Electronic communication in "chain-like" trimetallic ruthenium complexes with two C_7 carbon-rich conjugated bridges†

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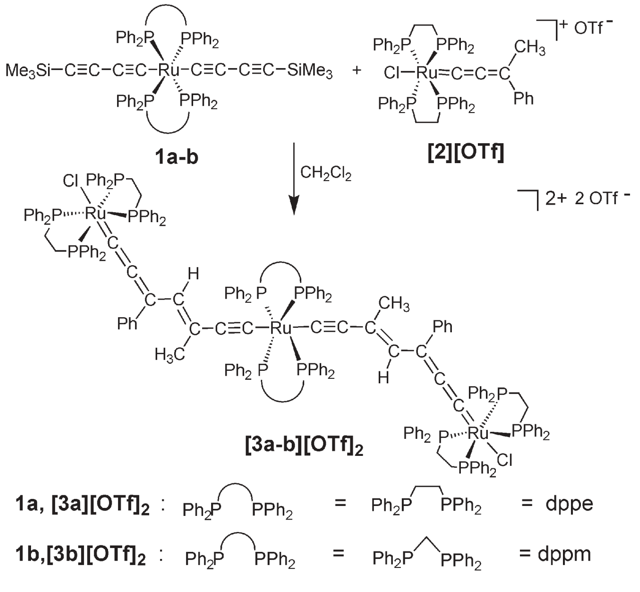
This paper describes the synthesis and properties of the first homotrinuclear metal complexes with large carbon-rich ligands that provide unique extended conduits for electron mobility.

Electron transfer studies are of considerable significance for the understanding of biological and physical processes.[1] Coordination complexes in which a bridging ligand allows intramolecular interaction between two remote redox-active metal center states are particularly well suited models for investigations under carefully controlled conditions.[1,2] Intriguingly, full exploration of higher nuclearity *linear* assemblies offering multiple redox and spin states remains scarce, despite their high suitability for the challenging development of "molecular wires" in which electrons can be transported over nanometric distances.[3] If some remote metal–metal interactions in trimetallic assemblies with phenantrolynopyrazine,[4] pyrazine,[5] cyanide[6] ligands or ferrocenes[7] have been addressed, longer bridging systems giving rise to strong coupling are still needed to engender electronic delocalization over long length scale, and ultimately to find application in devices.

Several transition metal systems with carbon-rich ligands have shown excellent abilities to complete a strong electronic interaction between two remote metals,[2,3,8] and the exceptional ability of ruthenium to operate as a connector allowing electron flow to occur between different elements in carbon-rich systems have been also demonstrated.[9] These observations provide the validation of the proposal to realize oligomeric molecular wires of precisely controlled lengths with more than two metal centers using the $Ru(dppe)_2$ fragment, in order to answer to the interesting question of whether large size carbon-rich spacers can facilitate electron delocalization over more than two metal centers of a unique type. Herein, we report (i) the synthesis of the first highly conjugated complexes displaying three similar metal centers spanned by two odd-numbered C_7 π-conjugated chains and showing well separated redox processes, and (ii) the initial studies of different oxidation states that evidence a remarkable behavior involving the metal centers and the non innocent carbon-rich ligands as parts of the redox system and that point out electronic communication in these 24 Å long molecular wires.

In the light of our earlier study of electron transfer across original C_7 carbon-rich bridges, the synthesis of the trimetallic species **[3a–b][OTf]**$_2$ were attempted from a *trans* bis-diyne complex **1a–b** with two different diphosphine ligands, and from two equivalents of the metal allenylidene **2** (Scheme 1).[8] The two triruthenium complexes **[3a–b][OTf]**$_2$ were obtained in 52 and 57% yield, respectively, as blue–green solids (ESI). As characteristic features, ^{31}P NMR analysis of complex **[3a][OTf]**$_2$ shows one singlet for the four equivalent phosphorus atoms of the central metal unit in *trans* arrangement, and another singlet for those of the two remote metallic centers. For both complexes, ^{13}C NMR spectra display one set of seven different signals for the seven carbon atoms of the two symmetrical chains. It is worth to note that one type of C_α resonance (δ 260.6 ppm for **[3a][OTf]**$_2$) presents a higher allenylidene character than the two different carbenic carbons of the analogous bimetallic C_7 complex,[8] displaying resonances at 230.2 and 224.0 ppm. The other carbenic carbon atoms present a lower resonance at 193.0 ppm, and both observed signals are still downfield compared to that of **1a** (δ 131.8 ppm) and upfield to that of **[2][OTf]** (δ 310.6 ppm). These observations evidence a strong conjugation along the two carbon chains, but with a higher weight for the mesomeric form displayed on Scheme 1. These results are also in line with FTIR analysis. Indeed spectra of **[3a–b][OTf]**$_2$ present an intense absorption around $\nu = 1880\ cm^{-1}$ characteristic of cumulenic stretches, and a weak absorption around $\nu = 1990\ cm^{-1}$ for an acetylide contribution. For both complexes, UV-visible spectra recorded from deep blue–green solutions in CH_2Cl_2 show a strong broad absorption



Scheme 1 Synthesis of the trimetallic complexes **[3a–b][OTf]**$_2$.

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($\lambda_{\max}$ = 802 nm, ε = 147 000 mol^{-1} L cm^{-1} for **[3a][OTf]**$_2$). This band can be attributed to a first approximation to metal-to-ligand charge transfer (MLCT) transitions. The presence of the third metallic center has the effect of increasing the absorptivity and shifting the transition to lower energy relative to the bimetallic congener which is indicative of a longer conjugated path.

The redox properties of **[3a–b][OTf]**$_2$ were investigated by means of cyclic voltammetry. Both complexes undergo two reversible one-electron reduction and three one-electron oxidation processes (Table 1). The second oxidation wave is partially reversible for **[3b][OTf]**$_2$, and the third one is irreversible for both complexes. Peak separations and comproportionation constants (K_c = exp($\Delta E^\circ F/RT$)) derived from wave separations indicate that for the three oxidation processes the oxidized species gain considerable thermodynamic stabilization. This might be the result of electronic delocalization, keeping in mind that K_c is not a true indication of the electronic coupling strength.[10] For example, the peak separation between the first two oxidations in **[3a][OTf]**$_2$, ΔE° = 410 mV, leads to $K_c = 1.1 \times 10^7$.

In order to probe the electronic communication along the molecules, a series of preliminary spectroscopic experiments were carried out on different redox states. The optical properties of **[3a–b]**$^{n+}$ (n = 0–4) were thus investigated by means of UV/Vis/NIR spectroelectrochemistry in an OTTLE cell. Especially, analysis of intervalence charge transfer bands (IVCT) observed in the NIR region of MV complexes can provide a powerful probe of interaction.[1–9] As expected, the most interesting features are located in the NIR region for **[3a–b][OTf]**$_2$ that both show a similar behavior. As an example, on one electron reduction of **[3a]**$^{2+}$ to **[3a]**$^{+}$, a new broad band shows up in the NIR region (Fig. 1), and collapses on further reduction to **3a**. Parameter extraction from this absorption is rather difficult owing to solvent overtone, and because the band extends outside the range of the spectrometer. To a first approximation the band is assumed to be Gaussian and the maximum could be located at *ca.* 3800 cm^{-1}. In our previous studies we showed (i) that the reduction process in the C$_7$ bimetallic analogues is not accompanied with any NIR absorption and is attributed to the chain,[8] and (ii) that the one-electron reduced form of the bis-allenylidene complex [(Ph$_2$C=C=C=)$_2$Ru(dppe)$_2$]$^{2+}$ shows electron delocalization over the two carbon chains.[9c] Therefore, complex **[3a]**$^{+}$ can be interpreted as a ligand based class II system involving electron delocalization over the two chains through the central metal.[9a,11] The energy, intensity and shape of the NIR band seem consistent with an IVCT and also with Hush theory, knowing that no accurate distance value for electron transfer distance can be assumed so far. Indeed, the calculation $\Delta\nu_{1/2} = (2310\nu)^{1/2}$ cm^{-1} yields $\Delta\nu_{1/2}$ = 2962 cm^{-1}. Within experimental error, this value is close to the experimental value of *ca.* 3070 cm^{-1}. This interpretation is in line with the very slight shift of the cumulenic vibration stretch to 1902 cm^{-1} for **[3a]**$^{+}$ upon IR monitoring of the first reduction, value which is similar to that of the bimetallic cationic analogue (ν = 1898 cm^{-1}). Further vanishing of the latter upon the second reduction highlights the reduction of the whole π system (both chains).

Table 1 Electrochemical data for [**3a–b**][OTf]$_2$[a]

	E°(+/0) **Red2**/V	E°(2+/+) **Red1**/V	E°(3+/2+) **Ox1**/V	E°(4+/3+) **Ox2**/V	E_{pa}(5+/4+) **Ox3**/V
[3a][OTf]$_2$	−1.26	−1.07	0.40	0.81	1.14[c]
[3b][OTf]$_2$	−1.32	−1.13	0.34	0.82[b]	1.05[c]

[a] Sample, 1 mM; Bu$_4$NPF$_6$ (0.1 M) in CH$_2$Cl$_2$; v = 100 mV s^{-1}; potential are reported in V *vs.* ferrocene as an internal standard; reversible redox processes $\Delta E_p \approx 60$ mV, $I_{pc}/I_{pa} \approx 1$. [b] E_{pa} of a partially reversible process, $I_{pc}/I_{pa} < 1$. [c] Peak potential of an irreversible process.

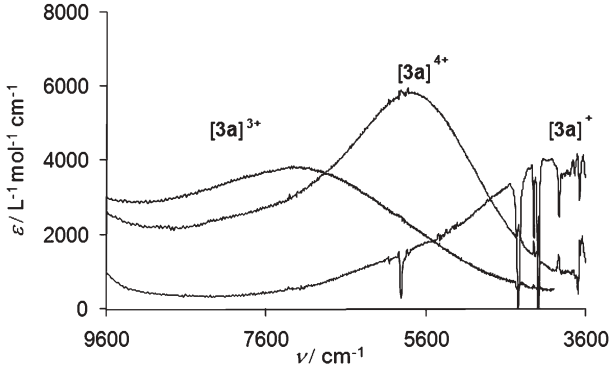

Fig. 1 Difference spectra [**3a**$^{n+}$–**3a**$^{2+}$] in the NIR region of [**3a**]$^{3+}$, [**3a**]$^{4+}$ and [**3a**]$^{+}$ in CH$_2$Cl$_2$ (0.1 M Bu$_4$NPF$_6$).

One-electron oxidation of **[3a][OTf]**$_2$ leads to the observation of a new broad band for **[3a]**$^{3+}$ centered at 7257 cm^{-1} (ε = 3850 mol^{-1} L cm^{-1}), a region in which no absorption is observed for **[3a]**$^{2+}$ (Fig. 1). Upon the second oxidation (**[3a]**$^{4+}$) a displacement of this absorption band toward lower energies ($\lambda_{\max}$ = 5787 cm^{-1}) with increasing intensity (ε = 5860 mol^{-1} L cm^{-1}) is observed. Further oxidation to **[3a]**$^{5+}$ leads to decomposition (irreversible process).

In order to get more insight in the nature of these oxidized species, EPR spectra were observed for both compounds at 77 and at 4 K after room temperature *in situ* electrolysis in CH$_2$Cl$_2$ at the first oxidation potential followed by a rapid quenching. When cooling down to 4 K, a weak contribution of Ru orbitals is detected for **[3b]**$^{3+}$, being responsible of an EPR line distortion (Fig. 2). An assessment of the principal values of the slightly rhombic g-tensor could be obtained from computer simulation: g_1 = 2.0265; g_2 = 2.016; g_3 = 2.0015, yielding the g anisotropy $g_1 - g_3$ = 0.025 and the average g-factor calculated from $\langle g \rangle = [(g_1^2 + g_2^2 + g_3^2)/3]^{1/2}$ as $\langle g \rangle$ = 2.0146. This is not observed in the case of **[3a]**$^{3+}$, which EPR spectrum is almost fully isotropic and centered close to the free-electron g-value of g_e = 2.0023. Following Kaim and co-workers,[12] and our recent work on related bimetallic C$_7$

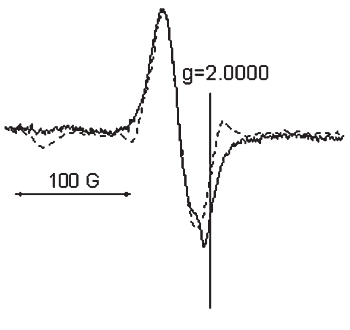

Fig. 2 First-derivative EPR spectra recorded at 77 K (dashed line) and at 4 K (continuous line) in CH$_2$Cl$_2$ frozen solution for **[3b]**$^{3+}$.

complexes,[8] the low g anisotropy and the average $\langle g \rangle$ factor close to g_e mostly suggests a contribution from the carbon rich ligands to the SOMO with an octahedral environment for the Ru centers. Continuous oxidation of the complexes results in decreasing the observed spectra so that no conclusion could be drawn for the possible spin pairing resulting in highest spin species.

Importantly, this EPR study points out the fact that the first oxidation process involves a much larger chain contribution than in the bimetallic analogue and probably engages both chains.[8] This is not unexpected owing to the good orbital matching between the metal and ligand orbitals.[8,9c] This behavior strongly contrasts with that usually observed for trimetallic complexes in which oxidations are always attributed to the metal centers. In those MV species, deconvolutions of NIR bands lead to subbands assigned to adjacent and remote IVCT between the metals depending on the position of the oxidized center in the assembly.[3–7] With our species, the involvement of both the metals and the chains makes the use of Hush model unlikely for these absorptions that should include a high $\pi \rightarrow \pi^*$ parentage.[1b,13] The unusual behavior of the processes is further supported by the fact that the two oxidized states show different absorption intensities and energies generally suggestive of an increase of delocalization in **[3a]**$^{4+}$ relative to **[3a]**$^{3+}$, which is not expected due to orbital destabilization.[5–7,14] These data also carry out the idea that the two oxidations are not simply the successive oxidations of the two chains. Additionally, upon IR monitoring of both oxidations, the vanishing of the chain contributions (v = 1880 and 1990 cm^{-1}) was gradually observed.[15] Overall, these observations strongly support the fact that the entire conjugated path is involved in the oxidation processes.

In conclusion, complexes **[3a–b][OTf]**$_2$ represent the first examples of a new type of homonuclear carbon-rich conjugated molecular wires with more than two metal centers, and in which the metals and the intervening bridging ligands provide a linear conduit of approximately 24 Å for electronic delocalization, either in an oxidation or a reduction process.[16] Further studies are currently in progress to get a better insight in these systems that give convincing argument for their potential in molecular electronic devices, and that will guide the developments and the fundamental understanding of long range metal mediated electron delocalization.

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