

Electronic communication between metal–organic electrophores in an organometallic ruthenium–acetylide–tetrathiafulvalene complex†

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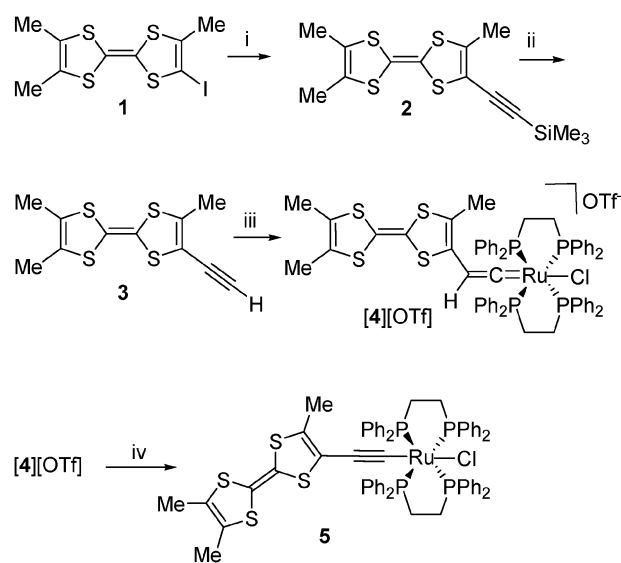
The organic and metal-based electroactive sites in the novel organometallic ruthenium–acetylide–tetrathiafulvalene complex are shown to be strongly electronically coupled.

The quest for interplay between redox active tetrathiafulvalene (TTF) and metallic centers has led to the synthesis of hybrid organic–inorganic building blocks essentially involving a coordination chemistry approach.¹ For that purpose, various coordination functionalities have been grafted, either directly or through a spacer group, on the TTF core, the latter being then turned into a potential electroactive ligand able to coordinate a number of transition metal complexes. A different approach which has been seldom explored so far, relies on the linking of the two electroactive moieties through a metal–carbon bond.² Within this framework, an interesting organometallic fragment with excellent electron donating ability is ruthenium(II)–alkynyl.^{3–5} Moreover, when connected to other electroactive cores, strong electronic interaction has been observed through the C≡C bond(s) of such molecules.⁶ The coupling of an alkynyl–ruthenium fragment to a TTF moiety has not yet been reported and we were therefore curious to explore how the fusing of these two electrophores with an organometallic linkage would affect the opto-electronic properties of such an *attelage*. Herein, we report on the synthesis and structure of a Ru–vinylidene–TTF complex and its conversion to the first example of a TTF–acetylide–Ru species. The electrochemical and spectroelectrochemical investigations of the latter are also reported in order to assess the extent of the electronic communication between the metal center and the TTF core through the acetylide bridge.

The synthetic strategy towards the target molecule is based on the reaction of a terminal alkyne with [CIRu(dppe)₂][OTf] (dppe = Ph₂PCH₂CH₂PPh₂), followed by deprotonation of the vinylidene derivative,⁷ as described in Scheme 1. First, the appropriate TTF acetylene **3** has been prepared from iodo TTF **1**⁸ (Scheme 1). CuI and PdCl₂(PPh₃)₂ catalyzed Sonogashira coupling between the iodo TTF **1** and trimethylsilylacetylene in the presence of diisopropylamine, afforded TTF **2** in 75% yield. Deprotection of **2** with KF in MeOH afforded the targeted TTF alkyne **3** in quantitative yield. Cyclic voltammetry of TTFs **1–3** shows two reversible monoelectronic oxidation

waves. No significant effect of the substituents is observed as the redox potentials are very close for all TTFs **1–3** ($E_1 = 0.36$ V for **1**, $E_1 = 0.35$ V for **2** and $E_1 = 0.38$ V for **3**, V vs. SCE, and $\Delta E = (E_2 - E_1) = 500$ mV in CH₂Cl₂–[nBu₄N][PF₆] for all three molecules).

In order to synthesise the organic–inorganic hybrid molecule, TTF **3** was reacted with [CIRu(dppe)₂][OTf] in dichloromethane at room temperature under an inert atmosphere and the reaction was monitored by ³¹P NMR spectroscopy. During the course of the reaction, the disappearance of the set of signals due to the starting material, [CIRu(dppe)₂]⁺, at $\delta_P = 57.1$ and 84.9 ppm is concomitant with the appearance of a novel set of signals at $\delta_P = 43.5$ and 41.9 ppm, and assigned to the vinylidene derivative [4][OTf] (Scheme 1). The presence of these two signals indicates a non-equivalent environment around the phosphorus atoms and is attributed to the presence of the TTF core in **4**⁺. Single crystals of the vinylidene derivative [4][OTf] were successfully obtained by slow diffusion of pentane into a concentrated solution of [4][OTf] in dichloromethane under an inert atmosphere. Complex [4][OTf] crystallises in the monoclinic system, space group C2/c, with two molecules of CH₂Cl₂.† The molecular structure of **4**⁺ is shown in Fig. 1. The organometallic Ru(II) fragment is chelated by two dppe units in the equatorial plane and the octahedral coordination geometry is completed by a chloride ligand, coordinated *trans* to the vinylidene. The Cl–Ru=C=C moiety is close to



Scheme 1 Reagents and conditions: (i) CuI, PdCl₂(PPh₃)₂, HN(CH(CH₃)₂)₂, HC≡CSiMe₃, THF; (ii) KF, MeOH; (iii) [CIRu(dppe)₂][OTf], CH₂Cl₂; (iv) NEt₃, CH₂Cl₂.

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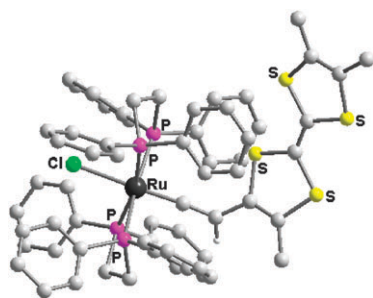


Fig. 1 Molecular structure of 4^+ in $[4][OTf]$ (H atoms are omitted for clarity except for the hydrogen on the vinylidene).

linearity with the Cl–Ru=C and Ru=C=C angles being $175.43(11)$ and $174.9(3)^\circ$, respectively, while the C=C–TTF angle is $127.84(33)^\circ$. The Cl–Ru ($2.452(1)$ Å), Ru=C ($1.841(4)$ Å) and C=C ($1.307(5)$ Å) bond lengths are in the usual range for such Ru–vinylidene fragments.^{9,10}

The boat conformation of the TTF core (with both dithiole rings folded along the S···S vectors with asymmetric folding angles of 20 and 14°) and the length of the central C=C bond ($1.336(5)$ Å) are consistent with a neutral TTF in $[4][OTf]$.

Deprotonation of the vinylidene 4^+ with NEt_3 yielded the ruthenium–alkynyl–TTF **5** (Scheme 1). The formation of **5** can be observed by the rapid decoloration of the deep green dichloromethane solution of **4** upon addition of the base. The ^{31}P NMR spectrum of **5** reveals one signal at 49.2 ppm indicating the equivalence of the four phosphorus atoms and the retaining of the *trans* arrangement of the chloride and alkynyl ligands. The C≡C bond IR vibration in **5** ($\nu_{C\equiv C} = 2029$ cm^{-1}) is found at a lower energy than in the starting alkyne TTFs **2** and **3** ($\nu_{C\equiv C} = 2140$ cm^{-1}). We note that the $\nu_{C\equiv C}$ stretching frequency in **5** is one of the lowest observed so far among the reported Ru(II) acetylide complexes, which indicates a high degree of conjugation in this species.⁵

Cyclic voltammetry of **5** shows three well defined reversible oxidation waves at $E_1 = 0.07$ V, $E_2 = 0.52$ V and $E_3 = 1.07$ V vs. SCE (Fig. 2). The rather low potential of the first oxidation (0.07 V) is unusual and worth a comment. Indeed, the primary oxidation of **5** occurs at a significantly less anodic potential than that of the first oxidation of TTF **3** (0.38 V vs. SCE), of the mononuclear ruthenium complex analogue, *trans*-[Ru(C≡CPh)Cl(dppe)₂] ($E = 0.55$ V vs. Ag/AgCl)⁴ and of the *trans*-[RuCl₂(dppe)₂] ($E = 0.50$ V vs. SCE). On these grounds, the primary oxidation of **5** could be tentatively assigned to the TTF core, strongly affected by the very electron-rich ruthenium(II) moiety, whose electronic effect is efficiently transmitted by the acetylide C≡C linkage, as observed in other examples available in the literature.³ The second oxidation of **5** is found at a potential (0.52 V) very similar to that of the oxidation potential of *trans*-[RuCl₂(dppe)₂] ($E = 0.50$ V vs. SCE). Considering, that the oxidation of the metal center in **5** must be affected both by the electronic effect of the TTF core and by the electrostatic effect of the mono-cationic charge, the second oxidation of **5** is then assigned to the second oxidation of the TTF core. The third oxidation process is then logically viewed as involving the Ru^{II}/Ru^{III} couple and is anodically shifted compared to *trans*-[Ru(C≡CPh)Cl(dppe)₂]⁴ due to the dicationic charge

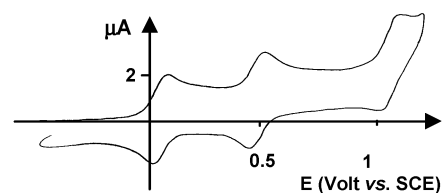


Fig. 2 CV of **5** in CH_2Cl_2 -[nBu_4N][PF_6] 0.1 M, $v = 100$ $mV s^{-1}$.

on the TTF moiety acting now as a strong electron acceptor. Similar mutual influences, however less pronounced, have been noticed previously between two metallic centers linked by the acetyl linkage in *trans*-[Fc–C≡C–RuCl(dppe)₂] (Fc = ferrocenyl).³

DFT calculations [Gaussian03, B3LYP/LanL2DZ] carried out on **5** and $5^{+•}$ are consistent with the electrochemical assignments but provide the following nuances. As expected, The HOMO of **5** has a strong TTF character, with however low coefficients found on the carbon atoms of the distal dithiol ring, Fig. 3.

There is also a significant metal and acetylide contribution in the HOMO of **5** so that the assignment of the primary oxidation as a pure TTF-based electron transfer is not possible. We also note that the HOMO of TTF **3** is symmetric with no contribution from the alkyne. The SOMO of $5^{+•}$ is also found to have a mixed and delocalized character with a strong TTF contribution, together with a metal–chloride and distal acetylide carbon contribution. In this case, the major distribution within the TTF core leans towards the distal dithiol ring. The EPR spectrum of $5^{+•}$ at room temperature ($g = 2.015$, Fig. S3, ESI†) indicates an organic radical character with hyperfine coupling with one methyl group, $a_H = 2.7$ G, consistent with the significant spin density found on one methyl group by theoretical calculation (Fig. 3, bottom right).

Finally, UV-vis-NIR spectroelectrochemical investigations were carried out on a dichloromethane solution of **5** ($c = 10^{-4}$ M). The neutral complex exhibits absorption bands in the visible range at $\lambda_{max} = 225$, 256 and 317 nm. The latter band is ascribed to a metal-to-ligand charge transfer (MLCT) transition as this transition is usually assigned to the lowest

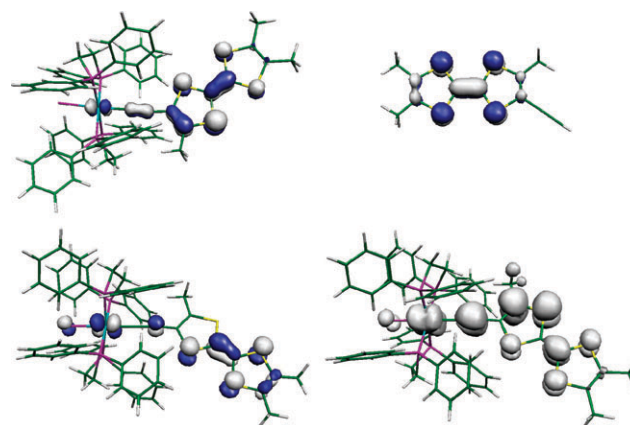


Fig. 3 HOMOs of **5** and **3** (top), SOMO and spin density of $5^{+•}$ (bottom).

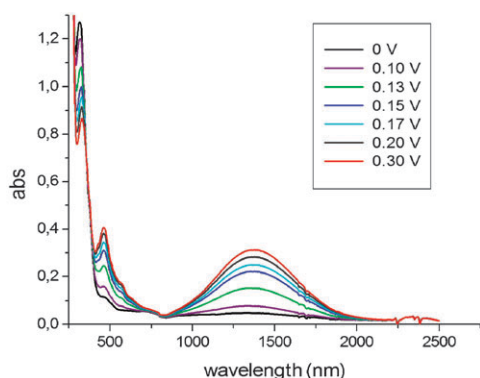


Fig. 4 UV-vis-NIR monitoring of the electrochemical oxidation of **5**.

energy band around 315 nm in Ru acetylide complexes.¹¹ Upon gradual oxidation the band at 317 nm ($\epsilon = 20\,960\text{ M}^{-1}\text{ cm}^{-1}$) decreases and a new band appears at $\lambda_{\text{max}} = 460\text{ nm}$ together with another broad absorption band centered at $\lambda_{\text{max}} = 1399\text{ nm}$ (Fig. 4). This broad band at 1399 nm is assigned to a SOMO–LUMO transition. Taken together, these experimental and theoretical data provide clear evidence of the electronic delocalization in $5^{+\bullet}$ and demonstrate the electronic coupling between the two heterogeneous metal–organic redox centers.

The present results are in sharp contrast with those observed for other TTF–Ru(II) complexes where the Ru(II) atom is connected to the TTF moiety through a coordination bond.^{12–14} In these cases, the sequence of the three oxidation processes are only moderately shifted towards more anodic potentials with respect to their parent models. For instance, in the case of an ethynylbipyridine linker between the metal and the organic redox active sites, the ruthenium center slightly decreases the electron density on the TTF site, while no significant influence of the Ru(II/III) oxidation potential is observed.¹⁵ The electronic effect of the Ru(II) center on the redox properties of the TTF is hence highly dependent on the binding mode. When a coordination linkage is involved, a positive shift of the TTF oxidation potential is found and assigned to an electrostatic effect,¹ representative examples being Ru(II) complexes linked to a neutral TTF through bipyridine,¹² ethynylbipyridine¹⁵ or dipyrrophenazine^{13,14} substituents. In the case of **5**, where an organometallic linkage is present, the strong negative shift detected for the direct σ -coordination of the TTF–ethynyl to the Ru(II) can be assigned to metal electron transference *via* π conjugation as suggested for bimetallic systems involving a ferrocenylethynyl group.¹⁶

In conclusion, the novel electroactive ruthenium–acetylide–TTF **5**, represents the first example of a TTF linked to a metal exhibiting such mutual strong electronic interactions along the bridge and a unique increase of the electron density on the

TTF effected by the metal fragment. Electrochemical, spectroscopic and theoretical investigations have evidenced that electronic interactions between the TTF and the Ru atom are to a large extent function of the coordination mode. Examples of complexes where the coordination of TTF involves a carbon–metal linkage are scarce, but this strategy opens new perspectives in the quest for the interplay between TTF and metallic centers.

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Notes and references

† Crystal data for **4**[(OTf)–2CH₂Cl₂], $M = 1522.66$, monoclinic, space group $C2/c$, $a = 19.7287(11)$, $b = 19.2039(9)$, $c = 36.6357(19)$ Å, $\beta = 101.699(2)^\circ$, $V = 13591.8(12)$ Å³, $Z = 8$, $T = 100(2)$ K, Mo–K α ($\lambda = 0.71073$ Å), $D_c = 1.488\text{ g cm}^{-3}$, 57 591 reflections measured, of which 15 532 independent ($R_{\text{int}} = 0.047$) $R_F = 0.0609$ [14 621 data, $I > 2\sigma(I)$], $wR(F^2) = 0.1233$, GOF = 1.235.

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