A Four-Oxidation-State Family of Coordinated Carbon: The First Isolable and Crystallographically Characterized Triradical $[M]{-}C_4{-}[M]^{3+}$

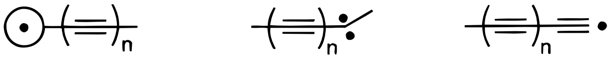
Maud Guillemot,[†] Loic Toupet,[‡] and Claude Lapinte*[,†]

UMR CNRS 6509, Organométalliques et Catalyse: Chimie et Electrochimie Moléculaires, and
UMR CNRS 6626, Groupe Matière Condensée et Matériaux, Université de Rennes I,
Campus de Beaulieu, 35042 Rennes Cedex, France

Received March 10, 1998

Summary: The deep blue complex $[Cp^*(dippe)Fe(\mu\text{-}C_4)Fe(dippe)Cp^*]^{3+}[PF_6]^-_3$ ($\mathbf{4}^{3+}[PF_6]^-_3$) *was prepared by a cascade of three successive one-electron oxidations of the neutral complex* $Cp^*(dippe)Fe(\mu\text{-}C_4)Fe(dippe)Cp^*$ (**4**). *This unprecedented trication was characterized by X-ray methods, and its triradical structure was established on the basis of Mössbauer, near-IR, and ESR spectroscopy.*

While acetylenic and polyacetylenic compounds are considered as key molecules in the design of high-spin carriers,[1] authentic carbon sp-centered radicals are rare. Up to now two classes of alkynyl compounds carrying unpaired electron have been accessible. The unpaired electron is located either in a remote organic or organometallic substituent of the acetylenic skeleton (**I**)[2−5]



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or in the α-position of the C≡C triple bond on a triplet carbene (**II**).[6−10] Compounds of class **III** with an even number of carbon atoms have only been observed on the time-of-flight scale in a mass spectrometer or by ESR characterization at liquid helium temperature during photoinduced polymerization of polyynes.[1,11,12]

Linear coordinated carbon chains stabilized by organometallic building blocks, $L_nMC_xM'L'_{n'}$, are now available for $x = 1{-}20$,[13] and a few of them have been prepared for different oxidation states of the metal termini, providing "*consanguineous*" families of molecules $[L_nMC_xML_n]^{n+}$. Two series of these compounds, with rhenium[14] and iron,[15] were isolated and fully characterized for three different oxidation states. Different ground-state electronic structures were proposed for the $-C_4-$ bridge between the metal centers in the dicationic complexes. Whereas a μ-butatrienediylidene formulation was found for the carbon bridge between the two 18-electron metal centers $\{[M]{=}C{=}C{=}C{=}C{=}[M]\}^{2+}$,[14,16] a μ-butadiynediyl carbon chain spans the two 17-electron iron centers $\{[Fe]{-}C{\equiv}CC{\equiv}C{-}[Fe]\}^{2+}$.[15] More recently, on the basis of cyclic voltammetry measurements, four discrete one-electron redox processes were reported for a $\{[Ru]{-}C{\equiv}CC{\equiv}C{-}[Ru]\}^{n+}$ system, and the Ru^{III}/Ru^{IV} and Ru^{IV}/Ru^{IV} structures were proposed for the highest oxidation states generated on the electrode surface.[17]

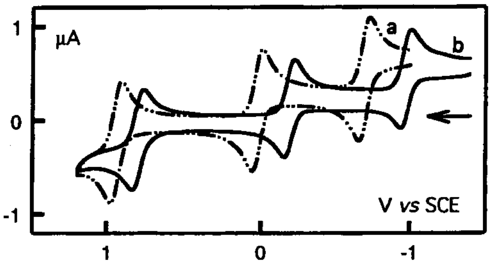

Figure 1. Cyclic voltammograms of **1** (a) and **4** (b) in CH_2Cl_2 on Pt electrodes (0.1 M $[Bu^n{}_4N][PF_6]$, scan rate 0.1 V s^{-1})

With the ultimate goal to discover a long-lived all-carbon chain centered radical, we reexamined the cyclic voltammogram (CV) of $[Cp^*(dppe)Fe(\mu\text{-}C_4)Fe(dppe)Cp^*]$ (**1**; dppe = ethylenebis(diphenylphosphine)) over a wider range of potentials (Figure 1). The CV showed a new reversible oxidation process near +1 V vs SCE, but efforts to prepare and isolate the tricationic compound $\mathbf{1}^{3+}$ failed. As there was no precedent for the isolation of a tricationic compound in the $[M]{-}C_4{-}[M]$ families,

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[†] UMR CNRS 6509.

[‡] UMR CNRS 6626.

(1) Iwamura, H.; Matsuda, K. *Acetylenic Compounds as Building Blocks for High-Spin Molecules and Molecular Assemblies*; Iwamura, H., Matsuda, K., Ed.; VCH: Weinheim, Germany, 1995; pp 385−414.

(2) Teuben, J. H.; De Liefde Meijer, H. J. *J. Organomet. Chem.* **1969**, *17*, 87−93.

(3) Köhler, F. H.; Prössdorf, W.; Schubert, U.; Neugebauer, D. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 850−851.

(4) Bianchini, C.; Laschi, F.; Masi, D.; Ottaviani, F. M.; Pastor, A.; Peruzzini, M.; Zanello, P.; Zanobini, F. *J. Am. Chem. Soc.* **1993**, *115*, 2723−2730.

(5) Howard, J. A.; Sutcliffe, R.; Tse, J. S. *Organometallics* **1984**, *3*, 859−866.

(6) Selvarajan, R.; Boyer, J. H. *J. Org. Chem.* **1971**, *36*, 1679−1682.

(7) Bernheim, R. A.; Kempf, R. J.; Gramas, J. V.; Skell, P. S. *J. Chem. Phys.* **1965**, *43*, 196−200.

(8) Seburg, R. A.; DePinto, J. T.; Patterson, E. V.; McMahon, R. J. *J. Am. Chem. Soc.* **1995**, *117*, 835−836.

(9) Koga, N.; Matsumura, M.; Noro, H.; Iwamura, H. *Chem. Lett.* **1991**, 1357−1360.

(10) Noro, M.; Masuda, T.; Ishimura, A. S.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1994**, *116*, 6179−6190.

(11) Neumann, W.; Sixl, H. *Chem. Phys.* **1980**, *50*, 273−280.

(12) Bubeck, C.; Hersel, W.; Neumann, H.; Sixl, J. *Chem. Phys.* **1980**, *51*, 1−8.

(13) Bartik, T.; Bartik, B.; Brady, M.; Dembinski, R.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 414−417.

(14) Brady, M.; Weng, W.; Zhou, Y.; Seyler, J. W.; Amoroso, A. J.; Arif, A. M.; Böhme, M.; Frenking, G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 775−788.

(15) Le Narvor, N.; Toupet, L.; Lapinte, C. *J. Am. Chem. Soc.* **1995**, *117*, 7129−7138.

(16) Woodworth, B. E.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1997**, *119*, 828−829.

(17) Bruce, M. I.; Denisovich, L. I.; Low, P. J.; Peregudova, S. M.; Ustynyuk, N. A. *Mendeleev Commun.* **1996**, 200−201.

S0276-7333(98)00179-4 CCC: $15.00

we decided to favor the stabilization of the highest oxidation state by replacing dppe in **1** by dippe (ethylenebis(diisopropylphosphine), a more electron releasing chelating ligand. We report here the synthesis and a brief characterization of [Cp*(dippe)Fe(μ-C_4)Fe(dippe)Cp*]$^{n+}$[PF_6]^-_n (**4**$^{n+}$[PF_6]^-_n), a family of four organoiron complexes differing one from each other only by their total number of electrons, and we have focused our efforts on the characterization of the unprecedented tricationic complex **4**$^{3+}$. **4**$^{3+}$ is revealed by spectroscopic analyses to be a three-spin carrier and constitutes, to the best of our knowledge, the first example of an isolated organic or inorganic stable species having an odd electron localized on a linear sp carbon fragment.

The neutral complex Cp*(dippe)Fe(μ-C_4)Fe(dippe)Cp* (**4**) was conveniently obtained (70% yield) from the reaction of Cp*(dippe)FeCl (**2**)[18] and Cp*(dippe)Fe(C≡CC≡CH) (**3**)[19] in THF/MeOH (3:2) and in the presence of KPF_6 and KO^tBu. The cyclic voltammogram of **4** in CH_2Cl_2 (Figure 1) exhibits three well-separated and reversible waves at $E° = -0.97, -0.18$, and 0.81 V vs SCE (ferrocene/ferrocenium couple used as internal calibrant, 0.460 V vs SCE, $\Delta E_p = 0.075$ V). In the accessible potential limits (−1.50 to +1.60 V) a fourth redox system was not detected. Comparison of these potential values with those obtained in the related dppe series ($E° = -0.68, -0.40$, 0.95 V vs SCE) clearly indicates that the wave separation between the redox systems increases with the electron density at the metal centers. Consequently, the iron−iron interaction across the $-C_4-$ spacer becomes stronger as the electron density on the metal centers is higher. Moreover, substitution of dppe by dippe induced a positive shift of the three redox potentials of 0.29, 0.14, and 0.14 V, respectively. Thus, the three related cationic complexes **4**$^+$, **4**$^{2+}$, and **4**$^{3+}$ were viewed as accessible synthetic targets.

Guided by the redox potentials, we carried out a cascade of three one-electron oxidations of **4** using 1 equiv of ferrocenium hexafluorophosphate (twice) and 1 equiv of silver hexafluorophosphate successively. The corresponding [Cp*(dippe)Fe(μ-C_4)Fe(dippe)Cp*]$^{n+}$[PF_6]^-_n complexes (**4**$^{n+}$[PF_6]^-_n; $n = 1-3$) were isolated in 90, 87, and 88% yields, respectively, after recrystallization from a CH_2Cl_2/diethyl ether mixture. They were characterized by microanalysis, mass spectrometry, and IR, ESR, and Mössbauer spectroscopy (see the Supporting Information). Efforts to grow crystals of the unprecedented trication **4**$^{3+}$ from a CH_2Cl_2/diethyl ether mixture were successful, and the crystal structure was determined (Figure 2). The molecule is centrosymmetric with an inversion center located in the middle of the carbon linkage. Two PF_6 anions are located on both edges of the trication, and the third one is positioned equidistant from the two metal centers. The two equivalent iron atoms adopt the pseudooctahedral geometry invariably observed for piano-stool iron complexes.[15,20]

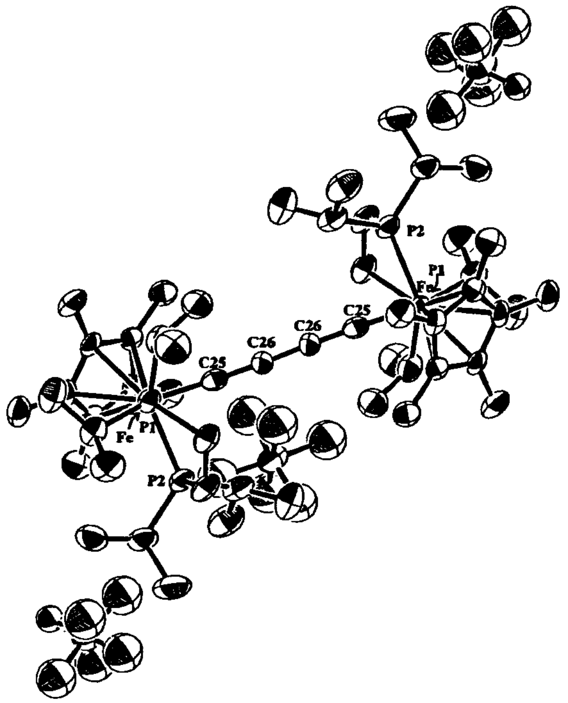
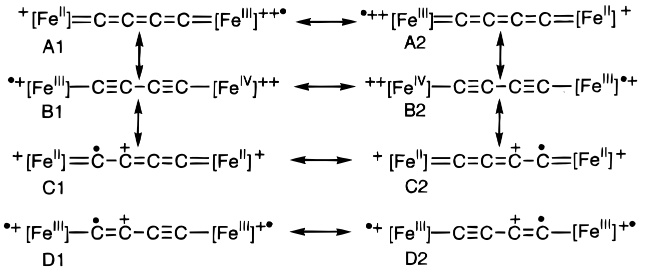


Figure 2. Structure of **4**$^{3+}$[PF_6]$^-_3$. Key bond lengths (Å) and angles (deg): Fe−C25, 1.79(1); C25−C26, 1.27(1); C26−C26′, 1.33(1); Fe−P1, 2.262(3); Fe−P2, 2.279(3); Fe−C25−C26, 175.2(9); C25−C26−C26′, 178.7(9); P1−Fe−P2, 85.2(1).

Scheme 1. Resonance Structures for 4^{3+}



The FeC_4Fe axis is nearly linear with bond angles of 175−177°, and the $C_\alpha-C_\beta$ and $C_\beta-C_{\beta'}$ bond lengths are 1.27(1) and 1.33(1) Å, respectively. These distances are intermediate between those determined for the butadiyne (1.218(2)/1.384(2) Å)[21] and those of the butatriene (1.283(5)/1.318(5) Å.[22] Comparison of the carbon−carbon bond distances with those determined for the mixed-valence [Cp*(dppe)Fe(μ-C_4)Fe(dppe)Cp*][PF_6] (**1**$^+$[PF_6]$^-$; 1.236(9)/1.36(1) Å) indicates an elongation of the $C_\alpha-C_\beta$ and a shortening of the $C_\beta-C_{\beta'}$ bonds.[15] The bond distances of the $-C_4-$ linkage of the dirhenium dication {[Re]=C=C=C=C=[Re]}$^{2+}$ (1.26(1)/1.30(1) Å) are close to those of **4**$^{3+}$. Finally, as a global effect, one observes a contraction of the Fe−Fe distance from 7.431 Å in **1**$^+$ to 7.411 Å in **4**$^{3+}$ despite an increase of the electrostatic repulsion which might support a cumulenic valence structure as in the **A** and **C** formulations (Scheme 1). In these two limiting resonance structures, the total number of bonds of the Fe−C_4−Fe linkage is higher than in the **B** and **D** formulations. The electronic structures **A** and **B** correspond to mixed-valence com-

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[18] Jiménez Tenorio, M.; Puerta, M. C.; Valerga, P. *Organometallics* **1994**, *13*, 3330−3337.

[19] Complete spectroscopic data for new compounds are given in the Supporting Information.

[20] Roger, C.; Hamon, P.; Toupet, L.; Rabaâ, H.; Saillard, J.-Y.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1991**, *10*, 1045−1054.

[21] Tanimoto, M.; Kuchitsu, K.; Morino, Y. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 386-391.

[22] Irngartinger, H.; Götzmann, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 340−342.

plexes, whereas the structures **C** and **D** can be viewed as all-carbon chain centered radicals. Examination of the spectroscopic properties of $\mathbf{4}^{3+}$ allowed determination of its electronic structure.

The ^{57}Fe Mössbauer spectrum of $\mathbf{4}^{3+}$ recorded at zero field showed a single doublet (80 K, mm s^{-1} vs Fe, IS = 0.163, QS = 0.985), unambiguously establishing that the two iron termini are equivalent on the Mössbauer time scale. The experimental Mössbauer quadrupole splitting might be compatible with two 17-electron Fe^{III} termini,[23] but this does not allow us to exclude an Fe^{II} cumulenic formulation. Indeed, we recently found that complexes with an Fe═C double bond give a Mössbauer spectrum very similar to those of the Fe^{III} 17-electron species [Cp*Fe(dppe)(R)][PF_6].[24,25] Moreover, it is noteworthy that the Mössbauer spectrum of the dication $\mathbf{4}^{2+}$ also displays a single doublet with quite close parameters (80 K, mm s^{-1} vs Fe, IS = 0.191, QS = 1.047), as the ^{57}Fe Mössbauer parameters of organoiron species strongly depend on the redox state of the metal centers.[20,26] These results indicate that the oxidation of $\mathbf{4}^{2+}$ could not take place at the metal centers but, rather, on the all-carbon chain.

Most mixed-valence compounds exhibit a characteristic near-IR band which can be used to probe their electronic ground state.[27,28] As the two metal centers are equivalent on the Mössbauer time scale, one can exclude a localized (class **I**) complex. On the other hand, the possible Fe^{II}/Fe^{III} and Fe^{III}/Fe^{IV} delocalized mixed-valence structures (class **III**, formulations **A** and **B**) are expected to be near-IR active. However, careful examination of the near-IR range of the electronic spectrum of $\mathbf{4}^{3+}$ did not show any absorption. As a result, the trication cannot be regarded as a mixed-valence compound and formulations **A** and **B** were both ruled out.

In contrast with the mixed-valence complex $\mathbf{4}^{+}$,[28] which is an ESR-active radical at 90 K ($g_1 = 2.2692$, $g_2 = 2.0616$, $g_3 = 2.0152$), the trication $\mathbf{4}^{3+}$ is ESR silent in the 300−80 K range. This behavior did not indicate a one-odd-electron electronic structure. However, antiferromagnetic coupling and a faster relaxation process could be expected in the case of a multispin carrier and for this reason we carried out ESR measurements at 4 K. Thus, at this temperature a partially resolved signal is observed with a peak to peak line width of ca. 200 G, probably due to exchange interactions among the unpaired electrons (Figure 3). The 4 K ESR spectrum of a solid powdered sample of $\mathbf{4}^{3+}$ displays two distinct **g**-tensor components for the $\Delta m_S = \pm 1$ transition. The g values ($g_1 = 2.5527$, $g_2 = 2.0308$)[29] are quite different from those observed in the spectrum of $\mathbf{4}^{+}$. The large anisotropy of the signal suggests a large delocalization of the SOMO's over the Fe−C_4−Fe assemblage with an important metal character. Interestingly, direct spectral evidence for the quartet state of $\mathbf{4}^{3+}$ is obtained from the $\Delta m_S = \pm 2$ transition observed at half-field ($g = 4.3597$).[30] The $\Delta m_S = \pm 3$ transition associated with a three-electron flip was not detected.[31] Thus, $\mathbf{4}^{3+}$ is a stable high-spin molecule in which the radical centers are linked together in a linear fashion with a significant contribution of the limit resonance structure **D** in the description of the bonding of the [Fe−C_4−Fe]$^{3+}$ system. This molecular three-spin system will be the subject of further magnetic measurements to determine the $S = {}^1/_2$ vs ${}^3/_2$ ground state.

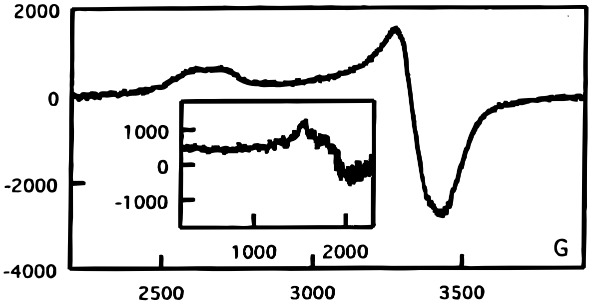

Figure 3. ESR spectrum of a powdered sample of $\mathbf{4}^{3+}[PF_6]^-{}_3$ at 4 K.

Acknowledgment. We thank the French Ministère MENSER for award of a thesis grant to M.G.

Supporting Information Available: Text giving details of the preparation and characterization data for **3**, **4**, $\mathbf{4}^{+}$, $\mathbf{4}^{2+}$, and $\mathbf{4}^{3+}$, experimental details for the X-ray analysis of $\mathbf{4}^{3+}$, listing of the experimental crystallographic parameters, and tables of atomic coordinates, bond distances and angles, and anisotropic thermal parameters for $\mathbf{4}^{3+}$ (15 pages). Ordering information is given on any current masthead page.

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

(24) Thominot, P.; Lapinte, C. Unpublished results, 1997.

(25) Mössbauer parameters of the vinylidene complex [Cp*Fe(dppe)(═C═CH_2)][PF_6] (80 K, mm s^{-1} vs Fe): IS = 0.086, QS = 1.032.

(26) Greenwood, N. N. *Mössbauer Spectroscopy*; Chapman and Hall: London, 1971.

(27) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391−444.

(28) Near-IR spectrum of $\mathbf{4}^{+}$ in CH_2Cl_2 (λ_{max} (nm), ϵ ($M^{-1}cm^{-1}$)): 1318, 14 000.

(29) As shown in the X-ray crystal structure, the geometry of the metal centers is pseudo-octahedral and we assume that the signal centered at 2.0308 corresponds to the unresolved g_2 and g_3 components.

(30) It has been suggested by one of the reviewers that the signal attributed to the $\Delta m_S = 2$ transition is too broad and might be reminiscent of a signal due to impurities in the quartz sample tube. This suggestion was not confirmed by blank ESR measurements.

(31) The transition $\Delta m_S = 2$ or 3 is also difficult to observe in high-spin organic molecules. See for example: Ishida, T.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 4238−4241.