (2006) 10819; (h) M. Samoc, J.P. Morrall, G.T. Dalton, M.P. Cifuentes, M.G. Humphrey, *Angew. Chem., Int. Ed.* 46 (2007) 731; (i) C.E. Powell, J.P. Morrall, S.A. Ward, M.P. Cifuentes, E.G.A. Notaras, M. Samoc, M.G. Humphrey, *J. Am. Chem. Soc.* 126 (2004) 12234; (j) A.M. McDonagh, C.E. Powell, J.P. Morrall, M.P. Cifuentes, M.G. Humphrey, *Organometallics* 22 (2003) 1402; (k) J. Vicente, M.T. Chicote, M.M. Alvarez-Falcon, *Organometallics* 24 (2005) 2764; (l) S.H.F. Chong, S.C.F. Lam, V.W.W. Yam, N. Zhu, K.K. Cheung, S. Fathallah, K. Costuas, J.F. Halet, *Organometallics* 23 (2004) 4924; (m) N.J. Long, A.J. Martin, A.J.P. White, D.J. Williams, M. Fontani, F. Laschi, P. Zanello, *J. Chem. Soc., Dalton Trans.* (2000) 3387; (n) N.J. Long, A.J. Martin, F.F. De Biani, P. Zanello, *J. Chem. Soc., Dalton Trans.* (1998) 2017; (o) C.E. Powell, M.P. Cifuentes, M.G. Humphrey, A.C. Willis, J.P. Morrall, M. Samoc, *Polyhedron* 26 (2007) 284.
- [6] R. Packheiser, P. Ecorchard, T. Rüffer, H. Lang, *Organometallics*, in press.
- [7] Ferrocene/ferrocenium redox couple: G. Gritzner, J. Kuta, *Pure Appl. Chem.* 56 (1984) 461.
- [8] A conversion of given electrode potentials to the standard normal hydrogen electrode is possible: H. Strehlow, W. Knoche, H. Schneider, *Ber. Bunsen. Phys. Chem.* 77 (1973) 760.
- [9] L.-B. Gao, L.-Y. Zhang, L.-X. Shi, Z.-N. Chen, *Organometallics* 24 (2005) 1678.
- [10] (a) M.I. Bruce, P.J. Low, K. Costuas, J.-F. Halet, S.P. Best, G.A. Heath, *J. Am. Chem. Soc.* 122 (2000) 1949; (b) M.I. Bruce, B.C. Hall, B.D. Kelly, P.J. Low, B.W. Skelton, A.H. White, *J. Chem. Soc., Dalton Trans.* (1999) 3719; (c) M.I. Bruce, B.G. Ellis, P.J. Low, B.W. Skelton, A.H. White, *Organometallics* 22 (2003) 3184.
- [11] (a) M.I. Bruce, P.J. Low, F. Hartl, P.A. Humphrey, F. de Montigny, M. Jevric, C. Lapinte, G.J. Perkins, R.L. Roberts, B.W. Skelton, A.H. White, *Organometallics* 24 (2005) 5241; (b) G.J. Perkins, M.I. Bruce, B.W. Skelton, A.H. White, *Inorg. Chim. Acta* 359 (2006) 2644; (c) C.E. Powell, M.P. Cifuentes, A.M. McDonagh, S.K. Hurst, N.T. Lucas, C.D. Delfs, R. Stranger, M.G. Humphrey, S. Houbrechts, I. Asselberghs, A. Persoons, D.C.R. Hockless, *Inorg. Chim. Acta* 352 (2003) 9.
- [12] S. Vatsadze, M. Al-Anber, W.R. Thiel, H. Lang, R. Holze, *J. Solid State Electrochem.* 9 (2005) 764.
- [13] (a) P.A. Anderson, F.R. Keene, E. Horn, E.R.T. Tiekink, *Appl. Organomet. Chem.* 4 (1990) 523; (b) P. Kurz, B. Probst, B. Springler, R. Alberto, *Eur. J. Inorg. Chem.* (2006) 2966; (c) W. Kaim, H.E.A. Kramer, C. Vogler, J. Rieker, *J. Organomet. Chem.* 367 (1989) 107; (d) K. Kalyanasundaram, *J. Chem. Soc., Faraday Trans.* 82 (1986) 2401.
- [14] (a) A. Klein, O. Lavastre, J. Fiedler, *Organometallics* 25 (2006) 635; (b) M.C.B. Colbert, J. Lewis, N.J. Long, P.R. Raithby, M. Younus, A.J.P. White, D.J. Williams, N.N. Payne, L. Yellowlees, D. Beljonne, N. Chawdhury, R.H. Friend, *Organometallics* 17 (1998) 3034.
- [15] M.I. Bruce, K. Costuas, T. Davin, J.-F. Halet, K.A. Kramarczuk, P.J. Low, B.K. Nicholson, J.P. Gary, R.L. Roberts, B.W. Skelton, M.E. Smith, A.H. White, *Dalton Trans.* (2007) 5387.
- [16] R. Packheiser, P. Ecorchard, T. Rüffer, M. Lohan, B. Bräuer, F. Justaud, C. Lapinte, H. Lang, *Organometallics*, in press.
- [17] A. Ovchinnikov, *Theor. Chim. Acta* 47 (1978) 297.
- [18] D.J.G. Ives, G.J. Janz, *Reference Electrodes*, Academic Press, New York, 1961.