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Elemental Carbon Chain Bridging Two Iron Centers: Syntheses and Spectroscopic Properties of $[Cp^*(dppe)Fe-C_4-FeCp^*(dppe)]^{n+}\cdot n[PF_6]^-$. X-ray Crystal Structure of the Mixed Valence Complex ($n = 1$)[†]

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Abstract: Reaction of [Fe(Cp*)(dppe)Cl] [**1**, Cp* = η^5-C_5Me_5, dppe = η^2-ethylenebis(diphenylphosphine)] and NH_4PF_6 in methanol with equiv of $Me_3SiC{\equiv}CH$ produced the vinylidene complex $[Fe(Cp^*)(dppe)({=}C{=}CH_2)][PF_6]$ (**2**) isolated in 89% yield. The complex **2** was readily deprotonated by $KOBu^t$ in tetrahydrofuran (THF), giving the ethynyl iron complex $Fe(Cp^*)(dppe)({-}C{\equiv}CH)$ (**3**) isolated after workup as a thermally stable orange solid in 98% yield. The addition of 0.95 equiv of $[Cp_2Fe][PF_6]$ to a −80 °C solution of **3** gave the low-spin Fe(III) intermediate **3[PF$_6$]** characterized by ESR spectroscopy. Upon stirring for 5 h, **3[PF$_6$]** produced a brown solution from which the bis(vinylidene) complex $[Fe(Cp^*)(dppe)]({=}C{=}CH{-}HC{=}C{=})[(dppe)(Cp^*)Fe][PF_6]_2$ was isolated (**4**, 87%) as a stable compound. The compound **4** was reacted with 2 equiv of potassium *tert*-butoxide to give the μ-η^1:η^1-butadiyndiyl C_4 complex **5**, isolated as a brown powder in 92% yield. Complex **5** is characterized by ^1H, ^{13}C, and ^{31}P NMR and by IR, Mössbauer, and microanalysis. A variable-temperature ^{31}P NMR experiment evidenced a rotation barrier ($\Delta G^\ddagger = 41.4$ kJ·mol^{-1} (9.90 kcal·mol^{-1})) in agreement with a slow rotation about the iron−C_4−iron axis. CV analysis of the butadiyne bridged complex **5** from −1.2 to 0.6 V displays two reversible one-electron oxidation waves. The two redox processes are separated by 0.720 V corresponding to a large comproportionation constant ($K_c = 1.6 \times 10^{12}$). Oxidation of **5** with 2 equiv of $[Cp_2Fe][PF_6]$ gave the salt **5[PF$_6$]$_2$**, isolated in 91% yield. It is a thermally and air stable compound which is characterized by IR, ESR, NMR, and Mössbauer spectroscopies. Its CV waves are identical to those of its parent complex **5**. The addition of 1 equiv of $[FeCp_2][PF_6]$ to **5** in CH_2Cl_2 produced the Fe(III)−Fe(II) complex **5[PF$_6$]** (92% yield). The air stable mixed-valence compound **5[PF$_6$]** is characterized by elemental analysis, IR, NIR, Mössbauer, and ESR spectroscopies, and magnetic susceptibility. The X-ray crystal structure of **5[PF$_6$]** shows that it crystallizes in the monoclinic space group *P*21/*n* with unit cell parameters $a = 19.401(3)$ Å, $b = 20.205(7)$ Å, $c = 8.458(3)$ Å, $\beta = 90.08(2)°$, and $Z = 2$. The structure was solved and refined (5732 reflexions) to the final values $R = 0.051$ and $R_w = 0.047$. It is established that **5[PF$_6$]** is a nontrapped mixed-valence complex on the infrared timescale and the intervalence transition band allowed the determination of a strong electronic coupling ($V_{ab} = 0.47$ eV).

The existence of long chains of carbon constitutes an intriguing aspect of carbon chemistry.[1] These infinite one-dimensional rods made of alkyne units have been observed during laser vaporization of graphite and are detected in the atmosphere of certain stars.[2] Some experiments have shown that clusters with more than 100 carbon atoms can be formed, and evidence for linearity of these clusters has been obtained up to 24 carbon atoms.[3] Such polyynes are expected to exhibit, among other characteristics, bulk spin alignment,[4] one-dimensional conductivity,[5] or nonlinear optical properties.[6] The incorporation of metals into these systems is under active investigations because such materials could have a large diversity of oxidation states and ligand environments, and due to the polarizable d electrons, increased nonlinear properties are likely.[6] The one-dimensional units are exceptional linking ligands in that π-electron delocalization over all carbon atoms in the chain enables electron transfer between two transition metals to occur. Owing to their potential interest in material science there is currently rapidly growing interest in the

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chemical, physical and material properties of these compounds ($L_nMC_xM'L'_{n'}$).[7-9]

We have previously found that the iron(III) alkyl [FeCp*(dppe)R]X,[10] alkyne [FeCp*(dppe)(C≡CR)]X,[11] and hydride [FeCp*(dppe)H]X[12] complexes are stable and readily generated in high yields, showing the capacity of the electron-rich moeity [FeCp*(dppe)] to stabilize 17-electron iron(III) half-sandwich compounds. We thought this fragment suitable for elaboration of new bimetallic compounds {[Cp*Fe(dppe)]-C_4-[(dppe)-FeCp*]}$^{n+}$ ($n = 0, 1, 2$) which differ only in the oxidation state of the metal centers. Our initial objective was the ligand–ligand coupling of iron ethynyl complex [Cp*Fe(dppe)(C≡CH)] (**3**) *via* an iron(III) intermediate to produce the μ-η^1:η^1-butadiyndiyl complex [Cp*Fe(dppe)]C_4[(dppe)FeCp*] (**5**), and we describe the synthesis and the redox properties of this compound below. We also report the synthesis and the characteristic features of the one and two odd electron complexes [Cp*Fe(dppe)]C_4[(dppe)FeCp*][PF_6]$_n$ ($n = 1$, **5[PF₆]**; $n = 2$, **5[PF₆]₂**. Part of this study has been communicated.[13] While this work was in progress, Gladysz reported the syntheses of the related rhenium complexes of the formula [Cp*Re(NO)(PPh_3)C_4(PPh_3)(NO)ReCp*]$^{n+}\cdot nPF_6^-$ ($n = 0, 1, 2$).[14] These important and complementary results emphasize the rapidly growing interest in these new compounds.

Results and Discussion

1. Synthesis and Characterization of the Ethynyl Complex Fe(Cp*)(dppe)(C≡CH) (3). The complex **3** was prepared in a two-step procedure involving the formation and isolation of the corresponding vinylidene iron complex [Fe(Cp*)(dppe)(=C=CH_2)][PF_6], following the route previously used to prepare the related mononuclear alkynyl complexes Fe(Cp*)(dppe)(C≡CR) (R = Bu^t, Ph).[11] The most general synthetic route to the vinylidene complexes [M]$^+$=C=C(H)(R) consists of terminal alkynes reacting with [M]–X complexes in the presence of a halide anion abstractor.[15,16] Thus, treatment of [Fe(Cp*)(dppe)Cl] (**1**) and NH_4PF_6 in methanol with 1 equiv of $Me_3SiC{\equiv}CH$ produced after 16 h a light-orange solution from which the vinylidene complex [Fe(Cp*)(dppe)(=C=CH_2)][PF_6] (**2**) was isolated as a light-orange solid in 95% yield (eq 1).

$$\underset{\mathbf{1}}{[\mathrm{Fe(Cp^*)(dppe)Cl}]} + \mathrm{Me_3SiC{\equiv}CH} \xrightarrow[\mathrm{MeOH}]{\mathrm{NH_4PF_6}} \underset{\mathbf{2}}{[\mathrm{Fe(Cp^*)(dppe)({=}C{=}CH_2)}][\mathrm{PF_6}]} \qquad (1)$$

Subsequent crystallization gave analytically pure **2** (89%), which was characterized by IR and ^{1}H, ^{13}C, and ^{31}P NMR. The infrared spectrum reveals a strong vinylidene C=C stretch at 1612 cm^{-1}. The vinylidene ligand in **2** displays a vinylic ^{1}H NMR triplet (δ_H 3.93, $^4J_{PH} = 3.6$ Hz), a highly deshielded C_α triplet (δ_C 354.7, $^2J_{PC} = 33$ Hz), and a vinylic C_β singlet (δ_C 103.8), which are typical of metal phosphine-substituted ethenylidene complexes.[15]

The vinylidene complex **2** was readily deprotonated by KOBu^t in tetrahydrofuran (THF), giving the ethynyl iron complex Fe(Cp*)(dppe)(–C≡CH) (**3**) isolated after workup as a thermally stable orange solid in 98% yield (eq 2). No further crystallization was needed to obtain an analytically pure sample. The acetylide complex **3** was characterized by IR and ^{1}H, ^{13}C, and ^{31}P NMR. The diagnostic medium IR $\nu_{C\equiv C}$ is observed at 1910 cm^{-1}. The NMR spectra display a phosphorus-coupled triplet for the ethynyl hydrogen (δ_H 1.70, $^4J_{PH} = 2.9$ Hz) and a triplet and singlet for the ethynyl carbons (δ_C (C_α) 129.5, $^2J_{PC} = 38$ Hz; δ_C (C_β) 102.7).

$$\underset{\mathbf{2}}{[\mathrm{Fe(Cp^*)(dppe)({=}C{=}CH_2)}][\mathrm{PF_6}]} \xrightarrow[\mathrm{THF}]{\mathrm{KOBu^t}} \underset{\mathbf{3}}{[\mathrm{Fe(Cp^*)(dppe)(C{\equiv}CH)}]} \qquad (2)$$

2. Cyclic Voltammogram and Chemical Oxidation of Fe(Cp*)(dppe)(C≡CH) (3). The initial scan in the cyclic voltammogram of complex **3** from +1 to −1 V (*vs* SCE) displays a chemically quasi-reversible oxidation wave at a platinum electrode (CH_2Cl_2, 0.1 M tetrabutylammonium hexafluorophosphate, 0.100 V s^{-1}, $E_p{}^a = -0.170$ V, $E_p{}^c = -0.070$ V). The ratio of the cathodic to anodic peak current is less than unity ($i_a/i_c = 0.8$). The occurrence of one-electron transfer reaction and subsequent hydrogen atom transfer from the solvent was established by the isolation of the vinylidene complex **2** as the single product quantitatively formed when the alkenyl complex **3** was treated with 1 equiv of [Cp_2Fe][PF_6] in CH_2Cl_2 at 20 °C (eqs 3 and 4). The low-spin iron(III) character of the intermediate **3[PF₆]** is established by ESR spectroscopy. Ferrocenium was added to a quartz tube containing a CH_2Cl_2/$ClCH_2CH_2Cl$ solution of **3** cooled to −80 °C. Argon was bubbled for 1 min to stir the mixture, and the ESR spectrum recorded at 77 K exhibits three unresolved broad tensor components ($g_1 = 1.977$, $g_2 = 2.034$, $g_3 = 2.457$) characteristic of the 17-electron alkynyl complexes.[11]

$$\underset{\mathbf{3}}{[\mathrm{Fe(Cp^*)(dppe)(C{\equiv}CH)}]} + [\mathrm{Cp_2Fe}][\mathrm{PF_6}] \xrightarrow{20\ ^\circ\mathrm{C,\ CH_2Cl_2}} \underset{\mathbf{3[PF_6]}}{[\mathrm{Fe(Cp^*)(dppe)(C{\equiv}CH)}][\mathrm{PF_6}]} \qquad (3)$$

$$\mathbf{3[PF_6]} + \mathrm{CH_2Cl_2} \xrightarrow{20\ ^\circ\mathrm{C}} \underset{\mathbf{2}}{[\mathrm{Fe(Cp^*)(dppe)({=}C{=}CH_2)}][\mathrm{PF_6}]} + [\mathrm{CHCl_2}]^\bullet \qquad (4)$$

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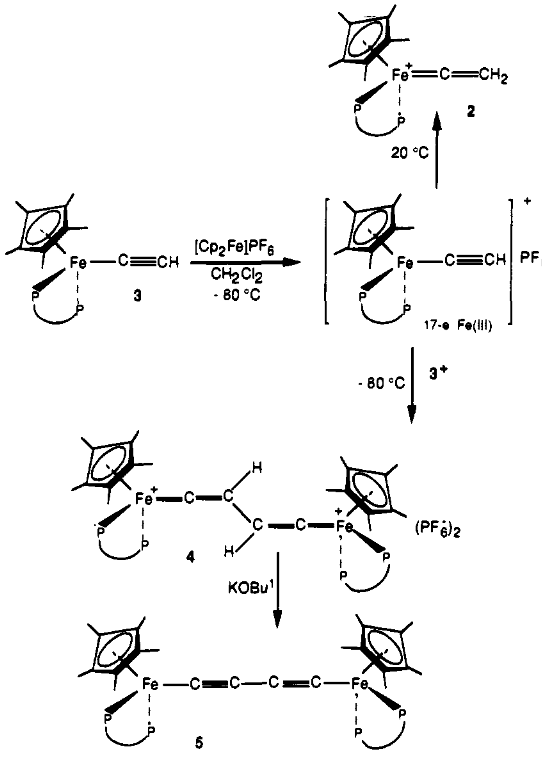
Scheme 1



Having established that the 17-electron iron(III) ethynyl complex [Fe(Cp*)(dppe)(C≡CH)][PF$_6$] ([**3**]$^+$) is stable enough in CH$_2$Cl$_2$ at −80 °C to be accumulated in the solution, the synthesis of the bis(vinylidene) complex by ligand−ligand coupling of two cationic iron ethynyl units was considered to be viable. The addition of 0.95 equiv of [Cp$_2$Fe][PF$_6$] to a solution of **3** at −80 °C and stirring for 5 h produced a brown solution from which a solid was precipitated by addition of diethyl ether (Scheme 1). After removal of the supernatant liquor, the solid was washed with diethyl ether. Recrystallization from CH$_2$Cl$_2$−pentane and drying in vacuo gave an air stable brown solid identified as the binuclear complex [Fe(Cp*)(dppe)](=C=CH−HC=C=)[(dppe)(Cp*)Fe][PF$_6$]$_2$ (**4**, 87%). The binuclear vinylidene complex **4** exhibits characteristic spectroscopic features. In the ^{1}H NMR, the resonance for the C$_\beta$ proton is observed downfield as a singlet (δ_H 4.37). In the ^{13}C NMR, the resonance for the C$_\alpha$ is a virtual triplet at δ_C 360.5 ($^2J_{PC}$ = 34 Hz) while the doublet signal at δ_C 108.0 ($^1J_{CH}$ = 159 Hz) is characteristic of the C$_\beta$ atoms. The characteristic medium-intensity vinylidene IR $\nu_{C=C}$ stretch (Nujol, 1585 cm^{-1}) is shifted toward a lower energy with respect to the mononuclear complex **2**.

In common with many organometallic radicals, the 17-electron intermediate, namely the iron(III) ethynyl cation [Fe(Cp*)(dppe)(−C≡CH)][PF$_6$] may tend to dimerize.[17] If the radical center is located on the transition metal and if the ligands are bulky enough to bring about steric protection of the metal center, then dimerization and other radical-type reactions (e.g., proton abstraction) do not occur, as is observed for the substituted σ-ethynyl complexes [Fe(Cp*)(dppe)(−C≡CR)][PF$_6$] (R = Bu^t, C$_6$H$_5$).[11] Dimerization of the 17-electron compounds through the metal center is most often observed. However the ligand−ligand coupling could be observed if the metal center is crowded to such an extent as to prevent metal−metal bond formation. To be favored, such a reaction needs the presence of one unsaturated ligand with a π system to enable the delocalization of the spin density. Similarly, the dimerization of the related iron(III) vinyl complexes has also been observed.[18] The formation of the μ-η^1:η^1-bis(vinylidene) complex **4** through outer-sphere oxidation of the σ-alkynyl complex **3** should be distinguished from Gladysz's coupling reaction of the rhenium ethynyl complex (Cp*)Re(NO)(PPh$_3$)(C≡CH) promoted by Cu(OAc)$_2$ in pyridine, which is closely connected with the general procedure for the oxidative coupling of organic acetylenic compounds.[19] Our reaction is more closely related to the Selegue synthesis of the dimethyl bis(vinylidene) complex [Fe(Cp)(dppe)](=C=CMe−MeC=C=)[(dppe)(Cp)Fe][BF$_4$]$_2$ resulting from the iodosobenzene oxidation of the cationic vinylidene complex [Fe(Cp)(dppe)(C=CMe$_2$)][BF$_4$] via a proposed iron(III) dication intermediate.[20]

3. Synthesis of the Butadiyndiyl Complex [Fe(Cp*)(dppe)](C≡C)−(C≡C)[(dppe)(Cp*)Fe] (5). Reaction of the vinylidene complex **4** with 2 equiv of potassium *tert*-butoxide gave the μ-η^1:η^1-butadiyndiyl C$_4$ complex **5** as a brown powder in 92% yield after workup (Scheme 1). Although the solubility of the dimeric complex was lower than those of the monuclear precursors **3**, a similar procedure was successfully used. Complex **5** was characterized by ^{1}H, ^{13}C, and ^{31}P NMR and by IR, Mössbauer, and microanalysis. Surprisingly, the ^{13}C resonances of the C$_4$ bridge are not observed in the room-temperature ^{13}C NMR spectrum which displays only the signal expected for the organometallic moieties [FeCp*(dppe)]. Note that the acetylenic carbons are not observed in the ^{13}C NMR spectrum in the case of the [CpRu(PPh$_3$)$_2$](μ-C$_4$) complex.[9g] The identity of the structure is based on the low-temperature ^{13}C NMR spectrum (C$_7$D$_8$, 193 K) where a phosphorus-coupled virtual triplet for the C$_\alpha$ atoms (δ_C 99.7, $^2J_{PC}$ = 41 Hz) and a singlet for the β carbon atoms (δ_C 110.2) are clearly shown. The IR spectrum exhibits two $\nu_{C\equiv C}$ absorptions (Nujol, cm^{-1}) at 1880 (w) and 1955 (m).

The most convenient probes to provide evidence for the fluxional behavior of **5** are the phosphorus atoms of the dppe. The ^{31}P{^{1}H} NMR spectrum at room temperature shows a single broad resonance (C$_6$D$_6$, 293 K, δ_P 99.9). A ^{31}P NMR spectrum recorded at −193 K exhibits two sharp singlets (C$_7$D$_8$, 99.5, 101.9) with exactly the same intensity. Upon warming, the two signals broaden and coalesce at 220 K (121.5 MHz). The observed barrier corresponds to a free energy of activation, $\Delta G^{\ddagger}$, for bond rotation of 41.4 kJ·mol^{-1} (9.90 kcal·mol^{-1}). In the case of a slow rotation process about the iron−C4−iron axis giving rise to different conformers which slowly interconvert in solution, a spectrum with more than two signals must be expected. It should be concluded that the two-site averaging process observed comes from the inequivalence of the two phosphorus atoms of the dppe ligand due to steric hindrance.[21] The X-ray data of the cation **5[PF$_6$]** which shows that the P(1)−Fe−C(11) and P(2)−Fe−C(11) angles are respectively of 93.4(2) and 84.4(2) (*vide infra*) greatly supports the assumption of unsymetrical dppe ligands.

4. CV Analysis of [Fe(Cp*)(dppe)](C≡C)−(C≡C)[(dppe)(Cp*)Fe] (5). The initial scan in the cyclic voltammogram of the butadiyne bridged complex **5** from −1.2 to +0.6 V displays two reversible oxidation waves in dichloromethane showing that, at the electrode, the neutral dimer undergoes two successive one-electrode oxidations to yield the mono- and dications,

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[21] This supposes a J_{PP} = 0 Hz for the unsymmetrical dppe ligand.

Table 1. Electrochemical Data for Compound **5** in CH_2Cl_2 (0.1 M $[nBu_4N][PF_6]$; 20 °C, Pt Electrodes, Sweep Rate 0.100 V s^{-1})

compds	E_1^0 [a]	$(E_p^a - E_p^c)_1$	E_2^0 [a]	$(E_p^a - E_p^c)_2$	$\lvert E_1^0 - E_2^0 \rvert$	K_c [b]
5	−0.675	0.060	+0.045	0.060	0.720	1.60×10^{12}
3	−0.120	0.100				

[a] E_0 are given in V *vs* SCE; ferrocene−ferrocenium couple was used as an internal calibrant for the potential measurements. [b] $\ln K_c = (n_1E_1^0 - n_2E_2^0)F/RT$ with $n_1 = n_2 = 1$.

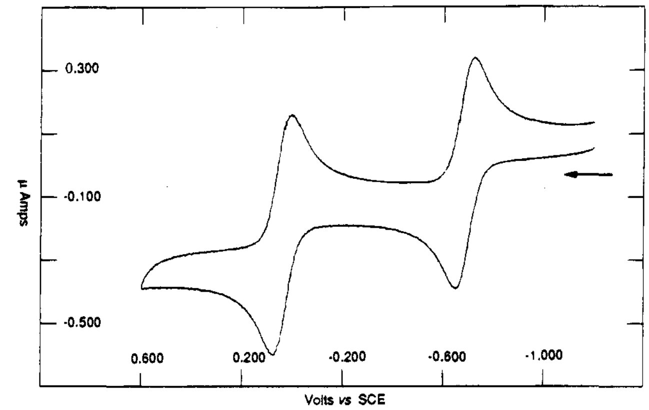

Figure 1. Cyclic voltammogram for $[\{Fe(Cp^*)(\eta^2\text{-dppe})\}_2\text{-}\mu\text{-}(C{\equiv}C{-}C{\equiv}C)]$ (**5**) in 0.1 M $[nBu_4N][PF_6]/CH_2Cl_2$; Pt electrode; V *vs* SCE; scan rate = 100 mV/s; 20 °C.

respectively (eq 5, Figure 1). The reversibility is determined,

$$\underset{\mathbf{5}}{Fe(II){-}C_4{-}Fe(II)} \overset{-e}{\rightleftharpoons} \underset{\mathbf{5}^+}{[Fe(II){-}C_4{-}Fe(III)]^+} \overset{-e}{\rightleftharpoons} \underset{\mathbf{5}^{2+}}{[Fe(III){-}C_4{-}Fe(III)]^{2+}} \quad (5)$$

for both waves, by the peak separation (ΔE_p) and the ratio of the anodic to cathodic peak current (i_{pa}/i_{pc}). The ΔE_p values are 0.060 V, and no variation with the scan rate is observed. A plot of i_{pa} against the square root of the scan speed is linear across a range of 0.050−0.500 V s^{-1} (correlation coefficient > 0.99), as expected for a diffusion-controlled electrode process, and the measurement of the ratio $i_{pa}/i_{pc} = 1$ for the two waves showed the chemical reversibility of the two one-electron transfers. The data for peak potentials and current peak ratio are compiled in Table 1. The comparison of these potentials with that of the corresponding monomer **3** demonstrates the electron−donor effect of the second iron center reducing the first oxidation potential by 0.55 V. The role of the electron-donating−C_4−bridge is also illustrated by comparison of the oxidation potential of the monocation $\mathbf{5}^+$ and the monomer **3**; it is large enough to balance the electron-withdrawing effect of the positive charge.

The two redox processes are well separated, and the potential difference between the two waves in this dimer is very large, slightly more than 0.7 V. The difference $|E_1^0 - E_2^0|$ can be attributed to strong exchange interactions between the two iron centers propagated throughout the orbitals of the −C≡C−C≡C− bridge. This reflects the extent of delocalization between metal centers in the ground state. The important stabilization of the mixed-valence Fe(II)−Fe(III) state is shown by the very large value of the comproportionation constant, $K_c = 1.6 \times 10^{12}$. The one-dimensional−C_4−bridge acts as a molecular wire to convey the odd electron from one metal center to the other. Indeed, incorporation of a phenyl ring between the two ethynyl units of the diyne ($[FeCp^*(dppe)]{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}C{-}[FeCp^*(dppe)]$) reduces the exchange interactions as shown by a significant lowering of the K_c value to 2.6×10^4.[22] Odd electron C_x bridged dimers available in several oxidation states of the metal are very rare, since, besides the compound reported here, only the Gladysz rhenium complex is known. For the latter, $\Delta E_p = 0.5$ V, corresponding to a K_c value of ca 3×10^8.[23] This shows that the delocalization greatly favored by the $-C_x-$ bridge strongly depends on the electronic structure of the metal unit. Note that the value for **5** is among the highest described in the literature. In the pioneering reports from Creutz and Taube, the data found for the ruthenium complexes range around $K_c = 10^6$ and the highest value ($K_c = 10^{13}$) was found for the μ-cyanogen−bis(pentaammineruthenium) complex.[24] For the accumulated data on mixed valence biferrocenes and related compounds, the K_c values range from 50 to 10^{10} and similar values were also reported for mixed-valence chromium compounds.[24−27] Very high values of up to 10^{10} were also reported for Fe(II)−Fe(I) fulvalene complexes.[28] The electrochemical features of the complex **5** proved that the intermediate cation radical $\mathbf{5}^+$ and the dication $\mathbf{5}^{2+}$ were viable synthetic targets, and the physical properties of these were expected to be unique.

5. Synthesis and Characterization of the 34-Electron Complex $[Fe(Cp^*)(dppe)](C{\equiv}C){-}(C{\equiv}C)[(dppe)(Cp^*)Fe][PF_6]_2$·$\mathbf{5}[PF_6]_2$. Guided by cyclic voltammetry data, we oxidized **5** with 2 equiv of $[Cp_2Fe][PF_6]$. The addition of the oxidizing reagent to a CH_2Cl_2 solution of **5** resulted in a rapid color change from brown to deep blue. After concentration and precipitation by pentane, the salt $\mathbf{5}[PF_6]_2$ was isolated as a beautiful deep blue microcrystalline solid. It is a thermally and air stable compound with CV waves identical to those of its parent complex **5**. Crystallization from a CH_2Cl_2−pentane mixture gave analytically pure $\mathbf{5}[PF_6]_2$ (91%), which was characterized by IR, ESR, NMR, Mössbauer, and electronic spectroscopies. The IR spectrum displays the two $\nu_{(C\equiv C)}$ band stretchings shifted to higher energy in the dication (1950, 2160 cm^{-1}), consistent with formation of two equivalent Fe(III) sites. However, oxidation of the mononuclear species $[Fe(Cp^*)(\eta^2dppe)(C{\equiv}CR)]$ (R = Bu^t, Ph) results in a shift of the C≡C band toward the lower energy, from (cm^{-1}) 2066 and 2049 to 2035 and 2022.[11] A similar behavior was also observed for the two-electron oxidation of $[Fe(Cp^*)(dppe)](C{\equiv}C){-}C_6H_4{-}(C{\equiv}C)[(dppe)(Cp^*)Fe]$.[22] The higher stretching frequency for the C≡C triple bond in complex $\mathbf{5}[PF_6]_2$ was unexpected and indicates that there is no contribution from the cumulenic resonance structure

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(23) Calculated from ref 14b and personnal communication from J. A. Gladysz.

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(27) (a) Van Order, N., Jr.; Geiger, W. E.; Bitterwolf, T. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 5680. (b) Geiger, W. E.; Van Order, N., Jr.; Pierce, D. T.; Bitterwolf, T. E.; Rheingold, A. L.; Chasteen, N. D. *Organometallics* **1991**, *10*, 2403.

(28) Desbois, M. H.; Astruc, D. *J. Am. Chem. Soc.* **1989**, *8*, 1841.

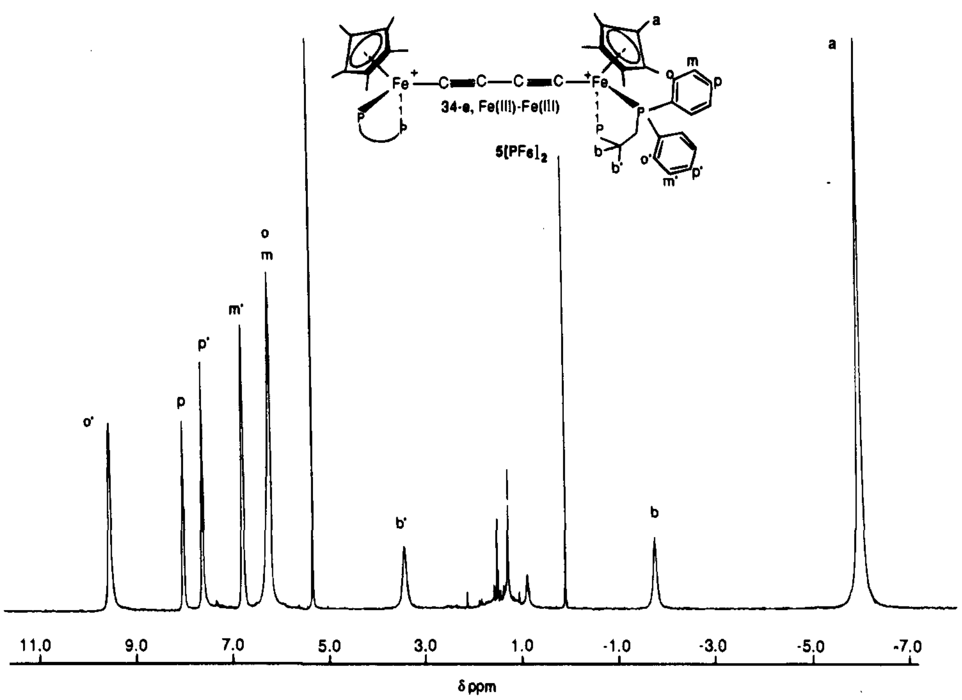


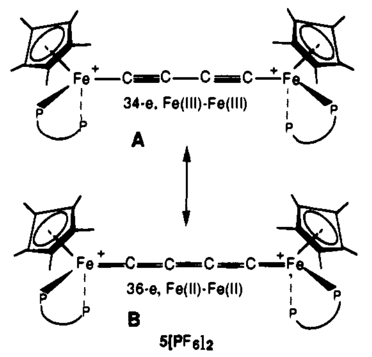
Figure 2. ^{1}H NMR spectrum (CD_2Cl_2, 293 K) for [{Fe(Cp*)(η^2dppe)}$_2$-μ-(C≡C—C≡C)][PF_6] (**5[PF$_6$]$_2$**) Unlabeled signals are due to solvent and diamagnetic impurities.

described by the canonical form B in Scheme 2.[29] In contrast with the Re—C≡C—C≡C—Re complex for which the two-electron oxidation produces the cumulenic linkage [Re=C=C=C=C=Re]$^{2+}$,[14a] in our iron series, the triple-bond character of two ethynyl groups of bridge is higher in the Fe(III)—C_4—Fe(III) complex than in the Fe(II)—C_4—Fe(II) one.

The electronic structure of the diyne linkage is in agreement with the Fe(III) low-spin character of the two metal centers established by Mössbauer spectrocospy. The Mössbauer spectra parameters (see the Experimental Section) of a crystallized sample of **5[PF$_6$]$_2$** recorded at zero field (77 K) are typical of a pure iron(III) center in the Cp*Fe(dppe) half-sandwich series.[10] A significant lowering of the isomeric shift from 0.27 to 0.18 mm^{-1} is observed between the mononuclear Fe(III) ethynyl complex and **5[PF$_6$]$_2$**. It has been shown that this variation in a homogeneous series can be interpreted by an increase of the electronic density at the iron nucleus.[30]

Magnetic susceptibility measurements of the complex **5[PF$_6$]$_2$** were performed on a SQUID magnetometer over the temperature range 5—300 K. The molar paramagnetic susceptibility (χ_M) *vs* temperature fits with the Curie—Weiss law, $\chi_M = \chi_0 + C/(T - \theta)$ with $\theta = -13.6$ K and $\chi_0 = 8.686 \times 10^{-3}$ emu/mol. There is a gradual decrease of χ_M with an increase in temperature. In the range 20—300 K, the magnetic moment is found to be rather weak ($\mu_{eff} = 1.37$ μ_B) and its determination in solution by the Evans method (1.29 μ_B) probes the measurements in the solid state, indicating the molecular origin of the magnetic behavior. This value, significantly lower than that determined for the mononuclear compound [Fe(Cp*)(η^2dppe)(C≡CPh)][PF_6] (1.60 μ_B),[11] is evidence of the paramagnetic character of **5[PF$_6$]$_2$**, and the negative θ value shows a dominant antiferromagnetic exchange between the two $S = 1/2$ spin densities on each atomic site. The $S = 0$ ground state is confirmed by the fact that the complex **5[PF$_6$]$_2$** (in a CH_2Cl_2—$C_2H_4Cl_2$ (1:1) glass) is ESR silent at 77 K.

Scheme 2



The strong antiferromagnetic interaction which prevents the recording of the ESR spectrum allows observation of well-resolved NMR spectra. The ^{1}H NMR spectrum (CD_2Cl_2, 293 K) exhibits eight resonances between −7 and +10 ppm. As depicted in Figure 2, the spectrum exhibits three groups of resonances. In the upfield region, a single and intense signal corresponding to the five methyl groups is observed (δ −6.03), the two types of methylene protons of the dppe are observed in the middle of the spectrum (δ −1.79, +3.40), and the down field region is occupied by five distinct signals with a 4—2—1—1—2 relative intensity attributed to phenyl resonances (δ 6.17, 6.74, 7.58, 7.98, 9.50). Depending on their orientation toward the all carbon bridge or to the outside of the molecule, two different phenyl groups exist in the molecule. The two signals with intensity of unity correspond to the protons in the para position as confirmed by a broad resonance for one proton and by a pseudo-triplet for the other due to coupling with the proton in the meta position. Selective irradiation of the meta proton resonances gives rise to a respective singlet for the proton located in the para position, thus allowing complete assignment of the spectrum (see the Experimental Section).

It was shown for related monomeric 17-electron alkyl iron complexes that the predominant ligand contribution to the delocalization of the unpaired electron occurs on the Cp* ring.[10] In agreement with this result, the upfield shift of the methyl

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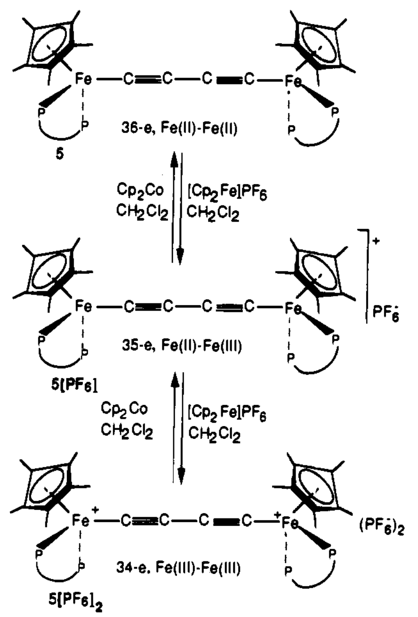
[29] The probability that the IR bands are not purely C≡C in character cannot be excluded, and the spectrum might be the result of a combination involving an overtone of lower frequency bands.

[30] Le Beuze, A.; Lissillour, R.; Weber, J. *Organometallics* **1993**, *12*, 47.

Scheme 3



resonance of the Cp* (δ_{iso} 7.58, $w_{1/2}$ = 30 Hz) provides evidence for the paramagnetic character of the dication. However, for the mononuclear compounds, the upfield shift was much more pronounced and broad resonances were observed for the methyl proton (δ_{iso} 19.11, $w_{1/2}$ = 2400 Hz). Predictably for a paramagnetic complex, variable-temperature ^{1}H NMR spectroscopy showed that the isotropic chemical shift (δ_{iso}) of all the peaks exhibited a linear relationship *vs* 1/*T* over the range 193−298 K in agreement with the Curie law.[31] As expected for a $S = 0$ ground state, an important deshielding was observed with the lowering of the temperature (193 K, δ_{iso} 1.32, $w_{1/2}$ = 60 Hz for the Cp* resonance). The line widths of the resonances increased with decreasing temperatures, probably due to decreasing electronic relaxation times at lower temperatures.

6. Synthesis and X-ray Structure of the 35-Electron Complex [Fe(Cp*)(dppe)](C≡C)−(C≡C)[(dppe)(Cp*)Fe][PF$_6$] (5[PF$_6$]). The addition of 1 equiv of [FeCp$_2$][PF$_6$] to a solution of **5** in CH$_2$Cl$_2$ resulted in a rapid color change from brown to deep green. After precipitation by pentane, the Fe(III)−Fe(II) complex **5[PF$_6$]** was isolated as green microcrystals in 92% yield. As expected from the high value of K_c, it is a thermally stable complex, and its CV exhibits two waves identical with those of its parent complex **5**. Oxidation of **5** with a stoichiometric amount of **5[PF$_6$]$_2$** gave 2 equiv of **5-[PF$_6$]**, whereas the reverse reduction of **5[PF$_6$]** with 1 equiv of cobaltocene afforded the orange-brown complex **5**, establishing the reversible character of the chemical electron transfer process (Scheme 3). The air stable compound **5[PF$_6$]** was characterized by elemental analysis, IR, Mössbauer electronic, and ESR spectroscopies, and magnetic susceptibility, and the crystal structure was determined.

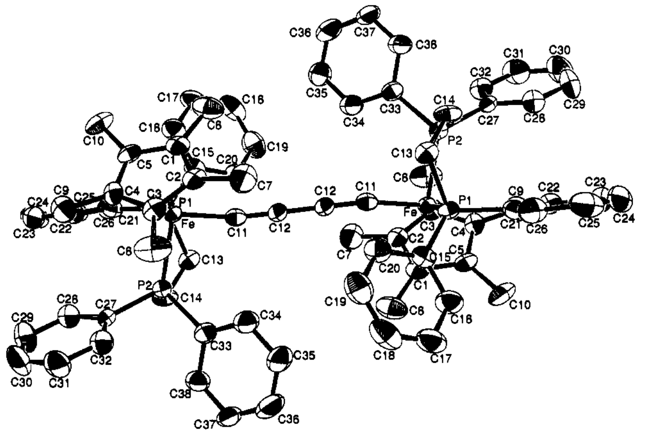


Figure 3. X-ray structure of the complex [{Fe(Cp*)(η^2dppe)}$_2$-μ-(C≡C−C≡C)][PF$_6$] (**5[PF$_6$]**).

Table 2. Experimental Crystallographic Data for **5[PF$_6$]**

formula	$C_{76}H_{78}Fe_2P_4{\cdot}PF_6$
fw	1372.02
cryst syst	monoclinic
space group	*P*2$_1$/*n*
a, Å	19.401(3)
b, Å	20.205(7)
c, Å	8.458(3)
α, deg	
β, deg	90.08(2)
γ, deg	
V, Å^3	3315(2)
Z	2
d_{calcd}, Mg m^{-3}	1.374
cryst size, mm	0.08 × 0.38 × 0.42
$2\theta_{max}$, deg	50
hkl range	0.22;0.23;1,−9.9)
diffractometer	CAD4 Enraf-Nonius
radiatn Mo Kα (*λ*), Å	0.71069
monochromator	graphite crystal
T, K	294
F(000)	1430
absn coeff (*μ*), cm-1	6.14
scan type	$\omega/2\theta = 1$
t_{max}, s	60
no. of reflns read	5725
no. of unique reflns	2538 [$I > 2\sigma(I)$]
R_{int} (from merging equiv reflns)	0.026
R(isotropic)	0.090
R(anisotropic)	0.072
Fourier difference	0.58−0.40
N(obs)/*N*(var)	2538/401
final *R*	0.051
R_w	0.047
Σ*w*	2.55
max residual, e Å^{-3}, Δ/σ	0.44, 0.19

Table 3. Selected Bond Distances (Å) and Angles (deg) for **5[PF$_6$]**

Fe−P(1)	2.238(2)	C(11)−C(12)	1.236(9)
Fe−P(2)	2.206(2)	C(12)−C(12)	1.36(1)
Fe−C(11)	1.830(8)	Fe−Fe	7.431
Fe−Cp*(centroide)	1.766		
P(1)−Fe−P(2)	84.65(8)	P(1)−Fe−C(11)	93.4(2)
P(2)−Fe−C(11)	84.4(2)	Fe−C(11)−C(12)	167.0(6)
C(11)−C(12)−C(12)	177(1)		

No C$_4$ complexes with the two terminal organometallic moieties in different oxidation states have been structurally characterized to date. Crystals of **5[PF$_6$]** were grown by slow diffusion of pentane into a CH$_2$Cl$_2$ solution of the mixed-valence complex. The unit cell contains two molecules. The molecular structure of the mixed-valence complex **5[PF$_6$]** is shown in Figure 3, and the X-ray data conditions are summarized in Table 2. Positional parameters, bond distances, and bond angles are collected in Table 3. Complex **5[PF$_6$]** crystallizes in the monoclinic space group *P*2$_1$/*n* and has a center of inversion. As the mixed-valence cation is centrosymmetric, the two organoiron units are strictly equivalent and the planes of the two Cp* rings are parallel. The two metal centers clearly adopt a pseudooctahedral geometry, as usually observed for many

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piano-stool complexes, with the Cp* ring occupying three coordination sites and the C_α carbon of the bridge and the phosphorus atoms occupying the other three sites. The Fe$-$P(1) and Fe$-$P(2) bond lengths and the angle P(1)$-$Fe$-$P(2) compare well with the data determined for other mononuclear complexes in the FeCp*(dppe) series.[10,32]

Within the C_4 chain, the $C_\alpha{\equiv}C_\beta$ and $C_\beta{-}C_{\beta'}$ distances are 1.236(9) and 1.36(1) Å, respectively. The carbon bridge is not strictly linear, the Fe$-C_\alpha-C_\beta$ and $C_\alpha-C_\beta-C_{\beta'}$ angles being found at 167.0(6) and 177(1)°, respectively. Distortions have also been observed for the binuclear [Re]$-$C4$-$[Re] and [Ru]$-C_4-$[Ru] complexes and for a few mononuclear *trans*-bis(σ-diacetylide) derivatives. They could be the result of intramolecular steric interactions between the two organometallic groups.[33] The comparison of the carbon$-$carbon bond distances with those of other organic[34] or organometallic[9g,14a,33i] butadiyndiyl fragments has to be made with caution. Often with this type of compound, the quality of the X-ray data does not permit discussion of the effect of the metal termini on the electronic structure of the C_4 chain.

The PF_6^- anions are symmetrically disposed relative to the two iron atoms. This is an important observation because valence trapping as the result of asymmetric positioning of the anion relative to the metal centers in mixed-valence biferrocene-like cations is well documented for complexes in the solid state.[26e,35] The intramolecular Fe$-$Fe distance (7.431(2) Å) is shorter than the iron$-$iron intermolecular distances measured at 8.460, 9.955, 10.958, and 12.430 Å. The extended packing of the mixed-valence complex **5[PF$_6$]** consists of linear strands of weakly interacting cations surrounded by and separated from other similar strands by PF_6^- anions. The closest cation$-$cation contacts result from intermolecular contacts of the Cp* ring. The crystallographic equivalence of the two iron sites and the associated metal$-$metal distance of 7.431 Å constitutes the major interest of this structure, and the spectroscopic data for this compound have been collected to address the question of the rate of the intramolecular electron transfer rate.

^{57}Fe Mössbauer Characteristics of 5[PF$_6$]. It is well-known that Mössbauer spectroscopy is very useful to identify the oxidation states of iron in mixed-valence compounds, and this technique was extensively used for ferrocene and ferrocenium ion derivatives.[26,35,36] As shown for mononuclear and binuclear half-sandwich species (*vide supra*) **5** and **5[PF$_6$]$_2$**, the quadrupole splittings and the isomer shifts are also very different for Fe(II) and Fe(III).[10,12,22,34] Figure 4 allows comparison of the Mössbauer spectra run at 77 K for the mixed-valence complex **5-[PF$_6$]** with those of **5** and **5[PF$_6$]$_2$**. It is clear that the spectrum of the monocation exhibits a single doublet with a quadrupole splitting close to the average value (1.58) of the quadrupole splittings for the doublets of **5** and **5[PF$_6$]$_2$**. A consequence of an average value of QS should be a weak contribution from the π-orbitals of the bridging$-C_4-$ligand to the delocalization of the unpaired electron. Mössbauer spectroscopy can be used to monitor the intramolecular electron transfer rate in mixed-valence compounds. When the intracation electron transfer rate is slower than 10^6 s^{-1}, localized valences are observed, whereas observation of a single average-valence quadrupole doublet is diagnostic of an electron transfer rate faster than 10^9 s^{-1}.[37] From our Mössbauer data, both iron atoms are equivalent. Furthermore, this equivalence is not a function of the temperature; spectra recorded at 298, 77, and 4.2 K all show the presence of only one type of iron, and the parameters (mm s^{-1} *vs* Fe, IS = 0.21 , QS = 1.32) are temperature independent.

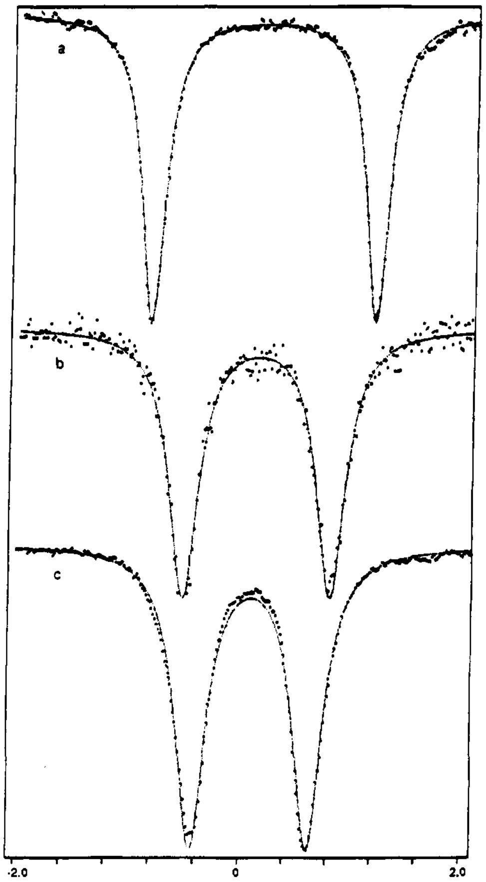

Figure 4. ^{57}Fe Mössbauer spectra for [{Fe(Cp*)(η^2dppe)}$_2$-μ-(C$\equiv$C$-$C$\equiv$C)][PF$_6$]$_n$ {(a) n = 0, **5**; (b) n = 1, **5[PF$_6$]**; (c) n = 2, **5-[PF$_6$]$_2$**} at 77 K. The velocity scale is referenced to iron metal.

Magnetism. The magnetic susceptibility was determined for the complex **5[PF$_6$]** with a SQUID magnetometer over the temperature range 5$-$300 K. The molar paramagnetic susceptibility (χ_M) corrected for diamagnetism follows the Curie-Weiss law, $\chi_M = \chi_0 + C/(T - \theta)$ with θ = 0 K and $\chi_0 = 5.828 \times 10^{-3}$ emu/mol. χ_M decreases gradually with increase in tem-

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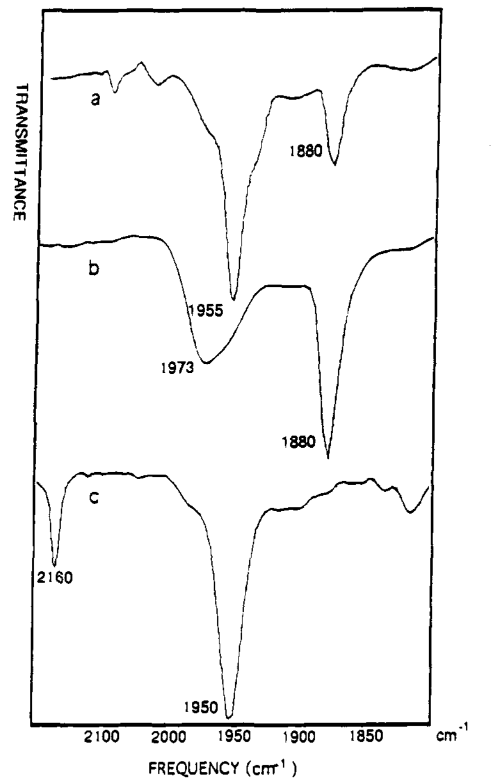

Figure 5. Infrared spectra (20 °C, Nujol) for $[\{Fe(Cp^*)(\eta^2dppe)\}_2\text{-}\mu\text{-}(C{\equiv}C{-}C{\equiv}C)][PF_6]_n$ {(a) $n = 0$, **5**; (b) $n = 1$, **5[PF$_6$]**; (c) $n = 2$, **5[PF$_6$]$_2$**} in the 1800−2200 cm^{-1} region.

perature. In the range 20−300 K, as observed for the dication **5[PF$_6$]$_2$**, the magnetic moment ($\mu_{eff} = 1.24\ \mu_B$) of the mixed-valence complex is rather weak with respect to the spin-only value of 1.73. It has also been determined in solution by the Evans method, and the value found of 1.34 μ_B at 300 K is in close agreement with the measurements in the solid state, indicating that there is no contribution of the solid state to the magnetic behavior.

Infrared Spectroscopy. Comparison of the infrared spectrum of the mixed-valence complex **5[PF$_6$]** with those of the neutral **5** and the dication **5[PF$_6$]$_2$** iron complexes should provide the most direct indication of electronic delocalization on a very short time scale. If the IR band stretching for a given mixed-valence compound occurs at a frequency intermediate between those for the corresponding unoxidized and dioxidized species, then it can be concluded that the intramolecular electron transfer rate is fast on the IR time scale (10^{-13} s). We have previously shown that the two-electron oxidation of the neutral complex Fe(II)−Fe(II) (**5**) to the Fe(III)−Fe(III) (**5[PF$_6$]$_2$**) produces a shift of the symmetric and asymmetric (−C≡C−) stretching bands toward the higher energy, from (cm^{-1}) 1880 and 1955 to 1950 and 2160. Similarly, a spectrum of the monocation **5[PF$_6$]** showed the corresponding vibrations at 1880 and 1973 cm^{-1} (Figure 5). As previously noted for the dication **5[PF$_6$]$_2$**, the higher stretching frequency observed for one of the vibrational modes of the C≡C triple bond in the complex **5[PF$_6$]** with respect to the neutral complex **5** was unexpected and shows that there is no reduction of the bond order, which would be expected if the π orbitals of the $-C_4-$ bridging group were to participate in the delocalization of the spin density. This strongly contrasts with the Re−C≡C−C≡C−Re complex, for which the one-electron oxidation produces a reduction of the −C≡C− bond stretching from (cm^{-1}) 1964 to 1872,[14b] but corroborates the Mössbauer data (*vide supra*). In our case, the two-electron oxidation strengthens the triple-bond character of two ethynyl groups of the $-C_4-$ bridge. Owing to the number of absorption bands, the complex **5[PF$_6$]** is delocalized on the time scale of the IR spectroscopy, implying that the rate of intramolecular electron transfer is faster that 10^{12} s^{-1}.

Near-Infrared Spectroscopy and Intervalence Transition. Optical absorption spectra with a time scale of ca. 10^{-15} s support the conclusion drawn from the IR measurements. In the near-infrared region, a new absorption band appears for the mixed-valence complex **5[PF$_6$]** which is not present for either the **5** or **5[PF$_6$]$_2$** dimeric compound. This band can be assigned as an intervalence transition (IT) on the basis of its low energy and large band width. The near-infrared spectrum was obtained in dichloromethane, acetonitrile, and methanol, solvents in which the mixed-valence compound is both soluble and stable. The results are summarized in Table 4, where the values of λ_{max}, ν_{max} (the energy of the absortion at λ_{max}), and ϵ_{max} (the extinction coefficient), as well as the values of the quantity ($1/D_{op} - 1/D_s$) for each solvent are given (D_s and D_{op} being the static and optical dielectric constants of the solvents used). The NIR spectra show a huge IT band above 7500 cm^{-1}. The position of its maximum is virtually independent of the solvent, which shows that the Fe(II)−C$_4$−Fe(III) complex behaves as the class III systems.[38] The value of the extinction coefficient ($\epsilon = 1.2 \times 10^4$ M^{-1} cm^{-1}) is important and of the same order of magnitude as in the fully delocalized systems.[23] The observed band full width at half-height ($\Delta\nu_{1/2}$; cm^{-1}) is found to be narrower than the calculated value from Hush's theory and eq 6 (3.25×10^3 *vs* 4.22×10^3).[38] Bands broader than those

$$\Delta\nu_{1/2} = \sqrt{2310\nu_{max}} \qquad (6)$$

calculated have been observed in many weakly coupled mixed-valence systems.[39,40] Exceptions to this behavior have been observed for ruthenium complexes bridged by pyrazine,[24,25a] cyanogen,[25b] *tert*-butylmalononitrile,[41] or tetrapyridylbiphenyl.[42]

Marcus[43,44] has shown that the activation barrier to electron transfer for a self-exchange outer-sphere redox reaction of a metal complex in solution is equal to $\lambda/4$, where λ is a reorganization energy. λ includes contributions from inner (λ_i) and outer (λ_o) sphere reorganizations of the complex. In the case of **5[PF$_6$]**, this band appears to be non-solvent-dependent, as expected for electronically delocalized mixed-valence complexes, and the data obtained from the spectra enabled us to calculate λ_i and λ_o (Table 4). The Marcus model establishes that the reactant and product of an electron transfer are associated by a ground-excited-state relationship, and the Hush theory correlates the parameters that are involved in the optical transition, connecting the two states and the corresponding thermal electron transfer. The evalution of the effective electronic coupling parameter V_{ab} (in cm^{-1}) between the two metal sites is generally calculated from eq 7, given by Hush, in which R is in Å, ϵ_{max} the extinction coefficient, ν_{max} is the

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Table 4. Near-Infrared Spectral Data for the Mixed-Valence Complex [**5PF$_6$**], Derived Inner and Outer Sphere Reorganization Energy, and Electronic Coupling

solvent	$1/D_{op} - 1/D_s$	λ_{max} (nm)	υ_{max} (cm^{-1})	$\Delta\upsilon_{1/2}$ (cm^{-1})	ϵ_{max} (M^{-1} cm^{-1})
CH_3CN	0.526	1298	7704	3.26×10^3	1.2×10^4
MeOH	0.536	1274	7692	3.31×10^3	1.1×10^4
CH_2Cl_2	0.383	1302	7541	3.25×10^3	1.2×10^4
$R_{ab} = 7.436$ Å		$\lambda_i = 7.1 \times 10^3$ cm^{-1} $\lambda_0 = 0.5 \times 10^3$ cm^{-1}	$E_{op} = 7.6 \times 10^3$ cm^{-1}		$V_{ab} = 0.19$ eV^a $V_{ab} = 0.47$ eV^b

^{a} Calculated from eq 7. ^{b} Calculated from eq 8.

$$V_{ab} = \frac{2.06 \times 10^{-2}}{R_{ab}}(\epsilon_{max}\nu_{max}\Delta\nu_{1/2})^{1/2} \qquad (7)$$

transition energy and $\nu_{1/2}$ the full width at half-maximum in cm^{-1}.[38] The former Hush treatment applies reasonably well for mixed-valence systems where the electronic coupling is small, but it should be mentioned that the validity of Hush's approach to calculate dipole strengths from spectroscopic data has been questioned[45] after the comparison of observed and predicted dipole strengths for the pyrazyne-bridged bis(pentaamineruthenium) complex in which the experimentally determined values were much smaller than those calculated. For class III compounds a more simply and more accurate determination for V_{ab} was proposed (eq 8).[40,46] Nevertheless, in

$$V_{ab} = \nu_{max}/2 \qquad (8)$$

common with many authors,[47] we used Hush's method to calculate V_{ab} in order to have an estimate of the electronic coupling between the two iron centers and to allow comparisons. We found $V_{ab} = 0.19$ eV from eq 7 and as expected, a higher value (0.47 eV) is obtained from eq 8. These data reveal a very strong electronic coupling characteristic of a class III compound, and by comparison with other bridged systems in which the distance between the metal centers is similar, the butadiyndiyl spacer leads to extremely strong coupling. Moreover, as shown by Taube and Sutton, the bonding properties of the spacer between the redox centers that promote a strong synergistic interaction between metal ions are much the same as those that increase the magnitude of V_{ab}.[47a] Therefore, a large electronic coupling is in full agreement with a strong value for the comproportionation constant K_c.

The very special coupling properties of the $-C_4-$ ligand in the dinuclear iron complex open the route to long-distance electron transfer across all carbon bridges. We are presently extending the $-C_x-$ spacer to longer and linear elemental carbon chains in order to investigate the possibility of connecting distant redox sites by this kind of "molecular wiring".

Experimental Section

General Data. Reagent grade tetrahydrofuran (THF), diethyl ether, and pentane were dried and distilled from sodium benzophenone ketyl prior to use. Pentamethylcyclopentadiene was prepared according to the published procedure,[17] and other chemicals were used as received. All the manipulations were carried out under argon atmosphere using Schlenk techniques or in a Jacomex 532 drybox filled with nitrogen. Routine NMR spectra were recorded using a Brucker AW 80 MHz. High-field NMR spectra experiments were performed on a multinuclear Bruker 300 MHz instrument (AM300WB). Chemical shifts are given in parts per million relative to tetramethylsilane (TMS) for ^{1}H and ^{13}C NMR spectra and H_3PO_4 for ^{31}P NMR spectra. Cyclic voltammograms were recorded using a PAR 263 instrument. X-band ESR spectra were recorded on a Brucker ESP-300E spectrometer at 77 K in liquid nitrogen. Mössbauer spectra were recorded with a 2.5×10^{-2} C (9.25×10^8 Bq) ^{57}Co source using a symmetric triangular sweep mode.[18] Magnetic susceptibility measurements were performed with a SQUID (susceptometer quantum interface device) instrument in the solid state and by ^{1}H NMR in solution.[48] The interatomic distances have been estimated with the molecular modeling system Chem3D from Cambridge Scientific Computing. Elemental analyses were performed at the Center for Microanalyses of the CNRS at Lyon-Solaise, France.

[Fe(Cp*)(dppe)($=$C$=$CH$_2$)][PF$_6$] (2). [Fe(Cp*)(dppe)Cl] (2.02 g, 3.23 mmol), $HC{\equiv}CSiMe_3$ (460 μL, 3.23 mmol), and NH_4PF_6 (0.53 g, 3.23 mmol) were dissolved in MeOH (30 mL). The solution was stirred overnight. The resulting yellow solution was evaporated to dryness and the crude residue extracted with dichloromethane. The solution was then concentrated to 5 mL, and diethyl ether (50 mL) was slowly added to precipitate 2.18 g (89%) of **2** as a light-orange powder. Anal. Calcd ($C_{38}H_{41}F_6FeP_3$): C, 60.02; H, 5.43. Found: C, 59.72; H, 5.55. FT-IR (Nujol, cm^{-1}): 1612 ($\nu_{C=C}$). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.37 (M, 20H, Ph), 3.93 (t, $^4J_{PH} = 3.6$ Hz, 2H, $=CH_2$), 3.0, 2.49 (2m, 4H, CH_2), 1.45 (s, 15H, Cp*). ^{13}C NMR ($CDCl_3$): δ_C 354.7 (t, $^2J_{PC} = 33$ Hz, C_α), 133.4 (d, $^1J_{PC} = 55$ Hz, *ipso*-Ph), 131.8 (d, $^1J_{CP} = 31$ Hz, *ipso*-Ph), 131.3 (m, *m,o,p*·*Ph*), 103.8 (t, $^1J_{CH} = 164$ Hz), 99.5 (s, *C*$_5$-Me$_5$), 30.0 (tt, $^1J_{CP} = 45$ Hz, $^1J_{CH} = 137$ Hz, P-CH$_2$), 9.8 (q, C$_5$*Me*$_5$, $^1J_{CH} = 128$ Hz). ^{31}P NMR ($CDCl_3$): δ_P 90.7.

Fe(Cp*)(η^2dppe)(C≡CH) (3). To a solution of [{Fe(Cp*)(η^2-dppe)}$_2$(μ-C$=$CH$_2$)][PF$_6$] (2.30 g, 3.03 mmol) in THF (40 mL) was added KO^{t}Bu (0.347 g, 3.10 mmol) under argon. The resulting brown solution was stirred for 15 min and evaporated to dryness *in vacuo*. The crude residue was then extracted with toluene (3 × 40 mL). After removal of the solvent, the solid was washed with pentane (10 mL) and dried *in vacuo* to give **3** (1.83 g, 98%). Anal. Calcd ($C_{38}H_{40}FeP_2$): C, 74.27; H, 6.56. Found: C, 74.52; H, 6.51. FT-IR (Nujol, cm^{-1}): 1910 ($\nu_{C\equiv C}$). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.27−7.97 (m, 20H), 2.03, 2.78 (2m, 4H, PCH$_2$), 1.70 (t, 1H, $^4J_{PH} = 2.9$Hz, C≡CH), 1.44 (s, 15H, Cp*). ^{13}C NMR{^{1}H} ($CDCl_3$): δ_C 139.6−126.9 (m, Ph), 129.5 (t, $^2J_{PC} = 38$ Hz, *C*≡CH), 102.7 (s, *C*≡CH), 87.2 (s, *C*$_5$Me$_5$), 30.6 (t, $^1J_{PC} = 45$ Hz, P*C*H$_2$), 10.2 (s, C$_5$*Me*$_5$). ^{31}P NMR ($CDCl_3$): δ_P 100.8 (s).

Oxidation of Fe(Cp*)(η^2dppe)(C≡CH) (3) at 20 °C. To a solution (20 °C) of **3** (0.545 g, 0.81 mmol) in dichloromethane (30 mL) was added 0.95 equiv of ferrocenium hexafluorophosphate. The mixture was stirred for 1 h, and the resulting yellow solution was evaporated to dryness. The crude residue was extracted with dichloromethane, then concentrated to 5 mL, and diethyl ether (50 mL) was slowly added to precipitate 0.59 g (96%) of **2** as a light-orange powder.

[{Fe(Cp*)(η^2dppe)}$_2$(μ-C$=$CH$-$CH$=$C)][PF$_6$]$_2$ (4). To a cooled solution (−80 °C) of **3** (0.545 g, 0.81 mmol) in dichloromethane (30 mL) was added 0.9 equivalents of ferrocenium hexafluorophosphate. The mixture was stirred at −80 °C for 5 h. A brown solid was precipitated by adding diethyl ether (150 mL) and filtered. The microcrystalline solid was washed with ether (2 × 20 mL) and dried *in vacuo* to give 0.525 g (87%) of complex **4**. Anal. Calcd ($C_{76}H_{80}F_{12}Fe_2P_6$): C, 60.10; H, 5.31. Found: C, 60.17; H, 5.41. FT-IR (Nujol, cm^{-1}): 1585 ($\nu_{C=C}$). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.59−7.10 (m, 40H), 4.37 (s, 2H), 2.89, 2.54 (2m, 8H, PCH$_2$), 1.52 (s, 30H, Cp*).

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^{13}C NMR{^{1}H} ($CDCl_3$): δ_C 360.5 (t, $^2J_{PC}$ = 34 Hz, *C*=CH), 134.6–129.0 (m, Ph), 108.0 (s, C=*C*H), 100.8 (s, *C*$_5$Me$_5$), 30.2 (t, $^1J_{PC}$ = 22Hz, P*C*H$_2$), 10.5 (s, C$_5$*Me*$_5$). ^{31}P NMR ($CDCl_3$): δ_P 88.6 (s).

[{Fe(Cp*)(η^2dppe)}$_2$(μ-C≡C–C≡C)] (5). KO^{t}Bu (0.062 g, 0.55 mmol) was added to a solution of [{Fe(Cp*)(η^2dppe)}$_2$(μ-C=C-H–CH=C)][PF$_6$]$_2$ (0.350 g, 0.23 mmol) in THF (40 mL) under argon. The resulting brown solution was stirred for 15 min and evaporated to dryness *in vacuo*. The crude residue was then extracted with toluene (3 × 40 mL). After removal of the solvent, the solid was washed with pentane (10 mL) and dried *in vacuo* to give **5** (0.260 g, 92%). Anal. Calcd ($C_{76}H_{78}Fe_2P_4$): C, 74.39; H, 6.41. Found: C, 74.28; H, 6.39. FT-IR (CH_2Cl_2, cm^{-1}): 1880, 1955 ($\nu_{C\equiv C}$). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ_H 8.16–7.00 (M, 40H, Ph), 2.72, 1.89 (2m, 8H, CH$_2$), 1.55 (s, 30H, Cp*). ^{13}C NMR{^{1}H} (C_7D_8, 193 K): δ_C 139.6–125.7 (M, Ph), 110.2 (s, C_β), 99.7 (t, $^2J_{PC}$ = 41 Hz, C_α), 87.8 (s, *C*$_5$Me$_5$), 30.9 (m, CH$_2$), 10.5 (s, C$_5$*Me*$_5$). ^{31}P NMR (MHz, C_7D_8, 193 K): δ_P 101.9, 99.5 (50/50). Mössbauer (mm/s *vs* Fe, 77 K): IS 0.27, QS 2.07.

[{Fe(Cp*)(η^2dppe)}$_2$(μ-C≡C–C≡C)][PF$_6$]$_2$ (5[PF$_6$]$_2$). To {Fe(Cp*)-(η^2dppe)}$_2$(μ-C≡C–C≡C) (0.48 g, 0.39 mmol) in CH_2Cl_2 (20 mL) at 20 °C was added [Fe(Cp)$_2$][PF$_6$] (0.246 g, 0.74 mmol). The solution was stirred at 20 °C for 2 h and then concentrated *in vacuo*. Addition of pentane gave a precipitate which was washed with pentane (3 × 10 mL) and dried *in vacuo* to give **5[PF$_6$]$_2$** (0.515 g, 91%). Anal. Calcd ($C_{76}H_{78}F_{12}Fe_2P_6$): C, 60.18; H, 5.18. Found: C, 59.93; H, 5.26. FT-IR (CH_2Cl_2, cm^{-1}): 1950, 2160 ($\nu_{C\equiv C}$). λ_{max} (CH_2Cl_2, ϵ): 621 (24 100), 828 (11 500). ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ_H 9.5 (s, 8H, *o'*-Ph), 7.98 (s broad, 4H, *p*-Ph), 7.58 (t, 4H, *p'*-Ph), 6.74 (s broad, 8H, *m'*-Ph), 6.17 (s broad, 16H, *m,o*-Ph), 3.40, −1.79 (s broad, 2 × 4H, –CH$_2$–), −6.03 (s, 30H, Cp*). ^{31}P NMR (C_7D_8, 293 K): δ_P 89.1, 88.2. Mössbauer (mm/s *vs* Fe, 77 K): IS 0.18, QS 1.05.

[{Fe(Cp*)(η^2dppe)}$_2$(μ-C≡C–C≡C)][PF$_6$] (5[PF$_6$]). To {Fe(Cp*)-(η^2dppe)}$_2$(μ-C≡C–C≡C) (0.28 g, 0.23 mmol) in CH_2Cl_2 (20 mL) at 20 °C was added [Fe(η-Cp)$_2$][PF$_6$] (0.068 g, 0.21 mmol). The solution was stirred at 20 °C for 2 h and then concentrated *in vacuo*. Addition of pentane gave a precipitate which was washed with pentane (3 × 10 mL) and dried in vacuo to give **5[PF$_6$]** (0.255 g, 92%). Anal. Calcd ($C_{76}H_{78}F_6Fe_2P_5 \cdot 0.5CH_2Cl_2$): C, 64.96; H, 5.63. Found: C, 65.29; H, 5.62. FT-IR (CH_2Cl_2, cm^{-1}): 1880, 1973 ($\nu_{C\equiv C}$). λ_{max} (CH_2Cl_2, ϵ): 437 (4100), 561 (702), 1326 (11 700). Mössbauer (mm/s *vs* Fe, 77 K): IS 0.21, QS 1.32.

X-ray Crystallography for 5[PF$_6$]. Crystals suitable for single X-ray diffraction studies were obtained from dichloromethane–pentane at 20 °C. The data were measured on a CAD-4 Enraf Nonius automated diffractometer. All the calculations were performed on a Digital MicroVax 3100 computer with the MOLEN package.[49] Crystal data collection and refinement parameters are collected in Table 2. The unit cell parameters were determined by least-squares fit of a set of 25 high-θ reflections. After Lorenz polarization corrections, the structure was solved by direct methods which located many non-hydrogen atoms of the structure. The remaining non-hydrogen atoms were located through subsequent difference Fourier syntheses. The PF$_6$ anion appeared as disordered between two positions (F1F2F3 and F4F5F6). After isotropic (R = 0.090) then anisotropic refinements (R = 0.072), many hygrogen atoms were found with a Fourier difference (between 0.58 and 0.40 e Å^{-3}) and the other being set in theoretical position. The whole structure was refined by the full-matrix least square techniques (use of F magnitude; x, y, z, and b_{ij} for Fe, P, and C atoms, x, y, z, and B for F atoms and x, y, and z for H atoms; 401 variables and 2538 observations).

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Supporting Information Available: Complete tables of atomic coordinates and their estimated standard deviations, bond lengths and angles for **5[PF$_6$]** and a table of general temperature factor expressions (14 pages); a listing of observed and calculated structure factors (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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