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Molecular Wire Consisting of a C_8 Chain of Elemental Carbon Bridging Two Metal Centers: Synthesis and Characterization of $[\{Fe(\eta^5\text{-}C_5Me_5)(dppe)\}_2(\mu\text{-}C_8)]$

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*Summary: The diiron complex $[\{Fe(\eta^5\text{-}C_5Me_5)(dppe)\}_2(\mu\text{-}C_8)]$ (**5**; dppe = 1,2-bis(diphenylphosphino)ethane) is synthesized by the oxidative coupling of $Fe(\eta^5\text{-}C_5Me_5)(dppe)(C{\equiv}CC{\equiv}CH)$ (**4**), and it is established from the properties of the thermally stable mixed-valence complex $[Fe^{II}{-}C_8\text{-}Fe^{III}][PF_6]$ (**6**) that the C_8 chain acts as a molecular wire between the two metal centers, giving rise to the strongest electronic coupling through nine bonds known to date.*

The synthesis of long chains of the elemental carbon allotrope with “sp” hybridization constitutes a new and important objective.[1,2] It has been shown that these chains are stabilized against further reaction by the presence of nonreactive terminal substituents.[1] The use of organometallic building blocks as end-capping groups offers fascinating perspectives for the stabilization of wirelike C_x moieties and for access to new materials science, expected to exhibit interesting physical properties.[2] Several species with C_4 bridges have been isolated,[3] and recently the first complexes with C_5, C_6, and C_8 chains were reported.[4] In this communication, we report the synthesis and the redox and preliminary spectroscopic properties of the first mixed-valence radical cation containing a C_8 chain, the longest known to date, namely the complex $[\{Fe(\eta^5\text{-}C_5Me_5)(dppe)\}_2(\mu\text{-}C_8)]^+[PF_6]^-$ (**6**).

The halide complex $Fe(\eta^5\text{-}C_5Me_5)(CO)_2I$ (**1**)[5] reacts with $Me_3SiC{\equiv}CC{\equiv}CLi$ (1.05 equiv) in THF at −80 °C to give after workup the yellow complex $Fe(\eta^5\text{-}C_5Me_5)(CO)_2(C{\equiv}CC{\equiv}CSiMe_3)$ (**2**; 70% yield, Scheme 1).[6] The ^{13}C NMR spectrum, which shows peaks at δ 69.5, 94.7, 96.5, and 106.3 assigned to the C_4 chain, is characteristic of the structure. The IR spectrum exhibits two strong absorptions in the carbonyl stretching region at 2010 and 1962 cm^{-1}, whereas those of the $C{\equiv}C$ bonds are weak and are located at 2171 and 2120 cm^{-1}. Upon UV irradiation in a toluene/acetonitrile (95/5) mixture in the presence of dppe, **2** is converted to the electron-

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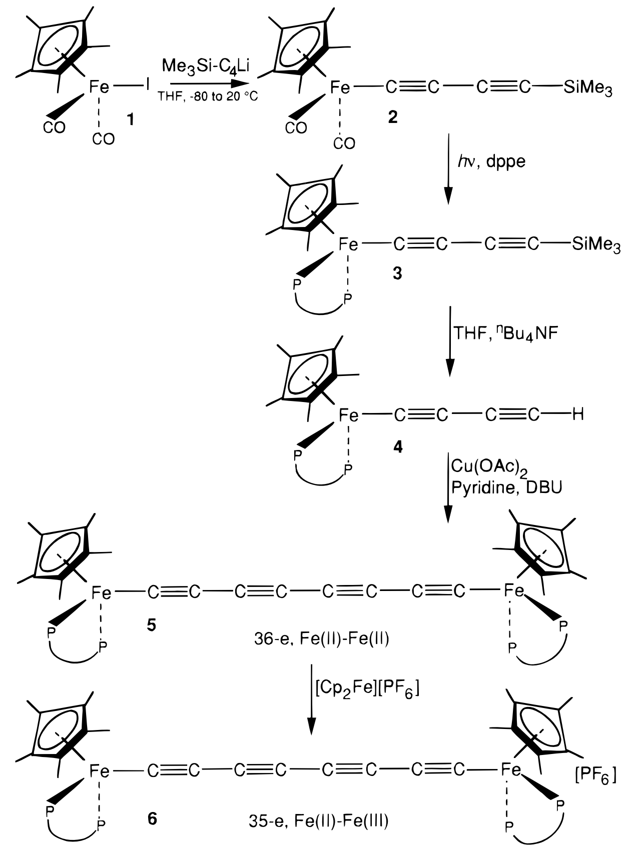
Scheme 1



rich complex $Fe(\eta^5\text{-}C_5Me_5)(dppe)(C\equiv CC\equiv CSiMe_3)$ (**3**), isolated after washing with diethyl ether as a pure burnt orange powder (85% yield).[7] The ^{13}C NMR spectrum displays three triplets at δ 142.2 ($^2J_{PC}$ = 38 Hz), 102.3 ($^3J_{PC}$ = 2 Hz), and 96.2 ($^4J_{PC}$ = 3 Hz), respectively, attributed to the C_α, C_β, and C_γ carbon atoms of the unsaturated C_4 chain; the C_δ atom is observed as a singlet at δ 64.5. Treatment of complex **3** with 0.2 equiv of tetrabutylammonium fluoride in THF at room temperature affords the terminal butadiyne complex $Fe(\eta^5\text{-}C_5Me_5)(dppe)(C\equiv CC\equiv CH)$ (**4**), isolated as an orange-red solid (95% yield).[8] The carbon resonances of the butadiynyl ligand are unequivocally assigned on the basis of the J_{CH} coupling constants. Thus, the ^{13}C resonances of the $-C_4H$ fragment are located in the spectrum at δ 50.5 (C_δ, d, $^1J_{CH}$ = 248 Hz), 75.1 ($C\gamma$, dt, $^2J_{CH}$ = 50 Hz, $^4J_{PC}$ = 3 Hz), 100.7 (C_β, d, $^3J_{CH}$ = 5 Hz), and 136.6 (C_α, t, $^2J_{PC}$ = 38 Hz). It is noteworthy that comparison of the J_{CH} and J_{CP} coupling constants establishes that $^4J_{CP}$ is larger than $^3J_{CP}$, consequently strongly supporting the attribution given above for complex **3**. The IR spectrum of **4** exhibits two (stretching) absorptions in the C≡C bond region stretching at 1960 (w) and 2099 (s) cm^{-1}.

The iron butadiyne complex **4** was treated with $Cu(OAc)_2$ (1 equiv) in the presence of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU; 1 equiv) in pyridine.[9] The reaction affords at +40 °C the C_8-bridged binuclear compound $[Fe(\eta^5\text{-}C_5Me_5)(dppe)(C\equiv CC\equiv CC\equiv CC\equiv C)Fe(\eta^5\text{-}C_5Me_5)(dppe)]$ (**5**), isolated after purification by filtration on celite as a thermally stable and air-sensitive burnt orange powder (80% yield).[10] The IR spectrum shows $\nu_{C\equiv C}$ bonds of the C_8 bridge at 2109 and 1949 cm^{-1}. The ^{13}C NMR spectrum exhibits four signals attributed to the carbon atoms of the μ-octatetraynediyl ligand. They are progressively shifted downfield as the carbon atoms are closer to the iron centers: δ 50.6 (C_δ, s), 62.7 ($C\gamma$, t, $^4J_{PC}$ = 3 Hz), 101.8 (C_β, s), and 139.5 (C_α, t, $^2J_{PC}$ = 42 Hz). As previously observed for complexes **3** and **4**, the $^4J_{CP}$ coupling constant for $C\gamma$ is larger than the $^3J_{CP}$ value.

The cyclic voltammogram (CV) of complex **5** establishes that the C_8 chain acts as a molecular wire connecting the two electron rich organoiron centers. The initial scan in the CV of complex **5** in dichloromethane from −0.8 to + 0.8 V [vs the standard calomel electrode (SCE)) is characterized by two reversible one-electron processes, with the ($i_p{}^a/i_p{}^c$) current ratio of unity ($E°_1$ = −0.23, $E°_2$ = +0.20, *cf.* ferrocene +0.420 V *vs* SCE; Figure 1). The anodic and cathodic peak separation ($E_p{}^a - E_p{}^c$) is 70 mV with a 100 mV s^{-1} scan rate. From the large wave separation ($|E°_1 - E°_2|$ = 0.43 V) a large constant K_c (2×10^7) was calculated for the comproportionation of Fe(II)−Fe(II) and Fe(III)−Fe(III) to Fe(II)−

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(6) To a −80 °C THF solution (20 mL) of **1** (1.83 g, 4.88 mmol) was added a −80 °C solution of $Me_3SiC\equiv CC\equiv CLi$ (5.14 mmol) in THF (10 mL). The temperature was gradually raised to room temperature and a dark brown solution was obtained. After 3 h, the solvent was removed under vacuum, the crude residue was extracted with pentane (200 mL), and the extract was chromatographed on an alumina column. After removal of the pentane under vacuum, the yellow solid was washed with cooled pentane (−80 °C) and dried in vacuo to give the complex **2** (1.25 g, 70%). Anal. Calcd for $C_{19}H_{24}FeO_2Si$: C, 61.96; H, 6.57. Found: C, 62.23; H, 6.57. FT-IR (Nujol, cm^{-1}): ν = 2010, 1962 (s, C≡O), 2171, 2120 (m, C≡C). ^1H NMR (300 MHz, C_6D_6, 25 °C, TMS ext): δ 1.32 (s, 15H, C_5Me_5), 0.15 (s, 9H, $SiMe_3$). ^{13}C NMR (75 MHz, C_6D_6, 25 °C, TMS ext): δ 214.3 (s, CO), 106.3 (s, C_α), 97.4 (s, C_5Me_5), 96.5 (s, C_β), 94.7 (s, C_γ), 69.5 (s, C_δ), 9.5 (s, C_5Me_5), 0.6 (s, $SiMe_3$).

(7) UV photolysis (Hanovia lamp, 450 W, 250 nm) of **2** (0.700 g, 1.90 mmol) and dppe (0.757 g, 1.90 mmol) in a mixture of toluene and acetonitrile (95/5) for 4 h gave a red-orange solution. After removal of the solvents under vacuum, the solid **3** was washed with cooled ether (2 × 5 mL, 1,15 g, 85%). Anal. Calcd for $C_{43}H_{48}FeP_2Si$: C, 72.65; H, 6.81. Found: C, 72.82; H, 7.24. FT-IR (Nujol, cm^{-1}): ν 2165 (w), 2093 (s), 1980 (w) (C≡C). ^1H NMR (300 MHz, C_6D_6, 25 °C, TMS ext): δ 7.93−6.99 (m, 20H, Ph), 1.69; 2.48 (2m, 4H, PCH_2), 1.39 (s, 15H, C_5Me_5), 0.24 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C, TMS ext): δ 142.2 (t, $^2J_{PC}$ = 38 Hz, C_α), 139.2−126.3 (m, Ph), 102.3 (t, $^3J_{PC}$ = 2 Hz, C_β), 96.2 (t, $^4J_{PC}$ = 3 Hz, C_γ), 89.1 (s, C_5Me_5), 64.7 (s, C_δ), 33.1−28.9 (m, CH_2), 10.7 (q, $^1J_{CH}$ = 126 Hz, C_5Me_5), 1.8 (q, $^1J_{CH}$ = 119 Hz, $SiMe_3$). ^{31}P NMR (121 MHz, C_6D_6, 25 °C, H_3PO_4 ext): δ 99.6 (s).

(8) To a solution of **3** (0.900 g, 1.27 mmol) in THF (20 mL) was added 0.2 equiv of tetrabutylammonium fluoride. After the mixture was stirred for 4 h at 20 °C, the solvent was removed under vacuum. The residue was extracted with a toluene/ether (20/80) mixture, and after evaporation of these solvents to dryness the solid was washed with cooled diethyl ether (2 × 5 mL, −40 °C). After drying a powder was obtained (0.770 g, 95%). Anal. Calcd for $C_{40}H_{40}FeP_2\cdot 0.5\ Et_2O$: C, 74.67; H, 6.71. Found: C, 74.25; H, 6.24. FT-IR (Nujol, cm^{-1}): ν 2099 (s), 1960 (w) (C≡C). ^1H NMR (300 MHz, C_6D_6, 25 °C, TMS ext): δ 7.99−6.98 (m, 20H, Ph), 2.54, 1.74 (2m, 4H, PCH_2), 1.44 (s, 15H, C_5Me_5), 1.39 (s, 1H, C≡CH). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C, TMS ext) δ 139.3−126.3 (m, Ph), 136.6 (t, $^2J_{PC}$ = 38 Hz, C_α), 100.7 (d, $^3J_{CH}$ = 5 Hz, C_β), 88.5 (s, C_5Me_5), 75.1 (dt, $^2J_{CH}$ = 50 Hz, $^4J_{PC}$ = 3 Hz, C_γ), 50.5 (d, $^1J_{CH}$ = 248 Hz, C_δ), 33.0−28.9 (m, CH_2), 10.3 (q, $^1J_{CH}$ = 126 Hz, C_5Me_5). ^{31}P NMR (121 MHz, C_6D_6, 25 °C, H_3PO_4 ext): δ 99.5 (s).

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(10) $Cu(OAc)_2$ (0.078 g, 0.39 mmol) and DBU (59 μL, 0.39 mmol) were added to a solution of **4** (0.250 g, 0.39 mmol) in pyridine (10 mL). The mixture was stirred at 40 °C for 3 h and then evaporated to dryness in vacuo. The crude residue was washed with diethyl ether and toluene. The remaining orange solid was dissolved in dichloromethane and purified by filtration on a Celite column. The solution was concentrated, and diethyl ether was added to precipitate **5** (0.200 g, 80%). Anal. Calcd for $C_{80}H_{78}Fe_2P_4\cdot 0.25CH_2Cl_2$: C, 74.36; H, 6.10. Found: C, 74.34; H, 6.09. FT-IR (Nujol, cm^{-1}): ν 2109, 1949 (s, C≡C). ^1H NMR (300 MHz, C_6D_5Br, 25 °C, TMS ext): δ 7.81−7.11 (m, 40 H, Ph), 2.45, 1.79 (2m, 8H, CH_2), 1.35 (s, 30 H, C_5Me_5). ^{13}C NMR (75 MHz, C_6D_5Br, 25 °C, TMS ext): δ 139.5 (t, $^2J_{PC}$ = 42 Hz, C_α), 138.3−127.2 (m, Ph), 101.8 (s, C_β), 88.4 (s, C_5Me_5), 62.7 (t, $^4J_{PC}$ = 3 Hz, C_γ), 50.6 (s, C_δ), 30.8−30.3 (m, CH_2), 9.9 (s, C_5Me_5). ^{31}P NMR (121 MHz, C_6D_5Br, 25 °C, H_3PO_4 ext): δ 98.5 (s). Mass spectrum (FAB): *m/z* calcd 1274.4, found 1274.0.

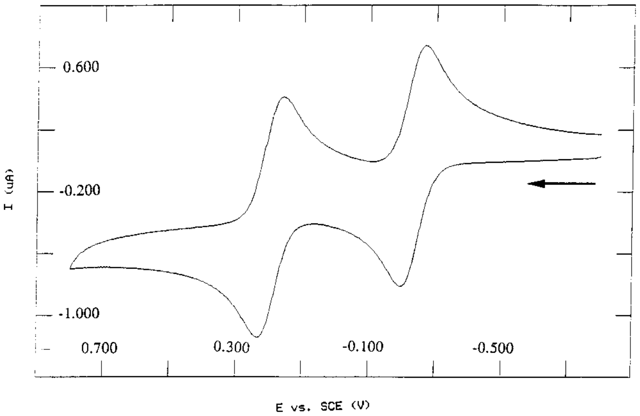

Figure 1. Cyclic voltammogram of **5** (10^{-5} M in 0.1 M $Bu_4N^+PF_6^-$, CH_2Cl_2, 20 °C; Pt electrodes, ferrocene standard, scan rate 100 mV s^{-1}, V *vs* SCE).

Fe(III) (eq 1). The first oxidation wave is thermodynamically more favorable in the C_8-bridged dimer **5** than in the C_4 monomer **4**. This shows that repulsive interactions between occupied orbitals on each metal are propagated throughout the carbon chain over a distance as great as 13 Å. It is noteworthy that the separation of the two redox systems is significantly larger for complex **5** than for the related Re$-C_8-$Re complex ($\Delta E° = 0.28$ V),[4b] illustrating that the properties of the carbon chain are strongly related to the organometallic termini.

$$\mathrm{Fe^{II}{-}C_8{-}Fe^{II}} \rightleftharpoons [\mathrm{Fe^{II}{-}C_8{-}Fe^{III}}]^+ + e^- \rightleftharpoons [\mathrm{Fe^{III}{-}C_8{-}Fe^{III}}]^{2+} + 2e^- \qquad (1)$$

The electrochemical features of complex **5** indicated that the cation radical **6** was a viable synthetic target. Hence, **5** and 0.97 equiv of ferrocenium salt were reacted in CH_2Cl_2 at −55 °C to produce the complex [Fe(η^5-C_5Me_5)(dppe)(C≡CC≡CC≡CC≡C)Fe(η^5-C_5Me_5)(dppe)]-[PF_6] (**6**), isolated after workup as a forest green powder in 90% yield.[11] Complex **6** was characterized by IR, UV−vis, and near-IR spectroscopy, CV, and microanalysis. Like **5**, the IR spectrum of **6** displays two $\nu_{C\equiv C}$ bond stretches (1879 and 1784 cm^{-1}). This indicates that **6** should be considered as a class III mixed-valence cation with the odd electron fully delocalized between the two iron centers on the very rapid IR time scale (10^{-13} s). The lower stretching frequency for the C≡C triple bond in cation **6** indicates that the sp-hybridized carbon bridge adopts an electronic structure intermediate between a polyacetylenic chain containing alternating triple and single bonds and a cumulenic form with double bonds.

The UV/visible spectra of the complexes **5** and **6** are quite different. The orange solution of complex **5** shows very intense metal-to-ligand charge transfer (MLCT) bands (λ_{max} 389, 481 nm; ϵ = 100 500 and 10 000 M^{-1} cm^{-1}, respectively) and does not display any absorption in the near-infrared domain. The MLCT bands also present in the visible spectrum of the green solution of the mixed-valence complex **6** are red-shifted and less intense (λ_{max} 403, 423, 556, 624, 707 nm; ϵ = 56 000, 54 000, 7600, 10 900, and 12 200 M^{-1} cm^{-1}, respectively). The near-IR spectrum shows a strong intervalence charge-transfer band (IT) centered at λ 1958 nm with a very intense extinction coefficient (ϵ = 31 000 M^{-1} cm^{-1}). This band is narrower ($\Delta\nu_{1/2} = 1300$ cm^{-1}) than expected from calculation based on Hush theory (3400 cm^{-1}) for localized mixed-valence systems.[12] The electronic coupling between the two iron centers was therefore calculated ($V_{ab} = 0.32$ eV).[13] The value found reveals 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 $-C_8-$ spacer leads to extremely strong coupling.[14]

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[11] To a cooled solution (−55 °C) of **5** (0.190 g, 0.149 mmol) in CH_2Cl_2 (30 mL) was added 0.97 equiv of ferrocenium as the PF_6 salt. The mixture was stirred for 2 h at −55 °C. After concentration at −55 °C, the solution was cooled at −80 °C and transferred to a Schlenk tube containing pentane at −80 °C (100 mL). After removal of the solvents by filtration, the product was dried in vacuo from −80 °C to room temperature to give the solid **6** (0.185 g, 90%). Anal. Calcd for $C_{80}H_{78}F_6Fe_2P_5 \cdot 0.5CH_2Cl_2$: C, 66.11; H, 5.44. Found: C, 65.76; H, 5.51. FT-IR (Nujol, cm^{-1}): ν = 1879 (s), 1784 (vs) (C≡C).

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