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Synthesis of the 1,2,3,4-Tetramethylfulvene-Bridged Diiron Complex $(\eta^1{:}\eta^5\text{-CH}_2\text{C}_5\text{Me}_4)\text{Fe}_2(\text{CO})_6$ and Its Reactions with Phosphines

Hisako Hashimoto, Hiromi Tobita, and Hiroshi Ogino*

Department of Chemistry, Faculty of Science, Tohoku University, Aoba-ku, Sendai 980, Japan

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1,2,3,4-Tetramethylfulvene was prepared by hydride abstraction from pentamethylcyclopentadienyl anion and was converted to the fulvene-bridged dinuclear complex $(\eta^1{:}\eta^5\text{-CH}_2\text{C}_5\text{Me}_4)\text{Fe}_2(\text{CO})_6$ by treatment with $\text{Fe}_2(\text{CO})_9$. Reaction of this complex with phosphine L (L = PMe_3, PPh_3, $\text{PH}_2\text{PCH}_2\text{PPh}_2$, or PPh_2H) caused replacement of a CO ligand with L to provide $(\eta^1{:}\eta^5\text{-CH}_2\text{C}_5\text{Me}_4)\text{Fe}_2(\text{CO})_5\text{L}$ in high yield. The structure of $(\eta^1{:}\eta^5\text{-CH}_2\text{C}_5\text{Me}_4)\text{Fe}_2(\text{CO})_5(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$ was determined by X-ray crystal structure analysis: $\text{C}_{40}\text{H}_{36}\text{Fe}_2\text{O}_5\text{P}_2$, monoclinic, $P2_1/a$; $a = 20.334(5)$ Å, $b = 10.978(2)$ Å, $c = 18.525(5)$ Å, $\beta = 116.17(2)°$, $V = 3711.2(4)$ Å^3, $Z = 4$. When $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ was used as L, each of the phosphorus atoms made a bond to a diiron unit to give the tetranuclear complex $[(\eta^1{:}\eta^5\text{-CH}_2\text{C}_5\text{Me}_4)\text{Fe}_2(\text{CO})_5]_2(\mu\text{-L})$. The PPh_2H complex $(\eta^1{:}\eta^5\text{-CH}_2\text{C}_5\text{Me}_4)\text{Fe}_2(\text{CO})_5(\text{PPh}_2\text{H})$ rearranged in hot benzene to a new phosphido-bridged dinuclear complex, $(\text{C}_5\text{Me}_5)\text{Fe}_2(\text{CO})_4(\mu\text{-CO})(\mu\text{-PPh}_2)$.

Introduction

Fulvene is a fascinating organic ligand in view of its different coordination modes toward transition metals.[1] 6-Nonsubstituted fulvenes are particularly interesting because of their simplicity, but only a few examples of these are known except for the benzofulvene derivatives:[2] i.e., parent fulvene,[3] 1,2,3,4-tetraphenylfulvene,[4] 1,2,3-triphenylfulvene,[5] and 1,2,3,4-tetramethylfulvene.[6–8]

Recently, there appeared several reports showing the conversion of a variety of pentamethylcyclopentadienyl complexes to tetramethylfulvene complexes in different transition metals.[8,9] These are good evidence for the versatility of 1,2,3,4-tetramethylfulvene as a ligand, but the free ligand has been known only as a product of photochemical[6] and organometallic reactions,[7,8] and there has been no report on its reactivity.[10]

We report here a new convenient method for the large-scale synthesis of 1,2,3,4-tetramethylfulvene, its conversion to a diiron carbonyl complex $(\eta^1{:}\eta^5\text{-CH}_2\text{C}_5\text{Me}_4)\text{Fe}_2(\text{CO})_6$, and the reactions of this complex with various phosphines. Although some diiron–fulvene complexes with the same coordination mode were synthesized in the early 1960s,[11] detailed studies, especially on the reactivity and fluxionality of this type of complex, have not been done.

Experimental Section

All manipulations were performed under an atmosphere of nitrogen or argon by means of standard Schlenk techniques. Dry, oxygen-free solvents were employed throughout. $\text{C}_5\text{Me}_5\text{H}$,[12] Ph_3CPF_6,[13] $\text{Fe}_2(\text{CO})_9$,[14] PMe_3,[15] and HPPh_2[16] were prepared according to literature methods. *t*-BuLi, PPh_3, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$, and $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ were purchased from Aldrich and used as received. NMR spectra were recorded on JEOL FX-90Q, Varian EM-390, or Varian XL-200 spectrometers, IR spectra on a Jasco IR-810 spectrometer, and mass or exact mass spectra on a Hitachi M-52 or JEOL-HX110. Gas chromatography was done on a Hitachi 263-30 (FID).

Preparation of Tetramethylfulvene (1). *t*-BuLi (9.50 mL, 18 mmol) was added dropwise to a solution of pentamethylcyclopentadiene (78% purity by GC) (2.63 g, 15 mmol) in hexane (50 mL) at −15 °C. A pale yellow salt ($\text{C}_5\text{Me}_5\text{Li}$) precipitated out during the addition. The mixture was stirred overnight at room temperature. First, 1,2-dimethoxyethane (DME) (30 mL) and then Ph_3CPF_6 (6.99 g, 18 mmol) were added at −15 °C, and the mixture was stirred for about 2.5 h at room temperature. To the orange-brown reaction mixture was added water (80 mL), and the aqueous layer was extracted with three 10-mL portions of hexane. The combined organic layer was dried with anhydrous MgSO_4 and then carefully concentrated at room temperature under 20–30 Torr. The residue was placed on an alumina column (3.6 × 68 cm), and an orange band was eluted with hexane.

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Concentration of the eluate gave 1 as an orange oil in 65% yield (1.31 g, 9.74 mmol). 1: ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.81 (6H, s, CH_3), 1.87 (6H, s, CH_3), 5.41 (2H, s, CH_2); ^{13}C NMR (22.5 MHz, C_6D_6) δ 9.4 (CH_3), 11.2 (CH_3), 109.9 (CH_2), 123.8 ($\mathit{C}_5\mathrm{Me}_4$), 138.7 ($\mathit{C}_5\mathrm{Me}_4$), 155.4 ($\mathit{C}_5\mathrm{Me}_4$); IR (NaCl) ν 3080 (w), 2960 (s), 2920 (s), 2855 (s), 1810 (w), 1645 (w), 1632 (w), 1440 (s), 1405 (m), 1378 (m), 1322 (m), 1205 (w), 900 (m); MS (EI) *m/z* 134 (100, M^+).

Preparation of $(\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Fe_2(CO)_6$ (2). A solution of 1 (0.34 g, 2.55 mmol) and $Fe_2(CO)_9$ (1.86 g, 5.11 mmol) in hexane (50 mL) was stirred overnight at 40 °C. Another portion of $Fe_2(CO)_9$ (1.20 g, 3.39 mmol) was added to the mixture, and heating was continued with stirring for 30 h in total. After cooling to room temperature, a small portion of Celite was added to the solution and the solvent was evaporated. The residue was placed on a silica gel flash column (i.d. 3.5 cm × 45 cm). Elution with hexane and concentration of the fractions afforded $Fe(CO)_5$ (trace), $Fe_3(CO)_{12}$ (0.12 g), and $(\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Fe_2(CO)_6$ (2) (orange-red crystals, 0.46 g, 44%) in this order. The eluent was then changed into hexane/benzene (1/3) to collect a red-violet band ($(\eta^5\text{-}C_5Me_5)_2Fe_2(CO)_4$, 0.12 g). 2: ^{1}H NMR (90 MHz, C_6D_6) δ 1.29 (6H, s, CH_3), 1.31 (2H, s, CH_2), 1.36 (6H, s, CH_3); ^{1}H NMR (90 MHz, CS_2) δ 1.58 (2H, s, CH_2), 1.66 (6H, s, CH_3), 1.90 (6H, s, CH_3); ^{13}C NMR (50 MHz, C_6D_6, tris(acetylacetonato)chromium(III) as a relaxation reagent) δ −5.5 (CH_2), 9.9 (CH_3), 10.2 (CH_3), 88.8 ($\mathit{C}_5\mathrm{Me}_4$), 90.2 ($\mathit{C}_5\mathrm{Me}_4$), 99.7 ($\mathit{C}_5\mathrm{Me}_4$), 215.7 (CO); IR (KBr pellet) ν_{CO} 2064 (s), 1993 (m), 1975 (s), 1958 (s), 1913 (m); MS (EI) *m/z* 414 (29, M^+), 386 (43.3, $M^+ - CO$), 358 (14.2, $M^+ - 2CO$), 330 (19.2, $M^+ - 3CO$), 302 (100, $M^+ - 4CO$), 274 (51.3, $M^+ - 5CO$), 246 (58.1, $M^+ - 6CO$). Exact mass calcd for $C_{16}H_{14}O_6Fe_2$ 413.9490, found 413.9490.

Preparation of $(\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Fe_2(CO)_5(PMe_3)$ (3a). To a solution of 2 (0.20 g, 0.48 mmol) in benzene (20 mL) was added PMe_3 (0.15 mL, 1.7 mmol), and the mixture was stirred for 1 h at 40 °C. After removal of the solvent, the red residue was chromatographed on a silica gel flash column (i.d. 2.5 cm × 18 cm; eluent: hexane/benzene = 3/1). Concentration of an orange-red fraction gave $(\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Fe_2(CO)_5(PMe_3)$ (**3a**) as red crystals in 85% yield (0.19 g, 0.41 mmol). **3a**: ^{1}H NMR (90 MHz, C_6D_6) δ 0.99 (9H, d, $^2J_{PH}$ = 8.8 Hz, PCH_3), 1.38 (2H, d, $^3J_{PH}$ = 1.4 Hz, CH_2), 1.55 (6H, s, CH_3), 1.62 (6H, s, CH_3); ^{1}H NMR (90 MHz, CS_2) δ 1.27 (2H, d, $^3J_{PH}$ = 1.2 Hz, CH_2), 1.46 (9H, d, $^2J_{PH}$ = 8.7 Hz, CH_3), 1.59 (6H, s, CH_3), 1.90 (6H, s, CH_3); ^{13}C NMR (50 MHz, $C_6D_5CD_3$) δ −6.3 (CH_2), 10.8 (CH_3), 11.1 (CH_3), 19.4 (d, $^1J_{PC}$ = 28 Hz, $P(CH_3)_3$), 87.5 ($\mathit{C}_5\mathrm{Me}_4$), 91.1 ($\mathit{C}_5\mathrm{Me}_4$), 98.5 ($\mathit{C}_5\mathrm{Me}_4$), 219.9 (d, $^2J_{PC}$ = 9.5 Hz, CO); ^{31}P NMR (36.2 MHz, $C_6D_5CD_3$) δ 16.3; IR (KBr pellet) ν_{CO} 2020 (s), 1940 (br, vs), 1924 (s), 1896 (s); MS (EI) *m/z* 462 (6.0, M^+), 434 (23.4, $M^+ - CO$), 406 (21.0, $M^+ - 2CO$), 378 (100, $M^+ - 3CO$), 350 (5.6, $M^+ - 4CO$), 322 (1.2, $M^+ - 5CO$). Exact mass calcd for $C_{18}H_{23}Fe_2O_5P$ 461.9981, found 462.0009.

Preparation of $(\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Fe_2(CO)_5(PPh_3)$ (3b). A solution of 2 (0.10 g, 0.24 mmol) and PPh_3 (0.070 g, 0.27 mmol) in hexane (15 mL) was stirred for 20 h at 70 °C. Red solid precipitated out during the reaction. The reaction mixture was concentrated to 4 mL under vacuum and then stored in a freezer (−35 °C) overnight to ensure the precipitation of the solid. The supernatant was removed with a syringe, and the remaining red solid was washed several times with 1-mL portions of cold hexane. Crude $(\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Fe_2(CO)_5(PPh_3)$ (**3b**) was obtained as a red solid in 71% yield (0.11 g, 0.17 mmol). Crude **3b** can be recrystallized from toluene/hexane to give red needles. **3b**: ^{1}H NMR (90 MHz, C_6D_6) δ 1.23 (2H, d, $^3J_{PH}$ = 5.2 Hz, CH_2), 1.56 (6H, s, CH_3), 1.58 (6H, s, CH_3), 6.9–8.0 (15H, m, PPh_3); ^{13}C NMR (22.5 MHz, C_6D_6) δ −2.1 (CH_2), 9.8 (CH_3), 10.6 (CH_3), 86.9 ($\mathit{C}_5\mathrm{Me}_4$), 91.2 ($\mathit{C}_5\mathrm{Me}_4$), 98.0 ($\mathit{C}_5\mathrm{Me}_4$), 219.0 (CO); ^{31}P NMR (36.2 MHz, C_6D_6) δ 62.3; IR (KBr pellet) ν_{CO} 2025 (s), 1980 (sh, w), 1942 (br, vs), 1923 (m), 1900 (m); MS (FAB, Xe, *m*-nitrobenzyl alcohol matrix) *m/z* 649 (12.8, $M^+ + 1$), 564 (100, $M^+ - 3CO$), 536 (23.8, $M^+ - 4CO$), 508 (39.4, $M^+ - 5CO$), 386 (47.7, $M^+ - PPh_3$), 358 (28.1, $M^+ - PPh_3 - CO$), 330 (66.7, $M^+ - PPh_3 - 2CO$). Anal. Calcd for $C_{33}H_{29}Fe_2O_5P$: C, 61.14; H, 4.51. Found: C, 61.05; H, 4.66.

Preparation of $(\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Fe_2(CO)_5(dppm)$ (4). A solution of 2 (0.21 g, 0.50 mmol) and bis(diphenylphosphino)methane (dppm) (0.19 g, 0.50 mmol) in benzene (20 mL) was stirred for 4 h at 35 °C. After removal of the solvent, the residue was chromatographed on a silica gel flash column (i.d. 1.6 cm × 15 cm; eluent: hexane/benzene = 2/1). Concentration of a dark red fraction gave $(\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Fe_2(CO)_5(dppm)$ (4) as red crystals in 94% yield (0.36 g, 0.47 mmol). 4: ^{1}H NMR (90 MHz, C_6D_6) δ 1.23 (2H, d, $^3J_{PH}$ = 6.0 Hz, $C\mathit{H}_2C_5Me_4$), 1.55 (6H, s, CH_3), 1.60 (6H, s, CH_3), 3.27 (2H, dd, $^2J_{PH}$ = 2.4, 9.0 Hz, $Ph_2PC\mathit{H}_2PPh_2$), 6.7–7.5 (10H, m, Ph); ^{13}C NMR (150 MHz, C_6D_6, tris(acetylacetonato)chromium(III) as a relaxation reagent) δ −2.2 (d, $^2J_{PC}$ = 3.9 Hz, CH_2), 11.2 (CH_3), 11.3 (CH_3), 32.7 (dd, $^1J_{PC}$ = 19.7, 32.9 Hz, $Ph_2P\mathit{C}H_2PPh_2$), 87.5 ($\mathit{C}_5\mathrm{Me}_4$), 91.7 (d, $^3J_{PC}$ = 3.8 Hz, $\mathit{C}_5\mathrm{Me}_4$), 98.5 ($\mathit{C}_5\mathrm{Me}_4$), 129–139 (m, Ph), 220.0 (br, CO); ^{31}P NMR (36.2 MHz, C_6D_6) δ −27.1 (d, $^2J_{PP}$ = 85 Hz, $FePPh_2CH_2\mathit{P}Ph_2$), 54.5 (d, $^2J_{PP}$ = 85 Hz, $Fe\mathit{P}Ph_2CH_2PPh_2$); IR (KBr pellet) ν_{CO} 2020 (s), 1945 (vs), 1940 (vs), 1898 (s); MS (FAB, Xe, *m*-nitrobenzyl alcohol matrix) *m/z* 770 (43.7, M^+), 658 (65.0, $M^+ - 4CO$), 630 (100, $M^+ - 5CO$). Anal. Calcd for $C_{40}H_{36}Fe_2O_5P_2$: C, 62.37; H, 4.71. Found: C, 61.99; H, 4.82.

Preparation of $[(\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Fe_2(CO)_5]_2(\mu\text{-dppe})$ (5). A solution of 2 (0.10 g, 0.25 mmol) and bis(diphenylphosphino)ethane (dppe) (0.048 g, 0.12 mmol) in hexane (10 mL) was stirred for 7 h at 40 °C. Cooling the reaction mixture to room temperature gave a red precipitate, which was filtered with a Schlenk funnel and washed with small portions of hexane until the washings were no longer colored. Dissolution of the residue in toluene and condensation afforded $[(\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Fe_2(CO)_5]_2(\mu\text{-dppe})$ (5) as red crystals in 92% yield (0.13 g, 0.11 mmol). Analytically pure sample was obtained by repeated recrystallization from toluene/hexane. 5: ^{1}H NMR (200 MHz, C_6D_6) δ 1.10 (4H, br s, $C\mathit{H}_2C_5Me_4$), 1.49 (12H, s, CH_3), 1.53 (12H, s, CH_3), 2.62 (4H, br s, $Ph_2PC\mathit{H}_2C\mathit{H}_2PPh_2$), 6.9–7.4 (20H, m, Ph); ^{13}C NMR (50 MHz, C_6D_6) δ −3.4 ($\mathit{C}H_2C_5H_4$), 10.5 (CH_3), 26.2 (t, J_{PC} = 9.4 Hz, $Ph_2P\mathit{C}H_2\mathit{C}H_2PPh_2$), 87.0 ($\mathit{C}_5\mathrm{Me}_4$), 91.1 ($\mathit{C}_5\mathrm{Me}_4$), 98.0 ($\mathit{C}_5\mathrm{Me}_4$), 129.0 (vt, J_{PC} = 4.5 Hz, Ph), 130.1 (s, Ph), 132.2 (vt, J_{PC} = 4.7 Hz, Ph), 135.0 (vt, J = 19.0 Hz, Ph), 219.0 (br, CO); ^{31}P NMR (36.2 MHz, C_6D_6) δ 58.2; IR (KBr pellet) ν_{CO} 2030 (s), 1924 (br, vs), 1905 (m); MS (FAB, Xe, *m*-nitrobenzyl alcohol matrix) *m/z* 1171 (0.7, $M^+ + 1$), 1086 (3.3, $M^+ - 3CO$), 784 (2.1, $M^+ - \{(CH_2C_5Me_4)Fe_2(CO)_5\}$), 538 (86.2, $Fe(dppe)(CO)_3$), 510 (92.3, $Fe(dppe)(CO)$), 454 (100, Fe(dppe)). Anal. Calcd for $C_{56}H_{52}Fe_4O_{10}P_2$: C, 57.48; H, 4.48. Found: C, 57.86; H, 4.73. The reaction of 2 with dppe in a 1:1 ratio under the same conditions gave 5 in 60% yield along with some unidentified products.

Preparation of $(\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Fe_2(CO)_5(PPh_2H)$ (6). To a solution of 2 (0.17 g, 0.48 mmol) in hexane (30 mL) was added PPh_2H (0.21 g, 1.11 mmol), and the mixture was stirred for 55 h at room temperature. After removal of the solvent, the residue was chromatographed on an alumina column (300 mesh, i.d. 2.6 cm × 30 cm; eluent: hexane/benzene = 3/1). Concentration of a red fraction gave red crystals of 6 in 68% yield (0.16 g, 0.28 mmol). 6: ^{1}H NMR (200 MHz, C_6D_6) δ 1.43 (2H, d, $^3J_{PC}$ = 4.2 Hz, CH_2), 1.49 (6H, s, CH_3), 1.57 (6H, s, CH_3), 6.39 (1H, d, $^1J_{PH}$ = 349.8 Hz, PH), 6.9–7.6 (10H, m, PPh_2H); ^{13}C NMR (22.5 MHz, C_6D_6) δ −4.0 (CH_2), 10.6 (CH_3), 87.2 ($\mathit{C}_5\mathrm{Me}_4$), 90.1 ($\mathit{C}_5\mathrm{Me}_4$), 98.2 ($\mathit{C}_5\mathrm{Me}_4$), 130–140 (m, PPh_2), 218.4 (CO); ^{31}P NMR (36.2 MHz, C_6D_6) δ 50.4; IR (KBr pellet) ν_{CO} 2025 (w), 1950 (s), 1934 (sh, s), 1900 (m); MS (FAB, Xe, *m*-nitrobenzyl alcohol matrix) *m/z* 573 (3.1, $M^+ + 1$), 544 (8.0, $M^+ - CO$), 516 (19, $M^+ - 2CO$), 488 (46, $M^+ - 3CO$), 460 (100, $M^+ - 4CO$), 431 (39, $M^+ - 5CO - H$), 354 (8.1, $Fe(PPh_2H)(CO)_4$). Exact mass calcd for $C_{27}H_{25}Fe_2O_5P$ 572.0139, found 572.0126.

Preparation of $(C_5Me_5)Fe_2(CO)_4(\mu\text{-}CO)(\mu\text{-}PPh_2)$ (7). A solution of 6 (0.16 g, 0.28 mmol) in benzene was stirred for 40 h at 60 °C, and then for 25 h at 70 °C. The solvent was removed and the residue was chromatographed on an alumina column (200 mesh, i.d. 1.4 cm × 17 cm; eluent: hexane/benzene = 2/1). A black band was collected and concentrated to give 0.082 g (0.14 mmol, 50%) of 7 as black crystals. 7: ^{1}H NMR (200 MHz, C_6D_6) δ 1.38 (d, $^4J_{PH}$ = 0.5 Hz, 15H, CH_3), 6.8–7.7 (m, 10H, PPh_2); ^{13}C

Table I. Crystal Data for (η^1:η^5-$CH_2C_5Me_4$)$Fe_2(CO)_5$(dppm) (4)

formula	$C_{40}H_{36}Fe_2O_5P_2$
fw	770.37
cryst system	monoclinic
space group	$P2_1/a$ (variant of No. 14)
a/Å	20.334(5)
b/Å	10.978(2)
c/Å	18.525(5)
β/deg	116.17(2)
V/Å^3	3711.2(4)
Z	4
D_{calcd}/g cm^{-3}	1.38
μ(Mo Kα)/cm^{-1}	4.34
cryst size/mm	0.25 × 0.15 × 0.10
temp/°C	18
2θ range/deg	3–50
scan mode	ω-2θ
ω scan width/deg	1.1 + 0.35 tan θ
no. of unique data	6912
no. of data used with $\|F_o\| > 3\sigma(F_o)$	3441
no. of refined params	459
R[a]	0.065
R_w[b]	0.086
quality of fit indicator (QFI)[c]	1.21

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = [\sigma^2(F_o) + aF_o^2]^{-1}$, where $a = 0.0024$. [c] $QFI = [\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

NMR (50 MHz, C_6D_6) δ 9.7 (s, CH_3), 97.1 (C_5Me_5), 128.9 (d, J_{PC} = 10.4 Hz, P*Ph*$_2$), 129.8 (d, J_{PC} = 3.1 Hz, P*Ph*$_2$), 133.9 (d, J_{PC} = 9.2 Hz, P*Ph*$_2$), 138.7 (d, J_{PC} = 33.2 Hz, P*Ph*$_2$), 225.7 (d, J_{PC} = 11.0 Hz, CO); ^{31}P NMR (36.2 MHz, C_6D_6) δ 169.9; IR (CH_2Cl_2) ν_{CO} 2040 (m), 2020 (s), 1960 (br, vs), 1769 (br, m); IR (KBr pellet) ν_{CO} 2015 (s), 2008 (s), 1970 (s), 1958 (s), 1940 (s), 1935 (s), 1918 (s), 1777 (m), 1763 (m); MS (EI) m/z 572 (21, M$^+$), 544 (17, M$^+$ – CO), 516 (29, M$^+$ – 2CO), 488 (25, M$^+$ – 3CO), 460 (100, M$^+$ – 4CO), 432 (81, M$^+$ – 5CO or M$^+$ – $Fe(CO)_3$), 404 (14, M$^+$ – $Fe(CO)_4$), 376 (56, M$^+$ – $Fe(CO)_5$). Anal. Calcd for $C_{27}H_{25}Fe_2O_5P$: C, 56.68; H, 4.40. Found: C, 56.53; H, 4.68.

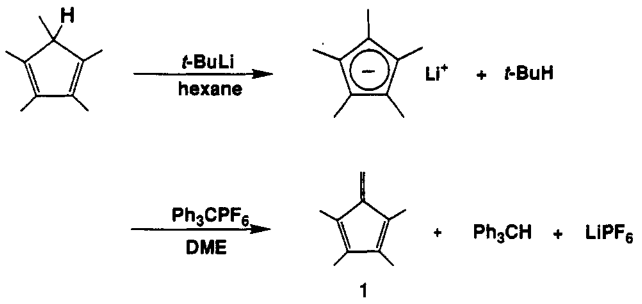
X-ray Crystal Structure Determination of 4. A red needle was grown by layering hexane on a toluene solution of 4 followed by keeping it at –15 °C. Intensity data were collected on a Rigaku AFC-6A four-circle diffractometer with graphite-monochromated Mo Kα radiation at 18 °C. Crystallographic parameters are listed in Table I. The structure was solved by the heavy atom method and refined by the block-diagonal least-squares method with individual anisotropic thermal parameters for non-hydrogen atoms. Positions of two hydrogen atoms of the *exo*-methylene and another two of the methylene in dppm were found on the difference Fourier synthesis and refined with isotropic thermal parameters. Positions of the hydrogen atoms of phenyl groups were calculated and added to the structure factor calculations but were not refined. All the calculations were performed on a Nippon Electric Co. ACOS-2000 computer system at the Computer Center of Tohoku University with the Universal Program System UNICS III.[17]

Results and Discussion

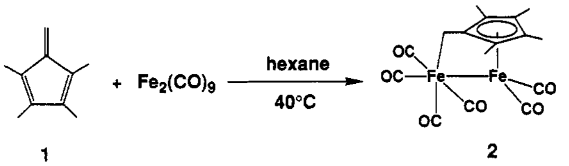
Preparation of 1,2,3,4-Tetramethylfulvene. 1,2,3,4-Tetramethylfulvene (1) was prepared by hydride abstraction from (pentamethylcyclopentadienyl)lithium by Ph_3CPF_6 in a mixture of hexane and DME (Scheme I). Pure 1 was isolated as an orange oil in 65% yield by column chromatography (alumina, hexane).

The ^{1}H NMR spectrum of 1 in $CDCl_3$ shows two methyl signals at δ 1.81 and 1.87 ppm and an *exo*-methylene signal at δ 5.41 ppm. These values agree well with the literature data (δ 1.82, 1.87, 5.40 ppm).[6] The formation of 1 is further supported by the ^{13}C NMR spectrum in which the signal of the *exo*-methylene carbon appears at δ 109.9 ppm, and the mass spectrum which shows the molecular ion peak as a base peak at m/z 134. Neat 1 gradually decomposes over several weeks even if it is stored under an argon atmosphere at –80 °C.

Scheme I



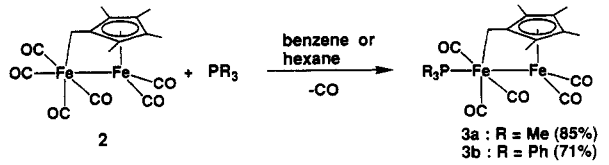
Reaction of 1 with $Fe_2(CO)_9$. The reaction of 1 with $Fe_2(CO)_9$ in hexane at 40 °C afforded the fulvene-bridged diiron complex (η^1:η^5-$CH_2C_5Me_4$)$Fe_2(CO)_6$ (2) as red crystals in 44% yield with small amounts of (η^5-$C_5Me_5)_2$-$Fe_2(CO)_4$ and $Fe_3(CO)_{12}$ (eq 1).



(1)

The ^{1}H NMR spectrum of 2 in C_6D_6 shows a singlet for the *exo*-methylene group at δ 1.31 ppm. This is shifted by about 4 ppm to higher field compared to that of the free fulvene 1 (δ 5.41 ppm), suggesting the occurrence of σ-bonding interaction between the *exo*-methylene carbon and a metal. Similarly, in the ^{13}C NMR spectrum of 2 in C_6D_6 the signal assigned to the *exo*-methylene carbon appears at δ –5.5 ppm, a typical chemical shift of the sp^3 carbon directly bound to a metal, and is shifted by more than 100 ppm to higher field from the signal of 1 (δ 109.9 ppm). A single sharp signal for carbonyl carbons at δ 215.7 ppm strongly suggests that the carbonyl ligands are mutually exchanging rapidly.

Reactions of 2 with Phosphines. When complex 2 was treated with monophosphine PR_3 (R = Me or Ph) in mildly heated benzene or hexane, one carbonyl ligand was replaced by the phosphine to give 3 as red crystals in high yield (eq 2). Each of the ^{1}H NMR spectra of 3a and 3b shows only two singlets for methyl protons on the five-membered ring and a doublet for the *exo*-methylene protons. The latter is apparently coupled with a phosphorus of the phosphine ligand. These features suggest that the molecule of 3 has an internal mirror plane dividing the tetramethylfulvene ligand into two equal parts, and the phosphine ligand is bound to the iron atom which is coordinated to the *exo*-methylene. There are two possible structures for 3 which satisfy these requirements, but the structure shown in eq 2 is more favorable than the other



(2)

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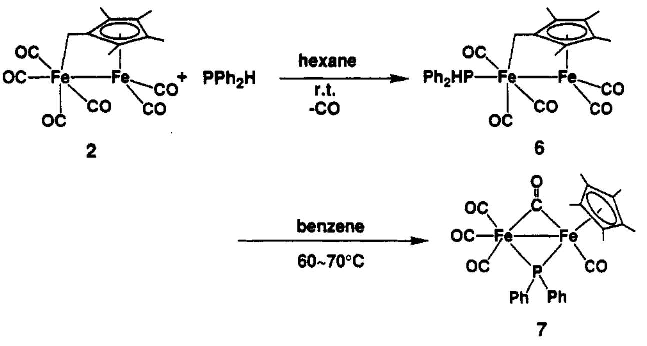
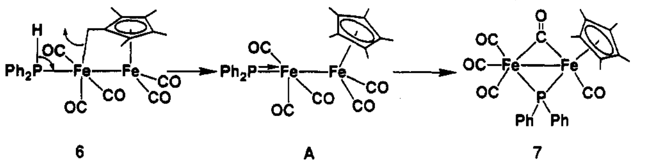
(17) Sakurai, T.; Kobayashi, M. *Rikagaku Kenkyuusho Houkoku* **1979**, *55*, 69.

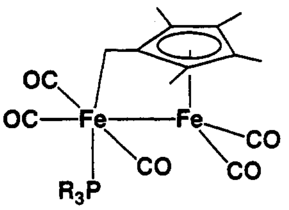
Scheme II



Scheme III



structure 3′ because the steric hindrance of the former is apparently less than that of the latter according to the molecular model study using space-filling models. The former structure is also supported by the crystal structure of the dppm derivative ($(\eta^1:\eta^5\text{-}CH_2C_5Me_4)Fe_2(CO)_5(dppm)$ (4) (vide infra). It can be inferred from the comparison of spectroscopic data that the coordination geometries around two iron atoms of **3a**, **3b**, and **4** (and also **5** and **6**; see below) are the same.



3′

The reaction of **2** with bis(diphenylphosphino)alkanes, $Ph_2P(CH_2)_nPPh_2$ ($n = 1, 2$), markedly depends on the length of the methylene chain. In the case of bis(diphenylphosphino)methane (dppm, $n = 1$), the product was exclusively a unidentate complex **4** (yield 94%). On the other hand, the reaction of **2** with bis(diphenylphosphino)ethane (dppe, $n = 2$) afforded a dppe-bridged tetranuclear complex **5** cleanly (92%) when 2 molecular equivalents of **2** against dppe was used (eq 3). This tetranuclear complex **5** was still a major product (yield 60%) even when **2** and dppe were allowed to react in a 1:1 ratio.

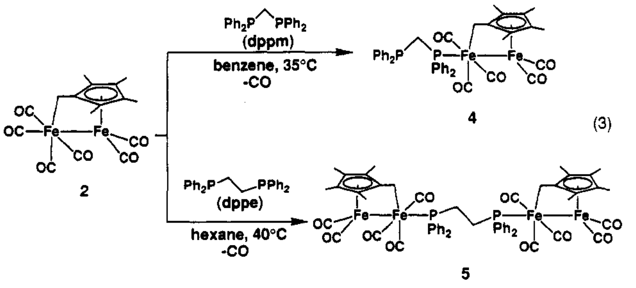


Table II. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for $(\eta^1:\eta^5\text{-}CH_2C_5Me_4)Fe_2(CO)_5(dppm)$ (4)[a]

atom	x	y	z	$B_{eqv}/\text{Å}^2$ [b]
Fe(1)	3057.7(6)	754.4(10)	2937.5(7)	3.5
Fe(2)	2757.1(7)	−261.7(11)	4107.0(7)	3.7
P(1)	3302(1)	1990(2)	2130(1)	3.2
P(2)	2401(1)	755(2)	494(1)	3.6
O(1)	1484(3)	542(8)	1882(4)	7.1
O(2)	4607(4)	683(8)	4106(4)	7.5
O(3)	3214(5)	−1638(6)	2336(5)	8.5
O(4)	1709(4)	−2052(7)	3118(5)	8.1
O(5)	3934(4)	−2015(7)	4780(5)	7.9
C(1)	2713(4)	1652(7)	4139(5)	3.6
C(2)	2008(5)	1139(7)	4018(5)	3.9
C(3)	2138(5)	399(8)	4703(5)	4.2
C(4)	2901(5)	423(7)	5233(5)	4.2
C(5)	3258(4)	1190(7)	4905(5)	3.8
C(6)	2869(4)	2273(7)	3540(5)	3.4
C(7)	1256(4)	1458(9)	3369(5)	4.9
C(8)	1553(6)	−251(10)	4843(7)	6.4
C(9)	3261(7)	−171(10)	6053(6)	6.9
C(10)	4044(5)	1592(9)	5341(5)	5.1
C(11)	2091(5)	652(9)	2314(5)	4.6
C(12)	4001(5)	726(9)	3682(5)	5.2
C(13)	3152(6)	−691(8)	2562(6)	5.2
C(14)	2128(5)	−1335(9)	3504(5)	5.3
C(15)	3466(5)	−1298(8)	4498(5)	4.9
C(16)	2577(4)	2174(7)	1093(5)	3.2
C(111)	4111(4)	1703(8)	1948(5)	4.1
C(112)	4471(5)	591(9)	2158(5)	5.3
C(113)	5090(6)	377(12)	2032(7)	7.6
C(114)	5318(5)	1258(14)	1667(7)	8.1
C(115)	4948(6)	2389(12)	1441(6)	7.1
C(116)	4337(5)	2591(9)	1575(6)	5.1
C(121)	3482(4)	3538(7)	2507(5)	3.6
C(122)	4171(5)	3803(9)	3138(6)	5.3
C(123)	4292(6)	4935(10)	3629(6)	6.4
C(124)	3754(7)	5757(9)	3302(7)	7.3
C(125)	3082(7)	5531(8)	2688(7)	6.7
C(126)	2938(5)	4404(8)	2285(5)	4.6
C(211)	2995(4)	965(7)	−10(5)	3.8
C(212)	3462(4)	5(8)	53(5)	4.3
C(213)	3946(5)	82(11)	−292(6)	6.0
C(214)	3929(5)	1098(12)	−723(6)	6.8
C(215)	3479(6)	2055(11)	−780(6)	6.5
C(216)	2999(5)	2014(9)	−420(5)	4.7
C(221)	1477(4)	1079(7)	−310(5)	3.6
C(222)	1314(5)	1266(11)	−1103(5)	6.0
C(223)	591(5)	1434(13)	−1676(6)	7.0
C(224)	46(5)	1415(12)	−1466(6)	7.2
C(225)	209(5)	1232(17)	−661(7)	9.5
C(226)	918(5)	1071(14)	−98(6)	7.4
atom	**x**	**y**	**z**	**$B_{iso}/\text{Å}^2$**
H(6A)	244(4)	264(7)	320(5)	5.1(19)
H(6B)	336(3)	271(5)	378(3)	2.2(13)
H(16A)	219(4)	245(7)	114(4)	3.9(17)
H(16B)	277(4)	287(7)	86(4)	4.0(17)

[a] Coordinates for non-hydrogen atoms are multiplied by 10^4 and those for hydrogen atoms by 10^3. [b] The equivalent isotropic temperature factors for non-hydrogen atoms were computed by the following equation: $B_{eqv} = {}^4/_3(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{12}ab\cos\gamma + B_{13}ac\cos\beta + B_{23}bc\cos\alpha)$. The B_{ij}'s are defined by the equation: $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$.

The ^{31}P NMR of **4** shows two doublets ($^2J_{PP} = 85$ Hz) at δ −27.1 and 54.5 ppm, indicating the existence of two different phosphorus atoms coupled with each other. The former value is close to the chemical shift of free dppm (δ −22.7 ppm),[16] while the latter is in the range of the chemical shifts of coordinated phosphines. These spectroscopic results are consistent with the structure of the complex with a unidentate dppm. The structure of **4** was further supported by the mass spectrum and confirmed by the X-ray crystal structure analysis (vide infra). The symmetrically bridged structure of the dppe complex **5** was determined on the basis of the mass and ^1H NMR

Table III. Selected Bond Distances (Å) for (η^1:η^5-$CH_2C_5Me_4$)$Fe_2(CO)_5$(dppm) (4)

Fe(1)–Fe(2)	2.735(3)	Fe(1)–P(1)	2.233(4)
Fe(1)–C(6)	2.133(11)	Fe(2)–C(1)	2.104(8)
Fe(2)–C(2)	2.118(10)	Fe(2)–C(3)	2.134(16)
Fe(2)–C(4)	2.113(16)	Fe(2)–C(5)	2.106(10)
Fe(1)–C(11)	1.792(9)	Fe(1)–C(12)	1.803(10)
Fe(1)–C(13)	1.776(12)	Fe(2)–C(14)	1.736(10)
Fe(2)–C(15)	1.725(9)		
C(1)–C(2)	1.46(1)	C(2)–C(3)	1.43(2)
C(3)–C(4)	1.42(1)	C(4)–C(5)	1.41(2)
C(5)–C(1)	1.45(2)	C(1)–C(6)	1.45(2)
C(2)–C(7)	1.51(1)	C(3)–C(8)	1.51(2)
C(4)–C(9)	1.51(2)	C(5)–C(10)	1.50(1)
P(1)–C(16)	1.845(11)	P(2)–C(16)	1.854(11)

Table IV. Selected Bond Angles (deg), Dihedral Angles (deg), and Plane–Bond Angles (deg) for (η^1:η^5-$CH_2C_5Me_4$)$Fe_2(CO)_5$(dppm) (4)

Bond Angles			
Fe(1)–C(6)–C(1)	100.6(7)	Fe(2)–Fe(1)–C(6)	75.5(3)
Fe(2)–Fe(1)–P(1)	166.5(2)	Fe(2)–Fe(1)–C(11)	85.4(3)
Fe(2)–Fe(1)–C(12)	85.5(3)	Fe(2)–Fe(1)–C(13)	92.6(4)
Fe(1)–Fe(2)–C(14)	97.2(4)	Fe(1)–Fe(2)–C(15)	99.4(3)
C(14)–Fe(2)–C(15)	116.9(4)	P(1)–Fe(1)–C(11)	96.4(3)
P(1)–Fe(1)–C(12)	92.7(3)	P(1)–Fe(1)–C(13)	100.7(4)
P(1)–Fe(1)–C(6)	91.2(3)	C(6)–Fe(1)–C(11)	89.2(4)
C(6)–Fe(1)–C(12)	89.4(4)	C(6)–Fe(1)–C(13)	168.1(5)
C(11)–Fe(1)–C(12)	170.8(4)	C(11)–Fe(1)–C(13)	88.2(5)
C(12)–Fe(1)–C(13)	91.3(5)	Fe(1)–P(1)–C(16)	116.9(4)
P(1)–C(16)–P(2)	112.7(4)		
Dihedral Angles			
C(11)–Fe(1)–P(1)–C(16)	166		
Fe(1)–P(1)–C(16)–P(2)	67		
Plane–Bond Angles			
C(6)–H(6A)–H(6B) plane vs C(1)–C(6) bond	135		
C(6)–H(6A)–H(6B) plane vs Fe(1)–C(6) bond	125		

spectra, and the ^{31}P NMR spectrum which shows only one singlet in the region of coordinated phosphines (δ 58.2 ppm).

The reaction of 2 with diphenylphosphine showed a unique secondary reaction after a normal ligand substitution reaction. When this reaction was performed at room temperature, the diphenylphosphine complex (η^1:η^5-$CH_2C_5Me_4$)$Fe_2(CO)_5(PPh_2H)$ (6) was obtained as red crystals in 58% yield (eq 4). This product was then completely changed to a black, phosphido-bridged diiron complex, (η^5-C_5Me_5)$Fe_2(CO)_4(\mu$-$CO)(\mu$-$PPh_2)$ (7), upon heating the benzene solution of 6 at 60–70 °C (Scheme II).

By the latter reaction, the ^1H NMR signals of a P–H (δ 6.39 ppm, $^1J_{PH}$ = 349.8 Hz), an *exo*-methylene, and two kinds of methyl groups on the tetramethylfulvene ligand in 6 disappeared, and a sharp signal newly appeared at δ 1.38 ppm, which is assigned to the methyl protons of pentamethylcyclopentadienyl ligand in 7. The ^{31}P NMR spectrum of 7 shows a signal at significantly low field (δ 169.9 ppm) which strongly supports the existence of a bridging phosphido ligand.[18] In addition, the IR spectrum of 7 in solution indicates that one carbonyl ligand is bridging while the others are terminal. The IR spectrum of solid 7 in the KBr pellet is more complicated perhaps due to the effect of crystal packing. In close connection with this phosphido-bridged complex 7, the cyclopentadienyl analogue, (η^5-C_5H_5)$Fe_2(CO)_4(\mu$-$CO)(\mu$-$PPh_2)$, has been already synthesized by Haines et al. by the reaction of $Fe(CO)_4(PPh_2Cl)$ with Na[$Fe(CO)_2(\eta^5$-$C_5H_5)$] followed by photochemical decarbonylation.[19]

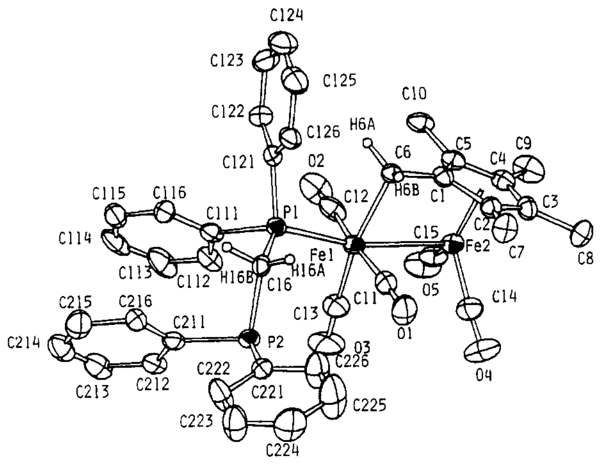


Figure 1. ORTEP diagram and numbering scheme of 4 with thermal ellipsoids drawn at the 30% level.

Scheme III shows a plausible mechanism for the rearrangement of 6 to 7. In this mechanism, the [1,3] shift of a hydrogen from the diphenylphosphine to the *exo*-methylene of the fulvene ligand occurs first to give an intermediate A containing a terminal phosphido ligand, which then rearranges to give 7.

X-Ray Crystal Structure of 4. The ORTEP diagram of the molecule is shown in Figure 1. Atomic coordinates, bond distances, and bond angles are summarized in Tables II, III, and IV.

It is clear from Figure 1 that the dppm in 4 is unidentate and occupies the coordination site *trans* to the Fe–Fe bond. This is probably because the coordination geometry has the least steric repulsion between dppm and other ligands. This geometry is also common for dinuclear complexes with both carbonyl and bulky phosphine ligands.[20] As for the conformation around the P(1)–Fe(1) bond, the Ph_2PCH_2 group is *anti* toward the η^1:η^5-$CH_2C_5Me_4$ ligand and locates between two CO ligands. Perhaps as a result of this conformation, the P(1)–Fe(1) bond is bent toward the fulvene ligand to relieve the steric repulsion between the Ph_2PCH_2 group and the CO ligands (P(1)–Fe(1)–Fe(2): 166.5(2)°).

Other structural characteristics of 4 are as follows: (1) Fe(1) and Fe(2) adopt octahedral and distorted piano stool coordination geometries, respectively. (2) Bond lengths between Fe(2) and carbons of the five-membered ring are almost equal, ranging between 2.104(8) and 2.134(16) Å. (3) The distance between Fe(1) and the *exo*-methylene carbon is 2.133(11) Å, which is in the range of normal Fe–C single bond lengths. (4) The Fe(1)–C(6)–C(1) angle (100.6(7)°) is close to the theoretically expected valence angle for sp^3 carbon (109.5°). These features are all consistent with the following coordination mode of the tetramethylfulvene ligand: The five-membered ring of the fulvene ligand is bound to the $Fe(CO)_2$ fragment in η^5-fashion, while the *exo*-methylene part is bound to the $Fe(CO)_3$(dppm) fragment in η^1-fashion. It should be noted, however, that the bond between the *exo*-methylene carbon and a ring carbon (C(6)–C(1): 1.45(2) Å) is somewhat shorter than the other four C–C single bonds projecting

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[18] (a) King, R. B.; Wu, F. J.; Holt, E. M. *J. Am. Chem. Soc.* **1988**, *110*, 2775. (b) Kyba, E. P.; Davis, R. E.; Clubb, C. N.; Liu, S. T.; Palacios, H. O. A.; McKennis, J. S. *Organometallics* **1986**, *5*, 869.

[19] Haines, R. J.; Nolte, C. R.; Greatrex, R.; Greenwood, N. N. *J. Organomet. Chem.* **1971**, *26*, C45.

[20] Wawersik, H.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1966**, 366.

out of the five-membered ring. This fact can be interpreted as a sign of remaining double-bond character on the C(6)–C(1) bond of the fulvene ligand.

The Fe(1)–Fe(2) distance (2.735(3) Å) corresponds to that of a normal Fe–Fe single bond. However, this bond is expected to be fairly polarized because the ligands on Fe(1) and Fe(2) are very different. In fact, on the basis of the observation that Fe(2)–C(carbonyl) distances (average: 1.740 Å) are shorter than Fe(1)–C(carbonyl) distances (average: 1.790 Å), we can estimate that the back-donation from Fe(2) to a carbonyl ligand is stronger than that from Fe(1). In other words, Fe(2) is more electron-rich than Fe(1). This is ascribable mainly to the strong electron-donor ability of the η^5-C_5Me_4 part of a tetramethylfulvene ligand.

The reaction of 2 with dppm gives a unidentate complex 4, while that with dppe provides a bidentate complex 5 in which two $(\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Fe_2(CO)_5$ fragments are connected by a dppe molecule. Apparently, the difference of reactivity toward the diphosphines arises from a steric factor: In 4, the coordinated and uncoordinated PPh_2's are separated by only one methylene group, and thus the steric interaction between them are fairly large. Probably, this interaction strongly requires the uncoordinated PPh_2 to take the conformation shown in Figure 1, in which the lone pair of P(2) is sterically protected from the access of the second $(\eta^1{:}\eta^5\text{-}CH_2C_5Me_4)Fe_2(CO)_5$ moiety. On the other hand, the ethylene chain of dppe is long enough to keep two PPh_2 parts apart from each other with considerably less steric interaction. This allows both of these PPh_2 parts to be coordinated to the diiron moieties.

Acknowledgment. This work was supported by a Grant-in-Aid for Special Project Research (04241102) from the Ministry of Education, Science and Culture.

Supplementary Material Available: Tables of calculated atomic coordinates, isotropic thermal parameters, mean square displacement tensors for non-hydrogen atoms, all bond lengths and angles, and least-squares planes and atomic deviations for 4 and a packing diagram for 4 (12 pages). Ordering information is given on any current masthead page.

OM9207929