Oxidative Activation of Aryldiyln—Iron Complexes: Regioselective Dimerization

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ABSTRACT: Chemical oxidations of the iron butadiynyl complexes Cp*(dppe)FeC≡CC≡CC≡CAr (Ar = Ph, 1a; Ar = C6H4-Me-4, 1b; Cp* = η5-C5Me5, dppe = 1,2-bis(diphenylphosphino)ethane) achieved with 1 equiv of ferrocenium hexafluorophosphate salt in THF at −78 °C provide the transient species 1a(PF6) and 1b(PF6), as demonstrated by ESR experiments. Above −35 °C, intramolecular C–C couplings take place regiospecifically, providing the binuclear complexes [{Cp*(dppe)Fe}2C8Ar2](PF6)2 (Ar = Ph, 2a; Ar = C6H4-Me-4, 2b), which were isolated after purification as thermally stable deep purple powders in 61 and 57% yields, respectively. The full characterization of the new products, including X-ray analysis of 2a(PF6)2, electrochemical data, spectroscopic properties, and electronic structures investigated at the DFT level of theory are reported. NMR investigations have shown that the iron building blocks rotate slowly around the cyclobutene ring, allowing the observation of three rotamers in equilibrium. The cyclic voltammetry of the dimer 2b(PF6)2 shows four redox events with the current peaks corresponding to two one-electron-oxidation and two one-electron-reduction processes. These compounds are diamagnetic in the solid state but ESR active in solution, indicating that the triplet excited state is readily accessible.

INTRODUCTION

Molecules comprised of two redox-active centers connected by an all-carbon bridge provide an ideal template from which intricate mechanistic details concerning the factors controlling electron transfer, electron delocalization, and magnetic exchange interactions can be extracted.1–3 The major limitation of such systems, which have often been referred to as molecular wires,4 comes from the chemical instability of these molecules when unpaired electrons are present on the compounds with chains longer than four carbon atoms.5 This chemical instability probably arises from intermolecular carbon–carbon bond formation, producing dimers and polymers. Few efforts have been devoted to the “insulation” of the unsaturated linkers to prevent bimolecular reactions.6 Incorporation of functional groups into the bridge between the redox centers increases the chemical stability of the oxidation states containing an odd number of electrons, allows the control of the molecular topology, and opens access to functional molecules with oriented electron-transfer capabilities,7 switching abilities,8 multipath connections,9,10 optical activities,11,12 and magnetic properties.3,10,13 Recently, it was shown that electroactive units such as 1’,1’”-biferrocenyl moieties incorporated in the carbon bridge linking the metal termini act as a molecular relay, mediating electron transfer between the two ends of the molecule by hopping processes.14,15

On the other hand, the properties and reactivity of 17e polyyne–metal complexes are very limited.24 Rigaut et al. published the first example of the dimerization of a diynyl complex activated by chemical oxidation.25 Whiteley and co-workers have found that monoelectronic oxidation of (C–H2)(LL)Mo(C≡CC≡CSR) (LL = bpy, dppe; R = SiMe3, H) produces molybdenum-stabilized diynyl radicals which were characterized by extensive spectroscopic studies and by a structural study of [(C–H2)(dppe)Mo(C≡CC≡CSiMe3)]-(PF6).22 Further oxidation of this compound afforded a dimeric product resulting from C–C coupling. Very recently, some of us reported that chemical oxidation of Cp(dppe)Ru(C≡CC≡CSR) with [Cp2Fe](PF6) affords the binuclear cations [{Cp-

Supporting Information

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Ru\(_2\)C\(_8\)R\(_2\) (R = Ph, Fc) by radical coupling at electron-rich sites involving the inner and outer C\(\equiv\)C triple bonds, to give cyclobutenediylidene derivatives. As depicted in Scheme 1, mixtures of symmetrical and asymmetrical isomers were obtained. DFT calculations revealed that the precursor cationic diynyl complexes have considerable electron density on C\(_{\beta}\) and C\(_{\delta}\), suggesting that radical couplings C\(_{\delta}\) + C\(_{\delta}\) and C\(_{\beta}\) + C\(_{\delta}\) afford the symmetrical and asymmetrical isomers, respectively.

Related to this chemistry is the earlier report of the dimerization of the butatrienylidene (dppe)\(_2\)(CO)W{[C\(\equiv\)C\(\equiv\)C\(\equiv\)CH(C\(_6\)H\(_4\)Bu\(_t\))]} to give {(dppe)\(_2\)(CO)W}{[C\(\equiv\)C\(\equiv\)C\(\equiv\)CH(C\(_6\)H\(_4\)Bu\(_t\))]} by C\(_{\gamma}\)−C\(_{\gamma}\) coupling. It has been suggested that this reaction proceeds via a 1,2-bis(ethynyl)cyclobutenyl diradical intermediate which undergoes retro-electrocyclic ring opening.

A recent experimental and theoretical investigation on iron and ruthenium \(\sigma\)-polyynyl complexes has concluded that the iron(III) radicals bearing ligands with four and six sp carbon atoms are stable in solution for a few minutes at 20 °C and for an unlimited time below −20 °C. It was also suggested that the 17e iron radicals may react via a smooth chemical process, since the ESR signal disappeared cleanly, no traces of other radicals being detected. Guided by these stimulating results, we have investigated the reactivity of the two aryldiynyl-iron complexes Cp\(^*\)(dppe)FeC\(\equiv\)C\(\equiv\)C\(\equiv\)CAr (Ar = Ph, 1a; Ar = C\(_6\)H\(_4\)-Me-4, 1b) and we report here the regiospecific formation and the full characterization of the binuclear cations \{[Cp\(^*\)(dppe)-Fe]C\(_6\)Ar\(_2\)\}(PF\(_6\))\(_2\) (Ar = Ph, 2a(PF\(_6\))\(_2\); Ar = C\(_6\)H\(_4\)-Me-4, 2b(PF\(_6\))\(_2\)), including X-ray analysis, electrochemical data, spectroscopic properties, and quantum chemical investigations at the DFT level.

### RESULTS AND DISCUSSION

1. Synthesis of 2a,b. Complex 1b was prepared according to the procedure already described for complex 1a. Chemical oxidations of the complexes 1a,b were achieved with 1 equiv of ferrocenium hexafluorophosphate salt in THF at −78 °C (Scheme 2). An immediate color change from orange to deep green was observed, and this color persisted as long as the solution was kept below −35 °C. ESR experiments established that these transient species are the iron(III) derivatives 1a(PF\(_6\))\(_2\) (Ar = Ph, 2a(PF\(_6\))\(_2\); Ar = C\(_6\)H\(_4\)-Me-4, 2b(PF\(_6\))\(_2\)), including X-ray analysis, electrochemical data, spectroscopic properties, and quantum chemical investigations at the DFT level.

2. Molecular Structure of 2a(PF\(_6\))\(_2\). Small thin purple crystals of 2a(PF\(_6\))\(_2\) were obtained by slow diffusion of pentane into a concentrated solution of the complex in 1,2-dichloroethane. Although the crystals diffracted only weakly due to their poor quality, the X-ray structure was solved (\(R = 0.087\)), establishing definitively the connectivity between atoms. An ORTEP view of the cation 2a\(^{2+}\) is shown in Figure 1, while respectively. High resolution mass spectra of the analytically pure sample of 2a(PF\(_6\))\(_2\) established the dimeric formula of the dicarboxionic complex, the structure of which was completely elucidated by single-crystal X-ray diffraction.
selected structural parameters are collected in Table 1 with the computed structural data (see below).

Figure 1. ORTEP drawing of the cation $2a^{2+}$ of $2a(\text{PF}_6)_2$. Thermal ellipsoids are at the 30% probability level. Hydrogen atoms and solvent molecule are omitted for clarity.

The X-ray analysis clearly shows that $2a(\text{PF}_6)_2$ is a symmetrical dimer with two Cp*(dppe)FeC₄ fragments linked by a C₄Ph₂ ligand containing a four-carbon ring. The C₄ ring is planar, and the angles are close to perfect right angles (88.0(2)° and 91.9(2)°); their sum is exactly equal to 360°. As expected, the 18e iron atoms adopt a pseudo-octahedral geometry with bond lengths in the Cp*(dppe)Fe fragments consistent with the presence of a positive charge on the metal atoms. Thus, the Fe−Cp* center (1.769 Å) and Fe−P distances (2.233(1) and 2.243(1) Å) are clearly elongated with respect to the reference neutral complex 1a. The Fe−C(1) distance in $2a(\text{PF}_6)_2$ (1.784(5) Å) is shorter by ca. 0.09 Å than that in 1a, which is consistent with the presence of an Fe−C double bond, as proposed in Scheme 2. Moreover, distances in the carbon ligand (C(1)−C(2) = 1.266(6) and C(2)−C(3) = 1.345(6) Å) are very close to the distances found in the allenylidene complex [Cp*(dppe)Fe(C≡C≡CPh₂)](PF₆) (Fe−C(1) = 1.784(4) Å, C(1)−C(2) = 1.257(7) Å, and C(2)−C(3) = 1.361(7) Å) previously reported.²⁸ These bond lengths are characteristic of allenylidene derivatives with the C(1)−C(2) distances shorter than the C(2)−C(3) distances, suggesting a contribution from the canonical form Cp*(dppe)Fe[C≡CC(C≡C)R(R)'].²⁹ The Fe−C(1)−C(2)−C(3) chain slightly deviates from linearity, with angles at C(1) and C(2) being 174.4(3)° and 170.3(4)°. Distances within the cyclobutene ring are consistent with the presence of three single bonds (2 × C(3)−C(4) = 1.477(6) Å and C(3)−C(3') = 1.509(8) Å) and one C≡C double bond (C(4)−C(4') = 1.417(9) Å). No short contacts were observed in this structure; however, the two Cp* rings are very close to each other, with distances between hydrogen atoms of the two closest methyl groups as short as 3.7 Å.

Starting from the X-ray structure obtained for this complex $2a(\text{PF}_6)_2$, full geometry optimization was first performed on compound $2a^{2+}$ at the DFT BP86/TZP level of theory. Pertinent computed bond lengths, for both singlet and triplet spin states of $2a^{2+}$, are given in Table 1 and are compared with the experimental values. The optimized distances of the singlet state compared rather well with the experimental data. The Fe−

Table 1. Pertinent Bond Lengths (Å) and Relative Energies (eV) Computed for Rotamers $2a^{2+}$, $2a^{2+}$, and $2a^{2+}$ and for the Hypothetical Asymmetrical Isomer $3a^{2+}$

<table>
<thead>
<tr>
<th>Bond Length (Å) &amp; Relative Energy (eV)</th>
<th>$2a^{2+}$</th>
<th>$2a^{2+}$</th>
<th>$2a^{2+}$</th>
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<tbody>
<tr>
<td>Fe−P(1)</td>
<td>2.266</td>
<td>2.277</td>
<td>2.303</td>
</tr>
<tr>
<td>Fe−P(2)</td>
<td>2.265</td>
<td>2.273</td>
<td>2.288</td>
</tr>
<tr>
<td>Fe−P(1)</td>
<td>2.266</td>
<td>2.317</td>
<td>2.293</td>
</tr>
<tr>
<td>Fe−P(2)</td>
<td>2.265</td>
<td>2.286</td>
<td>2.282</td>
</tr>
<tr>
<td>Fe−Cp*</td>
<td>1.827</td>
<td>1.826</td>
<td>1.856</td>
</tr>
<tr>
<td>Fe−Cp*</td>
<td>1.827</td>
<td>1.824</td>
<td>1.848</td>
</tr>
<tr>
<td>Cp−Cp</td>
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<td>1.811</td>
<td>1.876</td>
</tr>
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<td>C−C</td>
<td>1.274</td>
<td>1.271</td>
<td>1.498</td>
</tr>
<tr>
<td>C−C</td>
<td>1.346</td>
<td>1.353</td>
<td>1.384</td>
</tr>
<tr>
<td>C−C</td>
<td>1.477</td>
<td>1.439</td>
<td>1.231</td>
</tr>
<tr>
<td>C−Ph</td>
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<td>1.445</td>
<td>1.412</td>
</tr>
<tr>
<td>C−C</td>
<td>1.797</td>
<td>1.863</td>
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<tr>
<td>C−C</td>
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<td>1.258</td>
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</tr>
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<td>C−C</td>
<td>1.346</td>
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<td>1.368</td>
</tr>
<tr>
<td>C−C</td>
<td>1.477</td>
<td>1.423</td>
<td>1.461</td>
</tr>
<tr>
<td>C−Ph</td>
<td>1.450</td>
<td>1.449</td>
<td>1.449</td>
</tr>
<tr>
<td>C−C</td>
<td>1.513</td>
<td>1.537</td>
<td>1.524</td>
</tr>
<tr>
<td>C−C</td>
<td>1.413</td>
<td>1.464</td>
<td>1.408</td>
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Relative energy with solvent effect (see Computational Details). Relative energy with dispersion effects (see Computational Details). Relative energy with dispersion effects taken into account.

“A third rotamer, $2a^{2+}$ (90° rotation of one metal end group) was also calculated. It is lying too high in energy to be found in solution (+0.978 eV). Its characteristics are thus only reported in the Supporting Information. Experimental distances of $2a(\text{PF}_6)_2$ are given in brackets for the sake of comparison. Cp*: centroid of C₄Me₄. Relative energy after optimization. Relative energy with solvent effect (see Computational Details). Relative energy with dispersion effects (see Computational Details). Relative energy with dispersion effects taken into account.”
C distances are computed for both metal centers at 1.797 Å and thus are quite close to the experimental value of 1.784 Å. The optimized C--C bond lengths also match fairly well with experiment, especially the C--C distances of the central carbon square, where the largest discrepancy computed is 0.004 Å. Nevertheless, the common overestimation of the Fe--P and Fe--C\textsubscript{centroid} bond lengths is also computed in this case.\textsuperscript{24,30} These discrepancies are respectively 0.03 and 0.06 Å.

The Mulliken decomposition and energies of the first frontier molecular orbitals of \textit{2a}\textsuperscript{2+} obtained in the singlet state are collected in Table S1 (see the Supporting Information), and their plots are shown in Figure 2. The energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of ca. 1.1 eV reflects the thermodynamic stability of \textit{2a}\textsuperscript{2+} as a singlet. The HOMO and HOMO-1 are \(\pi/\pi\)-type in character, antibonding between iron centers and adjacent carbon atoms and bonding between carbon atoms \(C_1\) and \(C_2\) and between \(C_3\) and \(C_4\). These HOMOs are mainly metallic in character with computed iron percentage contributions of roughly 60%, whereas the organic character is only 17% and 4% for the HOMO and HOMO-1, respectively. In contrast, as previously computed for the ruthenium analogues of formula \(\text{[(Ru(η\textsuperscript{5}-C\textsubscript{5}H\textsubscript{4})\textsubscript{2}(dppe)\textsubscript{2}]\textsubscript{2}C\textsubscript{8}Ph\textsubscript{2}}\)\textsubscript{2}\textsubscript{(PF\textsubscript{6})\textsubscript{2}}\textsuperscript{-}\), the LUMO and LUMO+1 are fully delocalized over the metal--carbon skeleton with an important character computed on the carbon atoms of the central square, reminiscent of the \(\pi\)-MOs of the cyclobutadiene dication \([C\textsubscript{4}H\textsubscript{4}]^{2+}\).\textsuperscript{26}

In contrast to the singlet state, the optimized distances of the triplet state are not in good agreement with the corresponding experimental values. The computed Fe--C distances (1.811 and 1.864 Å) largely overestimate the experimental bond by 0.03 and 0.08 Å, respectively. Furthermore, bond lengths of the carbon square are far away from the experimental values. Indeed, the \(C_1--C_4\) and \(C_2--C_3\) bond lengths are underestimated by 0.05 and 0.04 Å, respectively, whereas the \(C_3--C_7\) and \(C_4--C_8\) bond lengths are overestimated by 0.05 and 0.04 Å, respectively (see Table 1). The computed deviations of the Fe--P and Fe--C\textsubscript{centroid} bond lengths are larger in this spin state in comparison to the singlet optimized structure. The largest deviation of the Fe--P distance is 0.08 Å, and the Fe--C\textsubscript{centroid} bond length is computed to be longer by ca. 0.05 Å. These results are consistent with the singlet spin state being more stable than the triplet state by roughly 0.95 eV and with the lack of any ESR signal in measurements of solid-state samples of \textit{2a}(PF\textsubscript{6})\textsubscript{2}\textsuperscript{-} (\textit{vide infra}). Solvent effects and dispersion corrections were added to the calculations in order to better estimate the energy difference between singlet and triplet states (see Table 1). Interestingly, the order of magnitude (1 eV) of the energy difference is kept, comforting the previous conclusions.

3. Conformational Analyses of \textit{2a}(PF\textsubscript{6})\textsubscript{2} and \textit{2b}(PF\textsubscript{6})\textsubscript{2} by Multinuclear NMR Spectroscopy. The \(^3\)P NMR spectra of \textit{2a}(PF\textsubscript{6})\textsubscript{2} and \textit{2b}(PF\textsubscript{6})\textsubscript{2} display four signals at \(\delta 89.36, 90.06, 90.45,\) and 91.00 for \textit{2a}(PF\textsubscript{6})\textsubscript{2}, and at \(\delta 89.64, 90.32, 90.76,\) and 91.25 for \textit{2b}(PF\textsubscript{6})\textsubscript{2}, with relative intensities 16:58:16:10 and 14:64:14:8 (for a total intensity of 100), respectively (Figure S1, Supporting Information). The hexafluorophosphate anions were also observed as septuplets at \(\delta -142.99\) (\(\uparrow J_{PP} = 708\) Hz) and \(-142.94\) (\(\uparrow J_{PP} = 708\) Hz) for \textit{2a}(PF\textsubscript{6})\textsubscript{2}, and \textit{2b}(PF\textsubscript{6})\textsubscript{2}, respectively. It was initially thought that the four signals might result from the formation of several isomers of the dimeric derivative, as previously observed in the ruthenium series (see Scheme 1).\textsuperscript{26} However, this hypothesis was disproved by three different pieces of experimental and theoretical evidence. (i) Attempts to separate the components of the mixture were carried out without any success. In particular, fractional precipitations or crystallization provided samples which always gave NMR spectra with the same number of signals with exactly the same ratio, even when measurements were achieved from solutions prepared from single crystals of \textit{2a}(PF\textsubscript{6})\textsubscript{2} used for X-ray analyses. (ii) The spectroscopic signature of carbon--carbon triple bond expected in asymmetrical isomers was not detected either in the IR or \(^{13}\)C NMR spectra, in contrast with the...
Asymmetrical form 3a isomer computed to be energetically less stable than the symmetrical and 2.293 and 2.282 Å for Fe2. The Fe–P bond lengths are also affected, with computed values of 2.303 and 2.288 Å for Fe1–P and 2.293 and 2.282 Å for Fe2–P in the latter, which render the two iron fragments inequivalent and eventually distinguishable by 31P NMR. However, this asymmetrical isomer 3a is computed to be energetically less stable than the symmetrical isomer 2a by 1.88 eV. In comparison, the energy gap between the two analogous ruthenium isomers was also in favor of the symmetrical dimer, but by only ca. 0.6 eV. This drastic difference between the iron and ruthenium examples suggests that the formation and existence of the iron-based asymmetrical dimer 3a is largely disfavored. This result is quite surprising at first sight. As discussed in the Introduction, the dimerization reaction involving radical coupling, might be explained using steric factors. Previous works also support this conclusion. In particular, it was found that the radical cations [Cp*(dppe)FeC≡CH](PF6) and [Cp*(dppe)FeC(OCH3)2]+C6H6 radicals both dimerize by formation of a carbon–carbon bond between the β-carbon atoms of two molecules. In each case the β-carbon atom carries either one or two hydrogen atoms. Replacement of the hydrogen atoms by any other substituents kinetically stabilizes the radical cations. In summary, the difference between the iron and ruthenium series (which are isostructural with the ruthenium dimers) show that the former is thermodynamically more stable.

At first sight, the 31P NMR spectrum of 2a shown in Figure S1 (Supporting Information), is not very different from that obtained for the mixture of products obtained after oxidation of the ruthenium-based complexes Cp(dppe)Ru(C4R) (R = Ph, Fc). Indeed, the oxidative dimerization of the monometallic ruthenium diynes leads to mixtures of symmetrical and asymmetrical isomers, as depicted in Scheme 1.

For the sake of comparison, the analogous iron-based asymmetrical isomer 3a (Chart 1), which is not found experimentally, was also optimized and the main data are reported in Table 1. The computed metal–ligand (dppe, Cβ*) distances differ strongly from those in the symmetrical isomer 2a. The Fe–Cβ* distances lengthen from 1.827 Å for 2a to 1.856 and 1.848 Å for 3a. The Fe–P bond lengths are also affected, with computed values of 2.303 and 2.288 Å for Fe1–P and 2.293 and 2.282 Å for Fe2–P in the latter, which render the two iron fragments inequivalent and eventually distinguishable by 31P NMR. However, this asymmetrical isomer 3a is computed to be energetically less stable than the symmetrical isomer 2a by 1.88 eV. In comparison, the energy gap between the two analogous ruthenium isomers was also in favor of the symmetrical dimer, but by only ca. 0.6 eV. This drastic difference between the iron and ruthenium examples suggests that the formation and existence of the iron-based asymmetrical dimer 3a is largely disfavored. This result is quite surprising at first sight. As discussed in the Introduction, the dimerization reaction involving radical Cβ–Cβ coupling is common for closely related compounds such as [Mo(C7H7)(dppe)C5SiMe3]2, [Mo(C7H7)(dppe)C5H5](PF6)2, and [Ru(C7H7)(dppe)C5H5](PF6)2. With the aim of understanding the oxidative coupling reaction affording the iron dimers, the electronic structure of the monometallic precursor must be discussed. Precursors 1a and 1b were recently studied at the DFT level. In both cases, the largest part of the spin density is found on the metal center. Nevertheless, the atomic spin density on the metal atom considerably increases, from 0.33 to 0.77 and to 0.99, when the iron and molybdenum fragments successively replace the ruthenium center. This result is consistent with the previous studies of Ru(III)−, Fe(III)−, and Mo(III)−. In both cases, the largest part of the spin density is found on the metal center. Nevertheless, the spin density on the metal atom considerably increases, from 0.33 to 0.77 and to 0.99, when the iron and molybdenum fragments successively replace the ruthenium center. This result is consistent with the previous studies of Ru(III)−, Fe(III)−, and Mo(III)−. In both cases, the largest part of the spin density is found on the metal center. Nevertheless, the atomic spin density on the metal center increases in the same order. Surprisingly enough, the computed atomic spin densities on the carbon-rich ligand are not strongly affected by this substitution.

Table 2. Computed Atomic Spin Densities (electron) of 2a2+(T), the Monometalic Precursor 1a and Related Compounds

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<th>compd</th>
<th>M</th>
<th>Cα</th>
<th>Cβ</th>
<th>Cγ</th>
<th>Cδ</th>
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<tbody>
<tr>
<td>1a</td>
<td>0.70</td>
<td>−0.06</td>
<td>0.20</td>
<td>−0.05</td>
<td>0.17</td>
<td>0.05</td>
<td>−0.02</td>
<td>0.07</td>
<td>24</td>
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<td>[RuCp(dppe)C2Ph]+26</td>
<td>0.33</td>
<td>0.01</td>
<td>0.22</td>
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<td>−0.03</td>
<td>0.10</td>
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<tr>
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<td>−0.07</td>
<td>0.21</td>
<td>−0.07</td>
<td>0.20</td>
<td></td>
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<tr>
<td>[Ru(dppe)C4SiMe3]26</td>
<td>0.99</td>
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<td>−0.13</td>
<td>0.23</td>
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<td></td>
<td>31</td>
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<tr>
<td>2a2+(T)</td>
<td>0.84/0.33</td>
<td>0.18/0.01</td>
<td>0.03/0.07</td>
<td>−0.01/−0.02</td>
<td>−0.01/0.32</td>
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**BP86/TZP (ADF) level of theory. **B3LYP/LANL2DZ-6-31G* (Gaussian) level of theory.
31P NMR spectra results from the presence of three rotamers in equilibrium, which interconvert slowly on the NMR time scale. 1H and 13C VT experiments were carried out in d6-acetone, but only a very small line broadening was detected at 55 °C, the highest temperature accessible in this solvent. The existence of the three rotamers was clearly validated by EXSY 1H NMR experiments. The EXSY (or NOESY) spectra are symmetrical along the diagonal, and correlation spots indicate exchange situation (or spatial proximity). The EXSY spectrum obtained with 2b(PF6)2 is shown in Figure S2 (Supporting Information).

The protons of Cp* ligands were used as probes to observe the exchange processes. Circled spots in Figure S1 (Supporting Information) clearly show that exchange occurred in solution between the Cp* signals located in the range δ 1.20−1.45. Correlation spots observed between the methyl group of the tolyl ligand in the aromatic region also confirm the exchange process. The 31P NMR spectra of 2a(PF6)2 and 2b(PF6)2 are shown in Figure S1 and are fully consistent with the rotamer hypothesis. The major peaks at δ 90.06 in the spectrum of the dimer 2a(PF6)2 and at δ 90.32 for 2b(PF6)2 correspond to the thermodynamically more stable rotamers. They are identified as 2a(PF6)2 and 2b(PF6)2 in Scheme 3. In crystalline samples only these rotamers are present and 2a(PF6)2 was identified by X-ray analysis. In these rotamers, the Cp* ligands are on the same side of the molecule. A rotation of 180° of one metal fragment provides the rotamers 2a′(PF6)2/2b′(PF6)2. The two inequivalent dppe ligands resonate as two singlets with the same intensity at δ 89.36 and 90.45/89.64 and 90.76, respectively. The last peaks at δ 91.00/91.25 could correspond to rotamers 2a″(PF6)2/2b″(PF6)2, respectively. These rotamers are derived from rotamers 2a(PF6)2 and 2b(PF6)2 by a rotation of 180° of the two metal fragments, and the two dppe ligands are still equivalent.

In the 1H NMR spectra, similar patterns containing three or four different peaks with the same relative intensities were observed for the Cp* protons at δ 1.34 (×2), 1.37, and 1.43 for the three rotamers 2a(PF6)2, 2a′(PF6)2, and 2a″(PF6)2 and at δ 1.31, 1.36, 1.38, and 1.55 for the three rotamers 2b(PF6)2, 2b′(PF6)2, and 2b″(PF6)2. In these two examples, the dppe CH2 protons were found between δ 2.40 and 3.65 as broad signals. The methyl substituents of the tolyl groups from the 31P NMR spectra results from the presence of three rotamers in equilibrium, which interconvert slowly on the NMR time scale. 1H and 13C VT experiments were carried out in d6-acetone, but only a very small line broadening was detected at 55 °C, the highest temperature accessible in this solvent. The existence of the three rotamers was clearly validated by EXSY 1H NMR experiments. The EXSY (or NOESY) spectra are symmetrical along the diagonal, and correlation spots indicate exchange situation (or spatial proximity). The EXSY spectrum obtained with 2b(PF6)2 is shown in Figure S2 (Supporting Information).

In 1H NMR spectra of dimer 2b(PF6)2 (the 1H NMR spectrum of dimer 2b(PF6)2 is similar), patterns analogous to the 31P NMR spectra, containing four signals of specific intensities which are characteristic of the three rotamers, are observed in the spectrum. The four signals corresponding to the Cp* carbons (Figure S3, Supporting Information) were found at δ 278.84, 281.05, 283.25, and 283.46 as triplets (the two last triplets being superimposed) with JCP = 36 Hz in each case. Two similar patterns of singlets were observed at δ 180.11, 180.63, 181.00, 181.95 and at δ 146.67, 147.51, 147.91, 149.42 ppm (Figure S4, Supporting Information), both including one intense peak and two medium peaks of similar intensity together with one small peak. These resonances were assigned to the Cα and Cβ carbon atoms, respectively. The pattern corresponding to the Cβ resonances was observed around 205 ppm, but unfortunately it was overlapped by the carbonyl resonance of the solvent d6-acetone. Chemical shifts observed for Cα, Cβ, and Cγ of the allenylidene fragments are consistent with values previously obtained for iron allenylidene complexes.35 Additionally, resonances of the Cp* ligands were also observed as patterns of singlets (Figure S5, Supporting Information) at δ 102.39, 102.56, 103.09, and 103.11 for the CpMe3 carbon atoms and at δ 10.36, 10.43, 10.64, and 10.78 for the Me carbon atoms. Chemical shifts around 100 ppm for the Cp* ring carbon atoms are characteristic of cationic Fe(II) complexes.36–38

In order to give further support for the existence of the three rotamers, a conformational study was carried out starting from the most stable isomer 2a2+. The relative orientation between the metallic fragments Fe(dppe)Cp* is known to be crucial.10 Relative energies and geometrical data of the most stable species are given in Table 1. Rotamer 2a2+, where one metallic fragment has rotated by 180°, is computed to be energetically less stable by 0.11 eV in comparison with 2a2+. Distances of the carbon backbone are not strongly affected by rotation. The largest deviation is computed for the C5−C6 bond length, which increases from 1.513 to 1.524 Å when going from 2a2+ to 2a2−, respectively. However, a change of the metal−ligand distances is observed upon rotation. Indeed, from rotamer 2a2+ to rotamer 2a2−, the Fe(2)−C5 and Fe(2)−Cp* separations are lengthened by 0.014 and 0.009 Å, respectively. Fe−P bond lengths are also affected. In 2a2+, Fe−P distances are computed to be quasi-identical for both metal centers, whereas in 2a2−, the Fe−P bond lengths strongly differ between metallic fragments (Fe(1)−P = 2.279/2.265 Å, Fe(2)−P = 2.255/2.268 Å), rendering the two dppe ligands inequivalent and distinguishable in 31P NMR. Rotamer 2a2+ (Scheme 3), where the two metallic fragments are rotated by 180°, is calculated to be 0.30 eV less stable than 2a2+. Geometrical changes observed upon the rotation of one metallic end group, from 2a2+ to 2a2−, are reproduced upon rotation of the second metallic fragment. However, in 2a2−, the computed Fe−P distances are computed to be identical for both metallic fragments (Fe−P(1) = 2.256 Å, Fe−P(2) = 2.258 Å), rendering the two dppe ligands equivalent. Using this conformational study, peaks observed
in the $^{31}$P NMR spectrum of $2a\text{PF}_6$ can now be assigned. The major peak centered at $\delta$ 90.06 corresponds to the most stable rotamer $2a$. Then, the two equivalent signals measured at $\delta$ 89.36 and 90.45 can be assigned to rotamer $2a$, where the two dppe ligands are inequivalent. This result contrasts with the analogous ruthenium compounds, where similar signals were assigned to the asymmetrical isomers. Finally, the last peak centered at $\delta$ 91.00 ppm corresponds to rotamer $2a$, where the two metallic fragments are rotated by 180°, again making the two dppe ligands equivalent.

Dimers $2a\text{PF}_6$ and $2b\text{PF}_6$ were further characterized by IR spectroscopy. The IR spectra exhibit one strong band at 1888 cm$^{-1}$ together with a medium band at 1968 cm$^{-1}$, while the P–F bands of the PF$_6$ anions were observed at $\nu_{PF}$ 839 cm$^{-1}$ in both cases. In the relevant literature, allenylidene $\nu_{C=C=C}$ bands for organometallic complexes [M]{$\equiv C=C=\ C(R)^{2}$} can be found over a large range between 1865 and 2200 cm$^{-1}$, depending on the metal, the ligands attached to the metal atom, and especially the nature of the $R$ and $R^*$ end groups.

However, the $\nu_{C=C=C}$ band in [Fe{$\equiv C=C$=CPH$_2$)(dppe)C*]PF$_6$ was found at 1896 cm$^{-1}$, suggesting that the band at 1888 cm$^{-1}$ corresponds to the $\nu_{C=C=C}$ band of the dimers $2a\text{PF}_6$ and $2b\text{PF}_6$. The medium band at 1968 cm$^{-1}$ might be due to the restricted rotation in the allenylidene fragments, giving the dihedral angles 43°.

4. Cyclic Voltammetry of $2b\text{PF}_6$. The initial scan in the CV of the dimer $2b\text{PF}_6$, from −1.4 to +1.4 V vs SCE shows four redox events with the same current peaks corresponding to two one-electron-oxidation and two one-electron-reduction processes. The reversibility of the oxidation waves found at $E^{1/2} = +1.07$ (PF$_6$) and $E^{1/2} = +1.25$ V vs SCE could not be clearly established because of their positions close to the solvent front; nevertheless, an $i_{pr}/i_{pc}$ current peak ratio smaller than 1 is suspected. In contrast, the two reduction waves centered at $E^{1/2} = −0.94$ and $E^{1/2} = −0.59$ V are reversible ($i_{pr}/i_{pc} = 1$) at the platinum electrode. In accord with the strong metallic character of the HOMO of these binuclear complexes (see above), the oxidation processes are probably iron-centered and correspond to the sequential formation of the (Fe$^{II}$/Fe$^{III}$)$_2$ and (Fe$^{III}$/Fe$^{II}$)$_2$ species. The two reduction waves are probably carbon-bridge centered, and they more especially concern the cyclobutene ring, due to its strong contribution in the electronic structure of the LUMO (see above). Despite an apparent stability on the platinum electrode, attempts to electrolyze $2b\text{PF}_6$ revealed that the monocationic derivative $2b\text{PF}_6^+$ is not stable in solution, new electroactive species appearing progressively as the reduction proceeds.

5. $^{57}$Fe Mössbauer Spectroscopy. $^{57}$Fe Mössbauer spectroscopy is a very sensitive probe for establishing the iron oxidation state and the nature of the Fe−C bond. Moreover, in a homogeneous series of iron compounds such as Cp$^*$-(dppe)Fe(C≡CR), it has been shown that the isomeric shift is related to the electron density at the metal center. Additionally, Mössbauer spectroscopy constitutes a sensitive and useful means of probing the selectivity of the redox reactions. The $^{57}$Fe Mössbauer spectrum of a microcrystalline sample of the complex $2b\text{PF}_6$ was run at 80 K and least squares fitted with Lorentzian line shapes. It displays a unique doublet, which proves the thermal stability of the complex and confirms the X-ray data obtained on a single crystal showing that all the iron atoms are in the same environment, excluding traces of unsymmetrical complexes. The isomer shift (IS = 0.538(5) mm/s vs Fe) and the quadrupole splitting (QS = 0.578(8) mm/s) are exceptionally large with respect to the values generally found for organometallic complexes of the Cp$^*$-(dppe)Fe series evidencing Fe$^{II}$ metal centers.

The IS parameter reflects the electron density at the iron nucleus. It decreases as the positive charge is more localized on the metal center or less stabilized by electrostatic interactions between cations and anions. In the case of $2b\text{PF}_6$, the value is very large and does not compare with the data obtained in the case of iron cumulenylenidene complexes, for which the IS parameters range between 0.8 and 1.7 mm/s vs Fe. Values of IS as large as that found for $2b\text{PF}_6$ have been occasionally found for substituted ferrocenium cations such as $\{1,1'-'\text{Cp}^*(\text{dppe})\text{Fe-C≡C=CR}\}(\text{PF}_6)_2$ (bfc = 1,1'-biferrocenyl). It is interesting to note that the redox potential of this ferrocenium derivative ($E^* = 0.49$ V) is not far from the first oxidation potential of $2b\text{PF}_6$.

In the Cp$^*$-(dppe)Fe series, the neutral iron(II) complexes have QS values close to 2.0 mm/s while the cationic iron(III) analogues exhibit QS values slightly below 1.0 mm/s. The metallacumulenylenidene are characterized by QS parameters ranging between 1.0 and 1.5 mm/s. The Mössbauer data strongly suggest that the C$_{2}$ ligand with a four-carbon cyclobutene strongly modifies the ligand field of the iron nucleus and plays a role different from those of conventional cumulene ligands. It apparently acts as a very electron withdrawing ligand, in accord with the redox potentials.

6. Glass ESR Spectroscopy. Powdered samples of complexes $2a\text{PF}_6$ and $2b\text{PF}_6$ are not ESR active, but surprisingly these binuclear compounds, which were fully characterized by NMR at 20 °C, are ESR active at liquid nitrogen temperature in frozen solution. For this reason, $2a\text{PF}_6$ was subjected to a detailed ESR study. Optimal resolution was obtained for samples dissolved in CH$_2$Cl$_2$ and transferred into an ESR quartz tube before being cooled to 67 K. The X-band ESR spectrum shows an intense signal characteristic of an Fe(III) complex in a pseudo-octahedral environment (Figure S6, Supporting Information). The characteristic three g tensors for the $\Delta m_s = \pm 1$ transition were found at $g_1 = 2.443$, $g_2 = 2.035$, and $g_3 = 1.989$. The magnetic anisotropy $\Delta g = g_1 - g_3 = 0.454$ is very large, indicating the metallic character of this magnetic complex. Interestingly, ca. 1.2 electrons out of the two unpaired electrons are found on the iron centers in the high-spin configuration of $2a$. The quantum chemical calculations performed for $2a^*$ (T) are in agreement with an important spin density on the metal centers (0.842 and 0.327). Nevertheless, with a total energy of roughly 1 eV higher than that of the singlet state (solvent and dispersion effects included), this compound is most probably not the magnetic compound observed experimentally. Furthermore, the $\Delta m_s = \pm 2$ transition characteristic of the triplet state was clearly observed at $g = 4.263$. This interesting observation demonstrates that complex $2a\text{PF}_6$ carries two unpaired electrons and magnetic exchange interactions between them take place. In its high-spin configuration this complex can be regarded as a bis-Fe$^{II}$ derivative.

CONCLUSION

In this contribution, we have found that the radical cations [Cp$^*$-(dppe)FeC≡C=CR]PF$_6$ (Ar = Ph, 1a; Ar = C$_6$H$_4$-Me-4, 1b) are stable below −35 °C in solution. Above this temperature they dimerize to provide specifically the symmetrical dimers [{Cp$^*$-(dppe)Fe}$_2$C$_3$Ar$_2$](PF$_6$)$_2$ (Ar = Ph,
2a(PF$_6$)$_2$: Ar = C$_6$H$_4$Me-4, 2b(PF$_6$)$_2$). The formation of these new complexes results from the initial formation of a carbon–carbon bond between atoms in C$_6$H$_4$ with respect to the iron nucleus of each radical cation. The iron building blocks rotate slowly around the cyclobutene ring on the NMR time scale, allowing the observation of three rotamers in equilibrium. Structures for the rotamers are proposed, and quantum chemical investigations have shown that their relative stabilities are largely dependent on the orientations of the metal end caps. From the redox potentials of the binuclear complex 2b(PF$_6$)$_2$, it has been shown that a strong electronic interaction occurs between the redox centers. The compound is diamagnetic in the solid state, while the triplet excited state becomes thermally accessible in solution. Further efforts will be devoted to the extension of the scope of this reaction, replacing the aryl groups by functional substituents.

**Experimental Section**

**General Data.** Manipulations of air-sensitive compounds were performed under an argon atmosphere using standard Schlenk techniques or in an argon-filled Jactomex 532 drybox. All glassware was oven-dried and vacuum or argon flow degassed before use. Fourier transform infrared (FT-IR) spectra were recorded using a Bruker IFS28 spectrophotometer (range 4000–800 cm$^{-1}$) as solids dispersed in KBr pellets. UV-visible spectra were recorded on a Cary 5000 spectrophotometer. $^{1}H$, $^{13}C$, and $^{31}P$ NMR spectra were recorded on a Bruker AVIII 400 MHz multinuclear spectrometer at ambient temperature, unless otherwise noted. $^{29}$Si NMR spectra were run on a Bruker 300-MSL spectrometer. Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane (TMS) for $^1H$ and $^{13}C$ spectra and external 85% aqueous H$_2$PO$_4$ for $^{31}P$ NMR spectra. Coupling constants (J) are reported in hertz (Hz), and integrations are reported as the number of protons. The following abbreviations are used to describe peak patterns: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Mass spectra were run on a HP 5971A/59890-II GC/MS coupling (HP 1 capillary column, length 25 m, diameter 0.2 mm, 0.33 μm polydimethylsiloxane). ESR spectra were recorded on a Bruker EMX-8/2.7 (X-band) spectrometer. The $^{57}$Fe Mössbauer spectra were recorded with a 2.5 × 10$^{-3}$（9.25 × 10$^{-4}$ Bq）$^{57}$Co 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.$^{39}$ The isomer shift (ν) values are reported relative to iron foil at 298 K. Elemental analyses were conducted on a Thermo-FINNIGAN Flash EA 1112 CHNS/O elemental analyzer, with a previously reported computer program.$^{39}$ The isomer shift (ν) values are reported relative to iron foil at 298 K. Elemental analyses were conducted on a Thermo-FINNIGAN Flash EA 1112 CHNS/O elemental analyzer, with a previously reported computer program.$^{39}$ The isomer shift (ν) values are reported relative to iron foil at 298 K. Elemental analyses were conducted on a Thermo-FINNIGAN Flash EA 1112 CHNS/O elemental analyzer, with a previously reported computer program.$^{39}$

**Synthesis of [(Cp*){dppe}Fe=C=Fe=C=Cp*{dppe}](PF$_6$)$_2$: (1a).** $^{31}P$ NMR ([Cp*{dppe}Fe=C=Fe=C=Cp*{dppe}]PF$_6$)$_2$: (1a) $^{31}P$ NMR (δ, C$_6$H$_4$Me-4) = 154.71, 105.10, 101.80, 90.06, 89.00 (4 H, Cp*). $^{31}C$ NMR (δ, C$_6$H$_4$Me-4): 203.16, 203.73 (4 H, Cp*). $^{1}H$ NMR (δ, C$_6$H$_4$Me-4): 1.34, 1.37, 1.38, 1.4, 1.7, 2.6, 3.8, 3.86, 4.8, 4.91 (16 H, C$_6$H$_4$). $^{13}C$ NMR (δ, C$_6$H$_4$Me-4): 19.96 (s, 6H, C$_6$H$_4$). 31P NMR (C$_6$H$_4$, 121 MHz): δ 100.3 (s, ES-MS (m/z): calc for C$_7$H$_5$Fe$_2$: 728.2424, found 728.2427 [M]$^+$. Extended data for this complex is provided in the Supporting Information.**
number of data/restraints/parameters, 12007/0/588; final R, R1 = 0.0867, wR2 = 0.2057; R indices (all data), R1 = 0.112, wR2 = 0.2237; goodness of fit/F2, 1.034; largest difference peak and hole, 2.101 and −1.932 e Å−3.

**Computational Details.** DFT calculations were carried out with the Amsterdam Density Functional package (ADF 2010) without any symmetry constraints on the bimetallic dimers 2a1, 3a1, 2a2, and 2a2−. Electron correlation was treated within the local density approximation (LDA) in the Vosko–Wilk–Nusair parametrization. The nonlocal corrections of Becke and Perdew were added to the exchange and correlation energies, respectively. The analytical gradient method implemented by Versluis and Ziegler was used. The standard ADF TZP basis set was used: i.e., a triple-ζ STO basis set for the valence core augmented with a 2p polarization function for H, a 3d polarization function for C, P, and Si, and a 4p polarization function for Fe. Orbitals up to 1s, 2p, and 3p were kept frozen for C, P, Si, and Fe, respectively. Geometry optimization convergence criteria were more drastic than default criteria (energy change <0.0005 hartree and atomic position displacement <0.005 Å). Single-point calculations were performed on the optimized geometries in order to partially evaluate solvent dispersion effects. To address solution effects, the conductor-like screening model (COSMO) was used with a dielectric constant simulating dichloromethane solvent. The geometries were not relaxed because of the prohibitive computational cost. For the dispersion effects, DFT-D3 corrections proposed by Grimme were added to the total bonding energy, gradient, and second derivatives.

Molecular orbitals were plotted with the ADF-GUI package.

### ASSOCIATED CONTENT

#### Supporting Information

Mulliken decomposition and energies of the first molecular frontier orbitals of 2a1 obtained in the singlet state (Table S1), energy and composition of the first electronic excitation energy for 2a1 (Table S2), Cartesian coordinates of the optimized geometries of 2a1 (Table S3), 31P NMR spectra of 2a(PF6)2 and 2b( PF6)2 (Figure S1), 1H EXSY NMR spectrum of 2b(PF6)2 (Figure S2), 11C NMR spectrum of 2a(PF6)2 (C1 pattern; Figure S3), 13C NMR spectrum of 2a(PF6)2 (C5 and quaternary aromatic carbon patterns; Figure S4), 13C NMR spectrum of 2a(PF6)2 (C5Me and pattern; Figure S5), ESR spectrum of the dimer 2a(PF6)2 in CH2Cl2 at 67 K (Figure S6), and a CIF file for 2a(PF6)2. This material is available free of charge via the Internet at http://pubs.acs.org. Full details of the structure determination have also been deposited with the Cambridge Crystallographic Data Centre as CCDC 916647. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Street, Cambridge CB2 1EZ, U.K. (fax +44-1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

#### AUTHOR INFORMATION

**Notes**
The authors declare no competing financial interest.

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