Cis and trans-bis(tetrathiafulvalene-acetylide) platinum(II) complexes: syntheses, crystal structures, and influence of the ancillary ligands on their electronic properties.

Antoine Vacher, Frédéric Barrière, Franck Camerel, Jean-François Bergamini, Thierry Roisnel, Dominique Lorcy

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Introduction

This last decade, the coordination chemistry of tetrathiafulvalene (TTF) derivatives has focused a lot of attention towards the elaboration of electroactive transition metal complexes with original electronic properties due to interplay between the TTF and the electron density on the metal.\(^1\)\(^-\)\(^3\) To study these interactions between the TTF moiety and the metal center, another approach has been recently developed which relies on organometallic chemistry and on the connection of a TTF to the metal center through a conjugated carbon chain. To date only four examples of such hybrid organic–inorganic building blocks have been reported, and all of them involve one or two TTF acetylide ligands coordinated to a metal center (Chart 1). Interestingly, electronic coupling was evidenced between the TTF and the metal electrophore within trans-RuCl(\text{C}==\text{CMe}_2\text{TF})_2(dppe)\(^6\) and Cp*(dppe)Fe(\text{C}==\text{CMe}_2\text{TF})\(^7\) with the strength of the coupling depending on the nature of the metal. Interplay between the two TTFs along the linker has also been evidenced in the trans-Ru(\text{C}==\text{CMe}_2\text{TF})_2(dppe)\(^5\) through the observation of multistage redox behavior whereas the TTF itself exhibits two reversible one-electron processes.\(^8\) It is worth mentioning that the use of an acetylide–Cr-acetylide organometallic bridge does not allow an electrochemical detection of interplay between the two TTFs within [CrCyclam(\text{C}==\text{CEDT}-\text{MeTF})]OTf.\(^9\) Nevertheless, electrochemical oxidations of this complex lead to two salts where mixed-valence TTF units were obtained. Among the various bisacetylide metal complexes, those involving a platinum center with various ancillary ligands have also proved their strong propensity to allow electronic interaction by connecting either organic or organometallic electrophores.\(^10\)\(^-\)\(^12\)

In this context, the aim of this work is to investigate the electronic properties of mononuclear platinum complexes containing two TTF acetylide ligands and either diimine or phosphine as ancillary ligands, namely triphenylphosphine, 1,2-bis(diphenylphosphino)ethane (dppe), 2,2'-dipyridyl (bipy) or 4,4'-di-tert-butyl-2,2'-dipyridyl (tBu\(_2\)bipy). Herein, the synthesis, characterization and properties of a series of Pt(II) complexes bearing two monodentate TTF acetylide ligands are reported.

Cis and trans-bis(tetrathiafulvalene-acetylylide) platinum(II) complexes: syntheses, crystal structures, and influence of the ancillary ligands on their electronic properties†

Antoine Vacher, Frédéric Barrière, Franck Camerel,\(^*\) Jean-François Bergamini, Thierry Roisnel and Dominique Lorcy\(^*\)

A series of four platinum(II) complexes bearing two tetrathiafulvalene acetylide ligands coordinated either cis or trans to the metal center are reported: cis-Pt(bipy)(\text{C}==\text{CMe}_2\text{TF})\(_2\), cis-Pt(tBu\(_2\)bipy)-(\text{C}==\text{CMe}_2\text{TF})\(_2\), cis-Pt(dppe)(\text{C}==\text{CMe}_2\text{TF})\(_2\) and trans-Pt(PPh\(_3\))\(_2\)(\text{C}==\text{CMe}_2\text{TF})\(_2\). The X-ray diffraction studies of the four complexes are reported and discussed. The electrochemical investigations carried out by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) evidenced different redox behavior as a function of the ancillary ligand. Only for the cis-Pt(dppe)(\text{C}==\text{CMe}_2\text{TF})\(_2\) complex is the first oxidation wave resolved (\(\Delta E = 70\) mV) into two one-electron processes. Spectroelectrochemical investigations performed on the four complexes did not evidence any electronic interactions between the two organic electrophores. The splitting of the first oxidation wave observed in cis-Pt(dppe)(\text{C}==\text{CMe}_2\text{TF})\(_2\) is mainly explained by the non-equivalence of the two TTF moieties induced by the geometrical constraint imposed by the ancillary dppe ligand as found by density functional theory calculations.

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Results and discussion

Synthesis

The synthesis of the target complexes is outlined in Scheme 1. The coupling reaction, catalysed by copper(I) iodide, between 2 equiv. of an alkyne and a bis(chloro)platinum derivative in a basic medium represents a versatile route towards platinum complexes. Accordingly, we prepared four different platinum complexes 1–4 bearing two Me₃TTF-acetylide ligands (Scheme 1). The use of the Pt(bipy)Cl₂ precursor affords complex 1 which was found to be insoluble in most of the commonly used organic solvents. To improve the solubility of the target complex, the analogue complex 2 carrying a tBu₂bipy fragment in place of the bipy fragment in 1 was synthesized using Pt(tBu₂bipy)Cl₂ as the starting material. In order to study the influence of the nature of the L-ligand and the cis or trans configuration of the two acetylide TTF moieties around the metal on the physicochemical properties of the platinum complexes, the bipy fragment was replaced by either a diphosphine (1,2-bis(diphenylphosphino)ethane, dppe) ligand or two triphenylphosphine ligands. For that purpose, the cis-Pt(dppe)Cl₂ and cis-Pt(PPh₃)₂Cl₂ complexes were used as starting materials for the synthesis of complexes 3 and 4 respectively. The substitution of the chloride ligands on the cis-Pt(PPh₃)₂Cl₂ complex by bulky alkynyl fragments leads to the formation of a more thermodynamically stable trans-complex. The ³¹P NMR spectrum of 4 shows one signal at 18 ppm indicating the equivalence of the two phosphorus atoms due to the trans arrangement of the acetylide TTF ligands around the Pt(II) center.

Molecular structures

Single crystals were obtained for each complex, 1–4, and the molecular structures have been elucidated by X-ray diffraction studies. Selected bond lengths and angles are reported in Table 1. All the complexes, 1–4, display a square planar geometry around the platinum atom. Bond lengths analyses of the central C≡C bonds reveal that the TTF moieties are all in a neutral state for each complex, 1–4. In complex 1, the two TTF fragments and the bipyridine ligand roughly lie in the same plane and the long axis of the TTF molecules is parallel to the long axis of the bipy fragment (Fig. 1). The observed Pt–N bond lengths as well as the ligand bite angle N1–Pt–N11 (Table 1) compare well with those usually measured in other bipyPt complexes. The observed Pt–C and C≡C are identical on the two TTF fragments (Table 1). These C≡C bond lengths are longer than that found in the Me₃TTF=C=CH precursor (1.152(8) Å) but lie in the same range as that found in
trans-RuCl\(\text{-C} \equiv \text{CMe}_3\text{TTF})(\text{dppe})_2\) (1.203(3) Å). The angle between the two alkynes in 1 amounts to 88.92(20)°.

The molecular structures of the two crystallographically independent complexes 2 are presented in Fig. 2 and Fig. S1.† In the two complexes, the TTF fragments and the tBu₂bipy ligand lie in the same plane. Interestingly, the orientation of the TTF molecules observed in the two crystallographically independent molecules of complex 2 is different from that observed in the crystalline structure of the parent complex 1. With complex 2, the long axis of the TTF moieties is perpendicular to the long axis of the bipy fragment (Fig. 2). The bond lengths Pt–C, Pt–N and C–C are slightly different in the two crystallographically independent molecules of complex 2 but they remain close to those discussed above for complex 1 (Table 1) or to the related Pt(II) diimine acetylide complex. A larger C–Pt–C angle (91.02(34)° and 92.21(24)°) is observed in the two molecules of complex 2 and can be explained by the peculiar orientation of the TTF moieties in this complex.

The molecular structures of the two crystallographically independent molecules of complexes 3 are presented in Fig. 3 and Fig. S2.† The molecular structure confirms that the platinum center is coordinated by one dppe fragment and two acetylide-TTF ligands in a cis arrangement. The TTF molecules are oriented with the long axis of the TTF parallel to the P⋯P axis of the dppe fragment. The Pt–C bond lengths are longer in the two molecules of complex 3 than those measured in complexes 1 and 2. This difference is due to a π-back metal to ligand (bipyridine) donation in complexes 1 and 2. The Pt–P bond lengths are consistent with those already determined on related phosphino-alkynyl-platinum derivatives. The C≡C bond lengths are similar in the two molecules and compare well with those measured in complexes 1 and 2. The TTF cores

<table>
<thead>
<tr>
<th>Compound</th>
<th>X–Pt</th>
<th>Pt–C11</th>
<th>C10≡C11</th>
<th>C5–C6</th>
<th>X–Pt-X</th>
<th>C–Pt–C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me$_3$TTFC≡CH</td>
<td>—</td>
<td>—</td>
<td>1.152(8)</td>
<td>1.349(7)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>1 TTF</td>
<td>N1: 2.068(4)</td>
<td>1.948(8)</td>
<td>1.207(8)</td>
<td>1.353(7)</td>
<td>79.10(15)</td>
<td>88.92(20)</td>
</tr>
<tr>
<td>2 TTF</td>
<td>N1: 2.054(4)</td>
<td>1.957(7)</td>
<td>1.184(10)</td>
<td>1.322(9)</td>
<td>78.15(19)</td>
<td>92.21(24)</td>
</tr>
<tr>
<td>TTF</td>
<td>N1: 2.062(5)</td>
<td>1.954(6)</td>
<td>1.180(9)</td>
<td>1.322(9)</td>
<td>80.09(27)</td>
<td>91.02(34)</td>
</tr>
<tr>
<td>3 TTF</td>
<td>P1: 2.291(2)</td>
<td>2.000(6)</td>
<td>1.206(8)</td>
<td>1.334(9)</td>
<td>85.08(6)</td>
<td>88.11(23)</td>
</tr>
<tr>
<td>4 TTF</td>
<td>P1: 2.305(1)</td>
<td>1.999(5)</td>
<td>1.220(5)</td>
<td>1.338(6)</td>
<td>180.00(13)</td>
<td>180.00(3)</td>
</tr>
</tbody>
</table>

Fig. 1 ORTEP drawing of the platinum complex 1 with the main numbering scheme. Thermal ellipsoids drawn at the 50% probability level.

Fig. 2 ORTEP drawing of one of the two crystallographically independent molecules of complex 2 with the main numbering scheme. Thermal ellipsoids drawn at the 50% probability level.

Fig. 3 ORTEP drawing of one of the two crystallographically independent molecules of complex 3 with the main numbering scheme. Thermal ellipsoids drawn at the 50% probability level.
adopt a boat conformation with the dithiole rings folded along the S⋯S axis (12/13° TTFA, 24/14° TTFB, 13/13° TTFC and 13/9° TTFD) contrasting with the planar TTF cores observed for complexes 1 and 2. On the two crystallographically independent molecules of complex 3, the two TTF fragments do not lie in the same plane and one TTF clearly appears to be more bent than the other one. This dissymmetry is induced by steric interactions and geometrical constraints imposed by the phenyl rings on the ddpe ligand.

In complex 4, the two acetylide-TTF ligands are in a trans arrangement with the platinum atom localized on the inversion center (Fig. 4). The bond lengths Pt–P, Pt–C, C=C compare well with the bond lengths reported for complex 3 and with other similar phosphino-alkynyl-platinum complexes.18 The central C=C—Pt—C=C—C=C–C spacer is almost linear with angles at C–Pt–C, Pt–C=C and C=C–C of 180.0(0), 174.4(3), 177.9(3)° respectively. The TTFs adopt a slight boat conformation (Fig. 4).

**Photophysical properties of complex 2**

Diimine platinum(II) di(acetylide) complexes are known to display good luminescence properties with bright emission and long decay lifetimes, usually arising predominantly from the MLCT excited state.19 For example, the complex Pt–(Bu3bipy)(C=CPh)2 in CH2Cl2 emits at 560 nm with a quantum yield of 0.34 and a luminescence lifetime of 1.36 μs.10 Acetylide ligands including functional units such as redox-active groups are particularly attractive to obtain redox active optical switches. In this respect, TTF is an efficient luminescent quencher by electron-donating effects and oxidation of the TTF usually leads to the regeneration of the luminescence properties of the luminophore on which this redox unit is attached.21 Hence, the luminescence properties of the soluble complex 2 have been explored in the neutral state and upon oxidation of the TTF units by adding successive aliquots of NOPF6 as the oxidizing agent.

The UV-vis absorption spectrum of complex 2 is shown in Fig. 5. The absorption maxima and extinction coefficients are given in Table 2. The strong bands below 360 nm (ε ~ 5–6 × 104 M−1 cm−1) are attributed to intraligand π–π* transitions localized on the tBu3bipy and the alkynyl-TTF fragments. The absorption band observed at 380 nm (ε = 1.9 × 104 M−1 cm−1) is assigned to ligand-localized π–π* transitions whereas the absorption band localized at 405 nm with a lower extinction coefficient (4.7 × 103 M−1 cm−1) is attributed to a π(C=C) → π*(C=C) transition containing a slight MLCT contribution.23

The absorption spectra of the phosphino complexes 3 and 4 appear to be the superimposition of the absorption spectra of the chloro-phosphino-platinum and of the Me3TTF–C=C–H precursors and only a hypochromic shift of 30 nm of the low energy band, strongly localized on the acetylide bridge, is observed (Fig. S4).

**Fig. 4** X-Ray molecular structure of complex 4: ORTEP drawing of the complex (top, thermal ellipsoids drawn at the 50% probability level), side view of the complex (bottom, the PPh3 ligands have been removed for clarity).

**Fig. 5** Evolution of the absorption spectrum of complex 2 in CH2Cl2 at room temperature upon addition of increasing amounts of NOPF6 as an oxidant.

<table>
<thead>
<tr>
<th>Complex</th>
<th>λmax [nm]</th>
<th>εmax [M−1 cm−1]</th>
<th>E1/2,1TTF</th>
<th>E1/2,2TTF</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>229(55 000), 294(60 000), 380(19 000), 483(5000)</td>
<td>0.23</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>228(52 500), 310(41 000), 405(9000)</td>
<td>0.19/0.26</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>229(68 700), 326(41 500), 405(11 300)</td>
<td>0.21</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td>Me3TTFDCCH</td>
<td>295(15 000), 331(14 000), 386(3000)</td>
<td>0.38</td>
<td>0.88</td>
<td></td>
</tr>
</tbody>
</table>

*In CH2Cl2, [NBu4][PF6] 0.1 M at room temperature; scan rate, 100 mV s−1, E1/2 = (∫Epa + ∫Epc)/2; Epa and Epc are the anodic and the cathodic peak potentials, respectively. Electronic absorption data of complexes 2–4 measured in CH2Cl2 at room temperature (ε ~ 104 M−1 cm−1).
At room temperature in CH$_2$Cl$_2$ (either under air or argon), complex 2 appears to be non-luminescent. Several excitation wavelengths have been tested and excitation in the MLCT band localized at 380 nm did not lead to the expected emission in the range 570–610 nm, usually observed with diimine platinum(II) di(acetylide) complexes. The luminescence quenching is probably due to photo-induced electron transfer from the TTF unit toward the excited states localized on the platinum–diimine fragments. Similar electron transfer quenching has already been reported in a related system bearing electron donor phenothiazine instead of TTF.

Chemical oxidation of complex 2 upon addition of increasing amounts of NOPF$_6$ was realized and the evolution of the absorption spectrum is presented in Fig. 5. The gradual oxidation of the TTF units leads to the growing of absorption bands below 330 nm, attributed to $\pi\pi^*$ transitions localized on the neutral TTF units, and a clear isosbestic point is observed at 400 nm. A decrease of the absorption bands below 330 nm, attributed to $\pi\pi^*$ transitions localized on the neutral TTF units, is also observed. Contrary to our expectations, treatment of the solutions of complex 2 with 1 and 2 equiv. of an oxidizing agent such as NOPF$_6$ or FeCl$_3$ did not lead to the formation of a luminescent complex. This can be ascribed to the fact that the TTF radical cation displays an additional reduction wave at $E_{\text{red}} = -1.32$ V vs. SCE attributed to the one-electron reduction of the tBu$_2$Bipy fragment.

IR studies

Platinum complexes 1–4 have also been characterized by solid-state IR spectroscopy. The alkynyl C≡C stretching vibration bands appear at 2090, 2091, 2092 and 2086 cm$^{-1}$ for complexes 1 to 4 respectively. These values are almost identical in the four complexes and this indicates that there is little effect of either the L-ligand (bipy for 1 and 2, dppe for 3 and PPh$_3$ for 4) or the cis/trans geometry on the frequency of the $\nu_{C≡C}$ stretching vibration.

Electrochemical studies

The electrochemical properties of complexes 2–4 were investigated by cyclic voltammetry in CH$_2$Cl$_2$ using [NBu$_4$][PF$_6$] as a supporting electrolyte. Due to its insolubility, the redox properties of complex 1 could not be determined. The cyclic voltammograms (CV) of complexes 2–4 are presented in Fig. 6 and the electrochemical data are collected in Table 2. Complexes 2, 3 and 4 display two main reversible oxidation waves. Complex 2 displays an additional reduction wave at $E_{\text{red}} = -1.32$ V vs. SCE attributed to the one-electron reduction of the tBu$_2$Bipy fragment. A closer look at the CV pattern of complex 3 reveals that the first redox system originates from two closely spaced and resolved oxidation processes at $E_{1/2} = 0.19$ V and $E_{1/2} = 0.26$ V vs. SCE, respectively corresponding to the successive generation of the TTF cation radical and the bis(TTF cation radical). The corresponding first oxidation systems in 2 and 4 are not resolved. However, they also involve two closely spaced one-electron transfers assigned to the oxidation of the TTF cores into the corresponding bis(TTF cation radical) $2^{(+\cdot)}$ and $4^{(+\cdot)}$. For all 2, 3 and 4, the second oxidation process is assigned to the closely spaced and unresolved second oxidation of the bis(TTF cation radical) $2^{(\cdot\cdot)}$, $3^{(\cdot\cdot)}$ and $4^{(\cdot\cdot)}$. 

### Figure 6

CV (top) and DPV (bottom) of complexes 2 (left), 3 (middle) and 4 (right) in CH$_2$Cl$_2$-[NBu$_4$][PF$_6$] 0.1 M (E vs. SCE, $\nu = 100$ mV s$^{-1}$). The small wave at $-1$ V in CV of compound 2 arises from an unassigned impurity.
into the bis(TTF dication) $2^{+*}$, $3^{+*}$ and $4^{+*}$. Note that none of these two-electron transfers involve inversion of the normal potential ordering. Rather, they all involve sequential and closely spaced one-electron transfer. Only the first oxidation system of 3 may be resolved electrochemically. The oxidation potentials of the TTF moieties are comparable in the three complexes indicating that the nature of the coordinating L-ligand (bipyridine or phosphine) has no significant influence on the electron-donating ability of the TTF core. Compared with the oxidation potentials of the $\text{Me}_2\text{TTF=CH}$ precursor ($E_{1/2}^{1} = 0.38 \text{ V}$ and $E_{1/2}^{2} = 0.88 \text{ V}$ vs. SCE, in CH$_2$Cl$_2$), all the oxidation potentials of the TTF cores within all these complexes, 2–4 (Table 2), are shifted by 160 mV towards less anodic potentials. This cathodic shift reveals that the organometallic fragment, through the acetylide linker, increases the electron density on the TTF cores and thus highlights the electronic interaction between the platinum center and the TTF cores. Such a cathodic shift has only been previously observed in a few cases such as for $[\text{Me}_2\text{TTF} \cdot \text{SiMe}_3]_3\text{Pt}([\text{PPh}_3])_2^{26}$ trans-ClRu(=C=CMe$_3$)(dppe)$_2^{6}$ and trans-Ru(=C=CMe$_3$)(dppe)$_2$. It is worth noting that this shift depends on the metal linked to the TTF acetylide ligand. Indeed, in the case of the chromium or iron acetylide-TTF type complex, namely $[\text{CrCyclam}(=C\text{EDTMeTTF})_2]^{2+}$ and $\text{Cp}^*([\text{dppe}]\text{FeC} \equiv \text{C} = \text{TTFMe}_3)^{-}$ no modification of the oxidation potentials of the TTF was observed. In other cases, when interactions exist between a TTF core connected to a metallic center through coordinating heteroatoms (L-type TTF ligands), an anodic shift is usually observed.

The splitting of the first oxidation process of 3 was confirmed by differential pulse voltammetry (DPV) analysis performed on the three complexes 2–4 (Fig. 6). The DPV of complex 3 displays two main oxidation peaks and clearly the first oxidation system contains two contributions at 0.19 and 0.26 V, corresponding to two monoelectronic oxidation processes. Hence, each TTF unit in 3 is oxidized to the cation radical sequentially, with a potential difference of $\Delta E = 70 \text{ mV}$, whereas the last oxidation process at 0.75 V is unresolved and involves two electrons. The DPV of complex 2 confirms the presence of three redox processes and integration of the waves confirms that the reduction process contains one electron whereas each oxidation peak is unresolved and involves two electrons. Similarly for complex 4, only two unresolved two-electron oxidation peaks are effectively observed in the anodic region.

The splitting of the first oxidation process for 3 is independent of the concentration (10$^{-4}$ to 10$^{-6}$ M), indicating that the sequential oxidation of the TTF cores is due to intramolecular interactions. This behavior is reminiscent of what was previously observed with dimeric TTFs where the splitting of the first redox process was the result of intramolecular interactions either through space, due to spatial proximity of the TTF cores, or through bond, due to electronic coupling of the TTF cores along the linker. For related platinum complexes containing two organometallic electrophiles such as ferrocene instead of the TTF cores, the $\text{trans-Pt}(\text{PPh}_3\text{Me}_3)_2(\equiv\text{CFe})_2$ and the $\text{cis-Pt}(\text{dppe})(\equiv\text{CFe})_3$, both ferrocene moieties are oxidized successively with a potential difference ($\Delta E$) of 80 and 70 mV, respectively.$^{11}$ The splitting value of 70 mV measured with complex 3 is in the same range and can indicate that weak intramolecular interactions occur between the two electrophores. However, a question remains, why this splitting is observed for the cis isomer 3 and not for the trans isomer 4 as in the case of the ferrocene complexes.

Regarding spatial interactions, it has been demonstrated that in TTF dimers linked by one heteroatom, the extent of the spatial intramolecular interactions increases when the angle between the two TTF moieties decreases.$^{28}$ The C-Pt-C angle determined in the crystalline structure of complex 3 appears smaller than that measured on the crystalline structure of complex 2. This smaller angle between the two TTF units in complex 3 can be at the origin of the splitting of the oxidation waves by increasing the spatial interactions (not observed with complex 2). However, measurements in the poorly coordinating electrolyte.$^{29}$ CH$_2$Cl$_2$-$\text{Na}[\text{B(CF}_3]_2\text{]}_2$ 0.02 M, do not yield a better resolution of the first two electron wave for any of the three complexes 2–4, showing that the TTF cores poorly interact electrostatically.

**UV-vis-NIR spectroelectrochemical investigations**

In order to get more insight into the interplay between the electroactive TTF through the bisacetylide–Pt bridge, UV-vis-NIR spectroelectrochemical investigations were carried out on complexes 2, 3 and 4 in a CH$_2$Cl$_2$-$\text{NBu}_4$[PF$_6$] 0.2 M solution (Fig. 7). The gradual oxidation of the TTF cores only induces the growth of low energy bands characteristic of radical cation species at 400 nm and 800 nm. No evidence of intervalence charge-transfer (IVCT) bands was observed for complexes 2–4 in the measured range from 200–2000 nm (5000–50 000 cm$^{-1}$) (Fig. 7). Although we cannot exclude the presence of an IVCT band at lower energy, these results suggest a lack of strong electronic communication between the TTF moieties in the mono-oxidized complexes in all three complexes (2–4). In a related trans-ruthenium complex,$^{8}$ a corresponding potential splitting of 110 mV was measured electrochemically and a band assigned as an IVCT recorded at 1360 nm.

**DFT computational studies**

DFT calculations [Gaussian03, B3LYP/LanL2DZ] were performed on complexes 2, 3 and 4. Full geometry optimization led to the molecular structure represented in Fig. 8 and 9. The optimized geometries are in good agreement with those obtained by X-ray diffraction studies concerning the bond lengths and the bond angles (vide supra). As shown in Fig. 8, the HOMOs (highest occupied molecular orbitals) of complexes 2 and 4 are symmetric and have a strong TTF character with a poor contribution of the bisacetylide–Pt spacer and also with poor coefficients found on the carbon atoms of the distal dithiole rings. The introduction of the bisacetylide organometallic fragment between the two TTF moieties induces a dis-symmetrization of the HOMO on the TTF core as the HOMO of the neutral Me$_3$TTF–C=CC–H precursor is symmetric on the
consistent with the crystal structure of complex 3 (vide supra). It is worth mentioning that such dissymmetry has not been evidenced on the $^1$H NMR and $^{31}$P NMR spectra. The HOMO is centered on one TTF unit and the HOMO – 1 is localized on the other TTF unit with energy levels calculated at –4.33 and –4.41 eV respectively. The dissymmetry is attributed to steric hindrance due to the bulky dppe ligand and the close proximity of the phenyl groups which force the TTF units to be in two distinct environments. With the rigid and symmetric tBu$_2$biy fragment in complex 2, the two TTF fragments have the same environment and are equivalent, leading to a closely spaced and unresolved first oxidation potential. In complex 4, the TTF cores are also equivalent and the conformation of the TTF cores is not constrained by the presence of PPh$_3$ groups. Interestingly, the SOMO of complex 3$^{+}$ is perfectly symmetric with a main contribution of two equivalent TTF cores. The spin density in the mono-oxidized species 3$^{+}$ is essentially localized on the TTF fragments with a slight delocalization on the organometallic bridge.

Contrary to complexes 2 and 4, complex 3 presents two resolved sequential oxidations. This peculiar electrochemical behavior is likely due to geometrical constraints and interactions with the phenyl groups of the structurally blocked and distorted dppe ligand. For all complexes, the lack of effect of the poorly coordinating electrolyte$^{29}$ on the splitting of the first wave and the lack of spectroscopic evidence for intervalence charge transfer excludes a strong interaction between the two TTF moieties and lends more support to the proposed explanation based on the demonstrated structural non-equivalence of the two organic electrophores.

Conclusions

In summary, we have presented a series of cis and trans platinum complexes bearing two TTF-ligands. Four complexes, cis-Pt(tBu$_2$biy)(C==CMe$_2$TF)$_2$ (2), cis-Pt(tBu$_2$biy)(C==CMe$_2$TF)$_2$ (1), cis-Pt(dppe)(C==CMe$_2$TF)$_2$ (3) and trans-Pt(PPh$_3$)$_2$-bis(C==CMe$_2$TF)$_2$ (4), were readily synthesized and characterized in order to study the influence of the nature of the L-ligands and the cis/trans geometry of the acetylide ligands on the electronic properties of the complexes. The luminescence of the bipy–platinum–alkyne fragment is quenched in the neutral state by intramolecular photoinduced electron transfer from TTF donors. However, chemical oxidation of the TTF moieties by NOPF$_6$ or FeCl$_3$ did not restore the luminescence properties of the diimine–platinum–acetylide complex. The luminescence of the oxidized complex is most likely quenched by energy transfer toward the formed TTF$^{+}$ radical cation. Electrochemical measurements and DFT calculations have revealed that in complexes 2 and 4, the two TTF units on each complex are equivalent and are oxidized to the radical cation at closely spaced and unresolved potentials. No evidence of electronic communications between the two TTF units through the organometallic fragment was found in these complexes, especially no intervalence charge-transfer (IVCT) bands are

TTF core with no contribution from the alkyne.$^{5,8}$ The SOMOs (highest singly occupied molecular orbitals) of the oxidized complexes 2$^{+}$ and 4$^{+}$ are essentially localized on the TTF cores with no contribution from the platinum center. The calculated spin densities of complexes 2$^{+}$ and 4$^{+}$ appear to be delocalized over the whole molecule with however weaker contribution of the organometallic bridge. The poor delocalization through the acetylide–platinum–acetylide organometallic linker in the cation radical is consistent with the unresolved first oxidation measured electrochemically (low $\Delta E$). Results obtained with complexes 2 and 4 are quite similar regardless of the cis or trans arrangement with even poorer contribution of the organometallic linker in the spin density of 2$^{+}$.

DFT calculations performed on complex 3 reveal that the HOMO is disymmetric with the electronic density localized on one of the two TTF cores (Fig. 9). Such dissymmetry is
Fig. 8 Graphical representations of the HOMO and SOMO of complexes 2 and 4 shown with a cut-off of 0.04 [e bohr$^{-3/2}$] and spin density of the mono-oxidized complexes 2$^{+*}$ and 4$^{+*}$ shown with a cut-off of 0.001 e bohr$^{-3}$.

Fig. 9 Graphical representations of the HOMO and SOMO of complexes 3 and 3$^{+*}$ shown with a cut-off of 0.04 [e bohr$^{-3/2}$] and spin density of the mono-oxidized complexes 3$^{+*}$ shown with a cut-off of 0.001 e bohr$^{-3}$. 
observed during the spectroelectrochemical studies. Based on these preliminary measurements, we conclude that alkynyl-platinum fragments do not allow efficient electronic communications between the two organic electrophores in contrast to alkynyl–ruthenium fragments. DFT calculations show a dissymmetry of the two TTF ligands in complex 3 also observed in the crystal structure. This is proposed to account for the more pronounced splitting of the first oxidation wave, as strong electronic coupling was ruled out by spectroelectrochemical investigations.

**Experimental section**

**General**

NMR spectra were recorded on a Bruker AV300III spectrometer at room temperature using perdeuterated solvents. Chemical shifts are reported in ppm referenced to TMS for $^1$H NMR, $^{13}$C NMR and to H$_2$PO$_4$ for $^{31}$P NMR. FT-IR spectra were recorded using a Varian-640 FT-IR spectrometer equipped with a PIKE ATR apparatus. Fluorescence spectra were recorded on a Fluorolog-3 fluorescence spectrometer (FL3-22, Horiba Jobin Yvon) with 1 cm quartz cells. Mass spectra were recorded with a Bruker MicroTOF-Q II instrument for complexes 1, 3 and 4 and with a Micromass ZABSpecoaTOF instrument for complex 2 by the Centre Régional de Mesures Physiques de l'Ouest, Rennes. CVs were carried out on a potensiostat from EG&G Instruments was used to set the applied potential and a Cary 5 spectrophotometer was employed to record the UV-vis-NIR spectra. All experiments were performed at room temperature using perdeuterated solvents. Chemical shifts are reported in ppm referenced to TMS for $^1$H NMR, $^{13}$C NMR and $^{31}$P NMR. NMR spectra were recorded on a Bruker AV300III spectrometer (400 MHz) and with a Micromass ZABSpecoaTOF instrument for complex 2 by the Centre Régional de Mesures Physiques de l'Ouest, Rennes. Chemical shifts are reported in ppm referenced to TMS for $^1$H NMR, $^{13}$C NMR and $^{31}$P NMR. NMR spectra were recorded on a Bruker AV300III spectrometer (400 MHz) and with a Micromass ZABSpecoaTOF instrument for complex 2 by the Centre Régional de Mesures Physiques de l'Ouest, Rennes.

**Complex 1**

$^{58}$ cis-Pt(bipy)($C=CMMe$_3$TF)$_2$. Pt(bipy)Cl$_2$ (47 mg, 0.11 mmol) was reacted with HC=CMMe$_3$TF (60 mg, 0.22 mmol) in distilled CH$_2$Cl$_2$ (10 mL) in the presence of freshly-distilled NEt$_3$ (5 mL) and CuI (4 mg, 0.022 mmol) as a catalyst. The reaction mixture was stirred under an inert nitrogen atmosphere at room temperature for 2 h. A black precipitate was filtered off and washed with methanol and CH$_2$Cl$_2$. After drying, 65 mg of black powder were isolated (yield = 65%). Single crystals were harvested by slow cooling of a clear hot DMF solution of 1. Due to its low solubility complex 1 could not be characterized by $^{13}$C NMR. $^1$H NMR (hot D$_2$O–DMSO) (ppm) 1.94 (s, 12H, CH$_2$), 2.26 (s, 6H, CH$_3$), 7.91 (m, 2H, CH), 8.42 (m, 2H, CH), 8.67 (m, 2H, CH), 9.30 (m, 2H, CH). IR (ATR): 2090 cm$^{-1}$ (υ(C=O)).

**Complex 2**

$^{59}$ cis-Pt(bBu$_2$bipy))($C=CMMe$_3$TF)$_2$. Pt(bBu$_2$bipy)Cl$_2$ (99 mg, 0.185 mmol) and HC=CMMe$_3$TF (100 mg, 0.37 mmol) were dissolved in distilled CH$_2$Cl$_2$ (10 mL) in a Schlenk tube. Nitrogen was bubbled through the mixture for 30 min, after which CuI (7 mg, 0.037 mmol) and freshly-distilled NEt$_3$ (5 mL) were added and the mixture stirred at room temperature for 24 h. The solvent was rotary evaporated and the residue treated with water and extracted with CH$_2$Cl$_2$. The organic layer was washed with water and dried over MgSO$_4$. The residue was purified by column chromatography on silica gel with CH$_2$Cl$_2$ as the eluent. The product was isolated as a red powder in 61% yield (0.10 g). Single crystals were obtained by slow evaporation of a concentrated CH$_2$Cl$_2$ solution of 2. $^1$H NMR (CDCl$_3$) (ppm) 1.47 (s, 18H, CH$_2$), 2.21 (s, 6H, CH$_3$), 7.54 (m, 2H, CH), 7.99 (m, 2H, CH), 9.34 (m, 2H, CH). $^{13}$C NMR (CDCl$_3$) (ppm) 12.7, 29.2, 34.8, 93.7, 118.1, 121.5, 121.7, 123.6, 149.7, 151.5, 162.5; IR (ATR): 2091 cm$^{-1}$ (υ(C=O)).

**Complex 3**

$^{60}$ cis-Pt(dppe)($C=CMMe$_3$TF)$_2$. cis-Pt(dppe)Cl$_2$ (100 mg, 0.15 mmol) was introduced in a Schlenk tube with HC=CMMe$_3$TF (81 mg, 0.30 mmol) in distilled CH$_2$Cl$_2$ (10 mL) in the presence of freshly-distilled NEt$_3$ (5 mL) and CuI (6 mg, 0.030 mmol) as a catalyst. The reaction mixture was stirred under an inert nitrogen atmosphere at room temperature for 12 h. The solvent was evaporated and the residue treated with water and extracted with CH$_2$Cl$_2$. The organic layer was washed with water and dried over MgSO$_4$. Complex 3 was precipitated by slow diffusion of pentane into a CH$_2$Cl$_2$ solution of the crude product. The complex was finally crystallized by slow evaporation of a concentrated CH$_2$Cl$_2$ solution (reddish-brown crystals, m = 45 mg, yield = 30%). $^1$H NMR (CDCl$_3$) (ppm) 1.91 (br, 18H, CH$_3$), 2.40 (m, 4H, CH$_2$), 7.44 (m, 12H, CH), 7.82 (m, 8H, CH); $^{13}$C NMR (CDCl$_3$) (ppm) 13.6, 15.5, 122.4, 128.8, 129.0, 131.4, 133.3, 133.5; $^{31}$P NMR (CDCl$_3$) (ppm) 41.2 (s, 2P, J$_{P}$, J$^{31}$P = 2298 Hz); IR (ATR): 2092 cm$^{-1}$ (υ(C=O)). HRMS (ESI): m/z calcd for C$_{48}$H$_{42}$N$_{4}$S$_{2}$P$_{2}$: 1007.740. Found: 1007.740.

**Complex 4**

$^{61}$ trans-Pt(PPPh$_3$)$_2$(C=CMMe$_3$TF)$_2$. cis-Pt(PPPh$_3$)$_2$Cl$_2$ (100 mg, 0.13 mmol) and HC=CMMe$_3$TF (68 mg, 0.26 mmol) were dissolved in a mixture of dry CH$_2$Cl$_2$ (10 mL) and distilled NEt$_3$ (5 mL) inside a Schlenk tube. The solution was degassed and CuI (5 mg, 0.026 mmol) was added. After stirring for 48 h at room temperature, a red precipitate appeared. After...
filtration, the red precipitate was washed with cold CH$_2$Cl$_2$. The material was dissolved in CH$_2$CN and red crystals were grown by slow diffusion of diethyl ether ($m = 90$ mg, 57% yield). Due to its low solubility complex 4 could not be characterized by $^{13}$C NMR. $^1$H NMR (CDCl$_3$) $\delta$ 1.90–1.95 (br, 18H, CH$_3$)$_3$, 7.39–7.73 (m, 30H, CH); IR (ATR): 2086 cm$^{-1}$; $^{31}$P NMR (CDCl$_3$) $\delta$ 18 [s]. HRMS (ESI): $m/z$ calcd for C$_{38}$H$_{48}$P$_2$S$_4$ $^{194}$Pt 1256.0518. Found: 1256.0618.

X-Ray crystallography

Details of the structural analyses for 1, 2, 3 and 4 are summarized in Table 3. X-Ray crystal structure determinations were performed on an APEXII Bruker-AXS diffractometer equipped with a CCD camera and a graphite-monochromated Mo K$\alpha$ radiation source ($\lambda = 0.71073$ Å), from the Center de Diffraction-métrie (CDFIX), Université de Rennes 1, France. Structures were solved by direct methods using the SHELXS-97 program, and then refined with full-matrix least-squares methods based on $F^2$ (SHELXL-97) with the aid of the WINGX program. For complexes 2 and 3, the contribution of the disordered solvents to the calculated structure factors was estimated following the BYPASS algorithm, implemented as the SQUEEZE option in PLATON.$^{37}$ A new data set, free of solvent contribution, was then used in the final refinement. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions.

Computational details

Density functional theory$^{38}$ calculations were performed with the hybrid Becke-3 parameter exchange functional$^{39}$ and the Lee–Yang–Parr nonlocal correlation functional$^{40}$ (B3LYP) implemented in the Gaussian 03 (revision D.02) program suite$^{41}$ using the LANL2DZ basis set$^{42}$ with the default convergence criteria implemented in the program. The figures were generated with Molekel 4.3.$^{43}$ Computational details are provided as ESL.$^†$

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