Synthesis and Properties of a Mixed-Valence Compound with Single-Step Tunneling and Multiple-Step Hopping Behavior


Keywords: Mixed-valent compounds / Hybrid materials / Iron / Molecular electronics / Conjugated systems

The organic precursor bis(trimethylsilylethynyl)TTFMe2 (3, TTF = tetrathiafulvalene) was prepared as a 1:1 mixture of the cis and trans isomers. Pure samples of 3-cis and 3-trans were obtained by crystallization and identified by XRD analysis. The treatment of pure 3-cis and a 1:1 mixture of 3-cis/trans with (i) potassium carbonate, (ii) the iron complex Cp*(dppe)FeCl [Cp* = η5-C5Me5, dppe = 1,2-bis(diphenylphosphanyl)ethane] in the presence of KPF6, and (iii) tBuOK provided Cp*(dppe)Fe–C–C–TTFMe2–C–Fe(dppe)Cp* as the pure geometric isomer 6-trans (85%) and as the 60:40 mixture 6-cis/trans (63%), respectively. The oxidation of 6-trans with [Fe(C5H4)2]PF6 gave [6-trans][PF6]6 (n = 1–3). Visible, IR, near-IR (NIR), and electron paramagnetic resonance (EPR) spectroscopy together with DFT data show that [6-trans][PF6]6 is a class II mixed-valence complex (Hab = 85 cm–1) in which the spin distribution depends on the conformation of the molecule. Intramolecular electron transfer occurs through single-step tunneling and a multistep hoping mechanism. The triplet state is thermally accessible for [6-trans][PF6]2.

Introduction

Dimetallic complexes with a π-conjugated carbon bridge have attracted great attention in recent years because of their potential applications in molecular electronics as building units in molecular scale electronic materials and nanotechnological devices. Much of this interest in these compounds, which are often called molecular organometallic wires, has been prompted by the rich redox chemistry of different metal termini[1,2] and the efficiency of diverse bridges[3,4] to promote electronic communication in mixed-valence species, that is, compounds with two or more redox sites in different oxidation states. We have shown that species containing redox-active Cp*(dppe)Fe fragments [Cp* = η5-C5Me5, dppe = 1,2-bis(diphenylphosphanyl)ethane] linked to π-conjugated polyyne linkers are ideally suited for studies of electronic and magnetic coupling between the redox centers.[4–6] These assemblies are usually stable (and isolable) in different redox states, and the polyyne linker is a particularly efficient mediator of electron transfer from one end to the other. The reason for this efficiency is the good match in energy between the Fe d orbitals and the π highest occupied molecular orbitals (HOMOs) of the carbon bridging ligand, which permits superexchange electron-transfer processes.[7] However, previous studies have demonstrated that the length expansion of polyyne linkers is limited by the poor chemical stability of the oxidized species.[7,8] Therefore, the introduction of aromatic rings such as thiophene or benzene [(Cp*dppe)Fe–C–C–(1,4-C6H4)–C–Fe(dppe)Cp*][PF6]6 (7) constitutes a well-known example[9,10] in the polyyne spacer is an attractive alternative to circumvent this instability as well as to tune the physical properties of the assemblies.[9,11,12]

Consequently, the various new nonlinear geometries that can be envisioned for different carbon-rich spacers lead to structural variation, which can deeply modify the electronic and magnetic properties of the molecules both in the bulk and at the single-molecule level.[5,7,13]

The incorporation of functional groups into the bridge between the redox centers and control of the molecular topology open routes to functional molecules with oriented electron-transfer capabilities,[14,15] switching abilities,[16] multipath connections[12,17] optical activities,[18,19] or magnetic properties.[5,12,20] Recently, it was shown that the 1′,1′′-biferrocenyl (bfc) unit in the family of complexes [Cp*(dppe)Fe–C–C–bfc–C–Fe(dppe)Cp*][PF6]n (8) acts as a molecular relay and mediates electron transfer.
between the two ends of the molecule by hopping processes.[21,22]

Simultaneously, efforts were also directed toward the construction of molecular compounds with substituted tetrathiafulvalene (TTF) electrophores and the exploration of the new properties arising from mutual d–π interactions within hybrid inorganic and organic components.[23,24] Owing to the unique properties of some TTF derivatives as organic metals, superconductors, and semiconductors, this promising approach has stimulated an increasing amount of research.[25]

In the context of our interest in the construction of molecular circuits incorporating several redox-active components, we have previously prepared the hybrid complexes \([\text{Cp}^*(\text{dppe})\text{Fe}–\text{C}_6\text{H}_2\text{N(Me)}_3][\text{PF}_6]_n\) (9)[PF$_6$], \(n = 0, 1, 2\). In this compound, two electroactive units, namely, the TTF and FeCp*(dppe) groups, are linked by an ethynyl bridge to favor π–d interactions between them. All experimental and theoretical data obtained for 9[PF$_6$] indicate that the relaxation of the molecular structure is characterized by an increase of the Fe–C bond order after one-electron oxidation with the localization of the positive charge on the iron nuclei and the delocalization of the spin density on the whole molecule. In the radical cation, the interaction between the iron center and the TTF fragment is much stronger than in the neutral species. Analysis of the ligand-to-metal charge-transfer (LMCT) transition by methods similar to those employed for mixed-valence complexes gives a coupling constant \(H_{\text{ab}} = 320 \text{ cm}^{-1}\), which is consistent with values obtained for typical class II mixed-valence (MV) systems. Furthermore, the dicationic species 9[PF$_6$]$_2$ was generated in situ and characterized by IR, near-IR (NIR), and electron paramagnetic resonance (EPR) spectroscopy.[24]

Finally, the synthesis and characterization of the three multicomponent molecular assemblies \([\text{Cp}^*(\text{dppe})\text{Fe}–\text{C}_6\text{H}_2\text{N(Me)}_3][\text{PF}_6]_n\) (10)[PF$_6$], \(n = 0, 1, 2\) has been reported.[26] The experimental data were analyzed with the support of a theoretical study performed at the DFT level on the full structures. It was concluded that the neutral complex shows the structure of a bis[alkynyl–iron(II)] complex connected by a bridge containing six sp$^2$ carbon atoms. In contrast with all previous work on dinuclear derivatives of this \([\text{Cp}^*(\text{dppe})\text{Fe}–\text{C}_6\text{H}_2\text{N(Me)}_3][\text{PF}_6]_n\) series,[7] the two one-electron oxidations of 10 do not change the oxidation state of the iron nuclei and are clearly bridge-centered, as unambiguously established by Mössbauer spectroscopy. With five components, namely, the two Fe centers, the two TTFMe$_2$ moieties, and the connecting organic bridge, the mixed-valence 10[PF$_6$] strongly differs from related mixed-valence metal–organic bridge–metal systems and, to the best of our knowledge, is unprecedented. The involvement of all these components in the electron-transfer process renders the usual Hush–Marcus two-center model inappropriate.[26,27]

Intrigued and motivated by the surprising properties of 10, we decided to prepare the similar but simpler compound 6, which contains only one TTF fragment. Here, we report the preparation of 6 as a cis/trans mixture and 6-trans as a pure compound. The redox and spectroscopic properties of 6-trans were investigated, and the associated mono-, di-, and tricationic oxidized species were prepared and briefly characterized by appropriate spectroscopic means. The main results are discussed.

Results and Discussion

1. Synthesis of Me$_3$Si–C=–TTFMe$_2$–C=–SiMe$_3$ and Separation of the trans and cis Isomers

The TTF derivative 4, which is the precursor of the bridging ligand between two iron centers of the title complex, was prepared as shown in Scheme 1. Namely, a 1:1 cis/trans mixture of TTFMe$_2$ (1-cis/trans) was diluted with an excess of lithium disopropylamide (LDA) and then treated with perfluorohexyl iodide to yield TTFMe$_2$I$_2$ (2-cis/trans).[28] This iodine-substituted compound was then coupled with trimethylsilylacetylene through a Sonogashira reaction.[29]
showed that these were ethanol solution, and single-crystal X-ray structure analysis. Orange elongated plates were obtained by cooling a hot can be separated by repeated recrystallization from ethanol. [31] This difficulty with respect to the methyl groups was inevitable. These two isomers cannot be separated either by crystallization or by chromatography, in contrast to the similar disubstituted molecules cis- and trans-DDT [28] which can be separated by repeated recrystallization from ethanol. [32] This difficulty in isomer separation persists in the iodine-substituted compounds TTFMe2I2. However, the cis and trans isomers of 3 can be separated by repeated recrystallization from ethanol. Orange elongated plates were obtained by cooling a hot ethanol solution, and single-crystal X-ray structure analysis showed that these were 3-trans [Figure 1 (top) and Supporting Information]. Dark red needles were grown by slowly evaporating the mother liquor at room temperature after the recovery of the trans isomer. An X-ray crystal structure analysis revealed that these needles were 3-cis [Figure 1 (bottom) and Supporting Information]. The difference in solubility between these two isomers in ethanol may be explained by the density of crystals; the less soluble trans isomer has a higher density (Dcalcd. = 1.202 g cm−3) than that of the cis isomer (Dcalcd. = 1.176 g cm−3), which is more soluble in organic solvents.

As the starting material TTFMe2 was obtained by a base-induced homocoupling reaction of 4-methyl-1,3-dithiolium iodide, [30] a mixture of trans and cis isomers with respect to the methyl groups in isomer separation persisted in the iodine-substituted compounds. However, the cis and trans isomers of 3 can be separated by repeated recrystallization from ethanol. Orange elongated plates were obtained by cooling a hot ethanol solution, and single-crystal X-ray structure analysis showed that these were 3-trans [Figure 1 (top) and Supporting Information]. Dark red needles were grown by slowly evaporating the mother liquor at room temperature after the recovery of the trans isomer. An X-ray crystal structure analysis revealed that these needles were 3-cis [Figure 1 (bottom) and Supporting Information]. The difference in solubility between these two isomers in ethanol may be explained by the density of crystals; the less soluble trans isomer has a higher density (Dcalcd. = 1.202 g cm−3) than that of the cis isomer (Dcalcd. = 1.176 g cm−3), which is more soluble in organic solvents.

An optimally resolved 1H NMR spectrum of 3 as a cis/trans mixture allows the observation of two resolved singlets for the resonances of the trimethylsilyl groups at δ = 0.23 and 0.24 ppm. However, although 1H NMR spectroscopy can be helpful in this chemistry to show the presence of both isomers, this technique does not allow a safe identification of pure samples containing only one isomer because their chemical shifts are too close. X-ray molecular structure determination constitutes the unique and unequivocal means to determine the geometry of the molecule within each crystal form and has allowed great progress to be made in this study as described below.

2. Synthesis and Characterization of [{Cp*(dppe)Fe–C=C–C}2(TTFMe2)] (6-trans)

The capability of the iron(II) chloride complex Cp* (dppe)FeCl (5) [32] to activate terminal alkynes was extensively exploited to prepare iron(II) alkynyl complexes in this series. [4,7,33] The iron vinylidene intermediate that results from the 1,2-shift of a terminal proton can be either reacted in situ with a base to give the target alkyne 6-trans or isolated as a salt for purification. By following this general procedure, which was previously used successfully to prepare the mononuclear complex [Cp*(dppe)Fe–C=C–C]2(TTFMe2) [9], [24] the freshly prepared terminal bis(alkyne) 4-trans was treated with 2.1 equiv. of 5 in a 2:1 MeOH/ tetrahydrofuran (MeOH/THF) mixture at 20 °C for 72 h. The brown suspension was then reacted with a small excess of tBuOK (2.3 equiv.) and the progressive appearance of an orange suspension was observed. After workup, 6-trans was isolated in 85% yield as an air- and moisture-sensitive orange powder (Scheme 2). An ESI+ mass spectrum of 6-trans showed the expected parent ion, and the microanalysis was satisfactory. Well-resolved 1H, 13C, and 31P NMR spectra were obtained and confirmed the structure of 6-trans. The most striking features of the 1H NMR spectrum include the Cp* methyl singlet at δ = 1.46 ppm, the single methyl resonance at δ = 1.73 ppm, and the two unresolved dppe methylene multiplets at δ = 1.84 and 2.96 ppm. The 31P NMR spectrum displayed one singlet at δ = 100.35 ppm, which is upfield shifted with respect to that of the mononuclear complex 9 (Δδ = 2.19 ppm). [24] Finally, the 13C NMR spectrum showed the resonances characteristic of the methyl substituent of the TTFMe2 moiety (δ = 14.59 ppm) and the Cp* ligand (δ = 87.78 and 10.04 ppm).

Figure 1. Molecular structures of 3-trans (top) and 3-cis (bottom) showing thermal ellipsoids at the 50% probability level.
As 3-cis was only available in very small amounts, the synthesis of 6-cis could not be achieved. However, the preparation of 6 was attempted from a 1:1 cis/trans mixture of terminal bis(alkyne) 4. By following the procedure optimized for 6-trans, a mixture of the geometric isomers 6-cis and 6-trans in a 1:1 ratio was isolated but with a lower overall yield (63%). The IR spectrum of the mixture is identical to that of pure 6-trans. The $^{31}$P and $^1$H NMR spectra display two sets of signals corresponding to the two isomers. The spectra of the cis isomer contain a larger number of resonances than those of the trans congener, reflecting the presence of observable rotamers for this complex.

The $^{31}$P NMR spectrum of 6-cis is characterized by three resonances at $\delta = 100.11$, 100.22, and 100.39 ppm with relative intensities of 5:5:4. The multiplicity of the signals results from the presence of several rotamers with different symmetries. In particular, rotamers 6-cis a, 6-cis a', and 6-cis b are in equilibrium and slowly interconvert on the NMR timescale (Scheme 3). In rotamers 6-cis a and 6-cis a', the two Cp* or dppe ligands are both oriented toward the methyl substituents of the TTFMe$_2$ core and, thus, they are magnetically equivalent and resonate as a singlet ($\delta = 100.39$ ppm). A rotation of 180° of one metal fragment provides the rotamer 6-trans b and renders the dppe (and also the Cp* and CH$_3$ groups) inequivalent. The two inequivalent dppe ligands resonate as two singlets with the same intensity ($\delta = 100.11$ and 100.22 ppm).

Scheme 3. Selected rotamers of 6-cis.

The $^1$H NMR spectrum of 6-cis gives further support for the existence of these rotamers with a slow interconversion regime on the NMR timescale. The equivalent methyl substituents of the rotamers 6-cis a and 6-cis a' resonate as a singlet ($\delta = 1.724$ ppm), whereas two singlets with the same intensity are observed for the methyl groups of the rotamer 6-cis b ($\delta = 1.696$ and 1.755 ppm). From the integration of these three resonances, the ratio 6-cis a + 6-cis a'/6-cis b was determined to be 1:2, which suggests that the population of the three conformers is close to the 1:1:4. Therefore, the 6-cis b isomer is probably slightly more stable than the 6-cis a and 6-cis a' isomers.

Analysis of the resonances of the Cp* ligands is less straightforward. In the $\delta = 1.44–1.48$ ppm range, three peaks are observed at $\delta = 1.449$, 1.456, and 1.464 ppm with relative intensities of ca. 1:2:1. The central and more-intense signal corresponds to the Cp* ligand of 6-trans. The side signals with the same intensity can be safely ascribed to the b rotamers of 6-cis. The Cp* resonance expected for rotamers 6-cis a and 6-cis a' is probably hidden by the resonance of the 6-trans isomer. The determination of the 6-cis/6-trans ratio gives substance to this assumption. From the integration of the well-resolved methyl resonances, a 6-cis/6-trans ratio of 60:40 was determined. The same ratio was also found from the assumption that the resonance at $\delta = 1.456$ ppm corresponds to the Cp* ligand of 6-trans and 1/3 of 6-trans (rotamers 6-cis a and 6-cis a').

The more-complex NMR spectrum for 6-cis is perhaps caused by steric interactions between the Cp*(dppe)Fe fragments, in contrast with the free rotation of the metal groups in 6-trans. In this respect, it is interesting to note that NMR investigations of the dinuclear complex $[\text{Cp}^*(\text{dppe})\text{Fe–C=C}]=_{2}(3,4-\text{C}_9\text{Ar}_2)[\text{PF}_6]_2$ ($\text{Ar} = \text{C}_9\text{H}_5$) have also shown that the iron building blocks rotate slowly around the cyclobutene ring on the NMR timescale, which allows the observation of rotamers.$^{[34]}$

Unfortunately, single crystals of 6-trans of sufficient quality could not be grown. The utility of density functional theory (DFT) has been previously demonstrated for the calculation, with good confidence, of the geometries of organometallic molecules for which X-ray data are not
of FeII centers in pseudooctahedral environments.[26] Upon oxidation, the metal–ligand distances are characteristic of FeIII centers in pseudooctahedral environments.[26] Upon oxidation, the metal–ligand and Fe–P distances for [6-trans]+ are longer than those computed for the neutral system by 0.012 and 0.022 Å, respectively. Upon oxidation, the Fe–C and C=C bonds are shortened and lengthened, respectively. The TTFMe2 distances are also affected upon oxidation, and the central carbon bond is shortened by 0.018 Å from 6-trans to [6-trans]+.

The HOMO and HOMO–1 of the neutral complex 6-trans are shown in Figure 2. As is commonly observed for related iron–alkynyl complexes, the HOMO and HOMO–1 are π/σ type in character, antibonding between the iron centers and their first adjacent carbon atoms, and bonding between the carbon atoms of the triple bond. However, the HOMO is heavily TTFMe2 in character (ca. 80%) with a relatively small contribution from the Fe–C=C moiety (12%), whereas the HOMO–1 is mainly localized on the iron centers (44%) and to a lesser extent on the TTFMe2 unit (21%).

3. Cyclic Voltammetry of 6-trans and Synthesis of the Oxidized Species [6-trans][PF6]2 (α = 1–3)

The initial scan in the cyclic voltammogram (CV) of 6-trans from –1 to +1 V shows three chemically reversible waves and one quasireversible wave separated by 0.12, 0.52, and 0.43 V, respectively (Figure 3). The currents of the four redox events have the same intensity and can be assigned to the sequential reversible oxidation of the first and second [Cp*(dppe)FeII/III] termini, [TTFMe2]0/+ and [TTFMe2]+/2+, respectively, on the basis of their potentials (Table 1). The first oxidation potential of 6-trans is shifted toward negative values with respect to that of its mononuclear relative 9 (ΔE0 = 0.15 V)[24] which suggests that the two iron–alkynyl termini are electronically coupled through the TTFMe2 bridge. Accordingly, the second oxidation wave, which corresponds to the sequential oxidation of the second iron end group, is shifted toward positive potential (E02 – E01 = 0.12 V). The wave separation corresponding to the iron-centered events is smaller than that in the bis(iron) 7 (E02 – E01 = 0.26 V)[9] but much larger than that in 8 (E02 – E01 = 0.00 V).[122] Apparently, the TTF core acts as a better electronic coupler than the bfc unit. Moreover, the third oxidation, which should be TTFMe2-centered, is found at a less-positive potential than that in the corresponding organic compound 3 [E03 (6) – E03 (3) = –0.03 V]. These data match very well with the conclusion drawn from the analysis of the redox potentials of 9, which have shown that the oxidized [Cp*(dppe)FeIII-C=C]1+ moiety does not act as an electron-withdrawing group with respect to the TTFMe2 part but rather as a weakly electron-donating fragment.[24]

Figure 3. CV of 6-trans (10−3 m solution in CH2Cl2 at 298 K, 0.1 m [nBu4N][PF6], scan rate 0.100 Vs−1).

Table 1. Comparison of the electrochemical potentials [V] for 6-trans and other selected compounds.[a]

<table>
<thead>
<tr>
<th>Compound</th>
<th>E0 (ΔE0)</th>
<th>E1 (ΔE1)</th>
<th>E2 (ΔE2)</th>
<th>E3 (ΔE3)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-trans</td>
<td>–0.26 (0.07)</td>
<td>–0.14 (0.10)</td>
<td>0.37 (0.12)</td>
<td>0.80 (0.20)</td>
<td>this work</td>
</tr>
<tr>
<td>3</td>
<td>–</td>
<td>–</td>
<td>0.40 (0.12)</td>
<td>0.90 (0.12)</td>
<td>this work</td>
</tr>
<tr>
<td>7</td>
<td>–0.27 (0.06)</td>
<td>–0.01 (0.06)</td>
<td>–</td>
<td>–</td>
<td>[9,10]</td>
</tr>
<tr>
<td>8</td>
<td>–0.23 (0.11)</td>
<td>0.49 (0.07)</td>
<td>0.78 (0.07)</td>
<td>–</td>
<td>[22]</td>
</tr>
<tr>
<td>9</td>
<td>–0.11 (0.07)</td>
<td>0.38 (0.07)</td>
<td>0.84 (0.08)</td>
<td>–</td>
<td>[24]</td>
</tr>
<tr>
<td>10</td>
<td>–0.29 (0.10)</td>
<td>0.10 (0.09)</td>
<td>0.66 (0.07)</td>
<td>0.87 (0.06)</td>
<td>[26]</td>
</tr>
</tbody>
</table>

[a] Potentials in CH2Cl2 {0.1 m [nBu4N][PF6], 25 °C, platinum electrode, sweep rate 0.100 V s−1, vs. saturated calomel electrode (SCE); the ferrocene/ferrocnium couple (0.460 V vs. SCE) was used as an internal standard for the potential measurements}.[35] [b] A two-electron event.

Examination of the different redox events showed that the peak-to-peak separation progressively increases as the number of charges on the complex increases. Probably, the accumulation of charges on the molecule makes electron transfers slower and slower and produces deeper and deeper structural reorganizations.

The analysis of the peak currents shows that the anodic and cathodic intensities are strictly identical for the four waves, so that the electron-deficient cations [6-trans]+, [6-trans]2+, [6-trans]3+, and [6-trans]4+ are apparently stable at the platinum electrode. Consequently, the complexes [6-trans][PF6], [6-trans][PF6]2, and [6-trans][PF6]3 were regarded as synthetic targets that would be accessible with ferrocenium salt as the oxidizing reagent. According to the established procedure, complex 6-trans was treated with 2.0 equiv. of [(C6H5)2Fe][PF6] in THF at –60 °C. Upon gradual warming to room temperature, the thermally stable dication formed. Partial precipitation and crystallization provided a pure sample of [6-trans][PF6]2, which was iso-

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lated in good yield (90%) as a dark purple powder. The monocationic complex [6-trans][PF₆] was prepared by a comproportionation reaction between the neutral complex 6-trans and its doubly oxidized relative [6-trans][PF₆]₂. The mixed-valence complex was isolated as a dark purple powder in 93% yield. For solubility purposes, the synthesis of the tricationic [6-trans][PF₆]₃ complex was performed in N,N-dimethylformamide (DMF) by treatment of the neutral complex 6-trans with 3 equiv. of [(C₅H₅)₂Fe][PF₆]. The [6-trans][PF₆] complex was isolated as a dark blue powder (90% yield). As expected, the CVs of the three oxidized complexes are identical to that of the neutral derivative 6-trans. These salts were characterized by FTIR and EPR spectroscopy, complemented by the UV/Vis and NIR absorption spectroscopy.

By the same procedure, a mixture of 6-cis/trans in a 60:40 ratio was subjected to a one-electron oxidation by treatment with 1 equiv. of [(C₅H₅)₂Fe][PF₆] in THF at –60 °C. The monocationic complex [6][PF₆] was isolated as a mixture of its cis and trans isomers. The IR spectrum is identical to that of [6-trans][PF₆] (see below). The resulting product was subjected to reduction by treatment with an excess of tBuOK in THF at –60 °C. After workup, complex 6 was isolated as an orange powder, and the cis/trans ratio was found to be unchanged by--------------------------------

4. IR Spectroscopy of [6-trans][PF₆]ₙ (n = 0–3)

The IR spectra of the [Cp⁺(dppe)FeHII–C=C–] acet- ylides display ν_{C–C} stretching modes at a frequency that is dependent on the oxidation state of the metal center and the electronic nature of the appended substituent. Its evolution has been qualitatively rationalized by a valence bond (VB) formalism.[33,37–39] The IR spectra of solid-state samples of [6-trans][PF₆]ₙ (n = 0–3) are displayed in Figure 4, and the bands in the 2100–1600 cm⁻¹ range are collected in Table 2, together with those previously reported for the reference compounds 7[PF₆]ₙ, 8[PF₆]ₙ, 9[PF₆]ₙ, and 10[PF₆]ₙ (n = 0–3) for comparison.

The complex 6-trans is characterized by a strong absorption band at 2018 cm⁻¹, a frequency very close to that found for 9 (Δν = 4 cm⁻¹). In comparison with other members of the [Cp⁺(dppe)FeHII–C=C–R] family, the frequency is relatively low (see representative examples 7 and 8).[40,41] These data suggest that the C=C bond order of the alkynyl linker is probably weakened by the presence of the TTFMe₂ moiety. Considering the electron-donating properties of the TTF derivative, an increase rather than a decrease of the C=C frequency could be expected. However, this finding is consistent with previous data for 9, which showed that the TTFMe₂ moiety acts as a very weak electron-releasing substituent vis-à-vis the Cp⁺(dppe)FeHII-C=C group.[24]

Upon double one-electron oxidation, the IR absorption of the ν_{C–C} stretch of [6-trans][PF₆]ₙ is shifted to lower wavenumber. This shift follows the same trend as previous observations. However, its amplitude is exceptionally large in the present case (Δν(6-trans) = 128 cm⁻¹), much larger than those in 7 (Δν(7) = 54 cm⁻¹) and 8 (Δν(8) = 81 cm⁻¹; see Table 2). As the potentials of the redox couples [6-trans][PF₆]₁/₂ and 7[PF₆]₁/₂ are close to each other, similar decreases of the ν_{C–C} frequencies are expected for these two families of complexes. Indeed, oxidation provokes a decrease of the IR frequency of the C=C bond, and the magnitude of the shift that depends on the electron-donating character of the substituent attached to the iron acetylide.[30,40] This effect probably reflects the very good electronic coupling between the iron–acylidyne groups and the TTFMe₂ moiety [Δν(9) = 105 cm⁻¹][26] but also suggest that a weak metal–metal coupling might also occur through the TTFMe₂ bridge.

The IR spectrum of the mixed-valence complex shows two bands at intermediate frequencies with respect to those observed for the homovalent complexes 6-trans and [6-trans][PF₆]. The mixed-valence complex [6-trans][PF₆] features localized iron(II) and iron(III) alkynyl centers on the IR timescale and, consequently, can be recognized as a class II mixed-valence complex as proposed by Robin and Day.[42] This behavior was confirmed by the electronic spectrum of the radical cation in the NIR range (see Section 7).
The tricationic [6-trans][PF6]3+ is characterized by a unique stretching band at a frequency almost identical to that found for the doubly oxidized compound [6-trans]-[PF6]2+. This result indicates that the two iron centers are equivalent in the trication and they are not involved in the third oxidation process. This oxidation is clearly TTFMe2-centered. Moreover, as the symmetry is not broken by the presence of an odd number of electrons, it can be assumed that the charge is largely delocalized on the two rings of the TTFMe2 core.

5. EPR Spectroscopy of [6-trans][PF6]n (n = 1–3)

The three complexes [6-trans][PF6]n (n = 1–3) were subjected to EPR studies. The monocationic complex [6-trans][PF6] was dissolved in THF, transferred into an EPR tube, and stored at liquid nitrogen temperature before measurement. The spectra were recorded for a rigid glass at 66 K, and the g values extracted from the spectra are collected in Table 3. The X-band EPR spectrum of the monocation [6-trans][PF6] shows a signal with three main lines at g1 = 2.449, g2 = 2.031, and g3 = 2.000. Two additional broad lines emerge at g1′ = 2.298 and g1′′ = 2.213 (Figure 5). The main lines correspond to the three components of the g tensor expected for a low-spin d5 FeIII complex in a pseudooctahedral environment.

Table 3. EPR parameters for [6-trans][PF6]n (n = 1–3) and related FeIII compounds at 66 K.

<table>
<thead>
<tr>
<th>Compound[a]</th>
<th>g1</th>
<th>g2 (a3)</th>
<th>g3</th>
<th>giso</th>
<th>Δg[b]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[6-trans][PF6]</td>
<td>2.449</td>
<td>2.031 (30 G)</td>
<td>2.000</td>
<td>2.161</td>
<td>0.450</td>
<td>[c]</td>
</tr>
<tr>
<td>[6-trans][PF6]2</td>
<td>2.298</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[6-trans][PF6]3</td>
<td>2.213</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>[6][PF6]</td>
<td>2.455</td>
<td>2.032</td>
<td>1.991</td>
<td>2.313</td>
<td></td>
<td>[c]</td>
</tr>
<tr>
<td>[7][PF6]</td>
<td>2.409</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>[8][PF6]</td>
<td>2.343</td>
<td>2.047</td>
<td>1.998</td>
<td>2.129</td>
<td>0.345</td>
<td>[22]</td>
</tr>
<tr>
<td>[9][PF6]</td>
<td>2.450</td>
<td>2.036</td>
<td>2.002</td>
<td>2.163</td>
<td>0.448</td>
<td>[24]</td>
</tr>
<tr>
<td>10[PF6]</td>
<td>2.090</td>
<td>2.051</td>
<td>2.011</td>
<td>2.051</td>
<td>0.079</td>
<td>[26]</td>
</tr>
</tbody>
</table>

[a] In THF unless otherwise specified. [b] Measurement performed on a cis/trans mixture of [6][PF6] in DMF. [c] This work.

Figure 5. X-band EPR spectrum of [6-trans][PF6] at 66 K in a frozen THF solution.

For closely related compounds, g1 is very sensitive to the conformation of the radical, whereas g2 and g3 are only slightly affected by the relative orientation of the redox centers.[43] As a result, the tensor of anisotropy (Δg = g3 − g1) is also sensitive to the geometrical changes that can occur in solution, that is, the rotation of the TTFMe2 core and relative orientation of the Cp* (dppe)Fe units. It has already been shown experimentally and theoretically that the orientation of the phenyl ring plays an important role in the Δg values of [Cp* (dppe)M–(C=C)x–Ph]+ (M = Fe, Ru, x = 0–3). [43] For [6-trans][PF6], the extra lines can be ascribed to different conformers trapped in the rigid glass. A reasonably good fit of the partially overlaid g2 and g3 tensor components also revealed the hyperfine coupling with the two phosphorus nuclei for the g2 tensor. This observation matches well with previous data for the related radical cation [9][PF6] and is consistent with the localization of the odd electron on one iron center on the EPR timescale, as expected for a class II MV complex (see Section 7).[4,24]

Moreover, for MV compounds of a homogeneous series, it has been suggested that the anisotropy tensor (Δg) decreases as the rate of the intramolecular electron transfer (ET) increases.[44] Such a behavior has previously been verified in several cases in the Cp* (dppe)Fe series[4,11,12,45] owing to the relatively large variation of Δg with the relative orientation of the Cp* (dppe)Fe termini, one can conclude that the intramolecular electron-transfer rate should significantly depend on the conformation of the molecule.[7,43,46]

The EPR spectrum of [6-trans][PF6] at 66 K is characteristic of low-spin iron(III) complexes in a pseudooctahedral environment and suggests that the odd electron has a strong metallic character in the ground state (GS, Scheme 4).[38] However, in contrast with the behavior of most of the complexes in the Cp* (dppe)FeIII series, [6-trans][PF6] is still EPR-active at 20 °C. Indeed, a clean, strong, and narrow signal was observed at g = 2.0030 with a peak-to-peak separation (ΔHpp) of 4.6 G. Such a signal is diagnostic of an organic radical and indicates that a redox isomer with a dominant TTF radical character is a thermally accessible excited state (ES, Scheme 4).


Interestingly, the DFT-calculated spin distribution of [6-trans]+ (Figure 6) shows that the unpaired electron is predominantly localized on the TTFMe2 part of the molecule. Indeed, some substantial atomic spin density is found on the iron centers (0.16 e on each); however, the sum of the atomic spin density on the organic fragment (C=C–
TTFMe\textsubscript{2}–C–=C) reaches 0.70 e. Consequently, the computed EPR $g$ factors of [6-trans]$^+$ reflect an organic (mainly TTFMe\textsubscript{2}) character of the unpaired electron with a very small computed anisotropy ($g_1 = 2.068$, $g_2 = 2.020$, $g_3 = 2.000$, and $\Delta g = 0.068$), which is similar to that for the analogous bis-TTF complex \textit{10}$^+$.\textsuperscript{[26]} It seems then that DFT calculations favor the redox isomer with a dominant TTF radical character, which is thermally accessible at room temperature (Scheme 4).

Clearly, such a TTF radical character strongly differs from the experimental data for [6-trans][PF\textsubscript{6}] at low temperature (see Table 3). However, as previously mentioned, the distribution of the unpaired electron and, hence, the EPR $g$ factors are strongly sensitive to the relative orientation of the metallic fragments with respect to the central TTF unit. Geometrical isoenergetic arrangements of [6-trans]$^+$ with different orientations of the Fe end groups with respect to the TTFMe\textsubscript{2} moiety must favor the localization of the unpaired electron on the iron centers. Taken as a whole, the EPR and theoretical data indicate that the iron-centered and TTFMe\textsubscript{2}-centered redox isomers are very close in energy and support a multiple-step hopping mechanism for the intramolecular electron transfer.

The spectrum of the dicationic complex [6-trans][PF\textsubscript{6}]\textsubscript{2} in a 1:1 mixture of CH\textsubscript{2}Cl\textsubscript{2}/1,2-C\textsubscript{2}H\textsubscript{4}Cl\textsubscript{2} was recorded at 66 K. A well-resolved EPR spectrum with three main components for the $\Delta m_s = \pm 1$ transition was obtained, and the EPR parameters were extracted (Table 3). As for the monocation, the splitting of the $g_1$ component of the tensor into three subcomponents is in accord with the dependence of this parameter on the conformation of the molecule. Additionally, the $\Delta m_s = \pm 2$ transition, characteristic of the triplet state, was clearly observed at $g = 4.310$. This result demonstrates that [6-trans][PF\textsubscript{6}]\textsubscript{2} is in a triplet state with two unpaired electrons. The solution is also EPR-active at 20°C, and a spectrum of a characteristic organic radical was observed ($g = 2.0083$, $\Delta H_{pp} = 5.8$ G). Similarly to [6-trans]$^+$, a redox isomer in which one electron moved from the TTFMe\textsubscript{2} moiety to one metal end is also thermally accessible in [6-trans][PF\textsubscript{6}]\textsubscript{2}.

The EPR spectrum of the tricationic complex was recorded for a cis\textit{trans} mixture of 6[PF\textsubscript{6}], which was obtained from the oxidation of 6-cis\textit{trans} with 3 equiv. of [(C\textsubscript{6}H\textsubscript{12})\textsubscript{2}Fe][PF\textsubscript{6}] in DMF. The spectrum shows the characteristic three $g$ tensor components of a low-spin d\textsuperscript{5} iron(III) center with a pseudooctahedral geometry (Table 3). In addition, a weak signal ($g = 4.255$) for the $\Delta m_s = \pm 2$ transitions was observed at half-field. The transition expected for $\Delta m_s = \pm 3$ at $g = 7$ was too weak to be detected in the background noise.\textsuperscript{[47]} At 293 K, the spectrum displays an isotropic broad signal ($g = 2.008$, $\Delta H_{pp} = 350$ G) assigned to a TTF$^{+*}$-centered radical. These data are consistent with the presence of three odd electrons on this complex, two of which are located on the iron termini, and the third one is mainly on the TTF fragment.

6. UV/Vis Absorption Spectroscopy

The UV/Vis spectra of [6-trans][PF\textsubscript{6}]\textsubscript{n} ($n = 0–3$) at 20°C in CH\textsubscript{2}Cl\textsubscript{2} were recorded in the range 300–800 nm, and the characteristic data are collected in Table 4. The spectrum of the neutral complex [6-trans] resembles that obtained for previously reported functionalized organoiron(II) compounds such as 7 and 9.\textsuperscript{[24,39]} The two intense absorptions in the visible range are at the origin of the orange color of these complexes and were assigned to metal-to-ligand charge-transfer (MLCT) transitions.\textsuperscript{[39]} Note that these transitions are at almost exactly the same energy in 6-trans and 9; therefore, they probably result from a d$(\text{Fe})$→e*(C–C–TTFMe\textsubscript{2}) admixture, as already suggested for 9.\textsuperscript{[24]}

<table>
<thead>
<tr>
<th>Absorption $\lambda$ [nm] ($10^3$ [dm$^3$ mol$^{-1}$ cm$^{-1}$])</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-trans</td>
<td>350 (20.1), 400 (15.3)</td>
</tr>
<tr>
<td>[6-trans][PF\textsubscript{6}]</td>
<td>438 (14.1), 489 (15.5), 554 (16.9)</td>
</tr>
<tr>
<td>[6-trans][PF\textsubscript{6}]</td>
<td>430 (16.1), 486 (16.8), 540 (15.0)</td>
</tr>
<tr>
<td>[6-trans][PF\textsubscript{6}]</td>
<td>350 (sh, 15.0), 545 (12.0), 780 (5.9)</td>
</tr>
<tr>
<td>9[PF\textsubscript{6}]</td>
<td>346 (22.3), 400 (12.3)</td>
</tr>
<tr>
<td>10[PF\textsubscript{6}]</td>
<td>336 (12.3), 514 (4.1), 572 (3.8)</td>
</tr>
<tr>
<td>10[PF\textsubscript{6}]</td>
<td>354 (60.5), 562 (24.0), 608 (39.8)</td>
</tr>
<tr>
<td>10[PF\textsubscript{6}]</td>
<td>420 (5.6), 536 (3.5), 672 (1.8)</td>
</tr>
<tr>
<td>10[PF\textsubscript{6}]</td>
<td>386 (28.7), 606 (23.4)</td>
</tr>
</tbody>
</table>

The visible spectra of the salts [6-trans][PF\textsubscript{6}]\textsubscript{n} ($n = 1–3$) are not very different, in agreement with their similar colors. The intense low-energy bands of these three complexes, which are responsible for their characteristic dark blue/purple color, can be ascribed to MLCT transitions derived from the whole structure [Fe\textsuperscript{II}]=C–C–TTFMe\textsubscript{2}=C–Fe\textsuperscript{III}].\textsuperscript{[24]} Indeed, low-energy absorption bands are also observed in the spectra of the oxidized forms of the TTF derivatives.\textsuperscript{[24]} It is interesting to observe that these bands are located at similar energies in the singly and doubly oxidized compounds ($n = 1, 2$), whereas their energy decreases significantly in the trication ($n = 3$). These data are consistent with the fact that the two first one-electron oxidations are iron-centered and the third oxidation is localized on the TTFMe\textsubscript{2} moiety.

Figure 6. Spatial distribution of computed spin density of [6-trans]$^+$ (isocontour values: $\pm 0.003$ $\text{e/bohr}^3$).
NIR Absorption Spectroscopy of [6-trans][PF₆]ₙ (n = 0–3)

The NIR spectra of [6-trans][PF₆]ₙ (n = 0–3) were recorded in CH₂Cl₂. The spectrum of the neutral complex (n = 0) does not contain any absorption bands in the NIR range, whereas the spectra of the doubly and triply oxidized species (n = 2, 3) present only residual absorption (ε < 200 m⁻¹ cm⁻¹) at ca. 5500 cm⁻¹, which corresponds to the characteristic absorption of the iron(III) complexes. The spectrum of the radical cation [6-trans][PF₆] in CH₂Cl₂ exhibits a broad absorption in the range 3300–10000 cm⁻¹ with three maxima and one shoulder (Figure 7).

The intensity of the experimental spectrum in the NIR range is moderate (ε = 1000 m⁻¹ cm⁻¹) and compares well with data previously reported for [9][PF₆]. But the spectrum is very different in shape and intensity from that of [10][PF₆].

Assuming that absorption bands can be approximated in terms of Gaussian band shapes, the deconvolution of the experimental spectrum of the singly oxidized complex [6-trans][PF₆] in the range 3300–10300 cm⁻¹ can be achieved by using a minimum of four distinct overlapping transitions. The fit is good enough to allow an almost exact overlay of the sum of the spectral components with the experimental spectrum (Figure 7). The spectral parameters extracted from the band-shape analysis are summarized in Table 5. The results show that four Gaussian curves with similar half-width at half-height can describe accurately the experimental spectra.

Table 5. NIR absorption data for [6-trans][PF₆] in CH₂Cl₂ and CH₃CN.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>νmax [cm⁻¹]</th>
<th>εmax [m⁻¹ cm⁻¹]</th>
<th>Δν1/2 [cm⁻¹]</th>
<th>H_ab [cm⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂Cl₂</td>
<td>3260</td>
<td>1070</td>
<td>1110</td>
<td>85[a]</td>
</tr>
<tr>
<td></td>
<td>5280</td>
<td>940</td>
<td>1110</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7120</td>
<td>920</td>
<td>1110</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8740</td>
<td>870</td>
<td>1110</td>
<td></td>
</tr>
<tr>
<td>CH₃CN</td>
<td>4000</td>
<td>3000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>5280</td>
<td>1800</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7120</td>
<td>2200</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8740</td>
<td>4500</td>
<td>1000</td>
<td></td>
</tr>
</tbody>
</table>

[a] Calculated from Equation (1), assuming a through-space iron–iron distance of 14.92 Å. The DFT-computed distance is ca. 15 Å.

A spectrum of [6-trans][PF₆] in CH₃CN, a much more polar solvent than CH₂Cl₂, evidences an increase of the extinction coefficients for all the components of the spectrum. Meanwhile, the absorption spectrum is perturbed by several vibration bands. The band-shape analysis can be performed in the same way, and the spectral parameters are listed in Table 5. The four bands have their intensities multiplied by two to five, but they all have the same width. The main feature is the blueshift of the lower-energy band (Δν = 740 cm⁻¹), and the three other bands of the spectrum remain at exactly the same energies.

The assignment of the NIR absorptions is far from obvious. The intervalence charge transfer (IVCT) character of the low-energy band is consistent with the absence of such a transition in the electronic spectra of the homovalent species [6-trans][PF₆] (n = 0, 2). In addition, the clear solvatochromism of the band confirms that this transition can safely be ascribed to an iron–iron photoinduced electron transfer. This band can further allow the calculation of the electronic coupling parameter H_ab, which can be computed from Equation (1), in which d_ab is the through-space distance between the iron centers and the other terms are given in Table 5. In the present case, d_ab was approximated as twice the through-space distance between the iron atom and the centroid of the central carbon–carbon double bond connecting the two rings of the TTFMe₂ unit. This value can be determined from the X-ray crystal structure of 9 (d_ab = 7.46 Å x 2 = 14.92 Å). The calculation gives a small H_ab value of 85 cm⁻¹.

\[ H_{ab} = 0.0206(\nu_{max}^2 \Delta \nu_{1/2})^{1/2} / d_{ab} \]  (1)

The higher-energy transitions, which are not solvent dependent, probably do not correspond to d–d ligand-field transitions because these band are generally weak in intensity (ε < 200 m⁻¹ cm⁻¹) and only one transition is expected at ca. 5300 cm⁻¹ (SOMO–2 to SOMO). Consequently, it can be assumed that these transitions involve the TTFMe₂ core of the bridge and might tentatively be ascribed to LMCT and intraligand charge-transfer (ILCT) transitions involving the bridge.

Finally, one can note that [6-trans][PF₆]₃ is not a mixed-valence derivative, despite the presence of an odd number of unpaired electrons.

Conclusions

In this contribution, the synthesis and characterization of the new Cp*(dppe)FeC=C–TTFMe₂–C=CFe(dppe)Cp* complex as the pure geometric isomer 6-trans and as a 60:40 6-cis/trans mixture have been reported. The CV of 6-trans shows four chemically reversible and separated waves, which indicate that the four redox centers are electronically coupled. The associated salts [6-trans][PF₆]ₙ (n = 1–3) were isolated and characterized by IR, EPR, visible, and NIR spectroscopy, substantiated by quantum chemistry. As a whole, our data show that the TTFMe₂ electrochrome mediates single-step tunneling electron transfer between the iron termini. With a moderate electronic coupling (H_ab ≈ 85 cm⁻¹), [6-trans][PF₆] belongs to the class II mixed-valence.
lence complexes as defined by Robin and Day. In addition, electron exchange also results from multiple-step hopping between the inorganic and organic redox centers. Finally, it was discovered that the rate of the intramolecular electron transfer depends on the conformational arrangement between the redox partners.

Experimental Section

General Data: Manipulations of air-sensitive compounds were performed under an argon atmosphere by using standard Schlenk techniques. THF, diethyl ether, and pentane were dried and deoxygenated by distillation from sodium/benzophenone ketyl. Dichloromethane was distilled under argon from P2O5 and then from Na2CO3. DMF was dried with activated 4 Å molecular sieves. Methane was distilled under argon from P2O5 and then from CS2, and the solvent was removed. The residue was chromatographed on silica gel with CS2 as eluent. The main orange fraction was collected, and the solvent was evaporated. The residue was crystallized from cyclohexane and then from ethanol to give trans-Me2Si-C≡C-TTFMe2-C≡C-SiMe3 (3): A Schlenk tube was charged with TTFMe2I2 (0.968 g, 2.0 mmol), trimethylsilylacetylene (0.85 mL, 6.0 mmol, 3.0 equiv.), Pd(PPh3)2Cl2 (0.28 g, 0.4 mmol, 0.2 equiv.), CuI (0.15 g, 0.8 mmol, 0.4 equiv.), diisopropylamine (5 mL), and THF (20 mL). The mixture was stirred for 18 h at room temperature. The solvents were removed, and the residue was chromatographed on silica gel with CH2Cl2 as eluent. cis and trans isomers, which were prepared for the next step without separation.

cis- and trans-Me2Si-C≡C-TTFMe2-C≡C-SiMe3 (3): A Schlenk tube was charged with TTFMe2I2 (0.968 g, 2.0 mmol), trimethylsilylacetylene (0.85 mL, 6.0 mmol, 3.0 equiv.), Pd(PPh3)2Cl2 (0.28 g, 0.4 mmol, 0.2 equiv.), CuI (0.15 g, 0.8 mmol, 0.4 equiv.), diisopropylamine (5 mL), and THF (20 mL). The mixture was stirred for 18 h at room temperature. The solvents were removed, and the residue was chromatographed on silica gel with CH2Cl2 as eluent. The main orange fraction was collected, and the solvent was evaporated. The residue was crystallized from cyclohexane and then from ethanol to give trans-Me2Si-C≡C-TTFMe2-C≡C-SiMe3 (3).
cis- and trans-[[Cp*(dppe)Fe-C=C]2(TTFMe2)] ([6-cis/trans]): A freshly prepared cis/trans mixture of H=C–C=TTfMe2–C=C–H (0.062 g, 0.22 mmol) was combined with an excess of 5 (0.29 g, 0.46 mmol, 2.3 equiv.) and KPF6 (0.084 g, 0.46 mmol, 2.3 equiv.) and stirred in a 2:1 mixture of MeOH/THF (15 mL) for 72 h at room temperature. Potassium tert-butoxide (0.069 g, 0.62 mmol, 2.3 equiv.) was added, and the reaction mixture was stirred for an additional 2 h with the progressive appearance of an orange solid. A workup as described for 6-trans yielded 6-cis/trans as an orange powder (0.020 g, 0.13 mmol, 63%; cis/trans ~60:40, see Section 2). FTIR (KBr): ν = 2018 (s, C=O), 1522 (m), 1456 (s, C–H), 1371 (m), 1246 (m), 1110 (m), 1092 (m), 1072 (s), 1044 (s), 976 (s), 746 (s), 739 (s), 693 (s). 13P NMR (162 MHz, C6D6, 25 °C): δ = 100.35 (s, dppe) ppm.

Oxidation/Reduction Cycle with [[Cp*(dppe)Fe-C≡C]2(TTFMe2)][PF6] ([6-trans][PF6]): A Schlenk tube cooled to –60 °C was charged with the neutral complex [[Cp*(dppe)Fe-C≡C]2(TTFMe2)] (0.040 g, 0.027 mmol) and its dioximated counterpart (see below) [[Cp*(dppe)Fe-C≡C]2(TTFMe2)][PF6] (0.047 g, 0.027 mmol) in THF (7 mL). The cold bath was removed, and the reaction mixture was allowed to reach room temperature over a period of 1 h, before the addition of pentane (20 mL) and dried under vacuum to yield a dark purple powder (0.040 g, 93%). FTIR (KBr): ν = 1974 and 1989 (s, C=O), 848 (m), 750 (w), 707 (w), 544 (m). 31P NMR (162 MHz, C6D6, 25 °C): δ = 10.04 (CH3 Cp*) ppm.

CCDC-983655 (for 6-trans) and -983656 (for 3-cis) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details: DFT calculations were performed by using the ADF2010.02 (Amsterdam Density Functional) package. The geometries of [6-trans]5+ (n = 0–2) were fully optimized. In these optimizations, electron correlation was treated within the local density approximation (LDA) in the Vosko–Wilk–Nusair parameterization. The nonlocal corrections (GGA) of Becke and Perdew (BP86) were added to the exchange and correlation energies. The analytical gradient method implemented by Versluis and Ziegler was used. Spin-unrestricted calculations were performed for all of the open-shell systems considered. The standard ADF TZP basis set was used for these geometry optimizations and corresponds, explicitly, to a triple-ζ Slater-type orbital (STO) basis set for the valence core, augmented with a 2p polarization function for H, a 3d polarization function for C, P, and S, and a 4p polarization function for Fe. Orbitals up to 1s and 2p were kept frozen for C and P, S, Fe, respectively. The EPR properties were calculated by using the ESR procedure developed by van Lenthe and coworkers. The g tensor components were obtained from self-consistent spin-restricted DFT calculations after incorporation of the relativistic spin–orbit coupling by first-order perturbation theory from a zeroth-order regular approximation (ZORA) Hamiltonian. For these calculations, the nonlocal corrections of Adamo–Barone and of Perdew–Burke–Ernzerhof (mPBE) were added to the exchange and correlation energies, respectively. Molecular orbitals were plotted with the ADF-GUI package.

Supporting Information (see footnote on the first page of this article): Selected computed distances for [6-trans]5+, details of crystal structure analysis of 3-trans and 3-cis.

Acknowledgments

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