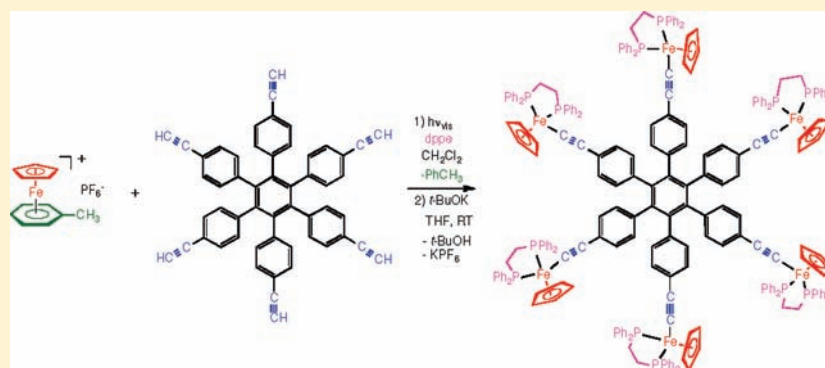# Visible-Light Generation of the Naked 12-Electron Fragment C₅H₅Fe⁺: Alkyne-to-Vinylidene Isomerization and Synthesis of Polynuclear Iron Vinylidene and Alkynyl Complexes Including Hexairon Stars[†]

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Ⓢ *Supporting Information*

ABSTRACT: Visible-light photolysis of $[FeCp(\eta^6\text{-}C_6H_5CH_3)][PF_6]$ using a simple 100-W bulb or a compact fluorescent light bulb in the presence of terminal alkynes and dppe yielded the vinylidene complexes $[FeCp(=C=CHR)(dppe)][PF_6]$ that were deprotonated by *t*-BuOK to yield the alkynyl complexes $[FeCp(\text{-}C≡CR)(dppe)]$. The reaction has been extended to the synthesis of bis-, tris, tetra-, and hexanuclear iron complexes including three alkynes of the ferrocenyl family.

■ INTRODUCTION

The 18-electron cationic sandwich complexes $[FeCp(\eta^6\text{-}arene)][PF_6]^{1-3}$ (Cp = η^5-cyclopentadienyl) are a very rich family and can be synthesized in large scale by cyclopentadienyl substitution upon heating ferrocene and a large variety of arenes in the presence of aluminum chloride.[2,3] The basic chemistry of these complexes involves a number of reactions of the cyclopentadienyl and arene ligands and their substituents.[2b,3] In particular, deprotonation of side methyl or alkyl groups followed by nucleophilic substitution leads to the easy synthesis of useful star[4] and dendrimer cores and dendrons in one-pot reactions under mild conditions.[5]

Additional interest arose when it was reported that both stable 17-electron Fe^III and 19-electron Fe^I complexes were synthesized with this structure and were involved as useful redox reagents and electron-transfer catalysts.[6] Finally, visible-light photolysis of simple complexes was shown to lead to ligand substitution with other arenes[7] and with phosphines,[8] nitriles,[9] and functional cyclopentadienyls.[10] Several reactions are summarized in Scheme 1 with the prototype toluene complex. Recently, we briefly communicated the visible-light photolysis of $[FeCp(\eta^6\text{-}C_6H_5CH_3)][PF_6]$, **1**, in the presence of simple terminal alkynes leading to cationic iron-vinylidene complexes (Scheme 1) that were deprotonated to neutral iron-alkynyl complexes.[11] Here we detail this reaction and report its extension to the synthesis of multinuclear complexes including tri-, tetranuclear, and star-shaped hexanuclear iron complexes.

Late transition-metal vinylidene complexes have a very rich chemistry that has been abundantly studied for several decades, and the literature has been the subject of fine comprehensive reviews.[12] Many of these complexes are formed upon reactions of terminal alkynes. The transition-metal vinylidene complexes are also involved as intermediates in the metathesis polymerization of terminal[13] (and sometimes also internal)[14] alkynes according to the Chauvin–Katz mechanism.[13,15,16] In 1992, the Grubbs group reported ruthenium vinylidene complexes that efficiently catalyzed the metathesis of functional olefins.[17]

Since vinylidene- and alkynyl-iron complexes have great potential applications in nonlinear optics, conducting materials, and catalysis,[12] the new simple synthetic procedure reported here should be a valuable tool to contribute to the development of these fields.

The simple piano-stool cationic complexes $[FeCp(=C=CHR)(dppe)][BF_4]$ are known. In 1992, Nakanishi et al. reported the photochemical substitution of CO by a vinylidene ligand in the presence of various mono alkynes (eq 1, R = H, SiMe₃, Ph, C_3H_7, CH_2OH, CH_2OSiMe_3, CH_2OPh, $CH_2OC\text{-}OCH_3$).[18]

The Fe-alkynyl complexes have also been reported. Sato et al. first published the reaction of ethynylferrocene with a family of complexes $C_5R_5FeL_2I$ (R = H or Me; L = CO, $P(OMe)_3$, or

**Scheme 1. Summary of the Properties of $[FeCp(\eta^6\text{-}C_6H_5CH_3)][PF_6]$, 1, Including Visible-Light Irradiation Reactions**
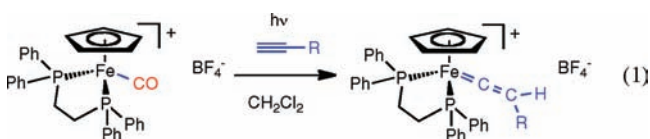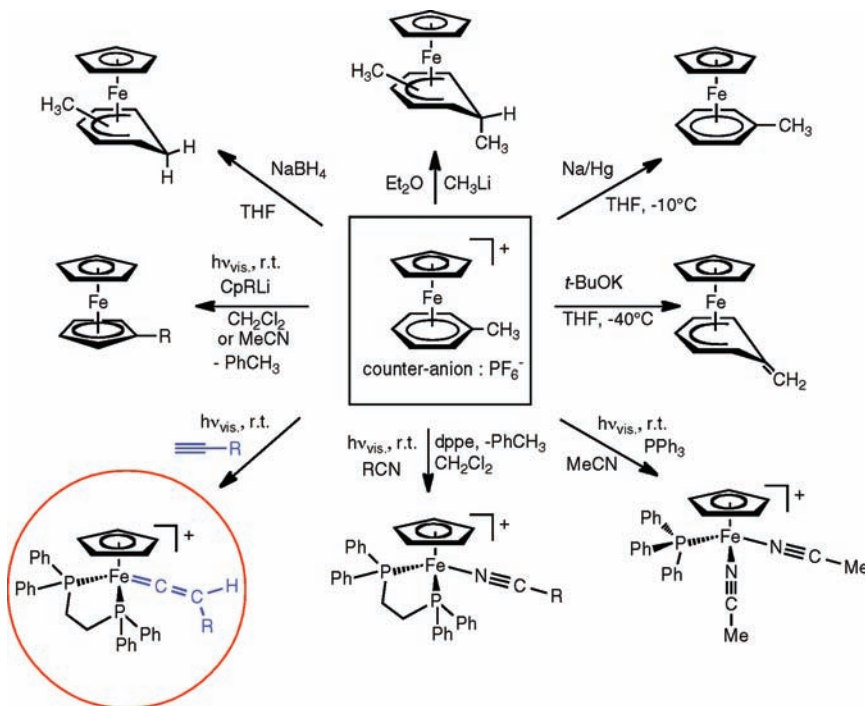
CO + PPh$_3$) and the photochemical substitution of the two carbonyl ligands of $[FeCp(CO)_2(C\equiv CFc)]$ by dppe (eq 2, Fc = ferrocenyl).[19]
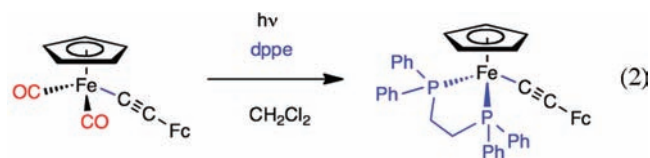
The Sato group also oxidized these complexes using ferricinium and obtained mixed-valence Fe^{II}Fe^{III} complexes that were shown to be delocalized.[20] Symmetrical dinuclear piano-stool pentamethylcyclopentadienyl alkynyl complexes were reported by the Lapinte group including inter alia their synthesis via the vinylidene intermediates[21] starting from the iron-chloro complex $[FeCp^*(dppe)Cl]$ (eq 3, Cp* = η^5=C$_5$Me$_5$).[22] In-depth studies of mixed valence compounds of these complexes and a number of related derivatives with
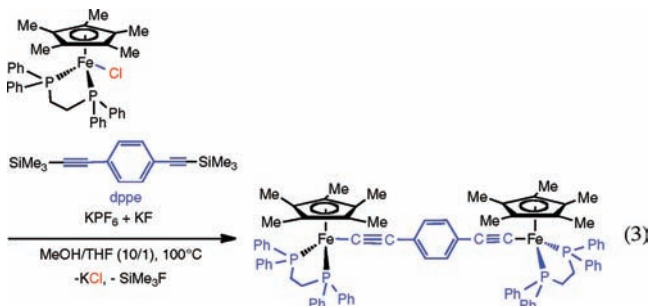
carbon bridges of variable length and nature were carried out by this research group.[21,23,24] The parent (Cp) analogue of the complex shown in eq 3 was also reported in 2006 by Medei et al.,[25] and in 2005 Bruce et al. reported the isostructural RuCp(dppe) series and electronic delocalization of the mixed-valence oxidized compounds.[26]

Finally, subsequently to work by Wakatsuki, the alkyne to vinylidene isomerization in cationic iron and ruthenium complexes has recently been viewed as an uncommon electrophilic rearrangement by Ishii's group.[16]

In the present work, we detail a new procedure for the synthesis of mono- and multinuclear vinylidene and alkynyl-iron complexes that rely on the visible-light photolysis of the easily available complex $[FeCp(\eta^6\text{-}C_6H_5CH_3)][PF_6]$, 1, using a simple 100-W bulb or a compact fluorescent light bulb.

■ RESULTS

Synthesis of the Parent Ethynyl Complex. Visible-light irradiation of 1 in the presence of stoichiometric amounts of trimethylsilylacetylene and dppe in dichloromethane (DCM) carried out with a standard 100-W bulb or a compact fluorescent light bulb overnight led to a color change from yellow to brown. After removing the solvent and toluene under vacuum, the vinylidene complex $[CpFe(dppe)\{=C=CH\text{-}(SiMe_3)\}][PF_6]$, 2, was the only reaction product obtained, as shown by the ^{31}P NMR spectrum that contained only the peak at 97.0 ppm corresponding to the two phosphorus atoms of the dppe ligand, besides the typical peaks of the PF$_6$ anion. The ^1H NMR is also in agreement with the expected complex showing only one peak for the Cp protons at 4.93 ppm as reported by Nakanishi et al. using the reaction shown in eq 1.[18] The infrared spectrum of the crude product showed the typical C=C band at 1642 cm^{-1}.[18] For comparison, a similar thermal reaction carried out in the dark in refluxing 1,2-diclororethane (84 °C) for 12 h did not give any product, and the starting materials were recovered (Supporting Information).

The complex **2** was deprotonated by a stoichiometric amount of *t*-BuOK, and addition of tetra(butyl)ammonium fluoride in tetrahydrofuran (THF) allowed the deprotection of the terminal alkyne in situ to give the corresponding red iron-alkynyl complex **3** (Scheme 2).

**Scheme 2. Synthesis of the Parent Acetylide Complex 3 upon Visible-Light Irradiation of 1**
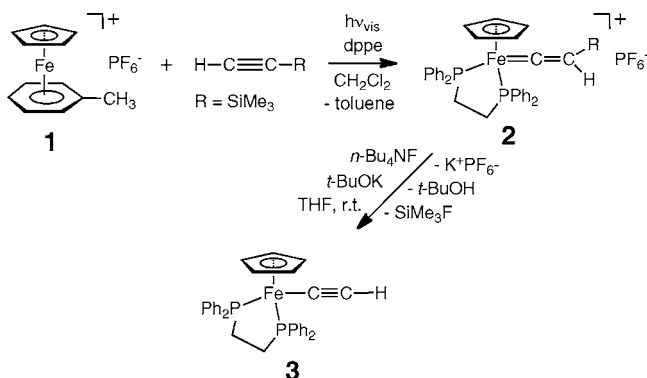
The complex **3** was separated from KPF_6 and $SiMe_3F$ formed, by extraction with ether. The dppe signal in the ^{31}P NMR spectra of **3** appeared at 106.4 ppm, and the PF_6 signal disappeared. In the ^{1}H NMR spectrum, the Cp protons changed from 4.93 ppm in complex **2** to 4.21 ppm in **3**, in accordance with the formation of a more electron-rich complex. The structure of complex **3** was also confirmed by mass spectrometry showing its molecular peak at 545.0 Da (calcd. for $C_{33}H_{30}P_2Fe$: 544.40), and elemental analysis.

Visible-Light Irradiation of $[FeCp(\eta^6-C_6H_5CH_3)][PF_6]$ with Phenylacetylene and 1,4- Bis(ethynyl)benzene. Likewise, visible-light irradiation of **1** in the presence of stoichiometric amounts of phenylacetylene or 1,4-bis(ethynyl)-benzene and dppe in DCM carried out using a standard 100-W bulb or a compact fluorescent light bulb overnight led to the known brown mono- and bis-vinylidene complexes [CpFe-(dppe)(=C=CHPh)][PF_6], **4**,[18] and [Cp(dppe)Fe=C=C−C_6H_4−C=C=Fe(dppe)Cp][PF_6]$_2$, **5**, respectively.[25] These vinylidene complexes were further deprotonated by *t*-BuOK to yield the corresponding mono- and bis(ethynyliron) derivatives [CpFe(dppe)(C≡CPh)], **6**, and [Cp(dppe)FeC≡CC_6H_4C≡CFe(dppe)Cp)], **7**, respectively (Scheme 3).[19,20,25] In particular, the dinuclear complex **7** was characterized inter alia in the MALDI-TOF mass spectrum by its molecular peak at 1162.23 Da (calcd. for $C_{72}H_{62}P_4Fe_2$: 1162.85). The reversibility of the deprotonation from vinylidene- to alkynyl iron complexes was verified in the case of the complexes **4** and **6** by formation of **4** upon reaction of **6** with HPF_6 (Supporting Information).

Visible-Light Irradiation of $[FeCp(\eta^6-C_6H_5CH_3)][PF_6]$ with Ethynylferrocene, 1,2,3,4,5-Pentamethyl-1′-ethynyl-ferrocene, and 1′-Ethynylbiferrocene. Visible-light photolysis of **1** in DCM in the presence of dppe and ethynyl-ferrocene, pentamethyl-ethynylferrocene, and ethynylbiferro-cene[27] gives brown cationic vinylidene complexes **8**, **9**, and **10** (Scheme 4 and Chart 1). None of these compounds was known before our study. They were characterized by infrared and NMR spectroscopies including in particular, a signal around 95 ppm in ^{31}P NMR, the vinylidene proton around 5 ppm in ^{1}H NMR, and the vinylidene carbon at 364−366 ppm in ^{13}C NMR. The MALDI-TOF mass spectra recorded for **8** and **10**
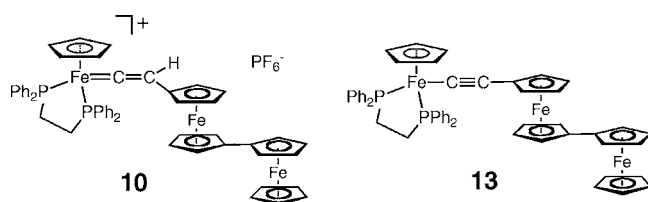
Scheme 3. Application of the Visible-Light Irradiation of 1 to the Synthesis of the Dinuclear Bis-(alkynyliron) Complex 7
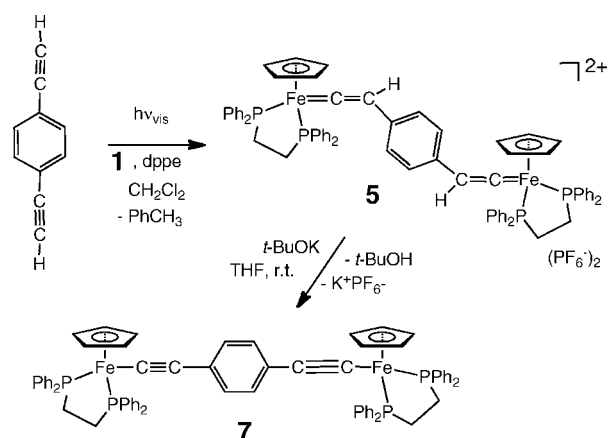
Scheme 4. Visible-Light Photolytic Synthesis of Ferrocenylalkynyliron Complexes
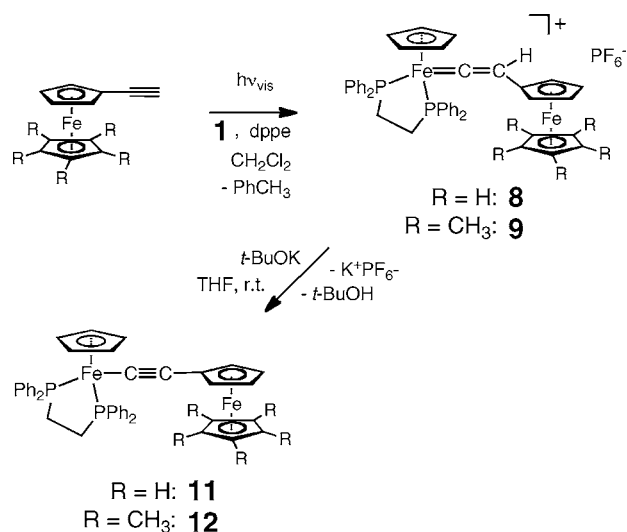
**Chart 1. Biferrocenyl Vinylidene and Alkynyl Iron Complexes Synthesized as in Scheme 4**

show the dominant molecular peaks at 728 and 912 Da respectively. These vinylidene complexes have been deprotonated to orange-red ethynyliron complexes **11**, **12**, and **13** (Scheme 4 and Chart 1). The parent ferrocenyl complex **11**[19] has been thoroughly studied by Sato's group from the point of view of its oxidation to a mixed-valence Fe^{II} Fe^{III} complex **11**$^+$.[19,20] For instance, the alkynyl complex [CpFe(dppe)C≡C-Fc], **11**, shows two completely reversible cyclic voltammetry (CV) waves at 0.0 and 0.65 V vs $FeCp_2^*$. The first redox wave at 0.0 V corresponds, as attributed by Sato, to the oxidation of Fe^{II} to Fe^{III} of the iron-alkynyl fragment, and the second wave to the oxidation of Fe^{II} to Fe^{III} of the ferrocenyl group. This wave assignment is confirmed by the CV of **12** that shows oxidation

of the iron-alkynyl fragment at the same potential, 0.0 V vs [FeCp*$_2$]$^{+/0}$[28] as **7**, but a 0.17 V cathodic shift at 0.48 V of the ferricinium/ferrocene redox system was observed as expected from the ring permethylation of this redox system in **9** compared to **7**. The ethynylbiferrocenyl derivative was also characterized inter alia by its molecular peak in the MALDI-TOF mass spectrum.

Visible-Light Photolysis of the Dinuclear Complexes [Fe$_2$(η^{10}, μ_2-fulvalene)(η^6-arene)$_2$][PF$_6$]$_2$ in the Presence of dppe and Ethynylferrocene. The series of dinuclear complexes [Fe$_2$(η^{10}, μ_2-fulvalene)(η^6-arene)$_2$][PF$_6$]$_2$, known for various arenes,[29] can be used in the same way as **1** for the visible-light photolytic cleavage of the arene ligands and their substitution by other ligands such as phosphines and acetonitrile (Scheme 5). The toluene complex is not soluble

Scheme 5. Extension of the Visible-Light Photolysis of 1 to Dinuclear Fulvalene Diiron Complexes for the Synthesis of Tetrairon Complexes
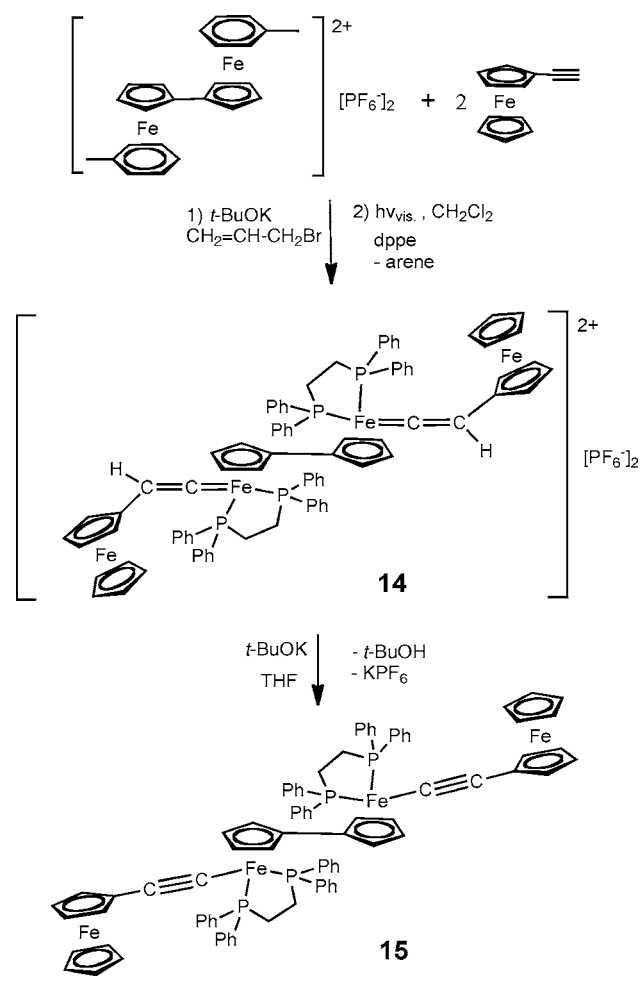
in DCM, however. It is soluble in acetonitrile, but the photolysis in acetonitrile does not allow the reaction with alkynes. Thus the complex [Fe$_2$(η^{10},μ_2-fulvalene)(η^6-C$_6$H$_5$CH$_3$)$_2$][PF$_6$]$_2$[29] was solubilized in DCM by reaction with a mixture of allyl bromide and *t*-BuOK in THF, to allylate the methyl group of the toluene ligands prior to the visible-light photolytic reaction.[29,30] In the presence of dppe and ethynylferrocene, this photolytic reaction in DCM leads to the tetranuclear (bis-vinylidene-iron) complex **14** that was

characterized by standard spectroscopies and elemental analyses. The complex **14** was deprotonated by *t*-BuOK to give the new brown tetranuclear bis(ethynyliron) complex **15** that was also characterized by ^{1}H, ^{13}C, ^{31}P NMR and infrared spectroscopies, elemental analysis, and MALDI-TOF mass spectrometry (calc. *m/z* for M$^+$ (C$_{86}$H$_{74}$Fe$_4$P$_4$): 1454.82; found 1454.15).

CV of **15** shows three chemically and electrochemically reversible oxidation waves at $E_{1/2}$ = −0.14 V, 0.23 V, and 0.68 V vs FeCp*$_2^{+/0}$. By comparison with the CV of the other ferrocenyl and diiron-fulvalene derivatives, the waves at −0.14 and 0.23 V correspond to the fulvalene diiron redox centers and are split because of the mixed valency usually encountered for the fulvalene diiron complexes of this series, whereas the wave at 0.68 V corresponds to the two ferrocenyl units that are too far apart from each other for sufficient electronic communication leading to CV wave splitting. Very recently, Lapinte et al. have reported biferrocene-bridged bis-vinylidene and bis-alkynyl complexes in the Cp* series.[24]

Synthesis of Flexible and Stiff Star-Shaped Hexanuclear Iron-Ethynyl Complexes. Visible-light photolysis of **1** in DCM in the presence of dppe and two known hexaalkyne derivatives **16**[31] and **17** immediately followed by deprotonation with *t*-BuOK yielded the hexa(ethynyliron) complexes **20** and **21** (Schemes 6 and 7) that were characterized by ^{1}H and ^{31}P NMR and infrared spectroscopies, and elemental analysis. The cyclic voltammograms of **20** and **21** gave a single reversible wave at 0.88 V vs Cp$_2$Co$^{+/0}$ (internal reference), that is, 0.08 V vs FeCp*$_2^{+/0}$ for **20** and 0.13 V vs FeCp*$_2^{+/0}$ for **21**, which indicates that **21** is easier to oxidize than the monoalkynyliron complex **3** ($E_{1/2}$ = 0.16 V vs FeCp*$_2^{+/0}$). This shows that the hexametalated alkynyl groups release electron density onto the metal centers, but the electronic communication is not strong enough to disclose several waves in CV. In the case of the hexa(alkynyliron) complex **20**, the intermediate hexacationic hexa(vinylideneiron) complex **18** was also characterized by ^{31}P NMR and elemental analysis.

■ DISCUSSION

The visible-light photolysis of the 18-electron cationic sandwich complexes [FeCp(η^6-arene)][PF$_6$] such as **1** is a very practical way to synthesize other iron-sandwich or piano-stool complexes because these starting materials are easily available in the scale of several hundred grams (the reactions are standard in our undergraduate laboratory). In addition, the simplicity of the use of a standard 100-W bulb for all the photolytic reactions using **1** is especially attractive. Complex **1** combines a straightforward synthesis, low cost of the toluene ligand, and smooth visible-light decomplexation releasing the "naked" 12-electron CpFe$^+$ fragment. The latter is probably very weakly coordinating by DCM molecules and the PF$_6^-$ counteranion. Optimal results are indeed only obtained with this counteranion.

In the presence of alkynes and dppe, the synthesis of the vinylidene complexes is virtually quantitative, and the follow-up deprotonation yields stable alkynyl complexes. With very electron-rich alkynes such as Cp*FeC$_5$H$_4$C≡CH, the new alkynyliron complex obtained, **12**, is also electron rich, and although it is fully stable thermally, it is quite air sensitive. The other alkynyliron complexes are less air sensitive.

The alkyne to vinylidene isomerization is largely precedented in the literature, even for the synthesis of simple alkynyl complexes such as **2**. It should be noted, however, that the procedures reported previously require UV-light for the photolytic

Scheme 6. Application of the Visible-Light Photolysis of 1 to the Synthesis of Flexible Star Complexes
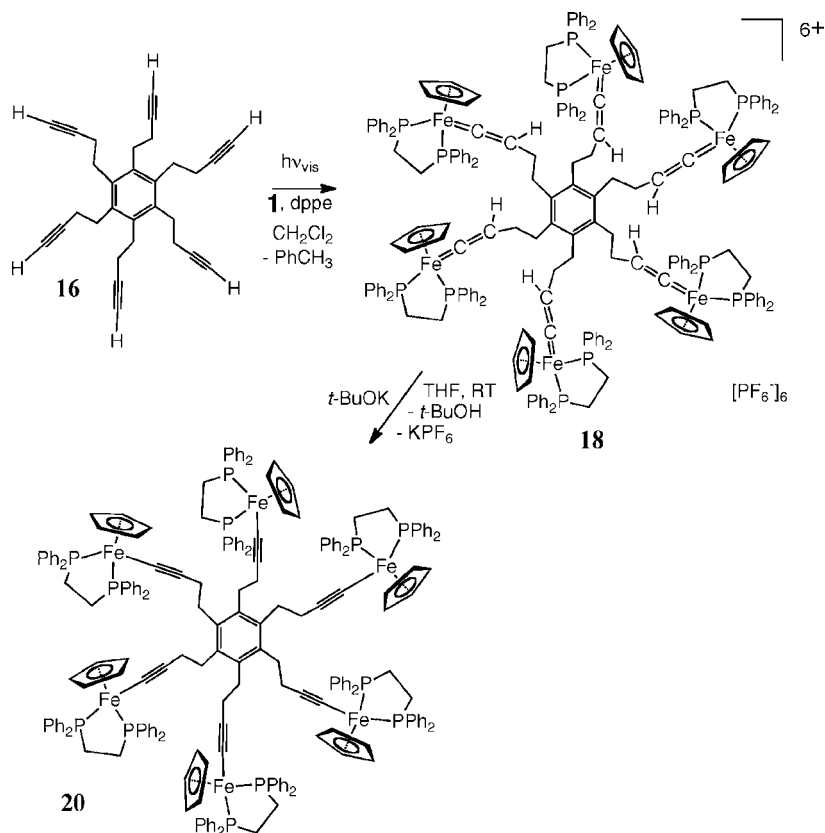
synthesis from a carbonyliron starting material (eq 1); moreover the synthesis of this precursor involves the use of unstable organoiron compounds, as indicated, and a longer synthetic route.[18]

The visible-light photolytic reaction is not reserved to the case of complex 1, but many other complexes [FeCp(η^6-arene)][PF$_6$] could be used. The visible-light photolysis reactions do not work with pentamethylcyclopentadienyl analogues of 1, because the absorption band responsible for decomplexation (involving a distorted $^3E_1$ ligand-field state) is shifted toward the UV region upon permethylation of the Cp ring of the sandwich complex. UV irradiation would work, however, for the synthesis of the Cp* analogues (synthesized otherwise by the Lapinte group[21−24]) of the vinylidene and alkynyl complexes described here with a Cp ligand.

The visible-light irradiation can indeed be used for the complexes [FeCp(η^6-arene)][PF$_6$] that bear only a single substitution on the Cp ring because the resulting blue shift of the absorption is then only minute when compared to the complexes [FeCp(η^6-arene)][PF$_6$] containing the unsubstituted Cp. This is the case for the fulvalene dinuclear complexes [Fe$_2$(η^{10},μ_2-fulvalene)(η^6-arene)$_2$][PF$_6$]$_2$ provided they remain soluble in DCM. The increase of solubility of these complexes upon alkylation or allylation reaction of t-BuOK and an organic halide is known,[29] and this strategy has been successfully applied here.

Alkynylferrocenes are attractive substrates, because ethynyliron complexes obtained benefit from extra conjugation, an aspect that was astutely used by Sato and co-workers for the synthesis of the ethynylferrocenyl iron complex 11 and its interesting oxidized mixed-valence derivatives.[19] We have used the new procedure to easily synthesize compound 11 in

quantitative yield and extended the family of these ferrocenylethynyliron complexes to three new compounds leading to the electron-rich bi-, tri-, and tetranuclear analogues 12, 13, and 15, respectively.

A metal-stabilized carbene is involved as a mesomeric form in the structure of the vinylidene complexes of the ferrocenyl family. This new type of carbene is not at all a classic transition-metal carbene complex, but a Bertrand-type organic carbene[32] in which the stabilizing group is a transition metal rather than a heteroatom (Chart 2).

Finally, the synthetic procedure was extended to flexible and stiff star-shaped derivatives for the introduction of redox-active and reversible ethynyliron termini that are electronically enriched by the hexa-star cores,[33] as indicated by the values of their redox potentials found in the cyclic voltammograms. Although the little-soluble brown hexacationic intermediate vinylidene complexes were not characterized, the intermediacy of vinylidene-iron cations is standard as demonstrated in the reactions of mono- and bis-alkynes. The final neutral alkylnyliron star complexes have a fair to good solubility in organic solvents and are easy to handle. As indicated in the introduction, the perspective of application of these alkynyliron terminated complexes to dendritic frameworks[34] using such a simple procedure is promising.

■ CONCLUSION

The visible-light photolytic generation of the naked CpFe$^+$ 12-electron fragment and (μ_2-fulvalene)Fe$_2^{2+}$ using the 18-electron sandwich toluene complexes and a simple 100-W bulb or a compact fluorescent light bulb allows to isomerize alkynes and synthesize a large variety of vinylidene-iron and alkynyl-iron compounds. The procedure was then extended to the synthesis

Scheme 7. Visible-Light Photolytic Synthesis of Stiff Hepta-Arene-Cored Hexavinylidene and Hexaalkynyl Complexes
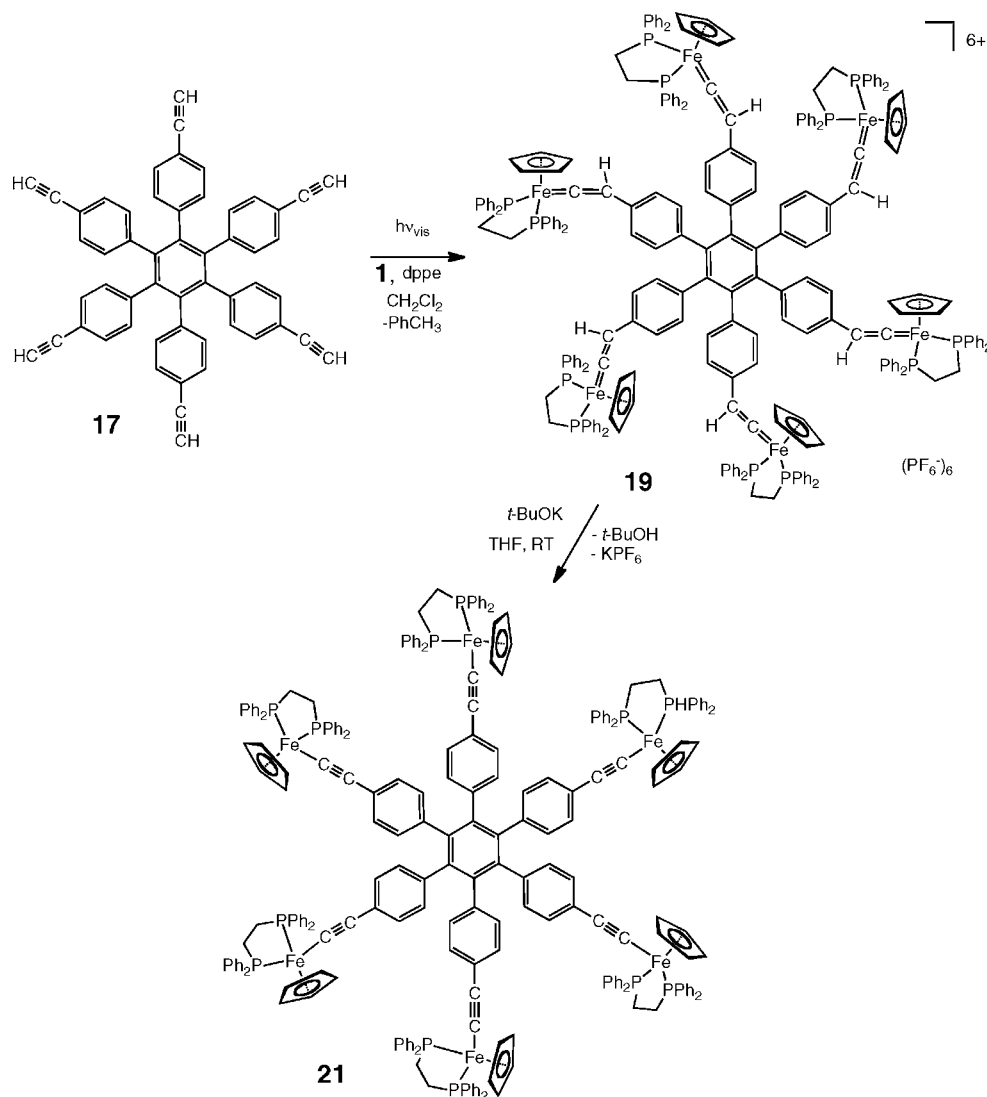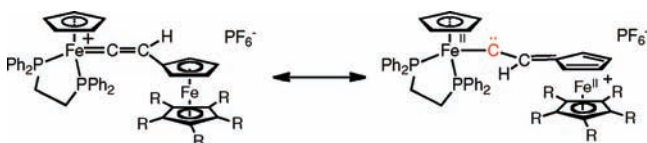

Chart 2. Metal-Stabilized Carbene Involved as a Mesomeric Form in the Structure of the Vinylidene Complexes of the Ferrocenyl Family (R = H or Me)

of new hydrocarbon-bridged bi-, tri, tetra-, and flexible and stiff hexanuclear arene-cored iron complexes. All the ferrocenylvinylidene complexes synthesized here in this Cp series are new, and their substitution by a ferrocenyl-type unit provides additional stabilization involving a proposed metallacarbene mesomeric form.

■ EXPERIMENTAL SECTION

General Information. Reagent-grade toluene, THF, diethyl ether, and pentane were dried over Na foil and distilled from sodium-benzophenone anion under nitrogen immediately prior to use. DCM and 1,2-dichloroethane were distilled from calcium hydride and distilled under nitrogen prior to use. CH_3CN was dried over P_2O_5 and distilled under nitrogen prior to use. All other solvents (pentane,

methanol, acetone) and chemicals were used as received. ^{1}H NMR spectra were recorded at 25 °C with a Bruker AC (200, 300, or 600 MHz) spectrometer. The ^{13}C NMR spectra were obtained in the pulsed FT mode at 75 or 150 MHz with a Bruker AC 300 or 600 spectrometer. All the chemical shifts are reported in parts per million (δ, ppm) with reference to Me_4Si for the ^{1}H and ^{13}C NMR spectra. [31]P stands for [31]P (^{1}H) in the data, with chemical shifts referenced to H_3PO_4. The mass spectra were recorded using an Applied Biosystems Voyager-DE STR-MALDI-TOF spectrometer. The infrared spectra were recorded on an ATI Mattson Genesis series FT-IR spectrophotometer. The elemental analyses were performed by the Center of Microanalyses of the CNRS at Lyon Villeurbanne, France. UV−vis. absorption spectra were measured with Perkin-Elmer Lambda 19 UV−vis. Spectrometer. Electrochemical measurements (CV) were recorded on a PAR 273 potentiostat under nitrogen atmosphere.

Syntheses of 3, 6, and 7, Spectra, and CV. See the Supporting Information,

General Procedure for the Synthesis of the Iron-Vinylidene Complexes. Under a nitrogen atmosphere, stoichiometric amounts of $[FeCp(\eta^6\text{-}C_6H_5CH_3)][PF_6]$, dppe, and alkyne ligand were successively introduced into a Schlenk flask with refrigerated double wall, to keep the temperature at 20 °C, suitable for photochemistry, containing dry DCM. The homogeneous reaction mixture was submitted to visible light irradiation using a 100-W bulb during 16 h, and the solution color changed from yellow to brown. The solvent was

removed under vacuum, and the crude vinylidene-iron product was washed several times with ether and analyzed by IR and ^{31}P NMR, and, for the new products, by elemental analyses and mass spectrometry.

General Procedure for the Synthesis of the Iron-Alkynyl Complexes. The crude iron-vinylidene complex synthesized as indicated above was dissolved in dry THF, and a stoichiometric amount of t-BuOK was added. The reaction mixture was stirred at room temperature (r.t.) for 2 h. The solvent was removed under vacuum, and the alkynyl-iron complex was extracted with ether or DCM, and filtered through Celite to remove the KPF$_6$ formed. The solvent was removed under vacuum. The orange-red powder obtained was analyzed by ^{1}H, ^{13}C, and ^{31}P NMR, and IR, elemental analysis, and MALDI-TOF mass spectrometry.

Synthesis of CpFe(dppe)C≡C-Fc, 11. The iron-alkynyl complex **11** was synthesized from the following: (i) **1** (0.250 g, 0.699 mmol), dppe (0.279 g, 0.699 mmol), and ethynylferrocene (0.147 g, 0.699 mmol) producing the vinylidene complex **8**; (ii) t-BuOK (0.091 g, 0.699 mmol) and **8** following the general procedure for the synthesis of the iron-alkynyl complexes. The complex **11** dissolved in DCM, filtered through Celite, and after removing the solvent under vacuum, it was obtained as a red-orange powder in 99% yield.

Complex **8**: ^{1}H NMR (600 MHz, (CD$_3$)$_2$CO), δ_{ppm}: 3.16 (m, 4H, CH$_2$ of dppe), 3.38 (t, 2H/C$_5$H$_4$), 4.02(s, 5H, Fc unsub), 4.47(t, 2H/C$_5$H$_4$), 5.16 (s, CH), 5.48 (s, 5H, Fc unsub), 7.18−7.70 (m, 20H, Ph of dppe), 1.12(m, CH$_3$ of ether), 3.41(m, CH$_2$ of ether), 2.06(m, (CD$_3$)$_2$CO), 2.96(s, H$_2$O). ^{13}C NMR (150 MHz, (CD$_3$)$_2$CO), δ_{ppm}:.27.84 (CH$_2$ of dppe), 66.30 (CH/C$_5$H$_4$), 67.83 (CH/C$_5$H$_4$), 69.13 (Fc unsub), 79.74 (Ci/C$_5$H$_4$), 89.29 (Fc unsub), 123.23 (≡CFc), 129.08−132.58 (Ph of dppe), 365.90 (t, Fe═C), 14.78 (CH$_3$ of pentane), 29.06 and 206.45 ((CD$_3$)$_2$CO). HMBC (600 MHz, (CD$_3$)$_2$CO): see Supporting Information, page S19; ^{31}P NMR (121 MHz, CD$_3$COCD$_3$), δ_{ppm}: 93.49(Fe-dppe), −144.23 (m, PF6-); IR (KBr): 1963 cm^{-1} ($\nu_{C≡C}$), 839 cm^{-1}; (ν_{PF6}) MALDI-TOF: calc. m/z for M$^+$ (C$_{43}$H$_{39}$ Fe$_2$P$_2$) 729.1, found 728.1. CV (electrolyte: [n-Bu$_4$N][PF$_6$] 0.1M; working and counter electrodes: Pt; reference electrode: Ag; internal reference: FeCp*$_2$; solvent CH$_2$Cl$_2$): $E_{1/2}$ = 0.510 and 0.690 V vs. FeCp*$_2$.

Complex **11**: ^{1}H NMR (CDCl$_3$, 300 MHz): 7.74−7.20 (m, 20H, arom. CH of dppe), 4.21 (s, 5H, Cp), 3.77−3.65 (m, 9H, Cp of Fc), 2.75 and 2.38 (m, 4H, CH$_2$CH$_2$ of dppe). ^{13}C NMR (CDCl$_3$, 75.0 MHz): 142.4−127.4 (arom.), 79.0 (Cp), 73.4−65.8 (Cp of Fc), 25.6 (CH$_2$ of dppe). ^{31}P NMR (CDCl$_3$, 121 MHz): 106.4 (Fe-dppe). Infrared (KBr) $\upsilon_{C≡C}$: 2 066 cm^{-1}. CV: (CH$_2$Cl$_2$; supporting electrolyte [(n-Bu)$_4$N][PF$_6$] 0.1 M; 293K): two reversible waves at $E_{1/2}$ = 0.00 V (iron-alkynyl) and 0.650 V (ferrocenyl) vs. FeCp*$_2$. MS (ESI m/z), calcd. for C$_{43}$H$_{38}$P$_2$Fe$_2$: 729.1, found: M$^+$ 728.1. Anal. Calc. for C$_{43}$H$_{38}$P$_2$Fe$_2$: C 70.90, H 5.26; found: C 70.56, H 5.21.

Synthesis of CpFe(dppe)C≡C−Fc*, 12. The complex **12** was synthesized from (i) **1** (319 mg, 0.89 mmol), dppe (355 mg, 0.89 mmol), and 1,2,3,4,5-pentamethyl,1′-ethynylferrocene (250 mg, 0.89 mmol) producing **9**; (ii) t-BuOK and **9** (100 mg, 0.89 mmol) following the general procedure for the synthesis of the iron-alkynyl complexes. A yellow powder was obtained, and the complex **12** (0.703 g, 99% yield) was separated by dissolving in ether, filtering through Celite, and evaporating the solvent.

Vinylidene complex **9**: ^{1}H NMR (400 MHz, (CD$_3$)$_2$CO), δ_{ppm}: 1.54 (s, 15H, CH$_3$ of Cp), 3.07−3.19 (m, 4H, CH$_2$ of dppe), 4.26 (t, 1H/C$_5$H$_4$), 4.48 (t, 1H/C$_5$H$_4$), 4.74 (t, 2H/C$_5$H$_4$), 5.40(s, 5H, Fc unsub), 5.74(s, CH), 7.38−7.67 (m, 20H, Ph of dppe), 2.06 (m, (CD$_3$)$_2$CO)). ^{13}C NMR (400 MHz, (CD$_3$)$_2$CO)), δ_{ppm}: 10.41 (CH$_3$/Cp*), 27.90 (CH$_2$/dppe), 69.74 (CH/C$_5$H$_4$), 79.91 (CH/C$_5$H$_4$), 80.20 (CH/C$_5$H$_4$), 81.02 (CH/C$_5$H$_4$), 88.67 (CH/C$_5$H$_4$), 89.15 (Fc unsub), 116.54 (═CFc), 129.09−132.72 (Ph of dppe), 364.08 (t, Fe═C), 29.14 and 205.46 (CD$_3$)$_2$CO). ^{31}P NMR (121 MHz, CD$_3$COCD$_3$), δ_{ppm}: 93.70 (Fe-dppe), −144.21 (m, PF$_6^-$). IR (KBr): 1957 cm^{-1} ($\nu_{C═C}$), 836 cm^{-1} (ν_{PF6}). MS (ESI m/z), calcd. for C$_{48}$H$_{49}$P$_2$Fe$_2$: 799.54, found: M$^+$ 798.19.

Alkynyl complex **12**: ^{1}H NMR (300 MHz, CDCl$_3$), δ_{ppm}: 1.60 (s, 15H, Cp*), 2.07 (m, 2H, CH$_2$), 2.56 (m, 2H, CH$_2$), 3.37 (s, 2H$_\alpha$,

Cp*Fc), 3.75 (s, 2H$_\beta$, Cp*Fc), 4.24 (s, 5H, Cp unsub), 7.24−8.0 (m, 20H, Ph, CH of dppe). ^{13}C NMR (75.0 MHz, CDCl$_3$), δ_{ppm}: 10.54 (CH$_3$, Cp*), 28.33 (CH$_2$), 69.77 (CH of Cp*Fc), 71.93 (CH of Cp*Fc), 78.76 (Cp unsub), 79.84 (Cq, Cp*), 127.28, 127.77 (Ph p), 128.51, 128.88 (Ph m), 131.75, 133.95 (Ph o), 138.74 (Ph ipso), 142.78 (Ph ipso). ^{31}P NMR (121 MHz, CDCl$_3$), δ_{ppm}: 106.27 (Fe-dppe). IR (KBr): 2068 cm^{-1} (ν_{CC}). MALDI-TOF: calc. m/z for M$^+$ (C$_{48}$H$_{48}$P$_2$Fe$_2$) 798.55; found 798.18. CV (CH$_2$Cl$_2$; supporting electrolyte [(n-Bu)$_4$N][PF$_6$] 0.1 M; 293 K): two reversible waves, $E_{1/2}$ = 0.00 and 0.48 V vs. FeCp$_2$*. Anal. Calcd for C$_{48}$H$_{48}$Fe$_2$P$_2$: C, 72.20, H, 6.06; found: C, 72.27, H, 6.18.

Synthesis of the Trimetallic Complexes 10 and 13. The complex **13** was synthesized from (i) **1** (179 mg, 0.5 mmol), dppe (199.6 mg, 0.5 mmol) and ethynylbiferrocene (197 mg, 0.5 mmol), which led to **10**; (ii) t-BuOK (112.2 mg, 2 equiv 1 mmol) and **10** following the general procedure for the synthesis of the iron−alkynyl complexes **13**. An orange powder was obtained, and **13** (0.365 mg, 80% yield) was separated by extraction with ether.

Complex **10**: ^{1}H NMR (400 MHz, (CD$_3$COCD$_3$), δ_{ppm}: 3.12 (m, 4H, CH$_2$ of dppe), 3.76 (t, 2H/C$_5$H$_4$), 3.98 (s, 5H, Cp unsub), 4.08(t, 4H/C$_5$H$_4$), 4.27(t, 2H/C$_5$H$_4$), 4.44(t, 4H/C$_5$H$_4$), 5.05 (s, CH), 5.39 (s, 5H, Fc unsub), 7.32−7.60 (m, 20H, Ph of dppe), 2.07(m, (CD$_3$COCD$_3$), 3.12(s, H$_2$O). ^{13}C NMR (100 MHz, (CD$_3$COCD$_3$), δppm: 27.95 (CH$_2$ of dppe), 66.55−68.82 (CH/C$_5$H$_4$), 69.29 (Cp unsub), 79.94 (Ci/C$_5$H$_4$), 89.40 (Fc unsub), 123.11 (≡CFc), 129.29−132.69 (Ph of dppe), 364.48 (t, Fe═C), 29.30 and 205.77 (CD$_3$COCD$_3$). ^{31}P NMR (121 MHz, CD$_3$COCD$_3$), δ_{ppm}: 94.29 (Fe-dppe), −142.90 (m, PF$_6^-$). IR (KBr): 1963 cm^{-1} ($\nu_{C═C}$), 839 cm^{-1} (ν_{PF6}). MALDI-TOF: calc. m/z for M$^+$ (C$_{43}$H$_{39}$Fe$_2$P$_2$) 913.4228, found 912.1177.

Complex **13**: ^{1}H NMR (300 MHz, C$_6$D$_6$), δ_{ppm}: 2.08 (m, 2H, CH$_2$), 2.67 (m, 2H, CH$_2$), 3.79 (t, 2H, BiFc), 3.81 (t, 2H, BiFc), 4.05 (s, 5H, Fc unsub), 4.06 (t, 2H, BiFc), 4.14 (t, 2H, BiFc), 4.15 (t, 2H, BiFc), 4.28 (s, 5H, Cp unsub), 4.38 (t, 2H, BiFc), 6.98−8.05 (m, 20H, Ph) ^{13}C NMR (200 MHz, C$_6$D$_6$), δ_{ppm}: 29.86 (CH$_2$), 66.93−70.89 (CH of BiFc), 79.18 (Cp unsub), 129.06−134.19 (Ph). ^{31}P NMR (121 MHz, CDCl$_3$), δ_{ppm}: 118.16 (Fe-dppe). IR (KBr): 2068 cm^{-1} (ν_{CC}). MALDI-TOF: calc. m/z for M$^+$ (C$_{53}$H$_{46}$Fe$_3$P$_2$) 912; found 912.118. CV (CH$_2$Cl$_2$; supporting electrolyte [(n-Bu)$_4$N][PF$_6$]; 293 K): three reversible waves, $E_{1/2}$ = 0.00 V, 0.049 V and 0.085 V (ΔE = 0.1 V) vs. FeCp$_2$*. Anal. Calc. for C$_{53}$H$_{46}$Fe$_3$P$_2$.CH$_2$Cl$_2$: C 65.03, H 4.85; found 65.28, H 4.93.

Syntheses of the Fulvalene Tetrairon Complexes 14 and 15. The complex **15** was synthesized from (i) [Fe$_2$(η^{10},μ_2-fulvalene)-(η^6-C$_6$H$_5$CH$_3$)$_2$] [PF$_6$]$_2$,[29] t-BuOK and allylbromide were stirred in THF at r.t. for 1 h, then the solvent was removed under vacuum, the residue was extracted with DCM and filtered. The solvent was removed under vacuum, and ^{1}H NMR in CD$_3$CN indicated monoallylation (butenyl chain). The complex (78 mg, 0.095 mmol), dppe (76 mg, 2 equiv., 0.19 mmol) and ethynylferrocene (40 mg, 2 equiv. 0.19 mmol) were introduced into a Schlenk flask, and visible-light photolysis was carried according to the general procedure for the synthesis of vinylidene complexes, which produced **14**; (ii) reaction between **14** and t-BuOK (21 mg, 2 equiv., 0.19 mmol) following the general procedure for the synthesis of the iron-alkynyl complexes produced **15** as a brown powder that was separated by extraction with ether (0.137 mg, 99% yield).

Complex **14**: ^{1}H NMR (400 MHz, (CD$_3$)$_2$CO), δ_{ppm}): 3.21(m, 8H, CH$_2$ of dppe), 3.23−4.22 (t, 16H/C$_5$H$_4$), 3.99 (s, 10H, Fc unsub), 5.26(s, 2H, CH), 7.28−7.58(m, 40H, Ph of dppe), 2.06 (m, (CD$_3$)$_2$CO). ^{13}C NMR (100 MHz, (CD$_3$)$_2$CO), δ_{ppm}: 26.94(CH$_2$/dppe), 67.44(CH/C$_5$H$_4$), 68.32 (CH/C$_5$H$_4$), 68.97 (CH/C$_5$H$_4$), 69.15 (Cp unsub), 86.36 (CH/C$_5$H$_4$), 88.19 (CH/C$_5$H$_4$), 88.55 (CH/C$_5$H$_4$), 122.75 (═CFc), 129.39−132.89 (Ph of dppe), 364.85 (t, Fe═C), 29.14 and 205.46 ((CD$_3$)$_2$CO). ^{31}P NMR (121 MHz, CD$_3$COCD$_3$, δ_{ppm}): 92.93 (Fe-dppe), −131.27 (m, PF$_6^-$). IR (KBr): 1966 cm^{-1} ($\nu_{C═C}$), 839 cm^{-1} (ν_{PF6}). MS (ESI m/z), calcd. for C$_{86}$H$_{76}$P$_4$Fe$_4$: 1456.7987, found: M$^+$ 1454.2416. Anal. Calcd for C$_{86}$H$_{76}$F$_{12}$Fe$_4$P$_6$.H$_2$O: C 58.53, H 4.45; found: C 58.27, H 4.75.

Complex **15**: ^{1}H NMR (300 MHz, CDCl$_3$), δ_{ppm}: 2.30−2.64 (d, 8H, CH$_2$CH$_2$ of dppe), 3.64−3.76 (d, 22H, CH of C$_5$H$_5$FeC$_5$H$_4$ and Fv), 4.61 (s, 4H, CH of Fv), 7.28−7.86 (m, 40H, arom. CH of dppe). ^{13}C NMR (75.0 MHz, CDCl$_3$), δ_{ppm}: 28.9−29.6 (CH$_2$ of dppe), 68.7, 68.9, 74.4 (CH of Cp and Fv), 81.8 (Cq of C$_5$H$_4$Fe and Fv), 90.4, 114.4 (C≡C), 127.2−142.7 (arom. of dppe). ^{31}P NMR (121 MHz, CDCl$_3$), δ_{ppm}: 105.05 (Fe-dppe). IR (KBr): 2068 cm^{-1} ($\nu_{C≡C}$). Anal. Calcd for C$_{86}$H$_{74}$Fe$_4$P$_4$: C, 71.00, H, 5.13; found: C, 71.27, H, 5.03. MALDI-TOF: calc. m/z for M$^+$ (C$_{86}$H$_{74}$Fe$_4$P$_4$) 1454.817; found 1454.15. CV (CH$_2$Cl$_2$; supporting electrolyte [n-Bu$_4$N][PF$_6$]; 293 K): three reversible waves, $E_{1/2}$= −0.14 V, 0.23 V, and 0.68 V (ΔE = 0.1 V) vs. FeCp$_2$*.

Synthesis of the Flexible Star Complex 20. The complex **20** was synthesized from (i) [FeCp(η^6-C$_6$H$_5$CH$_3$)] [PF$_6$] (1.100 g, 6 equiv. 3.072 mmol), dppe (1.224 g, 6 equiv. 3.072 mmol) and hexabutenylbenzene **16** (0.200 g, 0.512 mmol) producing **18**; (ii) t-BuOK (0.345 g, 6 equiv. 3.072 mmol) and **18** following the general procedure for the synthesis of the iron-akynyl complexes. A brown powder was obtained, and **20** (1.774 g, 99% yield) was separated by extraction with DCM.

Hexa(vinylidene) complex **18**: ^{31}P NMR (121 MHz, CD$_3$COCD$_3$), δ_{ppm}: 97.50 (Fe-dppe), −125.19, −160.24 (m, PF$_6$$^-$). IR (KBr): 1972 cm^{-1} ($\nu_{C≡C}$), 837 cm^{-1} (ν_{PF6}). Anal. Calcd for C$_{216}$H$_{204}$F$_{36}$Fe$_6$P$_{18}$.H$_2$O: C, 59.03, H, 4.72 Found: C, 58.74, H, 4.82.

Hexa(alkynyl) complex **20**: ^{1}H NMR (300 MHz, CDCl$_3$), δ_{ppm}: 1.58−2.75 (m, 36H, CH$_2$CH$_2$ of dppe and CH$_2$CH$_2$C≡C−), 3.80 (s, 12H, CH$_2$C≡C−), 4.21 (s, 30H, Cp), 7.30−7.93 (m, 120H, arom. CH of dppe). ^{31}P NMR (121 MHz, CDCl$_3$), δ_{ppm}: 106.67 (Fe-dppe). IR (KBr): 2086 cm^{-1} ($\nu_{C≡C}$). Anal. Calcd for C$_{216}$H$_{198}$Fe$_6$P$_{12}$.H$_2$O: C, 73.73, H, 5.72; found: C 73.51, H, 5.50. MALDI-TOF: calc. m/z for M$^+$ (C$_{216}$H$_{198}$Fe$_6$P$_{12}$) 3500.715; found 1167.263 (M$^+$/3). CV (CH$_2$Cl$_2$; supporting electrolyte [n-Bu$_4$N] [PF$_6$]; 293 K): one reversible wave, $E_{1/2}$ = 0.88 V vs. [CoCp$_2$] [PF$_6$]; ΔE = 0.07 V (0.08 V vs. FeCp$_2$*).

Syntheses of the Hexairon Complexes 19 and 21. The hexaalkynyl-iron star **21** was synthesized from (i) **1** (0.315 g, 0.882 mmol), dppe (0.351 g, 0.882 mmol), and hexaalkynylphenylbenzene **17** (0.100 g, 0.147 mmol) producing the vinylidene intermediate **19**; (ii) t-BuOK (0.109 g, 0.839 mmol) and **19** following the general procedure for the synthesis of the iron-alkynyl complexes. The star-shaped complex **21** was extracted with DCM and after, removing the solvent under vacuum, it was obtained as a brown powder in 99% yield.

^{1}H NMR (CDCl$_3$, 300 MHz): 7.74−7.20 (m, 120H, arom. CH of dppe), 6.27 and 6.00 (s, 24H, CH of benzene bridge), 4.21 (s, 30H, Cp), 2.54 and 2.16 (m, 24H, CH$_2$CH$_2$ of dppe). ^{13}C NMR (CDCl$_3$, 75.0 MHz): 140.4−127.1 (arom.), 78.9 (Cp), 31.2 (CH$_2$ of dppe). ^{31}P NMR (CDCl$_3$, 121 MHz): 105.8 (Fe-dppe). Anal. Calc. for C$_{240}$H$_{198}$P$_{12}$Fe$_6$(H$_2$O)$_2$: C 75.36, H 5.32; found: C 75.01 H 5.16. Infrared $v_{C≡C}$: 2 057 cm^{-1}. CV (CH$_2$Cl$_2$; supporting electrolyte [n-Bu$_4$N] [PF$_6$]; 293 K): one reversible wave: $E_{1/2}$ = 0.13 V vs FeCp$_2$*.

◾ ASSOCIATED CONTENT

ⓢ Supporting Information
General data, detailed experimental procedures, spectroscopic data for the known complexes, data, NMR and MALDI-TOF mass spectra, and cyclic voltammograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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◾ DEDICATION

[†]This article is dedicated to Claude Lapinte and Frédéric Paul who beautifully developed the synthesis and mixed-valence chemistry of the Cp*Fe(poly alcynyl) and cumulenylidene complexes.

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