Synthesis, Molecular Structure, Properties, and Electronic Structures of $[Cp^*(dppe)FeC \equiv C-TTFMe_3][PF_6]_n$ (n = 0, 1): Electronic Coupling between the Inorganic and Organic Electrophores

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Sequential treatment of trimethylsilylethynyl-TTF (TTFMe₃) 3a dissolved in methanol with potassium fluoride, the chloro complex Cp*(dppe)FeCl (8; Cp* = η^5 -C₅(CH₃)₅, dppe = 1,2-bis-(diphenylphosphino)ethane) in the presence of ammonium hexafluorophosphate, and finally with KOBu^t provided Cp*(dppe)FeC≡C-TTFMe₃ (1), which was isolated in 69% yield as an air- and moisture-sensitive orange powder. The X-ray crystal structure, IR, cyclic voltammetry (CV), UV-vis, Mössbauer, and DFT data obtained for 1 show that only weak interactions take place between the iron center and the TTFMe₃ core and that the latter acts as a rather poor electron donor vis-à-vis the organometallic group. When reacted with 1.0 equiv of $[(C_5H_5)_2Fe][PF_6]$ in tetrahydrofuran (THF) at -60 °C, 1 gives the thermally stable radical cation $1[PF_6]$, which was isolated in a pure form as a purple powder (77%). The Fe^{III} derivative was characterized by the same spectroscopic methods as 1 complemented by HRMS and elemental analyses also obtained for neutral 1. All experimental and theoretical data obtained for $1[PF_6]$ indicate that after one-electron oxidation the relaxation of the molecular structure is characterized by an increase of the Fe-C carbon bond order, 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 TTFMe₃ fragment is much stronger than in the neutral species, and a good electronic communication characterized by a rather large electronic coupling for a class II MV system takes place ($H_{ab} =$ 320 cm⁻¹ determined from the analysis of the NIR spectrum). Furthermore, the dicationic species 1[PF₆]₂ was in situ generated and characterized by IR, NIR, and EPR spectroscopies.

Introduction

Organometallics comprising two redox active centers connected by a carbon bridge provide an ideal template upon which intricate mechanistic details of the factors controlling electron transfer and electron delocalization can be extracted.¹⁻³ Consequently, over the last years, one thrust has involved extremes in oxidation states of this type of compound with different metal end-groups, and the consequences for electronic, magnetic, and geometric structure as well as electron transfer have been extensively studied.^{1,4} We have ourselves shown that species containing redox $Cp^*(dppe)$ Fe fragments ($Cp^* = C_5Me_5$, dppe = 1,2-bis(diphenylphosphino)ethane) linked to π conjugated polyynediyl ligands are ideally suited for studies of electronic and magnetic coupling between the redox-active centers. These assemblies proved usually to be stable (and isolable) in different redox states. However, previous studies have clearly shown that the stability of the oxidized species is limited by lengthening of the polyynediyl linkers.⁵ Introduction of aromatic rings such as benzene or thiophene in the polyynediyl spacer constitutes an attractive alternative

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 ⁽¹⁾ Crutchley, R. J. Adv. Inorg. Chem. 1994, 41, 273–325.
 (2) (a) Ward, M. D. Chem. Soc. Rev. 1995, 24, 121–134. (b) Ward, M. D. Chem. Ind. 1996, 568-573. (c) Paul, F.; Lapinte, C., Magnetic communication in binuclear organometallic complexes mediated by carbonrich bridges. In Unusual Structures and Physical Properties in Organometallic Chemistry; Gielen, M.; Willem, R.; Wrackmeyer, B., Eds.; John Wiley & Sons: London, 2002; pp 220–291. (d) Demandis, K. D.; Hartshorn, C. M.; Meyer, T. J. Chem. Rev. 2001, 101, 2655-2685. (e) Brunschwig, B. S.; Creutz, C.; Sutin, N. Chem. Soc. Rev. 2002, 31, 168-184.

⁽³⁾ Paul, F.; Lapinte, C. Coord. Chem. Rev. 1998, 178-180, 427-505.

^{(4) (}a) Ren, T. Chem. Rev. 2008, 108, 4185-4207. Ren, T. Organometallics 2005, 24, 4854–4870. (b) Schwab, P. F. H.; Levin, M. D.; Michl, J. Chem. Rev. 2005, 105, 1197-1279. (c) Qi, H.; Noll, B.; Snider, G. L.; Lu, Y.; Lent, S. S.; Fehlner, T. P. J. Am. Chem. Soc. 2005, 127, 15218-15227. (d) Blum, A. S.; Ren, T.; Parish, D. A.; Trammell, S. A.; Moore, M. H.; Kushmerick, J. G.; Xu, G. L.; Deschamps, J. R.; polack, S. K.; Shashidar, R. J. Am. Chem. Soc. 2005, 127, 10010-10011. (e) Xu, G. L.; Crutchley, R. J.; DeRosa, M. C.; Pan, Q.-J.; Zhang, H.-X.; Wang, X.; Ren, T. J. Am. Chem. Soc. 2005, 127, 13354–13365. (f) Akita, M.; Koike, T. Dalton Trans. 2008, 3523-3530

⁽⁵⁾ Coat, F.; Lapinte, C. Organometallics 1996, 15, 477-480.

to circumvent this instability and eventually to tune their physical properties.⁶⁻⁹ Various nonlinear rigid new geometries can then be envisioned for the carbon-rich spacers incorporating such aromatic units, leading to structural variation, which can deeply modify the electronic properties of the molecules.^{7,8,10}

On the other hand, since the first report on TTF (tetrathiafulvalene = 2,2'-bis(1,3-dithiolylidene)) in 1970,¹¹ TTF and its derivatives remain the most studied redox-active organic systems.^{12–14} They are now recognized as the gateway to organic metals, superconductors, and semiconductors.^{14,15} Because of the wide range of physical properties of TTFcontaining compounds as potential superconductors, chargetransfer complexes, ferromagnets, nonlinear optical materials, sensors, electroactive Langmuir–Blodgett films, and organic field effect transistors, they were the subject of a huge number of reports.¹² More recently, the high electron-donating ability of these redox-active moieties led to important studies focusing on their functionalization toward their use in coordination chemistry.^{15,16}

Multifunctional molecular systems based on the assemblies incorporating photo- and/or redox-active groups have been the subject of considerable recent research as suitable candidates for switchable optical, conductive, and magnetic

(6) (a) Le Narvor, N.; Lapinte, C. Organometallics 1995, 14, 634–639.
(b) Le Stang, S.; Paul, F.; Lapinte, C. Organometallics 2000, 19, 1035–1043.

- (7) de Montigny, F.; Argouarch, G.; Costuas, K.; Halet, J.-F.; Roisnel, T.; Toupet, L.; Lapinte, C. *Organometallics* **2005**, *24*, 4558–4572.
- (8) Lohan, M.; Justaud, F.; Roisnel, T.; Ecorchard, P.; Lang, H.; Lapinte, C. *Organometallics* **2010**, DOI: 10.1021/om100003z.

(9) Ghazala, S. I.; Paul, F.; Toupet, L.; Roisnel, T.; Hapiot, P.; Lapinte, C. *J. Am. Chem. Soc.* **2006**, *128*, 2463–2476.

(10) Tanaka, Y.; Shaw-Taberlet, J. A.; Justaud, F.; Cador, O.; Roisnel, T.; Akita, M.; Hamon, J.-R.; Lapinte, C. *Organometallics* **2009**, *28*, 4656–4669.

(11) Wudl, F.; Smith, G. M.; Hufnagel, E. J. J. Chem. Soc., Chem. Commun. 1970. 490–491.

(12) Chem. Rev. 2004, 104, 4887–4890, a thematic issue on "molecular conductors", P. Batail, Ed.

(13) (a) Ishiguro, T.; Yamaji, R.; Saito, G. Organic Superconductors; Springer-Verlag: Berlin, 1988. Ouahab, L.; Yagubskii, E. Organic Conductors, Superconductors and Magnets: From Synthesis to Molecular Electronics; Kluwer:Dordrecht, 2003. (b) Foumigué, M.; Ouahab, L. Topics in Organometallic Chemistry Dedicated to Conducting and Magnetic Organometallic Materials; Springer: Berlin, 2009. Ouahab, L.; Enoki, T. Eur. J. Inorg. Chem. 2004, 933. (c) Saito, G.; Y. Yoshida, Y. Bull. Chem. Soc. Jpn. 2007, 80, 1. (d) Lorcy, D.; Bellec, N.; Fourmigué, M.; Avarvari, N. Coord. Chem. Rev. 2009, 253, 1398.

(14) Yamada, J.; Sugimoto, T., *TTF Chemistry-Fundamentals and Applications of Tetratiafulvalene*; Kodansha and Springer: Tokyo, 2004.
(15) (a) Iwahori, F.; Golhen, S.; Ouahab, L.; Carlier, R.; Sutter, J.-P.

(16) Fourie, E.; Swarts, J.; Lorcy, D.; Bellec, N. Inorg. Chem. 2010, 49, 952–959.

Chart 1



materials. To establish stronger interactions between these functional groups, the introduction of a covalent-bonded linker is expected to be preferable to intermolecular van der Waals contacts used in the conventional π -d interaction-based systems. On the basis of this approach, we report here the synthesis and characterization of the new hybrid complex 1 (Chart 1).

In this compound, two electroactive units, namely, the TTFMe₃ and FeCp*(dppe) groups, are linked by an ethynyl bridge to favor π -d interactions between them. In contrast to the complexes 4 and 5, for which the first oxidation was found to be TTF or TTFMe₃ centered, ^{17,18} it can be anticipated that the first oxidation of 1 should be iron centered since the redox potential of the compounds 2, 3a, and 6 are -0.14, 0.35, and -0.10 V vs SCE, respectively.^{19,20} The isolation of the associated radical cation 1[PF₆] is also reported. This novel species was investigated by various means in order to assess the extent of the electronic interaction between the metal center and the TTF core through the acetylide bridge. Attempts to isolate the associated dication are also briefly described with some spectroscopic characterizations.

Results and Discussion

1. Synthesis and Characterization of 1. As illustrated in Scheme 1, 1 was synthesized from $Cp^*(dppe)Fe-Cl^{21}(8)$ and TTFMe₃ containing three methyl groups (3a). The TTFMe₃ precursor 3a was obtained from treatment of lithiated TTFMe₃ with perfluorohexyliodide, followed by the Sonogashira coupling reaction with trimethylsilylacety-lene. Treatment of 3a with potassium fluoride in methanol provided the ethynyl-TTFMe₃ 3b, which was in situ reacted with the chloro complex 8 in the presence of ammonium hexafluorophosphate. TLC monitoring showed that the organic reagent was consumed after 16 h, and following recipes established for the complexation of various alkynes

^{(15) (}a) Iwahori, F.; Golhen, S.; Ouahab, L.; Carlier, R.; Sutter, J.-P. *Inorg. Chem.* 2001, 40, 6541. (b) Setifi, F.; Ouahab, L.; Golhen, S.; Yoshida, Y.; Saito, G. *Inorg. Chem.* 2003, 42, 1791. (c) Pellon, P.; Gachot, G.; Le Bris, J.; Marchin, S.; Carlier, R.; Lorcy, D. *Inorg. Chem.* 2003, 42, 2056. (d) Devic, T.; Batail, P.; Fourmigué, M.; Avarvari, N. *Inorg. Chem.* 2004, 43, 3136. (e) Avarvari, N.; Fourmigué, M.; Avarvari, N. *Inorg. Chem.* 2004, 43, 3136. (e) Avarvari, N.; Fourmigué, M.; Chem. Commun. 2004, 1300. (f) Jia, C.; Liu, S.-X.; Ambrus, C.; Neels, A.; Labat, G.; Decurtins, S. *Inorg. Chem.* 2006, 45, 3152. (g) Ichikawa, S.; Kimura, S.; Mori, H.; Yoshida, G.; Tajima, H. *Inorg. Chem.* 2006, 7575. (h) Wang, L.; Zhang, B.; Zhang, J. *Inorg. Chem.* 2006, 45, 6860. (i) Massue, J.; Bellec, N.; Chopin, S.; Levillain, E.; Roisnel, T.; Clérac, R.; Lorcy, D. *Inorg. Chem.* 2005, 44, 8740. (j) Benbellat, N.; Le Gal, Y.; Golhen, S.; Gouasmia, A.; Ouahab, L.; Fabre, J.-M. *Eur. J. Org. Chem.* 2006, 4237. (k) Zhu, Q.-Y.; Liu, Y.; Lu, W.; Zhang, Y.; Bian, G.-Q.; Niu, G.-Y.; J. Dai, J. *Inorg. Chem.* 2007, 46, 1006. (l) Gavrilenko, K. S.; Le Gal, Y.; Cador, O.; Golhen, S.; Ouahab, L. *Chem. Commun.* 2007, 280. (m) Pointillart, F.; Gal, L.; Y.; Golhen, S.; Cador, O.; Ouahab, L. *Inorg. Chem.* 2008, 47, 9730. (n) Umezono, Y.; Fujita, W.; Awaga, K. *J. Am. Chem. Soc.* 2006, *128*, 1084. (o) Hervé, K.; Liu, S-X.; Cador, O.; Golhen, S.; Le Gal, Y.; Bousseksou, A.; Stoeckli-Evans, H.; Decurtins, S.; Ouahab, L. *Eur. J. Inorg. Chem.* 2006, 3498. (p) Cosquer, G.; Pointillart, F.; Gal, L.; Y.; Golhen, S.; Ouahab, L. *Eur.* J. *Ong. Chem.* 2006, 3498. (p) Cosquer, G.; Pointillart, F.; Gal, L.; Y.; Golhen, S.; Cador, O.; Gulhen, S.; Le Gal, Y.; Bousseksou, A.; Stoeckli-Evans, H.; Decurtins, S.; Ouahab, L. *Eur. J. Inorg. Chem.* 2006, 3498. (p) Cosquer, G.; Pointillart, F.; Gal, L.; Y.; Golhen, S.; Cador, O.; Ouahab, L. *Dalton Trans.* 2009, 3495.

⁽¹⁷⁾ Iyoda, M.; Takahiro, T.; Otani, N.; Ugawa, K.; Yoshida, M.; H., M.; Kuwatani, Y. *Chem. Lett.* **2001**, 1310–1311.

⁽¹⁸⁾ Vacher, A.; Barrière, F.; Roisnel, T.; Lorcy, D. Chem. Commun. 2009, 7200–7202.

⁽¹⁹⁾ Roué, S.; Lapinte, C. J. Organomet. Chem. 2005, 690, 594–604.
(20) Le Narvor, N.; Toupet, L.; Lapinte, C. J. Am. Chem. Soc. 1995, 117, 7129–7138.

⁽²¹⁾ Roger, C.; Hamon, P.; Toupet, L.; Rabaâ, H.; Saillard, J.-Y.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1991**, *10*, 1045–1054.



Figure 1. ORTEP drawing of 1A. Thermal ellipsoids are at the 30% probability level. Hydrogen atoms are omitted for clarity.

Scheme 1^{*a*}



^aKey reagents: (i) KF, NH₄PF₆, CH₃OH, 25 °C, 16 h, then KOBu'; (ii) [(C₅H₅)₂Fe][PF₆], THF, -60 °C, 2 h.

at the iron center, 1 equiv of KOBu^t was added to favor the deprotonation of the vinylidene intermediate.^{7,22} After workup **1** was isolated in 69% yield as an air- and moisturesensitive orange powder. A FAB mass spectrum of **1** showed the expected parent ion, and the microanalysis was satisfactory.

Well-resolved ¹H, ¹³C, and ³¹P NMR spectra were obtained and confirmed the structure. The most striking features of the ¹H NMR spectrum include the Cp* methyl singlet at 1.46 ppm, the methyl resonances at 1.74, 1.37, and 1.36 ppm, two dppe methylene multiplets at 2.63 and 1.84 ppm, and the aromatic peaks integrating to 20 protons. The ³¹P NMR spectrum displayed one singlet at 100.77 ppm, as usual for these acetylide iron derivatives.²³ Finally, the ¹³C NMR spectrum showed all expected resonances including the triplet (δ 151.32, ²J_{CP} = 38.4 Hz) and singlet (δ 116.6) signatures for the acetylide linkage and the three resonances characteristic of the methyl substituents of the TTFMe₃ moiety (δ 14.62, 12.99, and 12.97).

2. Molecular Structure of 1. Single crystals suitable for X-ray crystallography were grown by slow diffusion of *n*-pentane into a toluene solution containing **1** at 20 °C. Complex **1** crystallizes in the monoclinic space group $P2_1/c$. The X-ray data conditions, crystal data, data collection, and structure refinement parameters are summarized in the Experimental Section (Table 8).

The asymmetric unit is composed of two distinct but very similar units **A** and **B**. Molecules **A** and **B** contain the Fe1 and Fe2 atoms, respectively. We describe here only the unit **A**. The molecular structure of **A** is shown in Figure 1, and a set

of bond lengths and bond angles is given in Table 1. As it is invariably observed for all the members of the Cp*(dppe)-Fe-C=C family of complexes, the metal adopts a pseudo-octahedral geometry with bond lengths and angles in the previously established ranges.^{3,22-26}

The structural parameters within the TTFMe₃ units are in the range of what is usually observed for neutral molecules with, however, a small difference between the C=C double bonds.²⁷ Indeed, the double bond of the ring connected to the iron-alkynyl group is longer (1.340(3) Å) than the outer one, namely, the C44–C46 bond distance (1.332(4) Å). The TTFMe₃ unit is not planar; it is bent around the S1S2 segment with a dihedral angle of ca. 28.0° between the planes defined by (S1S2S3S4) and (S1S2C39C40). The dihedral angle between the planes defined by P1–Fe–P2 and (S1S2S3S4) is equal to ca. 69.7°.

3. Cyclic Voltammetry of 1 and Synthesis of the Oxidized Species $1[PF_6]$. The initial scan in the CV of 1 from -1 to +1.0 V shows three chemically reversible oxidation waves separated by 0.49 and 0.46 V, respectively (Figure 2). The analysis of the peak currents shows that the anodic and cathodic currents are strictly identical for the three waves,

⁽²²⁾ Weyland, T.; Lapinte, C.; Frapper, G.; Calhorda, M. J.; Halet, J.-F.; Toupet, L. Organometallics **1997**, *16*, 2024–2031.

⁽²³⁾ Denis, R.; Toupet, L.; Paul, F.; Lapinte, C. Organometallics 2000, 19, 4240–4251.

⁽²⁴⁾ Weyland, T.; Costuas, K.; Toupet, L.; Halet, J.-F.; Lapinte, C. Organometallics **2000**, *19*, 4228–4239.

⁽²⁵⁾ Coat, F.; Guillevic, M.-A.; Toupet, L.; Paul, F.; Lapinte, C. Organometallics **1997**, *16*, 5988–5998.

⁽²⁶⁾ Hamon, P.; Toupet, L.; Hamon, J.-R.; Lapinte, C. Organometallics 1996, 15, 10-12.

^{(27) (}a) Mas-Torrent, M.; Durkut, M.; Hadley, P.; Ribas, X.; Rovira, C., J. Am. Chem. Soc. 2004, 126. (b) Mas-Torrent, M.; Hadley, P.; Bromley, S. T.; Ribas, X.; Tarrés, J.; Mas, M.; Molins, E.; Veciana, J.; Riovira, C. J. Am. Chem. Soc. 2004, 126, 8546. (c) Guionneau, P.; Kepert, C. J.; Bravic, G.; Chasseau, D.; Truter, M. R.; Kurmoo, M.; Day, P. Synth. Met. 1997, 1973–1974. (d) Flandrois, S.; Chasseau, D. Acta Crystallogr. 1977, B33, 2744–2750.

Table 1. Experimental Selected Bond Distances (Å) and Angles (deg) for 1A and Calculated Bond Distances for 1^{n+} , $3b^{n+}$, and 6^{n+a}

	1A	1	1^+	$1^{2+}(S)$	$1^{2+}(T)$	$1^{2+}(BS)$	3b	3 b ⁺	6	6+
Fe-P1	2.1751(6)	2.213	2.252	2.279	2.302	2.291			2.207	2.283
Fe-P2	2.1731(6)	2.223	2.253	2.289	2.324	2.295			2.215	2.299
Fe-C37	1.898(2)	1.873	1.827	1.793	1.854	1.819			1.890	1.865
C37-C38	1.220(3)	1.247	1.257	1.269	1.250	1.261	1.218	1.216	1.236	1.237
C38-C39	1.418(3)	1.402	1.382	1.365	1.394	1.376	1.408	1.405		
C39-C40	1.346(3)	1.366	1.388	1.408	1.382	1.397	1.363	1.374		
C42-C43	1.340(3)	1.357	1.373	1.393	1.392	1.393	1.356	1.394		
C44-C46	1.332(4)									
Fe-Cp* ^b	1.744	1.767	1.783	1.802	1.807	1.803			1.763	1.800
C-S(av)		1.783	1.769	1.752	1.755	1.753	1.783	1.753		
P1-Fe-P2	85.42(2)									
Fe-C37-C38	176.4(2)									
C37-C38-C39	175.4(2)									
C38-C39-C40	127.9(2)									
S1-C42-C43-S3	2.73									
S2-C42-C43-S4	4.87									

^{*a*} The atom numbering of the computed compounds is the same as that in 1A. ^{*b*} Centroid of the η^{5} -C₅Me₅ ligand.

Table 2. Electrochemical Data for Selected Complexes^a

compd	$E_{1}^{0}(\Delta E_{\rm p})$	$E_{2}^{0}\left(\Delta E_{\mathrm{p}}\right)$	$\Delta E_{3}^{0} (\Delta E_{\rm p})$	ref
1	-0.11(0.07)	0.38 (0.07)	0.84 (0.08)	this work
2	-0.14(0.09)			19
3a	0.41 (0.06)	0.92(0.09)		this work
4	0.35	0.71	0.85	17
5	0.07	0.52	1.07	18
6	-0.10(0.07)			20

^{*a*} In CH₂Cl₂, 0.1 M [Bu₄^{*n*}N]PF₆, scan rate 0.1 V/s, Pt electrodes, V vs SCE (Fc/Fc⁺ = 0.46 V vs SCE used as internal reference for potential measurements).



Figure 2. CV of **1** (V vs SCE, 10^{-3} M solution in dichloromethane at 298 K, 0.1 M [Bu₄^{*n*}N]PF₆, scan rate = 0.100 V s⁻¹).

so that the electron-deficient species 1^+ , 1^{2+} , and 1^{3+} are apparently stable at the platinum electrode.

Comparison of the first oxidation potential of **1** with those found for **2** (Table 2) and other related compounds of the [Cp*(dppe)Fe-C=C-] series²³ strongly suggests that the first redox process should be metal centered ({[Fe^{II}]-C=C-TTFMe₃}/{[Fe^{III}]^{+•}-C=C-TTFMe₃}), while the two other oxidations are expected to mainly concern the TTFMe₃ moiety ({[Fe^{III}]^{+•}-C=C-TTFMe₃}/{[Fe^{III}]^{+•}-C= C-TTFMe₃^{+•}} and {[Fe^{III}]^{+•}-C=C-TTFMe₃^{+•}}/{[Fe^{III}]^{+•}-C=C-TTFMe₃²⁺}, respectively). In particular, comparison of the first redox potentials (E^{0}_{1}) given in Table 2 indicates that the TTFMe₃ moiety does not behave as a strong electron donor when connected to the alkynyl-iron site. Apparently, it is only slightly less electron-donating than the thiophene unit. Moreover, the potential of **1** is very similar to that of the reference complex 6, suggesting again that the TTFMe₃ moiety acts as a very weak electron-releasing substituent for the Cp*(dppe)Fe moiety.

The potential of the second redox event is 0.03 V more favored than the first oxidation of **3a**, indicating that the oxidized $[Cp*(dppe)Fe^{III}-C=C-]^{+\bullet}$ moiety does not act as an electron-withdrawing group with respect to the TTFMe₃ part, but rather as a weakly electron-donating fragment.

The hybrid systems TTF-ferrocene 4 and Me₃TTFalkynyl-ruthenium 5 also showed three reversible redox waves in the CVs. It is worth noting that the first oxidation potential of 4 is slightly less positive than that of 3a, indicating that ferrocene can stabilize the radical cation centered on the TTF moiety (provided that TTF is less electron rich than 3a).¹⁷ In the case of compound 5, the first oxidation potential was found at a significantly less anodic potential than that of the first oxidation potential of 3a. Nevertheless, the first oxidation of 5 was assigned to the TTFMe3 core, strongly affected by the electron-releasing ruthenium moiety.¹⁸ Interestingly, while the second oxidation can be assigned to the first oxidation of the TTFMe3 group in 1, it was attributed to the ferrocene in the case of 4 and to the second oxidation of the TTFMe₃ core in 5 (by the authors of ref 18). As a result, the three redox families $[1]^{n+}$, $[4]^{n+}$, and $[5]^{n+}$ somewhat differ.

On the basis of the full reversibility of the CV waves, the mono- and dioxidized complexes 1[PF₆] and 1[PF₆]₂ were thought as being accessible synthetic targets. According to a wellestablished procedure, complex 1 was reacted with 1.0 equiv of $[(C_5H_5)_2Fe][PF_6]$ in tetrahydrofuran (THF) at -60 °C. Upon gradual warming to room temperature, the thermally stable radical cation 1[PF₆] was formed. Partial precipitation and crystallization provide pure samples that were isolated in good yield (77%) as a dark purple powder. The Fe(III) derivative was characterized by usual spectroscopic methods complemented by HRMS and elemental analysis. As expected, this dark complex presents a CV identical to that of 1. Similar efforts to prepare the dication were unsuccessful. However, treatment of 1 with 2 equiv of $[(C_5H_5)_2Fe][PF_6]$ in tetrahydrofuran at -60 °C provided a greenish-brown liquor, from which addition of cold pentane allowed the isolation of $1[PF_6]_2$ in almost pure form. However, the large kinetic reactivity of this salt does not allow further purification. For this reason, the charactization of 1[PF₆]₂ was achieved only using FTIR and EPR spectroscopies.

Table 3. IR $v_{C=C}$ Bond Stretching for $1[PF_6]_n$ a	and Related Complexes"
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compd	n = 0	n = 1	n = 2	ref
1	2022 ^b (2035)	1917 ^b (1965)	2021 (w), 1885 (s) 1890) (S); (1970) (T); (1870) (BS)	this work
2	2044	1977, 1965		19
3a	2140			this work
3b	2140 (2124)	(2139)		this work
4	NA	NA		17
5	2029	NA		18
6	1910 (1936)	(1893)		20

^a Nujol, cm⁻¹ unless otherwise specified. Computed values are given in parentheses ^bKBr.

Scheme 2. Possible Electronic Structures for 1 and 1⁺



4. IR Spectroscopy. A large number of mononuclear Fe^{II} and Fe^{III} acetylides of $Cp^*(dppe)Fe-C\equiv C-R$ were subject to FTIR analyses. The stretching frequency of the triple bond ($\nu_{C\equiv C}$) was found to be dependent on the electronic nature of the appended substituent, and its evolution could be quantitatively rationalized using valence bond (VB) formalism.^{23,28-30} It was shown that respectively electron-withdrawing substituents in Fe^{II} acetylides or electron-releasing substituents in the Fe^{III} congeners favor the cumulenic character of the alkynyl bridge.²³

The neutral complex was characterized by a strong absorption at 2022 cm⁻¹, which corresponds to the C=C stretching mode. In comparison with other members of this Cp*(dppe)Fe-C≡C-R family of Fe^{II} complexes, the frequency is relatively low. This is confirmed by DFT calculations (see Table 3). For purpose of comparison, the lowest frequencies ever observed for this kind of complex were found for R = 9,10-C₁₄H₈-CN ($\nu_{C=C}$ = 1986 cm⁻¹), and a frequency as low as 2025 cm⁻¹ was found for R = 1, 4-C₆H₄CN.^{23,31} These data suggest that C=C bond order of the alkynyl linker is probably weakened by the presence of the TTFMe₃ core. However, the VB structure 1b (Scheme 2) should not play a significant role in the description of the electronic structure of this complex because the CV data indicate that the TTFMe₃ group is weakly electron releasing. Moreover, it is also noteworthy that the Fe-C bond distance in 1 is significantly longer (1.898(2) Å) than in the iron acetylides bearing an electron-withdrawing aryl group

(1.879(5) Å for $R = 1,4-C_6H_4CN$). These results suggest that **1b** is only a minor contributor (at best) to the overall structure of **1**.

Upon one-electron oxidation, the IR absorption corresponding to the $\nu_{C=C}$ stretch is shifted to lower wave numbers. This shift follows the same trend as previous observations.²³ However, its amplitude is exceptionally large in the present case ($\Delta \nu = 105 \,\mathrm{cm}^{-1}$). Indeed, up to now the largest lowering of the $\nu_{C=C}$ frequency induced by a single electron transfer was observed for the complex having a strongly electron-releasing substituent ($R = 1,4-C_6H_4NMe_2$),²³ and the effect was not as large as in the present case ($\Delta \nu = 94 \text{ cm}^{-1}$). The weight of the VB structure 1^+b (Scheme 2) is probably important in the description of the electronic structure of 1^+ . As a consequence, the positive charge is apparently mainly iron centered, while the spin density should be shared between the iron center and the organic moiety. Our results suggest that when coordinated to the Cp*(dppe)Fe moiety the TTFMe₃ group presents an original behavior. Indeed, up to now we have always observed that in the Cp*(dppe)Fe^{III} series the spin density is strongly metal centered regardless of the substituent on the alkynyl ligand. In contrast, in the closely related Cp*(dppe)Ru^{III} series, the spin density is largely distributed on the whole molecule.³

The IR spectrum of the deoxidized species $1[PF_6]_2$ displays two bands corresponding to the $\nu_{C=C}$ stretch at 2020 and 1885 cm⁻¹ with a constant ratio of relative intensities of 1:4. Following the DFT data discussed below these two bands might be assigned to the triplet (S = 1) and singlet or "broken symmetry" (S = 0) spin isomers.³³

5. ⁵⁷Fe Mössbauer Spectroscopy. ⁵⁷Fe Mössbauer spectroscopy is a very sensitive probe for identifying the iron oxidation state and the nature of the Fe–C bond.³⁴ Moreover, in a homogeneous series of iron compounds like Cp*-(dppe)Fe-C \equiv C-, it has been shown that the isomeric shift is related to the electron density at the metal center.³⁵ Additionally, Mössbauer spectroscopy constitutes a sensitive and useful means to probe the selectivity of the redox reactions.

The 57 Fe Mössbauer spectra of microcrystalline samples of the complexes 1 and 1[PF₆] were run at 80 K and least-squares fitted with Lorentzian line shapes.³⁶ The isomer shift (IS) and the quadrupole splitting (QS) parameters are given in Table 4. The spectrum of the neutral complex 1 displays a unique doublet, and

⁽²⁸⁾ Connelly, N. G.; Gamasa, M. P.; Gimeno, J.; Lapinte, C.; Lastra, E.; Maher, J. P.; Le Narvor, N.; Rieger, A. L.; Rieger, P. H. J. Chem. Soc., Dalton Trans. **1993**, 2575–2578.

⁽²⁹⁾ Paul, F.; Mevellec, J.-Y.; Lapinte, C. Dalton Trans. 2002, 1783–1790.

⁽³⁰⁾ Paul, F.; Toupet, L.; Thépot, J.-Y.; Costuas, K.; Halet, J.-F.; Lapinte, C. *Organometallics* **2005**, *24*, 5464–5478.

⁽³¹⁾ de Montigny, F.; Argouarch, G.; Roisnel, T.; Toupet, L.; Lapinte, C.; Lam, S. C.-F.; Tao, C.-H.; Yam, V. W.-W. *Organometallics* **2008**, *27*, 1912–1923.

⁽³²⁾ Paul, F.; Ellis, B. E.; Bruce, M. I.; Toupet, L.; Roisnel, T.; Costuas, K.; Halet, J.-F.; Lapinte, C. *Organometallics* 2006, *25*, 649–665.
(33) Guillaume, V.; Mahias, V.; Mari, V.; Lapinte, C. *Organometallics* 2006, *1*, 2007.

 ^{2000, 19, 1422–1426.} Lapinte, C. J. Organomet. Chem. 2008, 693, 793–801.
 (34) Guillaume, V.; Thominot, P.; Coat, F.; Mari, A.; Lapinte, C.

 ⁽³⁵⁾ Argouarch, G.; Thominot, P.; Paul, F.; Toupet, L.; Lapinte, C.
 (35) Argouarch, G.; Thominot, P.; Paul, F.; Toupet, L.; Lapinte, C.

⁽⁵⁵⁾ Argouarch, G.; Thomhot, P.; Paul, F.; Toupet, L.; Lapinte, C. C. R. Chim. **2003**, 6, 209–222.

⁽³⁶⁾ Varret, F.; Mariot, J.-P.; Hamon, J.-R.; Astruc, D. Hyperfine Interact. 1988, 39, 67-81.

Table 4. ⁵⁷Fe Mössbauer Parameters for 1^{n+} (n = 0, 1) and Related Compounds 2 and 7

	$\mathrm{IS}^{a}\left(\mathrm{QS} ight)\mathrm{I}$	b , mm s ⁻¹
compd	n = 0	n = 1
1 2^c 7^d	0.240 (1.979) 0.136 0.259 (1.969) 0.116	0.153 (1.114) 0.220 0.227 (0.974) 0.146 0.141 (1.123) 0.171

^{*a*} The velocity is referenced to iron metal. ^{*b*} Γ is the half-width at half-height. ^{*c*} From ref 19. ^{*d*} From ref 35.

the parameters are very close to those obtained for 2, chosen as a representative member of the $Cp^*(dppe)Fe^{II}-C=C-$ series.^{3,34,35}

In the case of complex 1[PF₆], the spectrum displays a single doublet, which probes the thermal stability of this radical. However, the QS parameter is exceptionally large for a Fe^{III}-alkynyl derivative, evidencing that the electronic structure of the new complex is unusual. Indeed, for the 17-electron Fe^{III} radical cation of this series, it has been observed that the quadrupole splitting is systematically below 1.0 mm s^{-1, ^{23,37} In the [Cp*(dppe)Fe⁻]⁺ series, QS} values ranging between 1.0 and 1.5 are characteristic of metallacumulenylidene cationic complexes with the general structure $Cp^*(dppe)Fe(=C(=C)nR_2)]X$, and complex 7 can be regarded as a representative example of this type of compound. For these derivatives an empiric dependence between the Fe=C distances and the QS values was observed.³⁵ According to this relationship the iron-carbon distance in $1[PF_6]$ is expected to be close to 1.80 ± 0.02 Å (computed value 1.827 Å). The Fe-C distance shortens upon one-electron oxidation by ca. 0.07 Å. Such a behavior strongly contrasts with all the previous observations for the known redox couple of [Cp*(dppe)- $\text{Fe-C}=\text{C-R}]^{0/+}$, for which it was found that the Fe-C bond distance shortens much less (ca. 0.04 Å at maximum).³⁰

The IS parameters reflect the electron density at the iron nucleus and decrease as the positive charge is more and more localized on the metal center or less stabilized by electrostatic interaction between cations and anions.³⁸ In the case of the complex $1[PF_6]$, the IS value is very small and compares well with the data obtained in the case of the iron carbene 7 (IS = 0.141 mm s⁻¹; QS = 1.123 mm s⁻¹), for which the charge is localized on the metal center.³⁵

Taken as a whole, the variation of the QS and IS parameters upon one-electron oxidation indicates that the Fe–C carbon bond order increases significantly, and the positive charge density is concentrated on the iron nuclei. As a consequence, in terms of VB description, the structures 1^+b might have a significant weight in the depiction of the electronic structure of $1[PF_6]$; in contrast, 1^+a and even more $1^+b'$ structures should have a negligible contribution. These observations are in line with the FTIR data and are fully supported by the DFT calculations (see Section 9). Note that such an electronic structure also explains why the second oxidation of 1 is less positive than the first oxidation of 3a.

6. Glass EPR Spectroscopy. Complex $1[PF_6]$ was dissolved in a 1:1 CH₂Cl₂/C₂H₄Cl₂ mixture, and the resulting solution was transferred into an EPR tube before being cooled to 68 K. The X-band EPR spectrum of the monocation shows three well-resolved features corresponding to

Table 5. EPR Parameters for 1[PF₆] and Related Fe(III) Compounds at 66 K

compd	g_1	$g_2 (a_2)^a$	$g_3 (a_3)^a$	$g_{iso}^{\ \ b}$	Δg^c	ref
1[PF ₆]	2.450	2.036(38)	2.002(5)	2.163	0.448	this work
I[PF ₆] ₂	2.312 D =	-88 G, E =	$2.063 \\ 8 G, \Delta ms = 1$	$\pm 2, g = 4$.267	this work
2[PF ₆]	2.366	2.036(14)	1.986(16)	2.129	0.380	39
6[PF ₆]	2.457	2.034	1.977	2.156	0.480	20
$a_{\rm In}$	b and b	- (-) -	$ \sim \rangle/2 c \Lambda$	~ - ~	~	

^{*a*} In Gauss. ^{*b*} $g_{iso} = (g_1 + g_2 + g_3)/3$. ^{*c*} $\Delta g = g_3 - g_1$.

the components of the *g*-tensors, characteristic of d⁵ low-spin Fe(III) in a pseudooctahedral environment. The *g* values extracted from the spectra are collected in Table 5. The spectrum of $1[\mathbf{PF}_6]$ is characterized by a large isotropic tensor (g_{iso}) and a large tensor of anisotropy (Δg).

Optimal resolution of the spectral features allows the observation of the hyperfine coupling with two phosphorus nuclei. In contrast with previous observations of related Fe^{III} radicals, ^{19,28,40} the coupling constants are quite different for the g_2 and g_3 components. Such an original anisotropy possibly originates from the partial delocalization of the unpaired electron on the TTFMe₃ moiety.

The dicationic complex $1[\mathbf{PF}_6]_2$ was obtained by treatment of complex 1 with 2.2 equiv of $[(C_5H_5)_2Fe][\mathbf{PF}_6]$ in THF at -80 °C. The resulting brownish solution was transferred at this temperature into an EPR tube before being cooled to 66 K. A well-resolved EPR spectrum displaying three components for the $\Delta m_s = \pm 1$ transition was obtained, and the EPR parameters were extracted by simulation (Table 5). Additionally, fine structures were clearly visible in the g = 2region, reflecting the zero-field splitting of the m_s components of the triplet state. Furthermore, the $\Delta m_s = \pm 2$ transition characteristic of the triplet state was clearly observed at g =4.267. These interesting results clearly demonstrate that complex $1[\mathbf{PF}_6]_2$ carries two unpaired electrons and magnetic exchange interactions between them take place.

7. UV-Vis Absorption Spectroscopy. The UV-vis spectra of the complexes $1[\mathbf{PF}_6]_n$ (n = 0, 1) were recorded in the range 260-800 nm. The spectrum of the neutral complex resembles the spectrum obtained for the previously reported functionalized organoiron(II) compounds (Table 6).41 Besides the high-energy transition that can apparently be attributed to $\pi - \pi^*$ ligand-centered transitions, two less intense transitions were also observed. These absorptions located in the visible range are at the origin of the orange color of 1 and can be assigned to MLCT transitions.²³ However, in comparison with 2 and other related complexes bearing a functional aryl group, these transitions are red-shifted by ca. 60 nm.^{19,23,42} This feature suggests that the low-energy transition results from some admixture of $d\pi(Fe) \rightarrow \pi^*(C \equiv C \text{-} TTFMe_3)$ and is in line with the atomic character of the HOMOs and LUMOs (see Section 9).

The UV–vis spectrum of the mono-oxidized species $1[PF_6]$ displays several absorptions that are also found for other Fe^{III}-alkynyl complexes.^{7,37} Indeed, upon one-electron

⁽³⁷⁾ Weyland, T.; Costuas, K.; Mari, A.; Halet, J.-F.; Lapinte, C. Organometallics 1998, 17, 5569–5579.

⁽³⁸⁾ Gütlich, P.; Link, R.; Steinhäuser, H. G. Inorg. Chem. 1978, 17, 2509.

⁽³⁹⁾ Roué, S.; Le Stang, S.; Toupet, L.; Lapinte, C. C. R. Chim. 2003, 6, 353–366.

⁽⁴⁰⁾ Hamon, P.; Justaud, F.; Cador, O.; Hapiot, P.; Rigaut, S.; Toupet, L.; Ouahab, L.; Stueger, H.; Hamon, J.-R.; Lapinte, C. J. Am. Chem. Soc. 2008, 130, 17372–17383.

⁽⁴¹⁾ Costuas, K.; Paul, F.; Toupet, L.; Halet, J.-F.; Lapinte, C. Organometallics 2004, 23, 2053–2068.

⁽⁴²⁾ Weyland, T. Synthèse et Propriétés de Complexes Organo-fer Bi- et Tri-nucléaires sous Differents Degrés d'Oxydation. Ph.D. Thesis, Rennes 1, Rennes, 1997.

Table 6. Visible Absorption Data for $1[PF_6]_n$ (n = 0, 1), in $CH_2Cl_2^a$

compd	absorption λ/nm (10 ³ $\varepsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)	ref	
1	288 (27.2), 346 (22.3), 400b (12.3)	this work	
1[PF ₆]	232 (54.0), 276 (33.0), 336 (12.3), 514 (4.1), 572 (3.8)	this work	
2	$233(31.0), 273^{b}(13.7), 362(6.9)$	19	
2[PF ₆]	402 (5.0), 434a (4.4), 736 (6.6)	19	
3a	297 (9000), 337 (7700), 386 (2000)	this work	
$3a[ClO_4]^d$	282 (6200), 338 (4900), 404 (2600), 466 (4400), 540 (1500), 682 (2600)	this work	
$3a[ClO_4]_2^e$	270 (4600), 351 (3000), 467 (6000), 540 (2100), 682 (3600)	this work	

^{*a*} Unless otherwise specified. ^{*b*} Shoulder. ^{*c*} UV range not available. ^{*d*} In situ generated by treatment of **3a** with 1 equiv of $Fe(ClO_4)_3$. ^{*e*} In situ generated by treatment of **3a** with 2 equiv of $Fe(ClO_4)_3$.

oxidation, the intense bands at ca. 346-400 nm in **1** are replaced by two less intense bands at ca. 514-572 nm. It is likely that upon oxidation of Fe^{II} to Fe^{III}, the band due to the $d\pi$ (Fe) $\rightarrow \pi^*$ (C=C-TTFMe₃) MLCT transition vanishes. Similar loss of the $d\pi$ (Fe) $\rightarrow \pi^*$ (C=C-Ar) MLCT intensities has been reported in the oxidation of the related compounds Cp*(dppe)Fe-C=C-Ar to [Cp*(dppe)Fe-C=C-Ar][PF₆].^{24,30,37} Absorption bands lower in energy are also observed in the spectrum of **3a**[CIO₄], suggesting that these transitions can be ascribed to a LMCT transition derived from the whole structure [Cp*(dppe)Fe^{III}-C=C-TTFMe₃] and not only from the organometallic moiety, as it was found in some instances.^{43,44} This finding is corroborated by the distribution of the spin density over the iron-ethynyl and TTFMe₃ moieties (see Section 9).

8. NIR Absorption Spectroscopy. The spectrum of the radical cation 1[PF₆] dissolved in CH₂Cl₂ exhibits absorptions of moderate intensities in the NIR range. A spectrum run in CH_3CN , a much more polar solvent than CH_2Cl_2 , evidences an overall solvatochromism toward the higher energies. Given the possibility that photoinduced electron transfer can take place from the TTFMe3 moiety to the Fe^{III} center of 1[PF₆], NIR bands might be assigned to ligandto-metal charge transfer (LMCT) transitions. An analogy can be made between these transitions and intervalence transitions (IVCT) observed in the case of mixed-valence compounds, and the Marcus-Hush theory may apply. Assuming that the absorption bands can be approximated in terms of Gaussian band shapes, the experimental spectra were deconvoluted in the range 3300-14000 cm⁻¹. Regardless of the solvent used, the results show that three Gaussian curves with similar intensities can describe very accurately the experimental spectrum (Figure 3). Indeed, the fits are good enough to allow an almost exact overlay of the sum of the spectral components with the experimental traces. Table 7 summarizes spectral parameters extracted from the band shape analysis.

Assignment of the NIR absorptions is not obvious. The IVCT character of low-energy and high-energy bands was excluded by the observation of the electronic spectrum of the unstable dioxidized species $1[PF_6]_2$. Despite its high kinetic instability due to unavoidable and unknown side reactions in the experimental conditions, this compound can be generated in situ. Thus, the complex $1[PF_6]_2$ was prepared in a Schlenk tube by addition of ferrocenium hexa-fluorophosphate to a CH_2Cl_2 solution of $1[PF_6]$ cooled



Figure 3. Near-IR spectrum for 1[PF₆] in dichloromethane and proposed deconvolution.

at -60 °C. NIR spectroscopic monitoring of this solution shows that the band around 7000 cm^{-1} has disappeared, while a weak absorption is still present around 5500 cm^{-1} and a more intense band can be observed at ca. $13\,000\,\mathrm{cm}^{-1}$. This result clearly indicates that the band found at 6960 cm^{-1} in the spectrum of $1[PF_6]$ can safely be ascribed to a photoinduced electron transfer. Consequently, the contribution at lowest energy probably corresponds to a d-d ligand field transition. Such transitions are usually observed for mononuclear and polynuclear alkynyl iron(III) complexes.^{3,37} It has been shown that they are characteristic of the Cp*(dppe)Fe^{III} fragment and are attributed to a ligand field (LF) transition from the (SOMO-2) to the SOMO.³⁰ The weak solvatochromism of the band, as well as its spectral parameters, is consistent with this attribution.9,45 On the other hand, the band at 11200 cm^{-1} , which is blue-shifted upon one-electron oxidation of 1[PF₆], can probably be ascribed to a LMCT transition.

The presence of an IVCT band in the NIR spectrum shows that complex 1[PF₆], which possesses both inorganic and organic redox centers, behaves as a mixed-valence complex. This band can furthermore allow the calculation of the electronic coupling parameter H_{ab} , which can be computed using eq 1, where d_{ab} is the through-space distance between the redox centers (Å) and the other terms are as given in Table 7. In the present case determination of d_{ab} is not easy. We have approximated this parameter taking the throughspace distance between the iron atom and the centroid of the central carbon-carbon double bond of the TTFMe₃ core $(d_{ab} = 7.46 \text{ Å})$. This formula gives a H_{ab} value of 320 cm⁻¹

⁽⁴³⁾ Wong, K. M.-C.; Lam, S. C.-F.; Ko, C.-C.; Zhu, N.; Yam, V. W.-W.; Roué, S.; Lapinte, C.; Fathallah, S.; Costuas, K.; Kahlal, S.; Halet, J.-F. *Inorg. Chem.* **2003**, *42*, 7086–7097.

⁽⁴⁴⁾ Paul, F.; Meyer, W. E.; Toupet, L.; Jiao, H.; Gladysz, J. A.; Lapinte, C. J. Am. Chem. Soc. 2000, 122, 9405–9414.

⁽⁴⁵⁾ Gauthier, N.; Olivier, C.; Rigaut, S.; Touchard, D.; Roisnel, T.; Humphrey, M. G.; Paul, F. *Organometallics* **2008**, *27*, 1063–1072.

⁽⁴⁶⁾ Robin, M. B.; Day, P. Adv. Inorg. Chem. Radiochem. 1967, 10, 247-422.

solvent	$v_{\rm max} ({\rm cm}^{-1})$	$\varepsilon_{\rm max} ({\rm M}^{-1} {\rm cm}^{-1})$	$\Delta \nu_{1/2}^{\rm exp} (\rm cm^{-1})$	$\Delta \nu_{1/2}^{\rm cal} (\rm cm^{-1})^a$	$\mathbf{H}_{ab}(\mathrm{cm}^{-1})^{b}$	ref
CH ₂ Cl ₂	4990	770	850			this work
	6780	1120	1750	2441	320	
	11200	750	2100			
CH ₃ CN	5350	380	950			this work
2	7580	880	1800	2794	337	
	11900	730	2300			

Table 7. NIR Absorption Data for 1[PF₆] in CH₂Cl₂ and CH₃CN

^{*a*} Calculated from eq 2. ^{*b*} Calculated from eq 1.





for 1[PF₆]. This value is high for a class II compound.⁴⁶

$$H_{\rm ab} = 0.0206 (\nu_{\rm max} \varepsilon_{\rm max} \Delta \nu_{1/2}^{\rm exp})^{1/2} / d_{\rm ab} \qquad (1)$$

$$(\Delta \nu_{1/2})_{\text{theo}} = [2310(\nu_{\text{max}} - \Delta G^0)]^{1/2}$$
(2)

Physically, the NIR transition corresponds to a photoinduced electron transfer from the TTFMe₃ core to iron, giving rise to the excited state II with dominant radical character on TTFMe₃ as depicted in Scheme 3, while the H_{ab} parameter represents the electronic coupling of the redox isomers (I and II) of 1[PF₆]. The former best represents the ground state with the charge localized on the iron center based upon the many spectroscopic probes given above and the DFT calculations discussed below. The free energy difference (ΔG^0) can be approximated by the difference in oxidation potentials between the mononuclear alkynyl iron complex 6 and the alkyne-substituted TTFMe₃ 3a in Table 2 $(0.52 \text{ V or } 4200 \text{ cm}^{-1})$. Equation 2 can then be used to calculate the theoretical bandwidth of the IVCT band.^{1,3} The value obtained is ca. 25% larger than that observed $(2441 \text{ vs } 1750 \text{ cm}^{-1})$. In view of the approximations made, uncertainty in the numbers, and the relatively large electronic coupling, which favors deviation from the Hush equations, this provides a valuable a posteriori validation of the use of the two-level model to extract the electronic coupling parameter.

9. Electronic Structures. In order to better understand some of the experimental results, a theoretical investigation was conducted at the DFT level (see computational details) on the neutral and oxidized forms of 1, as well as on 3b and $Cp^*(dppe)Fe(C \equiv CH)$ (6) for comparison. Optimized distances and angles computed for the neutral compound 1 compare rather well with available experimental data found in Table 1. The largest deviations of the experimental atomic separations (< 0.03 Å) are observed for the Fe–P distances, which are computed somewhat longer than the experimental ones, a tendency generally noted for this kind of compound. The Fe-C distance in 1 is slightly shorter than the corresponding one in complex 6 (1.873 vs 1.890 Å), whereas the C-C ethynyl bond is computed to be slightly longer (1.247 vs 1.237 A). C-C and C-S distances in 1 are nearly identical to those computed for 3b (see Table 1) and somewhat differ from those computed in Me₃TTF-CH=CH-Py, in which the TTFMe₃ and acceptor pyridine moieties are linked by an ethylene group.⁴⁷ Knowing that the atomic separations are particularly sensitive to the charge of the TTFMe₃, this seems to indicate that the Me₃TTF moiety acts as a rather weak electron donor to the iron redox group, confirming experimental results discussed above.

This good agreement between experimental and computed distances observed for the neutral compound 1 gives confidence in the computed bond distances in the cationic forms of 1, for which no X-ray data are available yet. Indeed, upon oxidation, the largest change in the atomic separation occurs on the Fe-ethynyl group, with some lengthening of the Fe-P distance, some shortening of the Fe-C37 distance, and a slight lengthening of the C37-C38 separation, as usually observed for organometallic compounds containing this kind of terminus.^{24,32,37,41–43,48} The TTFMe₃ part of the molecule is less affected-the C-S(av) and central C42-C43 distances change from 1.783 Å to 1.769 Å and from 1.357 Å to 1.373 Å upon oxidation, respectively—indicating that the first oxidation occurs mainly at the iron end group as proposed above. Indeed, these atomic separations are very sensitive to oxidation. The corresponding C-C distance increases to 1.394 Å, whereas the C-S(av) bonds decrease to 1.753 Å for the parent TTFMe₃ molecule $3b^+$ (see Table 1). Interestingly, the Fe-C37 distance shortens more in 1 than in the parent molecule 6 upon oxidation (from 1.873 Å to 1.827 Å, and from 1.890 Å to 1.865 Å for 1 and 6, respectively). This shows a more carbenic character for 1^+ and gives some weight to the Lewis formula 1^+b (Scheme 3) to describe its electronic structure.

A few other computational data such as the energies of the frequencies of the ethynyl C=C vibrator confirm the conclusions that first oxidation occurs mainly at the Fe-ethynyl moiety. They are given in Table 3 for the three compounds 1^{n+} , $3b^{n+}$, and 6^{n+} (n = 0-1). Less energetic vibrational frequencies are computed for the ethynyl groups upon oxidation in 1 and 6, but not in 3b, for which oxidation should occur on the TTFMe₃ part.

The molecular orbital diagrams of 1, 3b, and 6 are compared in Figure 4. They all present a large HOMO–LUMO gap, characteristic of electronically saturated molecules. Nevertheless, that for 1 is smaller, with the HOMO somewhat antibonding between the Fe-ethynyl and the TTFMe₃ moieties higher in energy (vide infra). Accordingly, the computed first ionization potential (IP) is smaller for 1 than for the two parent molecules 3b and 6 (4.78, 6.01, and 5.31 eV, respectively). The fact that the first IP of 1 is substantially lower than that of 6 indicates that the TTFMe₃ group acts as

⁽⁴⁷⁾ Prabusankar, G.; Molard, Y.; Cordier, S.; Golhen, S.; Le Gal, Y.; Perrin, C.; Ouahab, L.; Kahlal, S.; Halet, J.-F. *Eur. J. Inorg. Chem.* **2009**, 2153–2161.

⁽⁴⁸⁾ Bruce, M. I.; Costuas, K.; Davin, T.; Ellis, B. E.; Halet, J.-F.; Lapinte, C.; Low, P. J.; Smith, K. M.; Skelton, B. W.; Toupet, L.; White, A. H. *Organometallics* **2005**, *24*, 3864–3881.



Figure 4. Molecular orbital diagrams of 1 (center), 3b (right), and 6 (left).



Figure 5. Plots (contour values: $\pm 0.05 \, [e/bohr^3]^{1/2}$) and energy of the HOMO and HOMO-1 of **1** (bottom), **3b** (middle), and **6** (top).

a weak electron donor to the iron-ethynyl group during the first oxidation, as proposed on the basis of the electrochemical data (see above).





%Fe = 0.32

Figure 6. Spin density distribution and Mulliken population analysis for 1^+ (top) and $1^{2+}(BS)$ (bottom). Contour values are $\pm 0.005 \text{ e}^-/\text{bohr}^3$.

The HOMO of these systems is important in the description of their geometrical and physical properties upon oxidation. They are depicted in Figure 5. In the case of compound 1, it is substantially localized on the Fe center and the ethynyl group and to a lesser extent on the TTFMe₃ part. Analogously, the HOMO of its parent molecule **6** is heavily located at the Fe-C₂ backbone. Not surprisingly, being mainly Fe-C37 π -antibonding and C37-C38 π -bonding in character, oxidation of **1** and **6** leads to some shortening of Fe-C37 and a slight lengthening of C37-C38 (see Table 1). In line with the absence of ethynyl character in the HOMO of **3b**, the C37-38 bond length does not change upon oxidation (see Table 1).

The atomic spin densities of the monocationic compound 1^+ are given at the top of Figure 6. Their analysis gives some insight on the localization of the unpaired electron. Interestingly, the spin density is almost equally distributed over the Fe-ethynyl and the TTFMe₃ moieties. A possible explanation for this observation is some reorganization of electron density after relaxation of the molecular geometry following oxidation, which mainly occurs on the Fe-ethynyl group (vide supra).

What about the possible second oxidation experimentally observed at 0.38 V? The geometries of the dicationic form of complex 1 within three different spin states, i.e., the closedshell singlet (low-spin (LS) diamagnetic state), the triplet state (high-spin (HS) magnetic state), and the broken symmetry singlet (BS) featuring the antiferromagnetic state, were investigated. Pertinent atomic separations associated with these different magnetic states are given in Table 1. The three different geometries hardly differ except the Fe-C(α) distance, which is computed slightly longer in the singlet state with respect to the triplet and broken-symmetry states (see Table 1). Regardless of the magnetic state of 1^{2+} , the TTFMe₃ part is the most affected upon the second oxidation, with some substantial lengthening of the central C-C distance and some shortening of the outer C-C bonds (compare 1^+ and 1^{2+} in Table 1). It is important to note that the most stable electronic configuration is that of the

antiferromagnetic $1^{2+}(BS)$ structure (with a large exchange magnetic coupling J (J = E(BS) - E(T)) of -805 cm^{-1}). Its corresponding spin density plot is shown at the bottom of Figure 6. Interestingly, unpaired spin density resides both at the iron-ethynyl group and the TTFMe₃ fragment.

Conclusion

In summary, this contribution shows that while weak electronic interactions take place between the electron-rich iron center Cp*(dppe)Fe and the TTFMe₃ core in the neutral complex 1, in the oxidized species 1[PF₆] a very good electronic coupling exists between the two electrophores. Consequently, the TTFMe₃ moiety can be regarded as a synthetic metal,¹² and the assembly behaves as a heterobimetallic MV complex. Comparison with MV heterobimetallic complexes possessing the same Cp*(dppe)Fe unit associated with less electron rich ends containing iron,²⁵ rhenium,⁴⁸ and ruthenium⁴⁴ centers, which all behave as class II Robin-Day systems, shows that the electronic communication in the MV complex 1[PF₆] is very good, and the H_{ab} parameter is as large as the largest value found for these related systems with comparable distances between the redox centers. Additionally, trends previously reported for bimetallic related compounds have been further supported. The reversible redox behavior, polarized electronic structures with delocalization of the odd electron on the whole molecule, capabilities for photoinduced electron transfer, and other properties demonstrated above illustrate the potential for organometallics associated with synthetic metals (like TTF derivatives¹²) in nanoscale devices, including components for molecular electronics and NLO active assemblies. Work is currently underway to further explore, define, and elaborate the electronic and magnetic properties of these hybrid systems through construction of tailored bridge microenvironments.

Experimental Section

General Procedures. Manipulations of air-sensitive compounds were performed under an argon atmosphere using standard Schlenk techniques or in an argon-filled Jacomex 532 drybox. Tetrahydrofuran (THF), diethyl ether, toluene, and pentane were dried and deoxygenated by distillation from sodium/benzophenone ketyl. Acetone was distilled from P2O5. Dichloromethane and dichloroethane were distilled under argon from P2O5 and then from Na2CO3. Methanol was distilled over dried magnesium turnings. The following compounds were prepared following published procedures: ferrocenium hexafluorophosphate, $[Fe(\eta^5-C_5H_5)_2][PF_6]$,⁴⁹ and $Cp^*(dppe)FeCl$.²¹ Potassium tert-butoxide (ACROS) was used without further purification. Infrared spectra were obtained in KBr with a Bruker IFS28 FTIR infrared spectrophotometer $(4000-400 \text{ cm}^{-1})$. UV-visible spectra were recorded on a Varian CARY 5000 spectrometer. ¹H, ¹³C, and ³¹P NMR spectra were recorded on a Bruker DPX200, an Avance 300, and an Avance 500 NMR multinuclear spectrometer at ambient temperature, unless otherwise noted. Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane (TMS), using the residual solvent resonances as internal references. Coupling constants (J) are reported in hertz (Hz), and integrations are reported as numbers of protons. The following abbreviations are used to describe peak patterns: br = broad, s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, m = multiplet. ¹H and ¹³C NMR peak assignments are supported by the use of COSY, HMQC, and HMBC experiments. High-resolution mass spectra

(HRMS) were recorded on a high-resolution ZabSpec TOF VG analytical spectrometer operating in the ESI+ mode, at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO), Rennes. Polyethyleneglycol (PEG) was used as internal reference, and dichloromethane was used as solvent. All mass measurements refer to peaks for the most common isotopes (¹H, ¹²C, ³¹P, and ⁵⁶Fe). EPR spectra were recorded on a Bruker EMX-8/2.7 (X-band) spectrometer. The ⁵⁷Fe Mössbauer spectra were recorded with a 2.5×10^{-2} C (9.25×10^{8} Bq) 57Co source using a symmetric triangular sweep mode. Computer fitting of the Mössbauer data to Lorentzian line shapes was carried out with a previously reported computer program.³⁶ The isomer shift values are reported relative to iron foil at 298 K. Elemental analyses were conducted on a Thermo-Finnigan Flash EA 1112 CHNS/O analyzer by the Microanalytical Service of the CRMPO at the University of Rennes 1, France.

Cp*(dppe)Fe-C≡C-TTFMe₃ (1). A Schlenk tube was charged with 0.678 g (1.08 mmol, 1.05 equiv) of $(\eta_2$ -dppe)(η_5 -C₅-(CH₃)₅)Fe-Cl, 0.357 g (1.032 mmol, 1.0 equiv) of Me₃TTF-C₂-TMS, 0.185 g (1.13 mmol, 1.1 equiv) of NH₄PF₆, and 0.066 g (1.13 mmol, 1.1 equiv) of KF along with 40 mL of MeOH. The mixture was stirred for 16 h at 25 °C before adding KOBu^t (0.100 g). The solvent was then cryogenically trapped, and the dark orange residue was washed with 10.0 mL of pentane, partially precipitated from CH2Cl2/pentane, washed three times with 10 mL of pentane, and dried under vacuum, yielding complex 1 as an orange powder (0.643 g, 69%). Crystals were grown by slow diffusion of pentane from a toluene solution of 1 (layer/layer). Anal. Calcd for $C_{47}H_{48}P_2S_4Fe + 0.5C_7H_8$: C, 67.02; H, 5.79. Found: C, 67.18; H, 5.96. ESI MS (m/z): calcd for [C₄₇H₄₈P₂S₄Fe] 858.14636, found (CH₂Cl₂) 858.1484 ([M]+, 100%). FT-IR (ν , KBr, cm⁻¹): 2022 (s, C=C). ³¹P NMR (δ , C₆D₆, 81 MHz): 101.8 (s, dppe). ¹H NMR (δ , C₆D₆, 200 MHz): 7.89 (t, ${}^{3}J_{HH} = 8.0$ Hz, 4H, H_{para}), 7.23 (dd, ${}^{3}J_{HH} = 7.8$ and 8.0 Hz, 8H, H_{meta}), 7.08 (dd, ${}^{3}J_{HH} = 7.8$ and 8.0 Hz, 4H, H_{ortho}), 7.02 (t, ${}^{3}J_{HH} = 7.8$ Hz, 4H, H_{para}), 2.63 and 1.84 (m, 2H, 2 × CH_{dppe}), 1.74 (s, 3H, CH_3), 1.46 (s, 15 H, $C_5(CH_3)_5$), 1.36 and 1.37 (2 x CH_3). ¹³C³⁵ NMR (δ , C₆D₆): 151.3 (C_{α} , ² J_{PH} = 38.4 Hz), 138.9 and 137.4 (2 × $C_{ipso/Ar-dppe}$) 134.1, 134.0, 129.2, 128.8, 127.4, and 127.1 (6 × $CH_{Ar-dppe}$), 122.5, 122.3, and 122.2 (3 × *C*-CH_{3/TTF}), 116.6 (C_{β}), 109.6, 109.5 (2 × *C*=C_{TTF}) and 106.0 (C_{δ}), 87.8 (C_{Cp*}), 30.60 ($C_{H_{2/dppe}}$), 14.62, 12.99, 12.97 (3 × $C_{H_{3/TTF}}$), $10.06 (CH_3/_{Cp*}).$

[Cp*(dppe)Fe-C≡C-TTFMe₃][PF₆] (1[PF₆]). A Schlenk tube was charged with complex 1 (0.210 g, 0.244 mmol, 1.0 equiv), which was dissolved in THF (10 mL). The solution was then cooled to −60 °C prior to adding ferricinium hexafluorophosphate (0.072 g, 0.22 mmol, 0.9 equiv) at once. The temperature of the solution was allowed to reach room temperature in 2 h before adding pentane (20 mL) under vigorous stirring. The resulting precipitate was subsequently washed with pentane (2 × 20 mL) to yield 1[PF₆] (0.190 g, 77%) as an air-stable, dark violet powder. FT-IR (ν , KBr, cm⁻¹): 1917 (s, C≡C), 835 (PF₆). The CV was identical to that of 1. Anal. Calcd for C₄₇H₄₈F₆P₃S₄Fe: C, 56.23; H, 4.82. Found: C, 56.37; H, 5.10. ESI-MS (m/z): calcd for [C₄₇H₄₈P₂S₄Fe] 858.14636, found (CH₂Cl₂) 858.1448 [M − PF₆].

X-ray Crystal Structure Determination. Single crystals were mounted on a APEXII Bruker-AXS diffractometer equipped with a CCD camera and a graphite-monochromated Mo K α radiation source ($\lambda = 0.71073$ Å), from the Centre de Diffractométrie (CDFIX), Université de Rennes 1, France. Data were collected at 150 K. The structure was solved with a direct method using the SIR-97 program and refined with a full matrix least-squares method on F^2 using the SHELXL-97 program.⁵⁰ Crystal data, data collection, and structure refinement parameters for 1: empirical formula, C₄₇H₄₈FeP₂S₄; formula mass, g

(50) Sheldrick, G. M. SHELXL97, Program for Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1997.

⁽⁴⁹⁾ Connelly, N. G.; Geiger, W. E. Chem. Rev. 1996, 96, 877-910.

mol⁻¹, 858.88; collection *T*, K, 150(2); crystal system, monoclinic; space group, $P2_1/c \#14$; *a* (Å), 15.7427(3); *b* (Å), 26.8761(5); *c* (Å), 20.0397(4); β (deg), 92.510(1); *V* (Å³), 8470.7(3); *Z*, 8; D_{calcd} (g cm⁻³), 1.347; crystal size (mm), 0.08 × 0.06 × 0.06; *F*(000), 3600; abs coeff (mm⁻¹), 0.662; θ range (deg), 1.50 to 27.50; range *h*,*k*,*l*, $-20 \le h \le 20, -30 \le k \le 34$; no.

(51) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision A.02; Gaussian Inc.: Pittsburgh, PA, 2009.

(52) Becke, A. D. Phys. Rev. 1988, A38, 3098–3200. Perdew, J. P. Phys. Rev. 1986, B33, 8822.

(53) Flükiger, P.; Lüthi, H. P.; Portmann, S.; Weber, J. *Molekel 4.3*, Swiss Center for Scientific Computing: Manno, 2000–2002; http://www.cscs.ch/molkel.

total reflns, 67343; no. unique reflns, 19393 [R(int) = 0.0289]; data/restraints/parameters, 19393/0/989; final R, R1 = 0.0355, wR2 = 0.0853; R indices (all data), R1 = 0.0489, wR2 = 0.0938; goodness of fit/ F^2 , 1.114; largest diff peak and hole (e Å⁻³), 0.508 and -0.317.

Density Functional Theory Calculations. DFT calculations were carried out on compounds 1^{n+} , $3b^{n+}$, and 6^{n+} (n = 0-2) with the Gaussian 09 program.⁵¹ The geometric structures were fully optimized without any symmetry constraint using the B86 functional⁵² within triple- ζ valence basis sets augmented with polarization functions (TZVP) due to Ahlrichs and co-workers. Plots of molecular orbitals and spin densities were constructed using the MOLEKEL program 4.1.⁵³

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Supporting Information Available: Complete set of crystallographic data in CIF format for the X-ray crystal structure of 1. This material is available free of charge via the Internet at http:// pubs.acs.org.