# **ORGANOMETALLICS**

# Synthesis and Characterization of Redox-Active Mononuclear $Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)$ -Terminated $\pi$ -Conjugated Wires

Katy Green,<sup>†</sup> Nicolas Gauthier,<sup>†</sup> Hiba Sahnoune,<sup>†</sup> Gilles Argouarch,<sup>†</sup> Loic Toupet,<sup>‡</sup> Karine Costuas,<sup>†</sup> Arnaud Bondon,<sup>§</sup> Bruno Fabre,<sup>\*,†</sup> Jean-François Halet,<sup>\*,†</sup> and Frédéric Paul<sup>\*,†</sup>

<sup>†</sup>Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

<sup>‡</sup>Institut de Physique de Rennes, UMR 6251 CNRS, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France <sup>§</sup>RMN-ILP, UMR 6026 CNRS, Université de Rennes 1, IFR 140, PRISM, CS 34317, Campus de Villejean, 35043 Rennes Cedex, France

**Supporting Information** 

**ABSTRACT:** Several new redox-active  $Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)$  arylacetylide complexes featuring pendant ethynyl  $(Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)-[\{C \equiv C(1,4-C_6H_4)\}_nC \equiv CH]$  (1b-d; n = 1-3),  $Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)[C \equiv C(1,3-C_6H_4)C \equiv CH]$  (2)) or ethenyl  $(Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)[C \equiv C(1,4-C_6H_4)CH = CH_2]$  (3)) groups have been synthesized and characterized under their Fe(II) and Fe(III) states. In contrast to the known ethynyl Fe(III) complex  $[Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)(C \equiv CH)][PF_6]$  (1a[PF<sub>6</sub>]), most of the new Fe(III) derivatives turned out to be kinetically stable in solution. A consistent picture of the electronic structure of the latter complexes in both redox states emerged from experimental data and



DFT calculations. This study revealed that beyond the first 1,4-phenylene ring, modification or extension of the carbon-rich linker using (4-phenylene)ethynylene spacers will have only a minor influence on their electronic properties in their ground state, while still maintaining some (weak) electronic interaction along the carbon-rich backbone.

# INTRODUCTION

Functional molecular materials are playing an ever-increasing role in the fabrication of smart integrated devices that can perform *inter alia* logic operations.<sup>1–3</sup> In this respect, the modification of conducting surfaces at the molecular level with redox-active "building blocks" constitutes a powerful approach, particularly when the goal is to obtain integrated systems devoted to information storage or transfer.<sup>4-6</sup> In parallel with these studies, several families of redox-active carbon-rich group 8  $\sigma$ -alkynyl complexes have been identified as interesting candidates for reversible charge storage at the molecular level<sup>7,8</sup> and were shown to present promising prospects for the elaboration of molecular-based electro-switchable devices.9,10 Semiconducting surfaces, such as doped silicon, are attractive for the elaboration of molecular-scale devices, since " $\pi$ conjugation" between the redox tag and the surface can in principle be maintained when the grafting is conducted from an alkyne-terminated molecular precursor and oxide-free hydro-gen-terminated silicon (Si–H) surfaces.<sup>11,12</sup> To our knowledge, while such silicon-based interfaces derivatized with various types of redox-active centers, such as ferrocene<sup>13–15</sup> and metal-complexed porphyrins,<sup>1,2,4,16</sup> have recently attracted sustained attention, the interfacial electron-transfer kinetics have not yet been thoroughly investigated with metal alkynyl-based monolayers.<sup>5,6,14,17</sup> In order to learn how the nature and length of the spacer influence the interfacial electron-exchange

process, we decided to study the electron-transfer between the " $Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)$ " end group (dppe = 1,2-bis-(diphenylphosphino)ethane) and the underlying Si surface when anchored with various types of spacers. To this aim, the series of mononuclear complexes  $Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)$  $[\{C \equiv C(1,4-C_{6}H_{4})\}_{n}C \equiv CH\}$  (1a-d; n = 0-3),  $Fe(\kappa^{2}-dppe)$ - $(\eta^5 - C_5 Me_5)[C \equiv C(1, 3 - C_6 H_4)C \equiv CH]$  (2), and  $Fe(\kappa^2 - dppe)$ - $(\eta^{5}-C_{5}Me_{5})[C \equiv C(1,4-C_{6}H_{4})CH = CH_{2}]$  (3) featuring (poly)phenyleneethynylene ligands of various lengths and topologies terminated by linking end groups was targeted (Scheme 1). Indeed, as previously communicated,<sup>17</sup> 1b-d will lead to the corresponding monolayers when reacted with Si-H surfaces using the UV-activated hydrosilylation reaction initially developed by Chidsey and co-workers for phenylacetylene or styrene,<sup>18</sup> while 2 and 3 should react similarly. Then, in order to be able to optimize this photochemical grafting step, we have also conducted a thorough experimental and theoretical study on these derivatives in order to see how a change in the connectivity of the terminal group on the aryl ring (meta vs para), a change in the terminal group nature (ethynyl vs ethenyl), or simply the extension of the 1,4-phenylene ethynylene spacer would affect the terminal group involved in the photochemical grafting reaction. In particular, extension of

 Received:
 June 5, 2013

 Published:
 July 31, 2013

Scheme 1. Targeted Organoiron(II) Complexes: 1a-d, 2, and 3 ([Fe] =  $Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)$ )



Scheme 2. Synthesis of 1b-d and 2



the carbon-rich linker will result in a narrowing of the gap between the occupied and empty molecular orbitals centered on the (poly)phenylene ethynylene chain, and this phenomenon might significantly affect both the reactivity and the stability of the terminal functional group. Their electrontransfer properties within the monolayers should also be modified. Finally, the kinetic stability of the corresponding Fe(III) complexes might turn out to be an important issue, given that oxidation reactions might take place at the Si–H interface during the grafting process<sup>18b</sup> along with the fact that the shorter of these compounds ( $1a[PF_6]$ ) is known to spontaneously dimerize in solution.<sup>19</sup>

We therefore report in this paper (i) the synthesis of the phenylene ethynylene mononuclear Fe(II) precursors **1b**–**d**, **2**, and **3**, featuring a pendant ethynyl or ethenyl group, (ii) the characterization of their corresponding Fe(III) radical cations (**1b**–**d**[PF<sub>6</sub>], **2**[PF<sub>6</sub>], **3**[PF<sub>6</sub>]), and (iii) DFT computations on several of these compounds to better understand their reactivity toward the photochemical grafting reaction. The preparation and characterization of the corresponding hybrid molecule/Si interfaces as well as the measurements of the interfacial electron-transfer kinetics will be reported in a subsequent paper.<sup>20</sup>

# RESULTS

Synthesis and Characterization of Fe(II) Complexes with Pendant Ethynyl and Ethenyl Groups. Among the ethynyl-terminated mononuclear organoiron complexes that were targeted for the grafting on Si–H surfaces only  $1a^{19,21}$  and  $1b^{22}$  had been reported. The new compounds 1c-d, 2, and 3 were obtained by similar reactions, starting from the corresponding ethynyl precursors and the iron(II) chloride complex 4,<sup>23</sup> in two steps, following a well-established protocol (Scheme 2).<sup>24</sup> Several of the alkynes required for these syntheses have been previously reported.<sup>25,26</sup> All were newly synthesized (Supporting Information) and reacted with the Fe(II) chloride precursor 4. The synthesis proceeds in two steps via vinylidene intermediates that were deprotonated immediately after isolation with either t-BuOK or 1,8diazabicyclo [5.4.0] undec-7-ene (DBU). Deprotonation of trimethylsilyl-protected vinylidene complexes with t-BuOK resulted in the simultaneous removal of the silvl protective group, whereas the use of DBU allowed for the clean isolation of the silvl-terminated compounds (5a-c). The trimethylsilyl protective group in 5a-c was subsequently removed with potassium carbonate following standard procedures.<sup>27</sup> Complexes 1b and 1c were also accessed from the triisopropylsilylprotected complexes (5'b and 5'c) after desilylation using tetran-butylammonium fluoride (TBAF). The latter approach turned out to be less productive than the former one and requires harsher deprotection conditions. In line with a previous study,<sup>22</sup> trimethylsilyl complexes (5a-c) appear to be better precursors of the corresponding ethynyl derivatives than triisopropyl derivatives (5'a,b).

The synthesis of the ethenyl complex 3 was achieved from the known organoiron Fe(II) aldehyde complex precursor  $7^{28}$  in one step, by reaction with a phosphonium salt in a Wittig-type reaction (Scheme 3).<sup>29</sup>

Scheme 3. Synthesis of 3



The new Fe(II) complexes were fully characterized by MS, IR (in solution and solid state), and NMR spectroscopies. In addition, the solid-state structures of **1b**,**c**, **2**, and **3** and of the silyl precursors **5a** and **6** were obtained by X-ray diffraction (*vide infra*). <sup>31</sup>P{<sup>1</sup>H} NMR constitutes a good handle to probe the purity of the various products by observation of a unique singlet near 101 ppm for the chemically equivalent phosphine atoms of the dppe ligand of each compound. However this signal appears to be poorly sensitive to bridge extension in **1b**–

d. <sup>1</sup>H NMR is also poorly informative on the chemical modifications taking place on the bridge within **1a**–**d**, apart from evidencing the increasing number of aromatic signals. In contrast, <sup>13</sup>C NMR allows for the clear detection of the additional alkyne signals (near 90 ppm) when proceeding from **1a** to **1d**, while the  $\alpha$ -alkynyl carbon atom comes out each time around 146 ppm for all of these compounds.<sup>22,30,31</sup>

The IR spectra clearly reveal an increasing number of  $\nu_{C\equiv C}$  modes upon bridge extension between 1b and 1c (Table 1) or

Table 1. Experimental (in CH<sub>2</sub>Cl<sub>2</sub>) and Computed (in Parentheses) IR  $\nu_{C\equiv C}$  Frequencies (cm<sup>-1</sup>) for Selected Fe( $\kappa^2$ -dppe)( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)(R) Complexes

(Fe(III)
(-70)
(-70)
1)
(-56)
+5)
-15)
(3)
+21)
-28)
(-65)
-13)
(-71)

<sup>*a*</sup>Minimum Fe(II) vs Fe(III)  $\nu_{C\equiv C}$  difference (±4 cm<sup>-1</sup>; PF<sub>6</sub><sup>-1</sup> counterion). <sup>*b*</sup>Similar in CH<sub>2</sub>Cl<sub>2</sub> to that in KBr pellets.<sup>19</sup> <sup>*c*</sup>See also ref 22. <sup>*d*</sup>Two bands were observed for the Fe(III) parents, presumably due to Fermi coupling.<sup>33</sup> <sup>*c*</sup>Very weak. <sup>*f*</sup>Shoulder. <sup>*g*</sup>See ref 24.

5a and 5b series. In all complexes, except for 1a, the  $\nu_{C=C}$ mode corresponding to the alkynyl bonds ligated to the Fe(II) center is observed around 2040 cm<sup>-1</sup>, while those corresponding to the terminal alkyne bond appear as very weak absorptions near 2105 or 2155 cm<sup>-1</sup>, depending on whether the alkyne is ligated to H or SiMe3, respectively. The additional mode corresponding to the central alkyne in 1c or 5b is observed near 2210 cm<sup>-1.32</sup> Interestingly, further progression from 1c to 1d or 5b to 5c does not lead to any significant change in the  $\nu_{C \equiv C}$  range. Most likely, the additional  $\nu_{C \equiv C}$ mode expected is superimposed to the internal mode near 2210  $cm^{-1}$ , as suggested by the DFT calculations (vide infra). Congruent with this hypothesis, a shoulder is observed on this absorption peak near 2210 cm<sup>-1</sup> in the Raman spectrum, which could correspond to the expected additional mode (see Supporting Information). Finally, for 3, the additional stretching mode observed near 1620 cm<sup>-1</sup> and not observed for the other Fe(II) complexes is tentatively attributed to the  $\nu_{\rm CH=CH2}$  mode.

**Cyclic Voltammetry.** Cyclic voltammograms of the mononuclear compounds **1b–d**, **2**, and **3** were done in dichloromethane medium. A single reversible one-electron system was observed for all complexes (Table 2), corresponding to the metal-centered oxidation Fe(II)/Fe(III).<sup>8</sup> Compared to the phenylethynyl complex  $Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)(C \equiv CPh)$  (**8**), the oxidation process occurs at lower potential for

Table 2. Electrochemical Data for Selected  $Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)(R)$  Complexes

		1	1
compd	R	$E^{\circ} \left[\Delta E_{\rm p}\right] ({\rm V})^{a,b}$	$E^{\circ} \left[\Delta E_{\rm p}\right] ({\rm V})^{b,c}$
1b	$C \equiv C(1,4-C_6H_4)C \equiv CH$	$-0.11 \ [0.08]^d$	-0.11 [0.08]
1c	$\{C \equiv C(1,4-C_6H_4)\}_2 C \equiv CH$	-0.12 [0.08]	-0.11 [0.07]
1d	$\{C \equiv C(1,4-C_6H_4)\}_3 C \equiv CH$	-0.12 [0.08]	-0.11 [0.06]
2	$C \equiv C(1,3-C_6H_4)C \equiv CH$	-0.13 [0.09]	-0.12 [0.07]
3	$C \equiv C(1,4-C_6H_4)CH = CH_2$	-0.16 [0.07]	-0.15 [0.07]
5b	$C \equiv C(1,4-C_6H_4)C \equiv CTMS$	$-0.12 \ [0.08]^e$	
6	$C \equiv C(1,3-C_6H_4)C \equiv CTMS$	-0.14 [0.09]	
8	C≡CPh	-0.15 [0.08] <sup>f</sup>	$-0.14 \ [0.08]^g$

<sup>*a*</sup>Conditions: CH<sub>2</sub>Cl<sub>2</sub> solvent, 0.1 M [Bu<sub>4</sub>N][PF<sub>6</sub>] supporting electrolyte, 20 °C, Pt electrode, 0.1 V s<sup>-1</sup>. <sup>*b*</sup>The ratio between the anodic and cathodic peak current intensities was unity in each case ( $I_{pa}/I_{pc} = 1$ ). <sup>*c*</sup>Conditions: CH<sub>3</sub>CN solvent, 0.1 M [Bu<sub>4</sub>N][ClO<sub>4</sub>] supporting electrolyte, 20 °C, Pt electrode, 0.1 V s<sup>-1</sup>. <sup>*d*</sup>Potential difference between the anodic and cathodic peaks. <sup>*e*</sup>From ref 22. <sup>*f*</sup>From ref 35. <sup>*g*</sup>See ref 30.

**1b**–**d** and **3** and at higher potential for **2**. In line with previous observations,<sup>22,30</sup> this trend correlates well with the electronic effect of the substituent on the first ring. Indeed, based on the redox potentials, we find the following order: p-C $\equiv$ CH > p-C $\equiv$ CSiMe<sub>3</sub> (~p-C $\equiv$ CAr) > m-C $\equiv$ CH > m-C $\equiv$ CSiMe<sub>3</sub> > H > p-CH=CH<sub>2</sub>, which qualitatively fits with the electron-withdrawing character of the latter, according to the Hammett electronic substituent parameter scale (when available).<sup>34</sup> Notably, these values also indicate that beyond the second ring further extension of the arylethynyl ligand does not affect significantly the metal-centered oxidation redox potential, since **1c** and **1d** display the same value within experimental uncertainties.

Synthesis and Characterization of Corresponding Fe(III) Complexes. In accordance with the previous cyclic voltammetry (CV) studies, the corresponding Fe(III) complexes could be synthesized and isolated after chemical oxidation using ferrocenium hexafluorophosphate (Scheme 4). The completion of the reaction was apparent from the combined CV and IR spectra of the various products isolated. Thus, the CVs of  $1b,c[PF_6]$ ,  $2[PF_6]$ , and  $3[PF_6]$  remain identical to that of the starting Fe(II) complexes, indicating the absence of decomposition or formation of new electroactive side-products during the measurement time, while the IR showed a clear shift toward lower wavenumbers of the diagnostic  $\nu_{C \equiv CFe}$  stretching mode (Table 1), as expected from previous investigations.<sup>33,35</sup> Note that  $1d[PF_6]$  decomposes in solution at ambient temperature. This Fe(III) species could therefore not be isolated in a pure state and was only transiently characterized when generated in solution, exhibiting spectroscopic signatures consistent with these obtained for the shorter analogues 1b,c[PF<sub>6</sub>]. The  $\nu_{C \equiv CFe}$  shift reveals a weakening of the alkynyl bond order upon oxidation. However, its value for 1b, 2, and 3 is not simple to determine with accuracy, due to the existence of Fermi coupling.<sup>32,33</sup> Overall, the shift amounts to ca. 50  $\text{cm}^{-1}$  for 1c and 1d, which corresponds to that observed for the phenylalkynyl complex 8, and seems poorly affected when going from  $1b[PF_6]$  to  $1d[PF_6]$ . Relatively, the energies of the other  $\nu_{C \equiv C}$  modes of these complexes and of the  $\nu_{CH=CH2}$  mode in 3 are almost not affected by oxidation, further suggesting that the electronic hole is mainly metal-centered in these complexes and not delocalized beyond the first phenyl ring of the bridge. Thus,

Article

Scheme 4. Synthesis of 1b-d[PF<sub>6</sub>], 2[PF<sub>6</sub>], and 3[PF<sub>6</sub>]



Table 3. Experimental and Computed (in Parentheses) ESR Spectroscopic Data for Selected  $[Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)(R)][PF_6]$ Complexes<sup>*a,b*</sup>

compd	R	$g_1$	$g_2$	<i>g</i> <sub>3</sub>	$\Delta g$	$\langle g \rangle$
1 <b>b</b> [PF <sub>6</sub> ]	$C \equiv C(1,4-C_6H_4)C \equiv CH$	1.972 (1.978)	2.031 (2.032)	2.481 (2.259)	0.509 (0.281)	2.161 (2.090)
$1c[PF_6]$	$\{C \equiv C(1,4-C_6H_4)\}_2 C \equiv CH$	1.977 (1.985)	2.033 (2.026)	2.472 (2.197)	0.495 (0.212)	2.160 (2.069)
$1d[PF_6]^c$	$\{C \equiv C(1,4-C_6H_4)\}_3 C \equiv CH$	1.975 (1.982)	2.032 (2.022)	2.459 (2.214)	0.484 (0.232)	2.155 (2.073)
$2[PF_6]$	$C \equiv C(1,3-C_6H_4)C \equiv CH$	1.979 (1.971)	2.034 (2.029)	2.473 (2.305)	0.494 (0.334)	2.162 (2.102)
$3[PF_6]$	$C \equiv C(1,4-C_6H_4)CH = CH_2$	1.978 (1.976)	2.030 (2.028)	2.428 (2.263)	0.450 (0.287)	2.145 (2.089)
<b>5a</b> [PF <sub>6</sub> ]	$C \equiv C(1,4-C_6H_4)C \equiv CTMS$	1.975	2.032	2.478	0.503	2.161
<b>5b</b> [PF <sub>6</sub> ]	$\{C \equiv C(1,4-C_6H_4)\}_2 C \equiv CTMS$	1.974	2.032	2.476	0.502	2.160
<b>5c</b> [PF <sub>6</sub> ]	$\{C \equiv C(1, 4 - C_6 H_4)\}_3 C \equiv CTMS$	1.974	2.031	2.482	0.508	2.162
<b>5</b> 'a[PF <sub>6</sub> ]	$C \equiv C(1,4-C_6H_4)C \equiv CTIPS$	1.975	2.028	2.455	0.480	2.152
5'c[PF <sub>6</sub> ]	$\{C \equiv C(1,4-C_6H_4)\}_2 C \equiv CTIPS$	1.976	2.034	2.481	0.505	2.163
<b>6</b> [PF <sub>6</sub> ]	$C \equiv C(1,3-C_6H_4)C \equiv CTMS$	1.978	2.035	2.466	0.488	2.159
$8[PF_6]^d$	C≡CPh	1.975	2.033	2.464	0.489	2.157
<sup>a</sup> At ca. 70 K in	$CH_2Cl_2/1,\!2\text{-}C_2H_4Cl_2\ (1{:}1)$ glass.	<sup><i>b</i></sup> g values $\pm 0.005$ .	<sup>c</sup> Not pure: other m	inor species also pr	esent. <sup>d</sup> See ref 35.	

for the ethynyl-terminated complexes, oxidation leads to a  $\nu_{\equiv C-H}$  mode at slightly lower energies for  $1b[PF_6]$  ( $\Delta\nu = 19$  cm<sup>-1</sup>) and  $1c[PF_6]$  ( $\Delta\nu = 26$  cm<sup>-1</sup>) than for the Fe(II) parent compounds, but not for  $1d[PF_6]$  and  $2[PF_6]$ . Notably, the  $\nu_{C\equiv CH}$  mode is significantly less intense than the internal and alkynyl  $\nu_{C\equiv C}$  stretches in compounds 1b-d and 3.

The strong metallo-centered character of these Fe(III) radicals is also evidenced by their rhombic electron spin resonance (ESR) signatures at ca. 70 K, which exhibit only marginal changes in anisotropy ( $\Delta g$ ) or mean g value ( $\langle g \rangle$ ) between **1b**-**d**[PF<sub>6</sub>], **2**[PF<sub>6</sub>], and **3**[PF<sub>6</sub>] (Table 3). Thus, among the Fe(III) *para*-ethynyl/ethenyl complexes (**1b**-**d**[PF<sub>6</sub>] and **3**[PF<sub>6</sub>]) or silyl-protected precursors (**5a**-**c**[PF<sub>6</sub>]), extension of the conjugation pathway has apparently

only a marginal effect on the radical delocalization. As previously shown with other such arylalkynyl compounds,<sup>35</sup> the ESR anisotropy ( $\Delta g$ ) is often indicative of the electronattracting influence of the substituent on the ring. Presently, comparison between the  $\Delta g$  values obtained for  $1b[PF_6]$  and  $2[PF_6]$  or for  $5b[PF_6]$  and  $6[PF_6]$  suggests that an alkyne group is less electron withdrawing when located in the *meta* position than in the *para* position on the first aryl ring. Actually, the values found for the *meta* derivatives compare within experimental uncertainties with that obtained for the compound  $8[PF_6]$ , possessing an unsubstituted phenyl ring.<sup>35,36</sup> Likewise, comparison between the anisotropy of  $1b[PF_6]$  and  $3[PF_6]$  suggests that the vinyl group is a slightly more electron-releasing group than the ethynyl group and even



Figure 1. <sup>1</sup>H NMR spectra of 2[PF<sub>6</sub>] (a) and 1b[PF<sub>6</sub>] (b) in CD<sub>2</sub>Cl<sub>2</sub> at 20 °C with proposed assignment according to Chart 1 for selected protons.

Table 4. Observed <sup>1</sup>H NMR Shifts ( $\delta \pm 0.1$  ppm) Recorded for Selected Protons of the  $[Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)(R)][PF_6]$ Complexes at 20 °C in  $CD_2Cl_2^{a}$ 

					R				dppe	-	C <sub>5</sub> Me <sub>5</sub>
compd	R	$H_1$	H <sub>2</sub>	H <sub>3</sub>	$H_4$	H <sub>5</sub>	H <sub>6</sub>	H <sub>7</sub>	H <sub>Ar</sub>	CH <sub>2</sub>	H <sub>Cp*</sub>
1 <b>b</b> [PF <sub>6</sub> ]	$C \equiv C(1,4-C_6H_4)C \equiv CH$	-20.1	30.4	-39.6					7.9-1.3	-2.8	-10.3
$1c[PF_6]$	$\{C \equiv C(1,4-C_6H_4)\}_2 C \equiv CH$	0.9	31.3	-41.8	9.3	$3.6^{b}$			7.9-1.7	-2.8	-10.3
$1d[PF_6]$	$\{C \equiv C(1,4-C_6H_4)\}_3 C \equiv CH$	2.5 <sup>c</sup>	31.6	-42.4	9.5	$3.6^{b,c}$	n.a. <sup>d</sup>	n.a. <sup>d</sup>	$7.9 - 1.7^{c}$	-2.8	-10.3
$2[PF_6]$	$C \equiv C(1,3-C_6H_4)C \equiv CH$	8.9	-36.7	27.8	-38.2				7.9-1.6	-2.7	-10.5
$3[PF_6]$	$C \equiv C(1,4-C_6H_4)CH = CH_2$	-24.6	-22.3	28.1	32.5	-46.6			10.0-2.0	-2.9	-10.3
$8[PF_6]^e$	$C \equiv C(C_6H_5)$	$-41.7^{e}$	29.2 <sup>e</sup>	$-41.7^{e}$					7.9-1.8	-2.8	-10.5
		1 -			\ <b>1</b>			_			4

<sup>a</sup>Proposed assignment according to Chart 1 (CHDCl<sub>2</sub> taken at 5.35 ppm). <sup>b</sup>Partly hidden behind another signal. <sup>c</sup>Tentative assignment. <sup>d</sup>Not assigned. <sup>e</sup>See ref 38.

Chart 1. Labeling of Selected Protons of 1b-d[PF<sub>6</sub>], 2[PF<sub>6</sub>], 3[PF<sub>6</sub>], and 8[PF<sub>6</sub>] ([Fe] = Fe( $\kappa^2$ -dppe)( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>))



(a) (b)

Figure 2. Thermal ellipsoid plots (ORTEP) of the two ethynyl complexes 1b (a) and 1c (b) at the 50% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity.



Figure 3. Thermal ellipsoid plots (ORTEP) of the Fe(II) and Fe(III) ethynyl complexes 2 (a) and  $2[PF_6]$  (b) at the 50% probability level. Hydrogen atoms have been omitted for clarity.

slightly more than a hydrogen atom when compared to the  $\Delta g$  obtained for 8[PF<sub>6</sub>].

These Fe(III) compounds were also characterized by <sup>1</sup>H NMR (Figure 1). All, except  $1d[PF_6]$ , for which not all signals could be identified due to its kinetic instability in solution, gave rise to well-resolved spectra characteristic of a single Fe(III) metallo-centered radical.<sup>8,37</sup> The shift of their protons was identified by analogy with those of related complexes, by integration, and whenever possible by polarization transfer experiments. Most often, this led to an unambiguous assignment of all the observed signals.<sup>38</sup> The NMR shifts of the dppe and C<sub>5</sub>Me<sub>5</sub> protons were very constant from one complex to the other among  $1b_{c}[PF_{6}]$ ,  $2[PF_{6}]$ , and  $3[PF_{6}]$ , most of the changes taking place for the protons of the arylethynyl ligand. The shifts of these <sup>1</sup>H NMR signals (Table 4), which mostly depend on the so-called contact contribution, reflect the changes in spin delocalization along the backbone of the unsaturated carbon-rich ligand.<sup>39,40</sup> First, based on the DFT-computed spin densities (vide infra), their sign reflects the spin alternation of the vicinal carbon atoms, in line with a spin delocalization/polarization taking place mostly in the  $\pi$ manifold. This is plainly illustrated by the shift of the terminal ethynyl proton, which was identified by <sup>1</sup>H-<sup>13</sup>C HSQC correlation experiments for  $1b[PF_6]$  (see Supporting Information). The latter comes out at -20.1 ppm. For  $2[PF_6]$ , it is found at the positive value 8.9 ppm. Such a reversal of the sign of the observed shift can be expected based on the meta vs para

substitution on the aryl ring and is actually also supported by the DFT-computed carbon-based spin densities (see below).<sup>4</sup> The protons of the second aromatic ring in  $1c[PF_6]$  are much less shifted than those of the first ring and apparently even less than for the third ring in  $1d[PF_6]$ , which is consistent with no significant spin density being delocalized beyond the second ring in these compounds. This statement can also be deduced from the ethynyl proton shifts which appear at 20.1 ppm for  $1b[PF_6]$  and at 0.9 ppm for  $1c[PF_6]$ . These observations are in line with the dominantly metal-centered nature of these radicals, a statement already inferred from ESR experiments, but also apparent from IR measurements. Finally, the ethenyl protons  $H_1$  and  $H_2$  in  $3[PF_6]$  are slightly more shielded than the ethynyl one  $(H_1)$  in  $1b[PF_6]$ , in line with the slightly higher spin density found on the former substituent by DFT (see later).

Article

**Crystallography.** Figure 2 depicts the solid-state structures of Fe(II) complexes 1b and 1c. The structures of the Fe(II) and Fe(III) *meta*-substituted compounds 2 and 2[PF<sub>6</sub>] and of the ethenyl-terminated Fe(II) complex 3 are shown in Figures 3 and 4, respectively. Those of the triisopropylsilyl-protected precursor of 1b (5'a) and of the trimethylsilyl-protected precursor of 2 (6) are given in the Supporting Information. Compounds 1b and 5'c have been characterized previously, but their solid-state structures have not been reported,<sup>22</sup> while the structure of 1c has been previously reported in a communication.<sup>17</sup> In the present case, the structural data for



**Figure 4.** Thermal ellipsoid plots (ORTEP) of the ethenyl complex **3** at the 50% probability level. Hydrogen atoms have been omitted for clarity.

1b,c, 2, and 3 provide us with a mean to evaluate their spatial extension, which constitutes important information for estimating the surface area occupied by these molecules once grafted on Si-H surfaces. All these compounds crystallize in monoclinic or triclinic systems in centrosymmetric space groups (Supporting Information, Table S1). Both distance and angle values are expected for Fe(II) piano-stool complexes (Supporting Information, Table S2),<sup>22,24,28,30,35,42</sup> while a slight but characteristic lengthening of the Fe-C and Fe-P bonds and a concomitant shortening of the Fe–C37 bond are observed for the Fe(III) complex  $2[PF_6]$ .<sup>35,38,41,43</sup> Among the Fe(II) species, the terminal ethynyl bonds in 1b, 1c, and 2 are always slightly shorter (ca. 1.18 Å) than the internal ones (ca. 1.22 Å), while the ethenyl bond in 3 (1.312(3) Å) is significantly longer and close to typical values encountered for organic molecules (1.321 Å).<sup>44</sup> In contrast to related alkynyl complexes featuring extended ligands,<sup>46</sup> these compounds roughly preserve their "rigid rod structure" in the solid state, with only a slight S-shaped deviation from linearity taking place for 1c. This characteristic deviation<sup>46</sup> as well as the noncoplanarity between the two phenyl rings of the arylalkynyl ligand (torsion angle of 36.1° between them) is most likely induced by the packing rather than by intramolecular effects.<sup>3</sup>

Packing is certainly also at the origin of the unusual C45–C36–Si1 angle of 168.2° (significantly different from 180°) observed for 5'a. For the ethenyl complex 3, the coplanarity of the ethenyl group and the adjacent phenyl ring, which allows maximizing their  $\pi$  overlap, can apparently be accommodated by packing forces.

UV-Visible Absorption Spectroscopy. The UV-vis spectra of these compounds were recorded in their various redox states (Table 5). In line with previous studies on the electrochromism of related iron alkynyl complexes,<sup>32,47</sup> Fe(II) derivatives exhibit an orange color resulting from the presence of an allowed MLCT ( $\varepsilon \ge 8000 \text{ M}^{-1} \text{ cm}^{-1}$ ) absorption in the blue edge of the visible spectrum,<sup>30</sup> while Fe(III) complexes are dark brown-colored due to the apparence of an LMCT absorption at lower energy, near 700 nm ( $\varepsilon \leq$  7000 M<sup>-1</sup> cm<sup>-1</sup>), resulting from the reversal of polarity taking place upon oxidation (Figure 5a,b).<sup>35</sup> In the 1b-d/3 series, but also in 1b $d[PF_6]/3[PF_6]$ , the extension of the  $\pi$ -system on the alkynyl ligand induces a slight bathochromic shift of these transitions relative to those of the phenylethynyl complexes  $8/8[PF_6]$  (see also Computational Details).<sup>35</sup> A similar feature is also observed in the Fe(II) trimethylsilvl-protected complexes 5ac (Supporting Information). As expected, the introduction of an ethynyl group in a nonconjugated (meta) position of the arylethynyl ligand has a weaker effect than in para position. The hypsochromic shift of the MLCT of 2 relative to 1b can be attributed to the loss of conjugation between the organoiron center and the terminal ethynyl group located in meta position in 2. Notably, compared to 1b, a slightly lower bathochromic shift is observed for 3, which has an ethenvl group appended in para position, in line with the better electron-releasing capability of the vinyl substituent compared to the ethynyl one, also revealed by electrochemistry.

Likewise, for the Fe(III) complexes, the LMCT band of  $3[PF_6]$  shows up at slightly lower energies than for  $1b[PF_6]$  and  $2[PF_6]$ , in line with a little more pronounced electron-releasing character for the *para*-vinyl group relative to *para*- and *meta*-ethynyl substituents, while marginal differences between LMCT bands are stated between  $1c[PF_6]$  and  $1d[PF_6]$ .<sup>35</sup> In addition, for the Fe(III) radical cations (Figure 5b), forbidden

Table 5. UV–Vis Spectroscopy Data for Selected  $[Fe(dppe)(\eta^5-C_5Me_5)(R)]^{n+}$  Complexes in  $CH_2Cl_2$   $(n = 0, 1)^a$ 

compd	R	absorptions in nm $[10^{-3}\varepsilon$ in $M^{-1}$ cm <sup>-1</sup> ]	ref
1a	С≡СН	264 [15.1, sh], 402 [1.8, sh], 500 [0.6, sh]	this work
1b	$C \equiv C(1,4-C_6H_4)C \equiv CH$	268 [37.2], 412 [16.8]	this work
$1b[PF_6]$		266 [29.9], 331 [16.6, sh], 428 [5.1, sh], 495 [2.6, sh], 593 [1.4], 704 [1.7], 1863 [0.10]	this work
1c	$\substack{\{C \equiv C(1,4-C_6H_4)\}_2 C \equiv \\ CH}$	270 [37.2], 318 [32.2], 436 [19.7]	this work
$1c[PF_6]$		328 [38.1, sh], 336 [37.2, sh], 407 [8.4, sh], 500 [2.6, sh], 626 [1.3], 735 [2.6], 1864 [0.15]	this work
1d	$\substack{\{C \equiv C(1,4\text{-}C_6H_4)\}_3C \equiv \\ CH}$	337 [47.1], 476 [9.2]	this work
$1d[PF_6]^a$		338 [69.7, sh], 358 [56.2, sh], 442 [6.8, sh], 738 [3.6], 1864 [0.12]	this work
2	$C \equiv C(1,3-C_6H_4)C \equiv CH$	358 [8.6], 398 [sh, 6.1]	this work
<b>2</b> [PF <sub>6</sub> ]		275 [30.7, sh], 384 [4.0, sh], 571 [2.4], 655 [2.8], 1864 [0.12]	this work
3	$\begin{array}{c} C \equiv C(1,4\text{-}C_6H_4)CH = \\ CH_2 \end{array}$	274 [24.3], 406 [13.1]	this work
$3[PF_6]$		268 [36.3], 352 [9.8, sh], 412 [3.6, sh], 472 [2.5], 612 [1.5, sh], 726 [2.9], 1827 [0.10]	this work
8	C≡CPh	277 [sh, 14.5], 350 [13.6]	30
8[PF <sub>6</sub> ]		261 [32.6, sh], 280 [27.4, sh], 301 [18.8, sh], 342 [5.9, sh], 379 [3.6, sh], 575 [2.3, sh], 662 [3.1], 1846 [0.09]	35

<sup>a</sup>Data should be analyzed with caution due to the instability established for this particular Fe(III) compound in solution; sh = shoulder.



Figure 5. UV-vis spectra of 1b-d, 2, and 3 (a) and 1b-d[PF<sub>6</sub>], 2[PF<sub>6</sub>], and 3[PF<sub>6</sub>] (b) complexes in  $CH_2Cl_2$ . Scaled-up visible region for the Fe(III) complexes (c).



Figure 6. DFT molecular orbital diagrams of the  $[Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)\{C\equiv C(1,4-C_6H_4)\}_nC\equiv CH]$  para complexes  $(n = 1 \text{ (1b)}, 2 \text{ (1c)}, 3 \text{ (1d)}), [Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)\{C\equiv C(1,3-C_6H_4)\}C\equiv CH]$  meta complex (2), and  $[Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)\{C\equiv C(1,3-C_6H_4)\}CH= CH_2]$  (3). The Fe (left)/carbon-chain (right) percentage contributions are given in italics.

bands at lower energy ( $\varepsilon \approx 100 \text{ M}^{-1} \text{ cm}^{-1}$ ) corresponding to forbidden d–d excitations are also observed near 1900 nm.<sup>35</sup>

**DFT Calculations.** Density-functional theory (DFT) calculations were carried out on compounds **1b–d**, **2**, and **3** and their radical cations in order to analyze and compare their electronic structure and the ensuing physical properties (see the Experimental Section for computational details).<sup>48</sup> Their structural arrangements were first optimized and compared (Supporting Information, Table S3). Computed data match reasonably well with the available experimental values (Supporting Information, Table S4), with the largest bond

length deviations found for the Fe–Cp\* (centroid) (<0.05 Å) and Fe–P distances (<0.03 Å). As often observed for this kind of acetylide metal complex, the computed C $\equiv$ C distances are slightly overestimated by 0.02–0.03 Å on average, with respect to the experimental ones, in **1b** and **1c**. As expected, the extension of the unsaturated bridge (C $\equiv$ CPh)<sub>n</sub> from n = 1(**1b**) to 3 (**1d**) hardly affects the Fe–P(dppe) and Fe–Cp\* (centroid) bond lengths. Similar to experiment, the computed *inner* C $\equiv$ C distances (close to the metal center) are ca. 0.03 Å longer than the *outer* ones. Computed bond distances for **1d**, not measured experimentally, are reasonably similar to those computed for 1b and 1c.

Upon oxidation, a substantial lengthening of the Fe-P bond lengths (ca. 0.06 Å) and, to a lesser extent, of the Fe-Cp\* (centroid) along with a slight  $Fe-C \equiv C$  (ca. 0.03 Å) contraction is noted. A slight lengthening of the inner  $C \equiv C$ distances is computed. Surprisingly enough, no geometrical change is noted for the *outer* C≡C upon oxidation. These structural modifications are in line with those previously observed for related systems.<sup>35,38,41</sup> They can easily be understood by examining the HOMOs of those systems (see the molecular orbital diagrams in Figure 6). Indeed, the HOMO of 1b-d, 2, and 3 is  $\pi$  in character, heavily localized on the Fe center and on the adjacent ethynyl group and, to a lesser extent, on the next phenyl ring (Figure 7). It is, in turn, mainly Fe-C37 antibonding and C37-C38 bonding in character. Consequently, oxidation of these systems leads to some shortening of Fe-C37 and a slight lengthening of C37-C38



Figure 7. Plots of the HOMO and LUMO for the complexes 1b-d, 2, and 3. Contour values are  $\pm 0.03$  (e/Bohr<sup>3</sup>)<sup>1/2</sup>. The energy is given in parentheses.

(*vide supra*). This HOMO is part of the " $t_{2g}$ " set expected for these 18-electron pseudo-octahedral complexes (Figure 7). Being strongly metallic in character, only very small energy stabilization occurs upon elongation of the carbon chain.

Although the Koopmans approximation<sup>49</sup> is not valid within the DFT approach, the changes of the first adiabatic ionization potentials (IP) in the series are susceptible to be correlated to the energies of the HOMOs (which are close in energy, *vide supra*) if the electronic and geometric reorganizations upon oxidation are moderate. Indeed, IPs computed without or with solvent (dichloromethane) effect are almost equal (ca. 5.25 and 4.65 eV, respectively). This is in agreement with the experimental oxidation potentials of species **1b**–**d**, which are comparable.

The LUMO of **1b**, **2**, and **3** and the LUMO+1 of **1c** and **1d** are strongly localized on the  $Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)$  moiety. On the other hand, the LUMO of **1c** and **1d** is mainly localized on the carbon chain, specifically on the *outer* part (Figure 7). Indeed, the antibonding character of these  $\pi^*$ -orbitals diminishes with the lengthening of the carbon chain inducing a gradual energy stabilization. Consequently, the HOMO–LUMO energy gap decreases from **1b** (1.79 eV) to **1c** (1.52 eV) to **1d** (1.18 eV). As expected, the HOMO–LUMO gap of **2** (1.78 eV) and **3** (1.77 eV) is close to that of **1b**.

The energies of the vibrational frequencies of the ethynyl  $C \equiv C$  vibrators were computed for these compounds and their radical cations. Overall, they compare very well with the experimental values (Table 1). As experimentally observed for all the neutral compounds, the ethynyl bond neighboring the Fe center vibrates at somewhat smaller energy than the outer ones. No change in energy is observed for this vibrator upon chain lengthening. However, the vibrational energy decreases by ca. 50 cm<sup>-1</sup> upon oxidation (Table 1). Comparably, the energy of the other ethynyl groups remains nearly unchanged at ca. 2100–2200 cm<sup>-1</sup>. This is in agreement with the nodal properties of the HOMOs, partially depopulated upon oxidation, which are hardly localized on these C $\equiv C$  groups (*vide supra*).

Mulliken atomic spin densities were computed for the monocationic species  $1b-d^+$ ,  $2^+$ , and  $3^+$  to evaluate the delocalization of the unpaired electron in these complexes (Supporting Information, Table S5). Results are graphically represented in Figure 8. The spin density distribution tracks close to the HOMO spatial distribution of the neutral complexes, which is, indeed, partially depopulated. It is mostly localized on the iron and adjacent ethynyl group for each system (Figure 7). Indeed, for all complexes, most of the spin density is found on the metal center (ca. 0.70 electron) and to a lesser extent on the *inner* C group (ca. 0.35 electron). A slight spin-density decrease on the metal is noticed upon chain lengthening for the benefit of the adjacent ethynyl group of the chain itself. It is noteworthy that the spin density is somewhat more distributed over the whole backbone for  $1b^+$ ,  $2^+$ , and  $3^+$ .

It appears that regardless of the redox state (n = 0 or 1) of **1b**-d<sup>*n*+</sup>, **2**<sup>*n*+</sup>, and **3**<sup>*n*+</sup>, their MOs which are heavily localized on the terminal alkyne or alkene moieties will strongly resemble those observed for the purely organic molecules in which the organometallic  $[Fe(\kappa^2 \text{-dppe})(\eta^5 \text{-}C_5\text{Me}_5)(C \equiv C)]^{n+}$  capping groups have been replaced by a hydrogen or by a moderately electron-releasing substituent (such as a methoxy group), especially when the phenylene-ethynyl chain is extended. Thus, based on the assumption that the photochemical initiation previously used primarily involves homolysis of surface Si-H



Figure 8. Plots of the spatial distribution of the spin density for compounds  $1b-d^+$ ,  $2^+$ , and  $3^+$ . Isocontour values:  $\pm 0.003 \text{ e/bohr}^3$ .

bonds,<sup>18b</sup> the reactivity of 1b-d, 2, and 3 should resemble that of the purely organic analogues, which is indeed observed.<sup>17</sup>

EPR properties of the optimized  $1b-d^+$ ,  $2^+$ , and  $3^+$ complexes were also computed. The resulting g-tensor components are given in Table 3 for a comparison with experimental values. The agreement between the computed and experimental anisotropies  $\Delta g$  is moderately satisfactory, with the computed ones being somewhat smaller than the experimental ones. However, these computations were done on a single conformation,  $^{38,50}$  while the effect of the surrounding medium was not taken into consideration. With those restrictions in mind, the overall trend can be considered to be comparable to that experimentally observed and also in agreement with the computed spatial distribution of the spin density. Extension of the carbon chain hardly affects the spin density distribution of these monocationic species. This contrasts with metal-polyynyl complexes, which show much more pronounced delocalization of the spin density over the carbon chain.50

Finally, the TD-DFT-calculated energies of the lowest allowed electronic excitations of the neutral complexes 1b-d were also computed (Supporting Information, Tables S6 and S7). As observed experimentally, a substantial red shift of the lowest excitation energies is noted upon lengthening of the carbon chain (418, 486, and 527 nm for 1b, 1c, and 1d, respectively). These excitations mostly involve HOMO-LUMO transitions. Accordingly, with the energy of the HOMO hardly changing and that of the LUMO decreasing upon chain lengthening, some bathochromic shift is observed. The first lowest excitation energies were also computed for the cationic complexes  $1b^+-d^+$ . Interestingly, very weak excitations are found in the NIR region (1825, 1833, and 1897 nm for  $1b^+$ ,  $1c^+$ , and  $1d^+$ , respectively), which compare very well with the very low-energy bands of ca. 1865 nm measured experimentally. As expected, they involve metal d-d transitions. Very weak electronic excitations are computed around 600 nm for all the cations (see Table S7). They might correspond to weak bands experimentally observed somewhat red-shifted around 700 nm (see above). They mostly involve ligand-to-metal and/ or metal-ligand-to-metal transitions.

# DISCUSSION

Both the spectroscopic results and the DFT calculations confirm that the isolated ethynyl- or ethenyl-terminated compounds 1b-d, 2, and 3 exhibit the classical features of Fe(II) arylalkynyl complexes,<sup>30</sup> with a dominantly metalcentered HOMO. Spectroscopy (NMR and IR) and computations on 1b-d reveal that the terminal alkyne (or alkene) group in these organometallic complexes is not very different from those connected to purely organic aromatic scaffolds, especially for compounds featuring extended phenylene-ethynylene spacers, due to the strong localization of the HOMO on the Fe(II) fragment. For instance, based on its characteristic  $\nu_{C\equiv C}$  stretching mode, the terminal alkynyl group appears not to be significantly affected in solution by the structural changes within 1b,c or 2. Changes observed experimentally are much less than those computed and remain close to the experimental uncertainty. Also, the Fe(II/III) oxidation potential appears to be only weakly dependent on the substitution pattern of the closest phenylene ring of the carbonrich spacer, in line with an even weaker interaction with the terminal group in the longer compounds. However, the characteristic bathochromic shifts of their MLCT transitions in the UV-visible range reveal that some electronic communication is nevertheless present along the metal and phenylene ethynylene backbone in these Fe(II) compounds.

Upon oxidation, the  $\nu_{C \equiv C}$  stretching mode of the terminal alkyne appears also to not be significantly affected. ESR reveals a dominantly metal-centered rhombic radical, the anisotropy of which is primarily determined by the substitution pattern of the closest phenylene ring of the carbon-rich spacer. In this respect, the <sup>1</sup>H NMR of the Fe(III) complexes is more informative. It reveals that while sizable spin delocalization takes place on the first phenylene unit and also on the second C2 unit, this phenomenon drastically drops when further progressing along the carbon-rich chain. The magnitude (and sign) of the spin present on the second C<sub>2</sub> unit clearly depends on the topology of the first ring (para > meta) and on its nature (ethenyl > ethynyl). However, on the basis of the relative isotropic shifts of the protons of these units, it remains lower than in the first phenylene ring. The unpaired spin present on the terminal  $C_2$ unit of all compounds should therefore not exceed a few percent, in line with the available DFT computations.<sup>38</sup> Thus, in contrast to their shorter homologue 1a<sup>+</sup>, which presents a much larger spin density on the  $\beta$ -ethynyl carbon and promptly dimerizes upon oxidation,  $^{19,51}$  **1b**,c<sup>+</sup> are kinetically much more stable in solution. The gain in kinetic stability observed for  $1b_{c}[PF_{6}]$ ,  $2[PF_{6}]$ , and  $3[PF_{6}]$  over  $1a[PF_{6}]$  certainly results from the presence of an aryl ring in the  $\beta$ -position to the metal which sterically shields the reactive  $\beta$ -carbon atom, thereby preventing coupling at this position and inhibiting further spin delocalization along the carbon-rich ligand.<sup>51</sup> Note that in spite of a very small spin density on the terminal alkynyl unit,  $1d[PF_6]$  slowly undergoes degradation in solution, even in the absence of oxygen.<sup>52</sup> In this case, a larger portion of the 1,4phenylene-ethnylene chain is exposed to the reaction medium. The decomposition stated for  $1d[PF_6]$  might therefore be attributed to the occurrence of a radical coupling process taking place at other positions. Thus, except for 1d, the stability of 1b-d, 2, or 3 should not be a determining issue during the grafting reaction, even if partial oxidation takes place on the Si-H surface or within the monolayer,<sup>18b</sup> provided the reaction is conducted under an inert atmosphere.

As expected from previous investigations on arylalkynyl Fe(III) complexes,<sup>35</sup> DFT confirmed that the SOMO was largely metal-centered in these compounds, even when the aryl alkynyl ligand is extended. Experimentally, as discussed above, this translates to a quasi-invariance of the ESR signature (Table 3) and of the Fe(III/II) oxidation potentials (Table 2) of these compounds when featuring a carbon-rich ligand with two aryl rings or more, regardless of the exact nature of the terminal groups on the second ring (C $\equiv$ C-Ar, C $\equiv$ C-TMS, C $\equiv$ C-TIPS, or  $C \equiv C - H$ ).<sup>53</sup> This statement is also substantiated by the very slight changes in paramagnetic <sup>1</sup>H NMR shifts observed for the protons of the first phenyl ring upon chain extension, which are much more sensitive probes to changes in spin density than is ESR anisotropy.<sup>38</sup> However, a closer examination of these signals reveals very slight upfield and downfield shifts of the ortho and meta hydrogen atoms, respectively, when proceeding from 1b to 1d, in line with a concomitant slight enhancement of the spin delocalized from the metal toward the (poly)arylalkynyl ligand. The latter, also found in DFT computations, might be at the origin of the increased kinetic instability of these radicals upon extension of the carbon-rich linker,  $^{51,54'}$  as experimentally stated for  $1d[PF_6]$ in solution. In this connection, the very slight bathochromic shift experienced by the LMCT transition of 1c,d upon chain elongation further indicates that only a very weak electronic interaction takes place between the metallic end group and phenylethynyl linker for the extended compounds in the Fe(III) state.

# CONCLUSION

We have reported here the synthesis and characterization of new redox-active Fe(II) arylacetylide complexes 1b-d and 2featuring a pendant ethynyl group, and 3 with a pendant ethenyl group, as well. As discrete species, the experimental data and the DFT calculations reveal that beyond the first 1,4phenylene ring further extension of the carbon-rich linker induces only minor changes in their electronic properties in both redox states. Therefore, as previously observed,<sup>20</sup> the terminal ethynyl or ethenyl group of these compounds should react similarly to that of a purely organic aromatic styryl or phenylethynyl derivative, and, at least for 1b-d and 2, only minor differences in reactivity can be anticipated between them during the photochemical grafting reaction. The UV-vis absorption spectra nevertheless reveal the existence of some electronic interaction along the (poly)phenylene-ethynylene backbone, by showing a clear bathochromic shift of the MLCT transition upon chain lengthening. Accordingly, this kind of conjugated carbon-rich spacer should facilitate the electronic interaction between the terminal metallic Fe(II) center and the silicon surface subsequent to grafting. We have also isolated and characterized each of these electron-rich alkynyl complexes under their cationic Fe(III) state, and roughly similar conclusions can be drawn regarding the electronic structure of the terminal ethynyl or ethenyl group and regarding the electronic communication through the phenylethynyl linker.

Notably, all these radical cations except  $1d[PF_6]$  turned out to be kinetically stable in solution during periods exceeding those previously used for performing the grafting reaction. For the Fe(III) species, this remarkable stability is in line with the dominant metal-centered nature of these organometallic radicals. In this respect, the longest derivative  $(1d[PF_6])$ among them presents however a slightly higher delocalization of the electronic vacancy on the carbon-rich ligand, which is possibly at the origin of its increased reactivity in solution. In all the other cases, any adventitious oxidation of the Fe(II) precursor during the photochemical grafting reaction should not be detrimental to the monolayer formation, provided the reaction is performed under an inert atmosphere.<sup>52</sup> In accordance with these statements, we will see in a subsequent paper that these functional compounds can be conveniently grafted on Si–H surfaces by using a photochemical protocol operating under rather "mild" conditions.<sup>20</sup> In addition, we will show that the resulting monolayers exhibit remarkable electronic exchange rates through their covalent interfacial Si–C bond compared to related organometallic silicon-based interfaces.

### EXPERIMENTAL SECTION

General Procedures. All reactions and workup procedures were carried out under dry, high-purity argon using standard Schlenk techniques. All solvents were freshly distilled and purged with argon before use. Infrared spectra were obtained using a Bruker IFS28 FT-IR spectrometer (400-4000 cm<sup>-1</sup>) or using a Bruker Optics Vertex 70 FT-IR spectrometer in the transmission mode (100 scans, 2 cm<sup>-1</sup> resolution and automatic gain) using a DTGS detector. Raman spectra of the solid samples were obtained by diffuse scattering on the same apparatus and recorded in the 100-3500 cm<sup>-1</sup> range (Stokes emission) with a laser excitation source at 1064 nm (25 mW) and a quartz separator with an FRA 106 detector. NMR spectra were acquired at 298 K on a Bruker DPX200, a Bruker Ascend 400 MHz NMR, or a Bruker AVANCE 500, with a 5 mm broadband observe probe equipped with a z-gradient coil. Experimental details regarding measurements on paramagnetic Fe(III) complexes can be found in previous contributions.<sup>38,41,55</sup> Chemical shifts are given in ppm and referenced to the residual nondeuterated solvent signal for <sup>1</sup>H and <sup>13</sup>C and external H<sub>3</sub>PO<sub>4</sub> (0.0 ppm) for <sup>31</sup>P NMR spectra. Cyclic voltammograms were recorded in dry CH<sub>2</sub>Cl<sub>2</sub> solutions (containing 0.10 M [n-Bu<sub>4</sub>N][PF<sub>6</sub>], purged with argon, and maintained under an argon atmosphere) using an EG&G-PAR model 263 potentiostat/ galvanostat or using an Autolab electrochemical analyzer (PGSTAT 30 potentiostat/galvanostat from Eco Chemie B.V.) equipped with the GPES software in a homemade three-electrode Teflon cell. The working electrode was a Pt disk, the counter electrode a Pt wire, and the reference electrode a saturated calomel electrode. The  $FeCp_2^{0/4}$ couple ( $E_{1/2}$ : 0.46 V,  $\Delta E_p = 0.09$  V;  $I_{pa}/I_{pc} = 1$ ) was used as an internal calibrant for the potential measurements.<sup>56</sup> Near-IR and UV-visible spectra were recorded as CH<sub>2</sub>Cl<sub>2</sub> solutions, using a 1 cm long quartz cell on a Cary 5000 spectrometer. EPR spectra were recorded on a Bruker EMX-8/2.7 (X-band) spectrometer, at 77 K (liquid nitrogen). Elemental analysis and high-resolution mass spectra (ESI on Micromass MS/MS ZABSpec TOF spectrometer) were performed at the "Centre Regional de Mesures Physiques de l'Ouest" (CRMPO), Université de Rennes 1. The complex  $Fe(\kappa^2 - dppe)(\eta^5 - C_5Me_5)(Cl)$  (4) was obtained following published procedures.<sup>23</sup> Other chemicals were

purchased from commercial suppliers and used as received. Synthesis of  $Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)\{C \equiv C(1,4-C_6H_4)C \equiv CSiMe_3\}$ (5a). A solution of  $Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)(CI)$  (4; 509 mg, 0.81 mmol), ((4-ethynylphenyl)ethynyl)trimethylsilane (178 mg, 0.90 mmol), and KPF<sub>6</sub> (235 mg, 1.28 mmol) in THF (20 mL) and MeOH (20 mL) was stirred for 16 h. The solvent was removed *in vacuo*. The brown solid was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL), *n*-pentane (50 mL) was added to the stirred extract, and the crude vinylidene complex **5a**-vin[PF<sub>6</sub>] was collected as a brown precipitate. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 81 MHz):  $\delta$  87.6 (s, 2P, dppe), -143.0 (sept, 1P, PF<sub>6</sub><sup>-</sup>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  7.85–7.00 (m, 22H,  $H_{Ar/dppe})$ , 6.23 (m, 2H,  $H_{Ar}$ ) 5.06 (m, 1H, Fe=C=CH), 3.16 (m, 2H, CH<sub>2/dppe</sub>), 2.56 (m, 2H, CH<sub>2/dppe</sub>), 1.62 (s, 15H,  $H_{Cp^*}$ ), 0.28 (s, 9H,  $H_{SiMe3}$ ). This crude vinylidene complex was dissolved in THF (20 mL), DBU (0.2 mL, 1.32 mmol) was added, and the mixture was stirred for 10 min. The solvent was removed *in* vacuo, yielding the crude product as a red solid. The product was purified on a short column of deactivated silica under an inert atmosphere, eluting with toluene. The solvent was removed and the orange solid washed with *n*-pentane, affording **5a** as an orange solid in 84% yield (536 mg, 0.68 mmol). The identity of **5a** was confirmed by comparison of spectroscopic data with literature values.<sup>22</sup> UV–vis (CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{max}$ / nm [ $\epsilon$ /10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>]): 269 [38.3], 415 [17.1].

 $\begin{array}{l} \text{nm} \ [\varepsilon/10^3 \ \text{M}^{-1} \ \text{cm}^{-1}]): 269 \ [38.3], 415 \ [17.1]. \\ \text{Synthesis of } Fe(\kappa^2 - dppe)(\eta^5 - C_5 Me_5)\{C \equiv C(1, 4 - C_6 H_4)C \equiv CSi(^{l}Pr)_3\} \\ (5'a). \ \text{A solution of } Fe(\kappa^2 - dppe)(\eta^5 - C_5 Me_5)(Cl) \ (4; \ 1.90 \ g, \ 3.04 \\ \end{array}$ mmol), ((4-ethynylphenyl)ethynyl)triisopropylsilane (859 mg, 3.04 mmol), and NH<sub>4</sub>PF<sub>6</sub> (592 mg, 3.632 mmol) in MeOH (40 mL) was stirred for 12 h. The solvent was removed in vacuo. The brown solid was extracted with  $CH_2Cl_2$  (2 × 30 mL), and diethyl ether (40 mL) was added to the stirred extract after concentration to ca. 5 mL. The crude vinylidene complex 5'a-vin[PF<sub>6</sub>] (2.80 g) was collected as a brown precipitate. FT-IR (KBr, cm<sup>-1</sup>): v 2146 (m, C≡C), 1620 (s, Fe=C=CH), 838 (vs,  $PF_6^{-}$ ). This crude vinylidene complex was dissolved in THF (50 mL), KOt-Bu (618 mg, 5.507 mmol) was added, and the mixture was stirred for 60 min. The solvent was removed in vacuo, yielding the crude product as a red solid. The solvent was removed and the orange solid washed with n-pentane, affording 5'a as an orange solid in 88% yield (2.10 g, 2.411 mmol). Anal. Calcd for C55H64P2SiFe: C, 75.84; H, 7.41. Found: C, 75.81; H, 7.44. The identity of 5'a was also confirmed by comparison of spectroscopic data with literature values.<sup>22</sup> Crystals of this complex could be grown by slow evaporation of a diethyl ether solution of the complex. UV-vis  $(CH_2Cl_2, \lambda_{max}/nm [\varepsilon/10^3 M^{-1} cm^{-1}]): 280 [35.6], 416 [21.0].$ 

Synthesis of  $Fe(\kappa^2 - dppe)(\eta^5 - C_5 Me_5)\{C \equiv C(1, 4 - C_6 H_4)C \equiv CH\}$  (1b). From 5a: A solution of 5a (512 mg, 0.65 mmol) and  $K_2CO_3$  (116 mg, 0.84 mmol) in THF (20 mL) and MeOH (20 mL) was stirred for 16 h, and the solvent was removed in vacuo. The product was extracted with toluene, the solvent was removed, and the orange solid was washed twice with *n*-pentane, affording 1b as an orange solid in 85% yield (394 mg, 0.55 mmol). The identity of 1b was confirmed by comparison of spectroscopic data with literature values.<sup>22</sup> Crystals of the complex could also be grown by slow evaporation of a benzene solution of the complex. From 5'a: The complex 5'a (392 mg, 0.450 mmol) was solubilized in THF (30 mL), and 0.9 mL (0.900 mmol) of a 1 M commercial solution of tetrabutylammonium fluoride (TBAF) in THF was syringed into the reaction medium, which was stirred for 24 h before the solvent was removed in vacuo. The product was extracted with toluene, the solvent was concentrated, and the orange solid was precipitated with n-pentane and washed twice with npentane, affording 1b as an orange solid in 51% yield (165 mg, 0.231 mmol). Raman (neat, cm<sup>-1</sup>):  $\nu$  2097(m, C $\equiv$ CH), 2047, 2031(s, FeC≡C).

Synthesis of  $Fe(\kappa^2$ -dppe) $(\eta^5$ -C<sub>5</sub>Me<sub>5</sub>){[C=C(1,4-C<sub>6</sub>H<sub>4</sub>)]<sub>2</sub>C=CSiMe<sub>3</sub>} (**5b**). A solution of  $Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)Cl$  (4; 630 mg, 1.01 mmol) ((4-((4-ethynylphenyl)ethynyl)phenyl)ethynyl)trimethylsilane (302 mg, 1.01 mmol), and KPF<sub>6</sub> (375 mg, 2.03 mmol) in THF (20 mL) and MeOH (20 mL) was stirred for 16 h. The solvent was removed in vacuo. The brown solid was extracted with CH2Cl2 and the solvent removed *in vacuo*, providing the crude vinylidene complex **5b**-vin[PF<sub>6</sub>] as a brown precipitate. FT-IR (KBr, cm<sup>-1</sup>):  $\nu$  2210 (w, C $\equiv$ C), 2155 (m, C $\equiv$ C), 1625 (s, Fe=C=CH), 824 (vs, PF<sub>6</sub><sup>-1</sup>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 81 MHz):  $\delta$  86.5 (s, 2P, dppe), -143.0 (sept, 1P, PF<sub>6</sub><sup>-</sup>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  7.95–7.00 (m, 26H,  $H_{\rm Ar/dppe}$ ), 6.29 (m, 2H,  $H_{Ar}$ ) 5.07 (m, 1H, Fe=C=CH), 3.14 (m, 2H,  $C\dot{H}_{2/dppe}$ ), 2.55 (m, 2H,  $CH_{2/dppe}$ ), 1.64 (s, 15H,  $H_{Cp^*}$ ), 0.28 (s, 9H,  $H_{SiMe3}$ ). This crude vinylidene complex was dissolved in THF (20 mL), DBU (0.3 mL, 2.01 mmol) was added, and the mixture was stirred for 10 min. The solvent was removed in vacuo, yielding the crude product as a red solid. The product was purified on a short column of deactivated silica under an inert atmosphere, eluting with toluene. The solvent was removed and the red solid washed with *n*-pentane, affording 5b as an orange solid in 74% yield (628 mg, 0.75 mmol). HRMS: m/z 886.2968  $[M]^{+\bullet}$ , m/z calcd for  $[C_{57}H_{56}P_2Si^{56}Fe]$  886.29705. FT-IR (KBr, cm<sup>-1</sup>):  $\nu$  2206 (w, C=C), 2155 (w, C=C), 2046 (vs, C=CFe). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 81 MHz):  $\delta$  101.2 (s). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz):  $\delta$  7.95 (m, 4H,  $H_{dppe}$ ), 7.52 (m, 2H,  $H_{Ar}$ ), 7.35–6.90 (m, 22H,  $H_{\rm Ar/dppe}$ ), 2.65 (m, 2H,  $\dot{CH}_{\rm 2/dppe}$ ), 1.81 (m, 2H,  $CH_{\rm 2/dppe}$ ), 1.52 (s, 15H,  $H_{Cp^*}$ ), 0.24 (m, 9H,  $H_{SiMe3}$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 50 MHz):  $\delta$ 146.7 (t, <sup>2</sup>J<sub>P,C</sub> = 39 Hz, FeC $\equiv$ C), 139.9–128.5 ( $C_{Ar}$ , CH<sub>Ar</sub>), 124.9 ( $C_{Ar}$ ), 122.7 ( $C_{Ar}$ ), 121.7 (FeC $\equiv$ C), 117.1 ( $C_{Ar}$ ), 105.9, 95.9, 94.0, 89.9 (C $\equiv$ C), 88.1 ( $C_5$ (CH<sub>3</sub>)<sub>5</sub>), 31.1 (m, CH<sub>2</sub>), 10.4 ( $C_5$ (CH<sub>3</sub>)<sub>5</sub>), 0.1 (Si(CH<sub>3</sub>)<sub>3</sub>)). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{max}$ /nm [ $\epsilon$ /10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>]): 316 [40.3], 460 [20.6].

Synthesis of  $Fe(\kappa^2 - dppe)(\eta^5 - C_5 Me_5)\{[C \equiv C(1, 4 - C_6 H_4)]_2 C \equiv CSi(^i Pr)_3\}$ (5'b). A solution of ((4-((4-ethynylphenyl)ethynyl)phenyl)ethynyl)triisopropylsilane (200 mg, 0.522 mmol) in THF (15 mL) was added to a mixture of  $Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)(Cl)$  (4; 271 mg, 0.435 mmol) and NH<sub>4</sub>PF<sub>6</sub> (106 mg, 0.652 mmol) in MeOH (30 mL) and was stirred for 24 h. After evaporation of the solvent, the orange solid was extracted with CH2Cl2 and filtrated. Concentration of the extract and precipitation by excess diethyl ether (20 mL) allowed the isolation of the crude vinylidene complex 5'b-vin $[PF_6]$  as an orange solid in 78% yield (380 mg, 0.340 mmol). FT-IR (KBr, cm<sup>-1</sup>):  $\nu$  2208 (w, C $\equiv$ C), 2149 (vs, C=C), 1618 (Fe=C=CH), 824(PF\_6<sup>-</sup>).  ${}^{31}P{}^{1}H{}$  NMR (CDCl<sub>3</sub>, 81 MHz): δ 87.6 (s, 2P, dppe), -143.0 (sept, 1P, PF<sub>6</sub><sup>-</sup>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  7.91–6.80 (m, 26H,  $H_{\rm Ar/dppe}$ ), 6.3 (m, 2H,  $H_{Ar}$ ) 5.09 (m, 1H, Fe=C=CH), 3.11 (m, 2H,  $C\dot{H}_{2/dppe}$ ), 2.55 (m, 2H,  $CH_{2/dppe}$ ), 1.64 (s, 15H,  $H_{Cp^*}$ ), 1.20 (s, 3H, Si[ $CH(CH_3)_2$ ]), 1.18 (s, 18H, Si $[CH(CH_3)_2]$ ). The vinylidene complex (360 mg, 0.323 mmol) and t-BuOK (72 mg, 0.644 mmol) were dissolved in THF (20 mL) and stirred for 2 h. After evacuation of the solvent, the orange solid was extracted with toluene (20 mL) and filtrated. The solvent was evaporated and the orange solid was washed twice with *n*-pentane, affording 5'b as an orange solid in 71% yield (323 mg, 0.229 mmol). Anal. Calcd for C<sub>63</sub>H<sub>468</sub>P<sub>2</sub>SiFe: C, 77.92; H, 7.06. Found: C, 77.72; H, 7.18. HRMS: m/z 970.4230 [M]<sup>+</sup>, m/z calcd for [C<sub>63</sub>H<sub>68</sub>P<sub>2</sub>Si<sup>56</sup>Fe] 970.3914. FT-IR (KBr, cm<sup>-1</sup>):  $\nu$  2205 (w, C=C), 2151 (w, C=C), 2043 (vs, C=CFe). <sup>31</sup>P{<sup>1</sup>H} NMR ( $C_6D_6$ , 81 MHz):  $\delta$  101.2 (s). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz):  $\delta$  7.96 (m, 4H, H<sub>dppe</sub>), 7.53(d, <sup>3</sup>J<sub>H,H</sub> = 7.8 Hz, 2H, H<sub>Ar</sub>), 7.35-7.04 (m, 22H, H<sub>Ar/dppe</sub>), 2.61 (m, 2H, CH<sub>2/dppe</sub>), 1.83 (m, 2H,  $CH_{2/dppe}$ ), 1.53 (s, 15H,  $H_{Cp}*$ ), 1.21 (m, 21H, Si[CH(CH\_3)\_2]). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 125 MHz):  $\delta$  145.4 (t, <sup>2</sup>J<sub>P,C</sub>) = 38 Hz, FeC $\equiv$ C,), 141.5–128.5 (C<sub>Ar</sub>, C<sub>ArH</sub>), 122.5 (FeC $\equiv$ C), 117.8  $(C_{Ar})$ , 108.7, 94.7, 92.9, 90.7 (C=C), 88.9  $(C_5(CH_3)_5)$ , 31.8 (m,  $CH_2$ ), 19.7 (Si[CH(CH<sub>3</sub>)<sub>2</sub>]), 12.5 (Si[CH(CH<sub>3</sub>)<sub>2</sub>]), 11.2 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{max}$ /nm [ $\epsilon$ /10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>]): 318 [30.3], 456 [17.9]. CV (CH<sub>2</sub>Cl<sub>2</sub>, 0.1 M [NBu<sub>4</sub>][PF<sub>6</sub>], 20 °C, 0.1 V s<sup>-1</sup>) E° in V vs SCE( $\Delta E_p$  in V,  $i_{pa}/i_{pc}$ ): -0.12 (0.074, 1.0).

Synthesis of  $Fe(\kappa^2 - dppe)(\eta^5 - C_5Me_5) \{ [C \equiv C(1, 4 - C_6H_4)]_2 C \equiv CH \}$ (1c). From Sb: A solution of Sb (620 mg, 0.74 mmol), and K<sub>2</sub>CO<sub>3</sub> (142 mg, 1.03 mmol) in THF (40 mL) and MeOH (30 mL) was stirred for 16 h, and the solvent was removed in vacuo. The product was extracted with toluene, the solvent was removed, and the orange solid was washed twice with *n*-pentane, affording 1c as an orange solid in 86% yield (490 mg, 0.64 mmol). From 5'b: TBAF (1 M solution in THF, 0.041 mL, 0.041 mmol) was added to a solution of 5'b (200 mg, 0.205 mmol) in THF (30 mL), and the reaction mixture was stirred for 48 h. After evacuation of the solvent, the orange solid was extracted with toluene (20 mL) and filtrated. The solvent was evaporated under reduced pressure, and the orange solid was washed twice with npentane, affording 1c as an orange solid in 43% yield (250 mg, 0.092 mmol). Crystals of the complex were grown by slow diffusion of npentane vapors into a toluene solution of the complex. Anal. Calcd for C<sub>54</sub>H<sub>48</sub>P<sub>2</sub>Fe: C, 79.60; H, 5.94. Found: C, 79.32; H, 6.23. HRMS: *m*/*z* 814.2590 [M]<sup>+</sup>, m/z calcd for [C<sub>54</sub>H<sub>48</sub>P<sub>2</sub><sup>56</sup>Fe] 814.2581. FT-IR (KBr, cm<sup>-1</sup>):  $\nu$  3280 (w,  $\equiv$ C-H), 2206 (w, C $\equiv$ C), 2106 (vw, C $\equiv$ C), 2045 (vs, C≡CFe). Raman (neat, cm<sup>-1</sup>):  $\nu$  2206 (s, C≡C), 2107 (w, C=C), 2042 (m, C=CFe). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 81 MHz):  $\delta$  101.2 (s). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 200 MHz): δ 7.95 (m, 4H), 7.55–6.90 (m, 24H,  $H_{Ar/dppe}$ ), 2.75 (s, 1H, C $\equiv$ CH), 2.65 (m, 2H, C $H_{2/dppe}$ ), 1.62 (m, 2H,  $CH_{2/dppe}$ ), 1.52 (s, 15H,  $H_{Cp^*}$ ). <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_6$ , 50 MHz):  $\delta$ 146.9 (t,  ${}^{2}J_{P,C} = 38$  Hz, FeC=C), 139.9–128.3 ( $C_{Ar'}$  CH<sub>Ar</sub>), 125.7 ( $C_{Ar}$ ), 125.1 ( $C_{Ar}$ ), 121.7 (FeC=C), 116.9 ( $C_{Ar}$ ), 94.0, 89.8 (C=C), 88.9 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 83.8 (C≡CH), 79.2 (C≡CH), 31.0 (m, CH<sub>2</sub>), 10.5  $(C_{5}(CH_{3})_{5}).$ 

Synthesis of  $Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)\{[C \equiv C(1,4-C_6H_4)]_3C \equiv CSiMe_3\}$ (5c). A solution of  $Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)$  (4; 255 mg, 0.41 mmol),

((4-((4-((4-ethynylphenyl)ethynyl)phenyl)ethynyl)phenyl)ethynyl)trimethylsilane (165 mg, 0.41 mmol), and KPF<sub>6</sub> (136 mg, 0.74 mmol) in THF (30 mL) and MeOH (30 mL) was stirred for 16 h. The solvent was removed in vacuo, and the brown solid was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The solvent volume was reduced to 10 mL, n-pentane (50 mL) was added to the stirring solution, and the crude vinylidene complex 5c-vin[PF<sub>6</sub>] was collected as a brown precipitate. FT-IR  $(KBr, cm^{-1}): \nu 2205 (w, C \equiv C), 2154 (m, C \equiv C), 1618 (s, Fe = C =$ CH), 839 (vs,  $PF_6^{-}$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 81 MHz):  $\delta$  87.7 (s, 2P, dppe), -143.0 (sept., 1P, PF<sub>6</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ 8.10-7.10 (m, 30H,  $H_{Ar/dppe}$ ), 6.30 (m, 2H,  $H_{Ar}$ ), 5.10 (m, 1H, Fe=C= CH), 3.15 (m, 2H,  $CH_{2/dppe}$ ), 2.65 (m, 2H,  $CH_{2/dppe}$ ), 1.62 (s, 15H,  $C_5(CH_3)_5$ , 0.30 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>). This vinylidene complex (367 mg, 0.324 mmol) was dissolved in THF (30 mL), DBU (0.15 mL, 1.0 mmol) was added, and the mixture was stirred for 30 min. The solvent was removed in vacuo, yielding the crude product as a red solid. The product was purified on a short column of deactivated silica under an inert atmosphere, eluting with toluene. The solvent was removed and the red solid washed twice with n-pentane, affording 5c as an orange solid in 76% yield (243 mg, 0.246 mmol). HRMS: m/z 986.3276  $[M]^+$ , m/z calcd for  $[C_{65}H_{60}SiP_2^{56}Fe]$  986.32835. FT-IR (KBr, cm<sup>-1</sup>):  $\nu$  2205 (vw, C=C), 2156 (w, C=CSi), 2043 (s, FeC=C). <sup>31</sup>P{<sup>1</sup>H} NMR ( $C_6D_{67}$  81 MHz):  $\delta$  101.0 (s). <sup>1</sup>H NMR ( $C_6D_{67}$  200 MHz):  $\delta$ 7.95 (m, 4H,  $H_{dppe}$ ), 7.58–6.95 (m, 28H,  $H_{Ar/dppe}$ ), 2.56 (m, 2H,  $CH_{2/dppe}$ ), 1.82 (m, 2H,  $CH_{2/dppe}$ ), 1.52 (s, 15H,  $H_{Cp^*}$ ), 0.25 (m, 9H,  $H_{SiMe_3}$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 125 MHz):  $\delta$  139.2–127.4 (C<sub>Ar</sub>, CH<sub>Ar</sub>), 125.6 124.9, 123.6, 123.5, 122.4 ( $C_{Ar}$ ); 121.7 (FeC $\equiv$ C); 116.0 ( $C_{Ar}$ ); 104.8 (C≡CSi); 96.8 (C≡CSi); 93.4, 91.5, 90.8, 89.3 (C≡C); 88.2  $(C_5(CH_3)_5); 30.9 (m, CH_2); 10.2 (C_5(CH_3)_5); 0.1 (Si(CH_3)_3)). UV$ vis (CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{\text{max}}/\text{nm}$  [ $\epsilon/10^3$  M<sup>-1</sup> cm<sup>-1</sup>]): 340 [51.8], 476 [8.1].

Synthesis of  $Fe(\kappa^2 - dppe)(\eta^5 - C_5 Me_5) \{ [C \equiv C(1, 4 - C_6 H_4)]_3 C \equiv CH \}$ (1d). A solution of 5c (211 mg, 0.21 mmol) and  $K_2CO_3$  (62 mg, 0.45 mmol) in THF (40 mL) and MeOH (30 mL) was stirred for 16 h, and the solvent was removed in vacuo. The product was extracted with toluene, the solvent was removed, and the orange solid was washed twice with *n*-pentane, affording 1d as an orange solid in 72% yield (138 mg, 0.15 mmol). HRMS: *m/z* 914.2879 [M]<sup>+</sup>, *m/z* calcd for  $[C_{62}H_{52}P_2^{56}Fe]$  914.2894. FT-IR (KBr, cm<sup>-1</sup>):  $\nu$  3280 (w,  $\equiv$ C-H), 2203 (w, C≡C), 2107 (vw, C≡C), 2040 (vs, FeC≡C). Raman (neat, cm<sup>-1</sup>):  $\nu$  2207 (s, C=C), 2175 (w sh, C=C), 2104 (w, C= CH), 2037 (m, FeC=C).  ${}^{31}P{}^{1}H{}$  NMR (C<sub>6</sub>D<sub>6</sub>, 81 MHz):  $\delta$  101.2 (s). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 200 MHz):  $\delta$  7.95 (m, 4H,  $H_{dppe}$ ), 7.55–6.90 (m, 19H,  $H_{Ar/dppe}$ ), 3.11 (s, 1H, C=CH) 2.56 (m, 2H,  $CH_{2/dppe}$ ), 1.79 (m, 1)  $H_{Ar/dppe}$ , 5:11 (s, 11), C = C(1) 2, 5:10,  $C = C_{2/dppe}$ , 17) (m, 2H,  $CH_{2/dppe}$ ), 1.49 (s, 15H,  $H_{Cp}*$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125) MHz):  $\delta$  138.8–127.4 ( $C_{Ar}$ ,  $CH_{Ar}$ ), 123.8 ( $C_{Ar}$ ), 123.4 ( $C_{Ar}$ ), 122.5  $(C_{Ar})$ , 122.4 (FeC $\equiv$ C), 115.6  $(C_{Ar})$ , 91.2–91.1 (C $\equiv$ C), 88.3  $(C_5(CH_3)_5)$ , 83.4 (C=CH), 79.4 (C=CH), 30.7 (m, CH<sub>2</sub>), 10.2  $(C_5(CH_3)_5)$ , FeC $\equiv$ C not detected.

Synthesis of  $Fe(\kappa^2 - dppe)(\eta^5 - C_5 Me_5) \{C \equiv C(1, 3 - C_6 H_4) C \equiv CSi Me_3\}$ (6). A solution of  $Fe(\kappa^2 - dppe)(\eta^5 - C_5 Me_5)(Cl)$  (4; 500 mg, 0.80 mmol), ((3-ethynylphenyl)ethynyl)trimethylsilane (198 mg, 1.00 mmol), and KPF<sub>6</sub> (184 mg, 1.00 mmol) in THF (20 mL) and MeOH (20 mL) was stirred for 16 h. The solvent was removed in vacuo. The brown solid was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the solvent removed in vacuo, providing the crude vinylidene complex 6-vin[PF<sub>6</sub>] as a brown-orange solid. This crude vinylidene complex was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL), DBU (0.24 mL, 1.61 mmol) was added, and the mixture was stirred for 1 h. The solvent was removed in vacuo, yielding the crude product as a red solid. The product was purified on a short column of deactivated silica under an inert atmosphere, eluting with toluene. The solvent was removed and the red solid washed twice with n-pentane, affording 6 as an orange solid in 78% yield (490 mg, 0.62 mmol). Crystals of the complex were grown by slow diffusion of npentane vapors in a toluene solution of the complex. Anal. Calcd for C49H52SiP2Fe: C, 74.80; H, 6.66. Found: C, 75.11; H, 6.87. HRMS: m/z 786.2653 [M]<sup>+</sup>, m/z calcd for  $[C_{49}H_{52}SiP_2^{56}Fe]$  786.2663. FT-IR (KBr, cm<sup>-1</sup>):  $\nu$  2149 (s, C $\equiv$ CSi), 2043 (vs, FeC $\equiv$ C). <sup>31</sup>P{<sup>1</sup>H} NMR  $(C_6D_6, 81 \text{ MHz})$ :  $\delta$  101.3 (s). <sup>1</sup>H NMR  $(C_6D_6, 200 \text{ MHz})$ :  $\delta$  7.95 (m, 4H, H<sub>dppe</sub>), 7.54 (m, 1H, H<sub>Ar</sub>), 7.35–6.90 (m, 19H, H<sub>Ar/dppe</sub>), 2.56 (m, 2H,  $C\hat{H}_{2/dppe}$ ), 1.79 (m, 2H,  $CH_{2/dppe}$ ), 1.49 (s, 15H,  $H_{Cp*}$ ), 0.24 (m,

9H,  $H_{SiMe_3}$ ). <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_6$ , 101 MHz):  $\delta$  141.9 (t, <sup>3</sup> $J_{C,P}$  = 39 Hz, FeC $\equiv$ C), 140.3 and 138.6 (m,  $C_{Ar/dppe}$ ), 135.1 (m, CH<sub>Ar/dppe</sub>), 134.8 (CH<sub>Ar</sub>), 132.3 ( $C_{Ar}$ ), 131.5 (CH<sub>Ar</sub>), 129.9 and 129.7 ( $C_{Ar/dppe}$ ), 129.0 (CH<sub>Ar</sub>), 128.1 (m,  $C_{Ar/dppe}$ ), 127.2 (CH<sub>Ar</sub>), 124.1 ( $C_{Ar}$ ), 120.3 (FeC $\equiv$ C), 107.9 ( $C\equiv$ C), 92.6, ( $C\equiv$ C), 88.5 ( $C_5$ (CH<sub>3</sub>)<sub>5</sub>), 31.6 (m, CH<sub>2</sub>), 11.0 ( $C_5$ (CH<sub>3</sub>)<sub>5</sub>), 0.8 (Si(CH<sub>3</sub>)<sub>3</sub>). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{max}/nm$  [ $\epsilon/10^3$  M<sup>-1</sup> cm<sup>-1</sup>]): 354 [10.3], 406 [sh, 6.2].

Synthesis of  $Fe(\kappa^2 - dppe)(\eta^5 - C_5 Me_5)[C \equiv C(1, 3 - C_6 H_4)C \equiv CH]$  (2). A solution of 6 (420 mg, 0.53 mmol) and K<sub>2</sub>CO<sub>3</sub> (89 mg, 0.64 mmol) in THF (20 mL) and MeOH (20 mL) was stirred for 16 h. The solvent was removed in vacuo. The product was purified on a short column of deactivated silica under an inert atmosphere, eluting with toluene. The solvent was removed in vacuo and the orange solid was washed with npentane, affording 2 as an orange solid in 94% yield (360 mg, 0.50 mmol). Crystals of the complex were grown by slow evaporation of a diethyl ether solution of the complex. HRMS: m/z 714.2260 [M]<sup>+</sup>, m/zz calcd for  $[C_{46}H_{44}P_2^{56}Fe]$  714.2268. FT-IR (KBr, cm<sup>-1</sup>):  $\nu$  3298 (m, ≡C-H), 2105 (w, C≡CH), 2044 (vs, FeC≡C). Raman (neat, cm<sup>-1</sup>):  $\nu$  2107 (w, C=CH), 2044 (vs, FeC=C). <sup>31</sup>P{<sup>1</sup>H} NMR  $(C_6D_6, 81 \text{ MHz})$ :  $\delta$  101.3 (s). <sup>1</sup>H NMR  $(C_6D_6, 200 \text{ MHz})$ :  $\delta$  7.96 (m, 4H, H<sub>dppe</sub>), 7.54 (m, 1H, H<sub>Ar</sub>), 7.35–6.90 (m, 19H, H<sub>Ar/dppe</sub>), 2.73 (s, 1H, C $\equiv$ CH), 2.56 (m, 2H, CH<sub>2/dppe</sub>), 1.79 (m, 2H, CH<sub>2/dppe</sub>), 1.50 (s, 15H, H<sub>Cp\*</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 50 MHz):  $\delta$  139.5–119.3 (FeC $\equiv$ C, C<sub>Ar</sub>, CH<sub>ArH</sub>, FeC $\equiv$ C), 88.0 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 84.6(C $\equiv$ CH), 76.2 (C $\equiv$ CH), 30.8 (m, CH<sub>2</sub>), 10.2 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{\text{max}}/\text{nm} [\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1}]): 358 [8.6], 398 [sh, 6.1].$ 

Synthesis of  $Fe(\kappa^2 - dppe)(\eta^5 - C_5 Me_5)[C \equiv C(1, 4 - C_6 H_4)CH = CH_2]$  (3). A solution of Ph<sub>3</sub>PCH<sub>3</sub>Br (500 mg, 1.40 mmol) in THF (25 mL) was cooled to 0 °C, and n-BuLi in hexanes (2.0 M solution, 0.7 mL, 1.40 mmol) was added. After 30 min the temperature was lowered to -90 °C, and a solution of 7 (400 mg, 0.56 mmol) in THF (25 mL) was added. After 30 min at -90 °C the solution was allowed to return to room temperature and stirred there for 16 h. The solvent was removed in vacuo. The product was purified on a short column of deactivated silica under an inert atmosphere, eluting with toluene, and the solvent was removed in vacuo. The product was washed with n-pentane, affording 3 as an orange solid in 88% yield (350 mg, 0.49 mmol). Crystals of the complex could also be grown by slow diffusion of npentane in a CH2Cl2 solution of the complex. Anal. Calcd for  $C_{46}H_{46}P_2Fe: C, 77.09; H, 6.47.$  Found: C, 77.09; H, 6.38. HRMS: m/z716.2420  $[M]^+$ , m/z calcd for  $[C_{46}H_{46}P_2^{56}Fe]$  716.2420. FT-IR (KBr, cm<sup>-1</sup>):  $\nu$  2054, 2036 (vs, FeC $\equiv$ C), 1620 (C=C). Raman (neat, cm<sup>-1</sup>):  $\nu$  2053, 2038 (vs, FeC=C), 1622 (w, C=C). <sup>31</sup>P{<sup>1</sup>H} NMR  $(C_6D_6, 81 \text{ MHz}): \delta 101.4 \text{ (s)}.$  <sup>1</sup>H NMR  $(C_6D_6, 200 \text{ MHz}): \delta 8.01 \text{ (m,}$ 4H,  $H_{dppe}$ ), 7.36–7.04 (m, 20H,  $H_{Ar/dppe}$ ), 6.66 (dd, 1H, CH=CH<sub>2</sub>), 5.59 (dd, 1H, CH=CH<sub>2</sub>), 5.03 (dd, 1H, CH=CH<sub>2</sub>), 2.56 (m, 2H,  $CH_{2/dppe}$ ), 1.79 (m, 2H,  $CH_{2/dppe}$ ), 1.54 (s, 15H,  $H_{Cp^*}$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 50 MHz):  $\delta$  139.6–120.4 (FeC $\equiv$ C, C<sub>Ar</sub>, CH<sub>Ar</sub>, Fe-C $\equiv$ C,  $-CH = CH_2$ ), 111.0 ( $-CH = CH_2$ ), 87.9 ( $C_5(CH_3)_5$ ), 30.7 (m,  $CH_2$ ), 10.2 ( $C_{e}(CH_{2})_{e}$ 

Synthesis of  $[Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)(C \equiv C(1,4-C_6H_4)C \equiv CH)][PF_6]$ (1b[PF<sub>6</sub>]). [Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>][PF<sub>6</sub>] (57 mg, 0.172 mmol) and 1b (130 mg, 0.182 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and stirred for 1 h. The solvent volume was reduced to ~5 mL *in vacuo*, and *n*-pentane was added (40 mL) to give a dark precipitate. Decantation and subsequent washings with toluene (2 × 5 mL), diethyl ether (2 × 5 mL), and *n*-pentane (2 × 5 mL) yielded [Fe( $\kappa^2$ -dppe)( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)-{C  $\equiv$  C(1,4-C<sub>6</sub>H<sub>4</sub>)C  $\equiv$  CH}][PF<sub>6</sub>] (1b[PF<sub>6</sub>]) (78 mg, 0.091 mmol, 53%). FT-IR (KBr, cm<sup>-1</sup>):  $\nu$  3274 (m,  $\equiv$ C-H), 2102 (w, C  $\equiv$ CH), 1994 (s, FeC  $\equiv$ C). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz):  $\delta$  30.4 (s, H<sub>2</sub>), 7.9 (s, H<sub>dppe</sub>), 7.2 (s, H<sub>dppe</sub>), 6.8 (s, H<sub>dppe</sub>), 6.2 (s, H<sub>dppe</sub>), 3.6 (s, H<sub>dppe</sub>), 1.3 (s, H<sub>dppe</sub>), -2.8 (s, CH<sub>2/dppe</sub>), -10.3 (br s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), -20.1 (s, C  $\equiv$  CH), -39.6 (br s, H<sub>3</sub>).

Synthesis of  $[Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)({C \equiv C(1,4-C_6H_4)}_2C \equiv CH)]$ - $[PF_6]$  (1c[PF\_6]).  $[Fe(\eta^5-C_5H_5)_2][PF_6]$  (64 mg, 0.193 mmol) and 1c (165 mg, 0.203 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and stirred for 1 h. The solvent volume was reduced to ~5 mL *in vacuo*, and *n*-pentane was added (50 mL) to give a dark precipitate. Decantation and subsequent washings with toluene (3 × 5 mL), diethyl ether (3 × 5 mL), and *n*-pentane (2 × 5 mL) yielded  $[Fe(\kappa^2-dppe)(\eta^5-2\pi)]$  C<sub>5</sub>Me<sub>5</sub>){C≡C(1,4-C<sub>6</sub>H<sub>4</sub>)C≡C(1,4-C<sub>6</sub>H<sub>4</sub>)C≡CH}][PF<sub>6</sub>] (1c[PF<sub>6</sub>]) (123 mg, 0.128 mmol, 66%). FT-IR (KBr, cm<sup>-1</sup>):  $\nu$  3269 (s, ≡C−H), 2207 (w, C≡C), 2107 (vw, C≡C−H), 1991 (s, C≡C−Fe). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz):  $\delta$  31.3 (s, H<sub>2</sub>), 9.3 (s, H<sub>4</sub>), 7.9 (s, H<sub>dppe</sub>), 7.2 (s, H<sub>dppe</sub>), 6.8 (s, H<sub>dppe</sub>), 6.2 (s, H<sub>dppe</sub>), 3.6 (s, H<sub>Ar/dppe</sub> + H<sub>5</sub>), 1.7 (s, H<sub>dppe</sub>), 0.9 (s, C≡CH), −2.8 (s, CH<sub>2/dppe</sub>), −10.3 (br s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), −41.8 (br s, H<sub>3</sub>).

Synthesis of  $[Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)(\{C \equiv C(1,4-C_6H_4)\}_3C \equiv CH)]$ -  $[PF_6]$  (1d[PF\_6]).  $[Fe(\eta^5-C_5H_5)_2][PF_6]$  (33 mg, 0.100 mmol) and 1d (95 mg, 0.104 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and stirred for 30 mn. The solvent volume was reduced to ~5 mL *in vacuo*, and *n*pentane was added (30 mL) to precipitate a dark brown precipitate. Decantation and subsequent washings with toluene (2 × 5 mL), diethyl ether (2 × 5 mL), and *n*-pentane (2 × 5 mL) yielded  $[Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)\{C \equiv C(1,4-C_6H_4)C \equiv C(1,3-C_6H_4)C \equiv C(1,3-C_6)C \equiv C($ 

Synthesis of  $[Pe(k^{-}dppe)[\eta^{-}-c_{5}Me_{5}]C \equiv C(1),5-c_{5}H_{4}/C \equiv CH)][PF_{6}]$ (2[PF<sub>6</sub>]). [Fe( $\eta^{5}-C_{5}H_{5}$ )\_][PF<sub>6</sub>] (40 mg, 0.121 mmol) and 2 (90 mg, 0.126 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and stirred for 2 h. The solvent volume was reduced to ~5 mL *in vacuo*, and *n*-pentane was added (50 mL) to give a red-brown precipitate. Decantation and subsequent washings with toluene (2 × 5 mL), diethyl ether (2 × 5 mL), and *n*-pentane (2 × 5 mL) yielded [Fe( $k^{2}$ -dppe)( $\eta^{5}$ -C<sub>5</sub>Me\_{5})-{C $\equiv$ C(1,3-C<sub>6</sub>H<sub>4</sub>)C $\equiv$ CH}][PF<sub>6</sub>] (2[PF<sub>6</sub>]; 74 mg, 0.086 mmol, 71%). Crystals of the complex were grown by slow diffusion of *n*-pentane in a CH<sub>2</sub>Cl<sub>2</sub> solution of the complex. FT-IR (KBr, cm<sup>-1</sup>):  $\nu$  3287 (s,  $\equiv$ C-H), 2008 (w, C $\equiv$ CFe). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz):  $\delta$  27.8 (s, H<sub>3</sub>), 8.9 (s, C $\equiv$ CH), 7.9 (s, H<sub>dppe</sub>), 6.9 (s, H<sub>dppe</sub>), 6.4 (s, H<sub>dppe</sub>), 6.2 (s, H<sub>dppe</sub>), 3.6 (s, H<sub>dppe</sub>), 1.6 (s, H<sub>dppe</sub>), -2.7 (s, CH<sub>2/dppe</sub>), -10.5 (br s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), -36.7 (br s, H<sub>2</sub>), -38.2 (br s, H<sub>4</sub> + H<sub>4</sub>'). Synthesis of [Fe( $k^{2}$ -dppe)( $\eta^{5}$ -C<sub>5</sub>Me<sub>5</sub>){C $\equiv$ C(1,4-C<sub>6</sub>H<sub>4</sub>)CH $\equiv$ CH<sub>2</sub>]]-

Synthesis of  $[Fe(\kappa^2-dppe)(\eta^5-C_5Me_5)(C \equiv C(1,4-C_6H_4)CH = CH_2)]$ -  $[PF_6]$  (3[PF\_6]). [Fe( $\eta^5-C_5H_5$ )\_2][PF\_6] (55 mg, 0.166 mmol) and 3 (125 mg, 0.174 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and stirred for 2 h. The solvent volume was reduced to ~5 mL *in vacuo*, and *n*pentane was added (50 mL) to give a dark brown precipitate. Decantation and subsequent washings with toluene (2 × 5 mL), diethyl ether (2 × 5 mL), and *n*-pentane (2 × 5 mL) yielded [Fe( $\kappa^2$ dppe)( $\eta^5-C_5Me_5$ ){C = C(1,4-C<sub>6</sub>H<sub>4</sub>)CH = CH<sub>2</sub>})][PF<sub>6</sub>] (3[PF<sub>6</sub>]; 97 mg, 0.113 mmol, 68%). FT-IR (KBr, cm<sup>-1</sup>):  $\nu$  1992 (w, C = CFe), 1595 (w, C = CH). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz):  $\delta$  32.5 (s, H<sub>3</sub>), 28.1 (s, CH = CH<sub>2</sub>), 10.0 (s, H<sub>dppe</sub>), 7.2 (s, H<sub>dppe</sub>), 6.8 (s, H<sub>dppe</sub>), 6.3 (s, H<sub>dppe</sub>), 3.7 (s, H<sub>dppe</sub>), 2.0 (s, H<sub>dppe</sub>), -2.9 (s, CH<sub>2/dppe</sub>), -10.3 (br s, C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), -22.3 (s, CH = CH<sub>2</sub>), -24.6 (s, CH = CH<sub>2</sub>), -46.6 (br s, H<sub>5</sub>), -46.6 (br s, H<sub>4</sub>).

**Solvent-Glass ESR Measurements.** A 1-2 mg sample of an Fe(II) complex was introduced in an ESR tube under an argon-filled atmosphere along with an excess of [FcH][PF<sub>6</sub>], and a 1:1 mixture of degassed dichloromethane/1,2-dichloroethane was transferred to dissolve the solid. For solvent glass measurements at 77 K, the solvent mixture was frozen immediately in liquid nitrogen, and the tubes were sealed and transferred in the ESR cavity.

**Computational Details.** DFT calculations were carried out on the **Ib-d**<sup>0/+</sup>, 2<sup>0/+</sup>, and 3<sup>0/+</sup> complexes using the Amsterdam Density Functional (ADF) program.<sup>57,58</sup> Electron correlation was treated within the local density approximation (LDA) in the Vosko–Wilk–Nusair parametrization.<sup>59</sup> Nonlocal corrections were added to the exchange and correlation energies using the Perdew–Wang 1991 (PW91)<sup>60</sup> or revPBE<sup>61</sup> functionals. Calculations were performed using the standard ADF triple- $\zeta$  quality basis set for the atom valence shells augmented with a 2p polarization function for H, a 3d polarization function for C and P, and a 4p for Fe. Orbitals up to 1s, 2p, and 3p were kept frozen for C, P, and Fe, respectively. Full geometry optimizations (assuming  $C_1$  symmetry) were carried out on each complex, using the analytical gradient method implemented by Versluis and Ziegler.<sup>62</sup> The nature of the stationary points after

optimization was checked by calculations of the harmonic vibrational frequencies using the revPBE functional. Computed EPR properties were accomplished using the ESR procedure developed by van Lenthe and co-workers.<sup>63</sup> The *g*-tensor components were obtained using self-consistent spin-unrestricted DFT calculations after incorporating the relativistic spin–orbit coupling by first-order perturbation theory from a ZORA Hamiltonian, using the PW91 functional<sup>60</sup> for nonlocal corrections to the exchange and correlation energies.

Time-dependent density functional theory (TD-DFT) calculations<sup>64</sup> were performed on the optimized structures of neutral and open-shell systems using the hybrid PBE0 functional<sup>65</sup> and taking into account the solvation effects using the conductor-like screening model (COSMO)<sup>66</sup> with a dielectric constant simulating dichloromethane solvent. Molecular orbitals and spin densities were plotted with the ADF-GUI package.<sup>58</sup>

Crystallography. Crystals of 1b,  $1c \cdot C_7 H_8$ , 2,  $2[PF_6]$ , 3, 5'a, and 6 were studied on an Oxford Diffraction Xcalibur Saphir 3 with graphitemonochromatized Mo K $\alpha$  radiation. The cell parameters were obtained with Denzo and Scalepack with 10 frames (psi rotation: 1° per frame).<sup>67</sup> The data collection<sup>68</sup> details ( $2\theta_{\max}$ , number of frames,  $\Omega$ rotation, scan rate, and HKL range) for 1b,  $1c \cdot C_7 H_8$ , 2,  $2[PF_6]$ , 3, 5'a, and 6 are given in the Supporting Information (Table S1). Subsequent data reduction with Denzo and Scalepack<sup>67</sup> gave the independent reflections. The structures were solved with SIR-97, which revealed the non-hydrogen atoms.<sup>69</sup> After anisotropic refinement, the remaining atoms were found in Fourrier difference maps. The complete structures were then refined with SHELXL97<sup>70<sup>+</sup></sup> by the full-matrix least-squares methods against  $F^2$ . All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Hydrogen atoms were included as a riding model based on the atom to which they are bonded. Atomic scattering factors were taken from the literature.<sup>71</sup> Thermal ellipsoid plots of 1b, 1c, 2, 2[PF<sub>6</sub>], 3, 5'a, and 6 were realized with ORTEP.

# ASSOCIATED CONTENT

#### Supporting Information

Synthesis of selected organic precursors, selected spectroscopic and crystallographic data for **1b**–**d** and **1b**–**d**[PF<sub>6</sub>] complexes. Crystallographic (CIF) file for **1b**, **1c**·C<sub>7</sub>H<sub>8</sub>, **2**, **2**[PF<sub>6</sub>], **3**, **5**′a, and **6**. Cartesian coordinates for all calculated geometries. Final atomic positional coordinates, with estimated standard deviations, bond lengths, angles, and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre and were allocated the deposition numbers CCDC 299572, 942561, 676885, 918574, 668871, 298157, and 664966, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

# AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: bruno.fabre@univ-rennes1.fr, jean-francois.halet@ univ-rennes1.fr, frederic.paul@univ-rennes1.fr.

#### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

# Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

F.P. and N.G. thank Region Bretagne for financial support. H.S. acknowledges a Ph.D. fellowship from the PROFAS French-Algerian Programme. The Agence Nationale de la Recherche (ANR 09-BLAN-0109) and CNRS are fully acknowledged for financial support. T. Guizouarn and F. Justaud (Rennes) are

acknowledged for experimental assistance in ESR and A. Barnes for her editorial assistance.

# REFERENCES

(1) (a) Liu, Z.; Yasseri, A. A.; Lindsey, J. S.; Bocian, D. F. Science 2003, 302, 1543–1545. (b) Lindsey, J. S.; Bocian, D. F. Acc. Chem. Res. 2011, 44, 638–650.

(2) Roth, K. M.; Yasseri, A. A.; Liu, Z.; Dabke, R. B.; Malinovskii, V.; Schweikhart, K.-H.; Yu, L.; Tiznado, H.; Zaera, F.; Lindsey, J. S.; Kuhr, W. G.; Bocian, D. F. J. Am. Chem. Soc. **2003**, 125, 505–517.

(3) (a) Tour, J. M. Acc. Chem. Res. 2000, 33, 791–803. (b) Joachim, C. New J. Chem. 1991, 15, 223–229.

(4) Li, Q.; Mathur, G.; Gowda, G.; Surthi, S.; Zhao, Q.; Yu, L.; Lindsey, J. S.; Bocian, D. F.; Misra, V. *Adv. Mater.* **2004**, *16*, 133–137. Li, C.; Ly, J.; Lei, B.; Fan, W.; Zhang, D.; Han, J.; Meyyapan, M.;

Thompson, M.; Zhou, C. J. Phys. Chem. B 2004, 108, 9646-9649.

(5) Qi, H.; Sharma, S.; Li, Z.; Snider, G. L.; Orlov, A. O.; Lent, C. S.; Fehlner, T. P. J. Am. Chem. Soc. **2003**, 125, 15250–15259.

(6) Qi, H.; Ghupta, A.; Noll, B. C.; Snider, G. L.; Lu, Y.; Lent, C. S.; Fehlner, T. P. J. Am. Chem. Soc. **2005**, 127, 15218–15227.

(7) (a) Aguirre-Etcheverry, P.; O'Hare, D. Chem. Rev. 2010, 4839–4864. (b) Ren, T. Organometallics 2005, 24, 4854–4870. (c) Ceccon, A.; Santi, S.; Orian, L.; Bisello, A. Coord. Chem. Rev. 2004, 248, 683–724.

(8) (a) Paul, F.; Lapinte, C. Coord. Chem. Rev. **1998**, 178/180, 431–509. (b) Halet, J.-F.; Lapinte, C. Coord. Chem. Rev. **2013**, 257, 1584–1613.

(9) (a) Higgins, S. J.; Nichols, R. J.; Martin, S.; Cea, P.; van der Zant, H. S. J.; Richter, M. M.; Low, P. J. Organometallics 2011, 30, 7–12.
(b) Humphrey, M. G.; Cifuentes, M. P.; Samoc, M. Top. Organomet. Chem. 2011, 28, 57–73. (c) Akita, M.; Koike, T. J. Chem. Soc., Dalton Trans. 2008, 3523–3530.

(10) 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.

(11) (a) Buriak, J. M. Chem. Rev. 2002, 102, 1271-1308. (b) Wayner,
D. D. M.; Wolkow, R. A. J. Chem. Soc., Perkin Trans. 2 2002, 23-34.
(c) Ciampi, S.; Harper, J. B.; Gooding, J. J. Chem. Soc. Rev. 2010, 39, 2158-2183. (d) Boukherroub, R. Curr. Opin. Solid State Mater. Sci. 2005, 9, 66-72.

(12) (a) Scheres, L.; Giesbers, M.; Zuilhof, H. Langmuir 2010, 26, 4790–4795. Scheres, L.; Rijksen, B.; Giesbers, M.; Zuilhof, H. Langmuir 2011, 27, 972–980. (b) Scheres, L.; Giesbers, M.; Zuilhof, H. Langmuir 2010, 26, 10924–10929. (c) Ng, A.; Ciampi, S.; James, M.; Harper, J. B.; Gooding, J. J. Langmuir 2009, 25, 13934–13941.

(13) Fabre, B. Acc. Chem. Res. 2010, 43, 1509-1518.

(14) Cummings, S. P.; Savchenko, J.; Ren, T. Coord. Chem. Rev. 2011, 255, 1587–1616.

(15) (a) Zigah, D.; Herrier, C.; Scheres, L.; Giesbers, M.; Fabre, B.; Hapiot, P.; Zuilhof, H. Angew. Chem., Int. Ed. 2010, 49, 3157–3160.
(b) Hauquier, F.; Ghilane, J.; Fabre, B.; Hapiot, P. J. Am. Chem. Soc. 2008, 130, 2748–2749. (c) Fabre, B.; Hauquier, F. J. Phys. Chem. B 2006, 110, 6848–6855. (d) Decker, F.; Cattaruzza, F.; Coluzza, C.; Flamini, A.; Marrani, A. G.; Zanoni, R.; Dalchiele, E. A. J. Phys. Chem. B 2006, 110, 7374–7379. (e) Dalchiele, E. A.; Aurora, A.; Bernardini, G.; Cattaruzza, F.; Flamini, A.; Pallavicini, P.; Zanoni, R.; Decker, F. J. Electroanal. Chem. 2005, 579, 133–142. (f) Tajimi, N.; Sano, H.; Murase, K.; Lee, K.-H.; Sugimura, H. Langmuir 2007, 23, 3193–3198. (16) (a) Yasseri, A. A.; Syomin, D.; Loewe, R. S.; Lindsey, J. S.; Zaera,

(b) Huang, K.; Duclairoir, F.; Pro, T.; Buckley, J.; Marchand, G.;
Martinez, E.; Marchon, J.-C.; De Salvo, B.; Delapierre, G.; Vinet, F. *Chem. Phys. Chem.* 2009, 10, 963–971.

(17) Gauthier, N.; Argouarch, G.; Paul, F.; Humphrey, M. G.; Toupet, L.; Ababou-Girard, S.; Sabbah, H.; Hapiot, P.; Fabre, B. *Adv. Mater.* **2008**, *20*, 1952–1957.

(18) (a) Cicero, R. L.; Linford, M. R.; Chidsey, C. E. D. Langmuir 2000, 16, 5688-5695 and references therein. (b) Kondo, M.; Mates,

- (19) Le Narvor, N.; Toupet, L.; Lapinte, C. J. Am. Chem. Soc. 1995, 117, 7129–7138.
- (20) Green, K.; Gauthier, N.; Sahnoune, H.; Halet, J.-F.; Paul, F.; Fabre, B. To be submitted.
- (21) Dahlenburg, L.; Weiss, A.; Bock, M.; Zhal, A. J. Organomet. Chem. 1997, 541, 465-471.

(22) Courmarcel, J.; Le Gland, G.; Toupet, L.; Paul, F.; Lapinte, C. J. Organomet. Chem. 2003, 670, 108–122.

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

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

(25) Rodríguez, J. G.; Tejedor, J. L.; La Parra, T.; Díaz, C. Tetrahedron 2006, 62, 3355-3361.

(26) Taratula, O.; Rochford, J.; Piotrowiak, P.; Galoppini, E.; Carlisle, R. A.; Meyer, G. J. J. Phys. Chem. B **2006**, 110, 15734–15741.

(27) We also report the synthesis of the known complexes 5a and 5'a by this route, since these were previously isolated by catalytic coupling from 1a.<sup>22</sup>

(28) Makowska-Janusik, M.; Kityk, I. V.; Gauthier, N.; Paul, F. J. Phys. Chem. C 2007, 111, 12094–12099.

(29) Wittig, G.; Schöllkopf, U. Chem. Ber. 1954, 87, 1318-1330.

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

(31) This signal exhibits a diagnostic coupling of ca. 39 Hz to the phosphorus atoms of dppe.

(32) Cifuentes, M. P.; Humphrey, M. G.; Morrall, J. P.; Samoc, M.; Paul, F.; Roisnel, T.; Lapinte, C. *Organometallics* **2005**, *24*, 4280–4288.

(33) Paul, F.; Mevellec, J.-Y.; Lapinte, C. J. Chem. Soc., Dalton Trans. 2002, 1783-1790.

(34) Hansch, C.; Leo, A.; Taft, R. W. Chem. Rev. 1991, 91, 165-195.

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

(36) Paul, F. Work in progress.

(37) Paul, F.; Lapinte, C. In Unusual Structures and Physical Properties in Organometallic Chemistry; Gielen, M., Willem, R., Wrackmeyer, B., Eds.; Wiley: San Francisco, CA, 2002; pp 219–295.

(38) Paul, F.; da Costa, G.; Bondon, A.; Gauthier, N.; Sinbandhit, S.; Toupet, L.; Costuas, K.; Halet, J.-F.; Lapinte, C. *Organometallics* **2007**, *26*, 874–896.

(39) Bertini, I.; Luchinat, C.; Parigi, G. Solution NMR of Paramagnetic Molecules. Application to Metallobiomolecules and Models; Elsevier: Amsterdam, 2001.

(40) In this connection, the isotropic shifts obtained by subtracting the shifts of the corresponding protons in the diamagnetic Fe(II) parents<sup>38</sup> roughly correlate with the spin densities computed on the attenant carbon atoms (see the Supporting Information).

(41) Paul, F.; Bondon, A.; da Costa, G.; Malvolti, F.; Sinbandhit, S.; Cador, O.; Costuas, K.; Toupet, L.; Boillot, M.-L. *Inorg. Chem.* **2009**, 48, 10608–10624.

(42) (a) Ibn Ghazala, S.; Paul, F.; Toupet, L.; Roisnel, T.; Hapiot, P.; Lapinte, C. J. Am. Chem. Soc. 2006, 128, 2463-2476. (b) Ibn Ghazala, S.; Gauthier, N.; Paul, F.; Toupet, L.; Lapinte, C. Organometallics 2007, 26, 2308-2317. (c) Justaud, F.; Argouarch, G.; Gazalah, S. I.; Toupet, L.; Paul, F.; Lapinte, C. Organometallics 2008, 27, 4260-4264. (d) Costuas, K.; Cador, O.; Justaud, F.; Le Stang, S.; Paul, F.; Monari, A.; Evangelisti, S.; Toupet, L.; Lapinte, C.; Halet, J.-F. Inorg. Chem. 2012, 50, 12601-12622. (e) Drouet, S.; Merhi, A.; Grelaud, G.; Cifuentes, M. P.; Humphrey, M. G.; Matczyszyn, K.; Samoc, M.; Toupet, L.; Paul-Roth, C. O.; Paul, F. New J. Chem. 2012, 36, 2192-2195. (f) Grelaud, G.; Cador, O.; Roisnel, T.; Argouarch, G.; Cifuentes, M. P.; Humphrey, M. G.; Paul, F. Organometallics 2012, 31, 1635-1642. (g) Trujillo, A.; Veillard, R.; Argouarch, G.; Roisnel, T.; Singh, A.; Ledoux, I.; Paul, F. Dalton Trans. 2012, 41, 7454-7456. (43) In the latter complex (2[PF<sub>6</sub>]), the bond length found (1.135  $\pm$ 0.009 Å) for the terminal ethynyl bond is much shorter than expected (1.181 Å),<sup>44</sup> while the C43–C45 bond is slightly longer (1.465  $\pm$  0.012 Å vs 1.436 Å). This artifactual feature results possibly from the thermal motions of the terminal carbon atoms.<sup>45</sup>

(44) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. J. Chem. Soc., Perkin Trans. **1987**, *2*, S1–S19.

(45) See for instance: Dunitz, J. D. J. Chem. Soc., Chem. Commun. 1999, 2547–2547.

(46) Szafert, S.; Gladysz, J. A. Chem. Rev. 2006, 106, PR1-PR33.

(47) Gauthier, N.; Argouarch, G.; Paul, F.; Toupet, L.; Ladjarafi, A.; Costuas, K.; Halet, J.-F.; Samoc, M.; Cifuentes, M. P.; Corkery, T. C.; Humphrey, M. G. *Chem.—Eur. J.* **2011**, *17*, 5561–5577.

(48) A model of compound 1b has been theoretically studied previously; see ref 10.

(49) Koopmans, T. Physica 1934, 1, 104–113.

(50) Gendron, F.; Burgun, A.; Skelton, B. W.; White, A. H.; Roisnel, T.; Bruce, M. I.; Halet, J.-F.; Lapinte, C.; Costuas, K. *Organometallics* **2012**, *31*, 6796–6811.

(51) Schauer, P. A.; Low, P. J. Eur. J. Inorg. Chem. 2012, 390-411. (52) Paul, F.; Toupet, L.; Roisnel, T.; Hamon, P.; Lapinte, C. C. R.

Chim. 2005, 8, 1174–1185. (53) For related observations with isoelectronic Ru(II/III) analogues,

see: Khairul, W. M.; Fox, M. A.; Schauer, P. A.; Albesa-Jové, D.; Yufit, D. S.; Howard, J. A. K.; Low, P. J. *Inorg. Chim. Acta* **2011**, *374*, 461–471.

(54) Bruce, M. I.; Burgun, A.; Gendron, F.; Grelaud, G.; Halet, J.-F.; Skelton, B. W. Organometallics **2011**, *30*, 2861–2868.

(55) Paul, F.; Malvolti, F.; da Costa, G.; Stang, S. L.; Justaud, F.; Argouarch, G.; Bondon, A.; Sinbandhit, S.; Costuas, K.; Toupet, L.; Lapinte, C. *Organometallics* **2010**, *29*, 2491–2502.

(56) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877–910. (57) (a) te Velde, G.; Bickelhaupt, F. M.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Baerends, E. J.; Snijders, J.; Ziegler, T. *Theor. Chem. Acc.* **2001**, *22*, 931–967. (b) Fonseca Guerra, C.; Snijders, J.; te Velde,

G.; Baerends, E. J. Theor. Chem. Acc. 1998, 99, 391–403.
(58) ADF2010.02, SCM; Theoretical Chemistry, Vrije Universiteit:

Amsterdam, The Netherlands, http://www.scm. (59) Vosko, S. D.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, 58, 1200–

(39) Vosko, S. D.; Wilk, L.; Nusair, M. Can. J. Phys. **1960**, 58, 1200– 1211.

(60) Perdew, J. P.; Wang, Y. Phys. Rev. B 1992, 45, 13244-13249.

(61) Zhang, Y.; Yang, W. Phys. Rev. Lett. 1998, 80, 890.

(62) Versluis, L.; Ziegler, T. J. Chem. Phys. 1988, 88, 322-328.

(63) (a) van Lenthe, E.; van der Avoird, A.; Wormer, P. E. S. J. Chem.

*Phys.* **1998**, *108*, 4783–4796. (b) van Lenthe, E.; van der Avoird, A.; Wormer, P. E. S. *J. Chem. Phys.* **1997**, *107*, 2488–2498. (c) Autschbach,

J.; Pritchard, B. Theor. Chem. Acc. 2011, 129, 453-466.

(64) van Gisbergen, S. J. A.; Snijders, J. G.; Baerends, E. J. Comput. Phys. Commun. 1999, 118, 119–138.

(65) Adamo, C.; Barone, V. J. Chem. Phys. 1999, 110, 6158-6178.
(66) (a) Pye, C.; Ziegler, T. Theor. Chem. Acc. 1999, 396-408.

(b) Klamt, A. J. Phys. Chem. 1995, 99, 2224-2235.

(67) Otwinowski, Z.; Minor, W. In *Methods in Enzymology*; Carter, C. W., Sweet, R. M., Eds.; Academic Press: London, 1997; Vol. 276, pp 307–326.

(68) Nonius, B. V. Kappa CCD Software; Delft: The Netherlands, 1999.

(69) Altomare, A.; Foadi, J.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Burla, M. C.; Polidori, G. *J. Appl. Crystallogr.* **1998**, *31*, 74–77.

(70) Sheldrick, G. M. SHELX97-2. Program for the Refinement of Crystal Structures; Univ. of Göttingen: Germany, 1997.

(71) Reidel, D. International Tables for X-ray Crystallography; Kynoch Press (present distrib. D. Reidel, Dordrecht): Birmingham, 1974; Vol. *IV.* 

# NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on the Web on July 21, 2013, with errors in the first paragraph on page 4 and the last paragraph on page 9. The corrected version was reposted on August 12, 2013.