Four Different Coordination Modes of 1,1′-Bis(diphenylphosphino)ferrocene: Synthesis, X-Ray Crystal Structure, and Iron-57 Mössbauer Spectroscopy of Four Metal Carbonyl Complexes with 1,1′-Bis(diphenylphosphino)ferrocene (dppfe)

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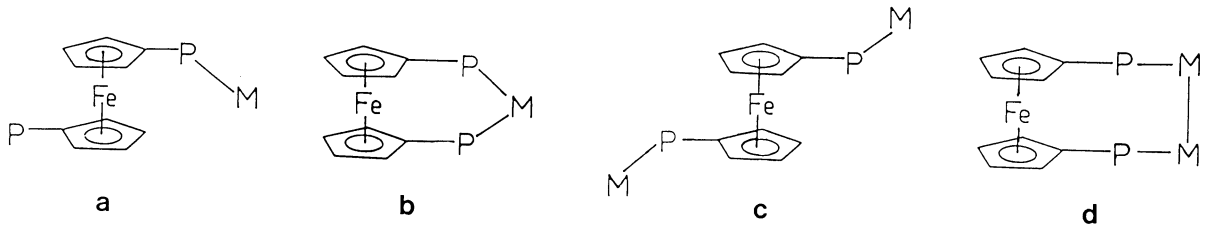
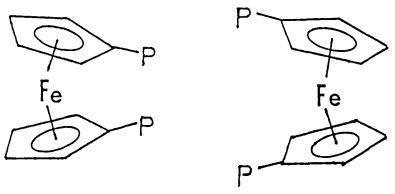
Four kinds of methal carbonyl complexes with 1,1′-bis(diphenylphosphino)ferrocene (dppfe) are synthesized and their molecular structures are determined by single-crystal X-ray analyses. Crystal data for (η^5-$CH_3C_5H_4$)-$Mn(CO)_2$dppfe (**1**), (η^5-$CH_3C_5H_4$)Mn(CO)dppfe (**2**), $[ClMn(CO)_4]_2$(μ-dppfe) (**3**), and $CH_3CCo_3(CO)_7$dppfe (**4**) are as follows: **1**, *Pbca*, a=20.551(3), b=28.951(5), c=11.786(1) Å, V=7012(2) Å^3, Z=8; **2**, $P2_1/n$, a=18.682(5), b=20.495(4), c=9.750(2) Å, β=91.24(2)°, V=3732(1) Å^3, Z=4; **3**, $A2/a(C2/c)$, a=18.978(5), b=15.293(4), c=16.513(5) Å, β=112.62(2)°, V=4423.9(2) Å^3, Z=4; **4**, $P\bar{1}$, a=13.031(2), b=15.338(2), c=11.583(2) Å, α=99.13(2)°, β=98.35(2)°, γ=99.64(2)°, V=2218.1(7) Å^3, Z=2; Mo $K\alpha$ radiation; R=0.075, 0.084, 0.074, and 0.056 for 2639, 4219, 2575, and 6098 reflections, respectively. Dppfe functions as a monodentate ligand in **1** with the rotational angle 128.0° for two cyclopentadienyl rings, as a bidentate chelating ligand in **2** with the rotational angles 3.1°, as a bidentate bridging ligand (no metal–metal bond) in **3** with the rotational angle 180°, and as a bridging ligand (over metal-metal bond) in **4** with the rotational angle 69.6°, respectively; Mn–P=2.242(4) Å (**1**), Mn–P=2.215(2) and 2.216(3) Å (**2**), Mn–P=2.364(4) Å (**3**), and Co–P=2.297(2) and 2.314(2) Å (**4**). The two cyclopentadienyl rings of dppfe are slightly tilted (2.3—5.7° for tilt angles in **1**, **2**, and **4**) and are parallel in **3**. The coordinated P atoms are significantly displaced from the cyclopentadienyl ring planes. From the comparison of these geometrical parameters, it is concluded that the rotation of the two cyclopentadienyl rings is a predominant factor to determine various coordination modes of dppfe rather than the tilt of the two rings and/or the deviation of the P atoms from the ring plane. The ^{57}Fe Mössbauer spectra of this series of compounds show doublets with parameters (IS=0.50—0.52 mm s^{-1} relative to Fe, QS=2.22—2.35 mm s^{-1}). Although isomer shifts are essentially constant, the quadrupole splittings have a tendency to increase with the increase of the rotational angle of the two cyclopentadienyl rings. ^{1}H and ^{31}P NMR spectra are measured for all of these compounds.

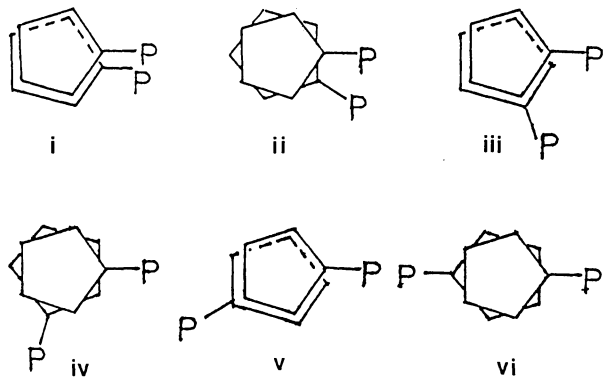
Since the first synthesis of the platinum complex with 1,1′-bis(diphenylphosphino)ferrocene (dppfe) by Whitesides et al. in 1972,[1] considerable papers on the transition metal complexes with dppfe, its congeners and/or its derivatives have been reported.[2] These papers have stemmed from the interest in their catalytic properties,[3] their possible antitumor activity,[4] and/or their cooperative activity as heterobimetallic compounds in which the two metal atoms are held in close proximity.[5] We have, however, been interested in potential versatility of dppfe as a ligand and noticed that dppfe should form metal complexes in a similar manner to that of bis(diphenylphosphino)methane, dppm (Scheme 1); dppfe possesses two freedoms to adjust the coordination mode to metals and/or to minimize the strain which should be imposed on dppfe in complexation with metals. These are the tilt of the two Cp rings (Scheme 2) and the rotation about the Cp–Fe–Cp axis (Scheme 3). Although dppfe can adjust its bite angle and/or distance between two metal atoms which dppfe bridges in such manners as described above, only the coordination mode **b** in Scheme 1 as a bidentate chelating ligand had been reported for X-ray structurally characterized compounds until quite recently.[2c,2g,2l,2k,3c,6a] Hill et al., however, reported in 1989 the synthesis and X-ray structure analysis of $[AuCl]_2$(μ-dppfe) which shows the coordination mode **c** in Scheme 1 (Fe atom is located at the inversion center similar to the free dppfe ligand).[7] An analogous compound, $[ClMn(CO)_4]_2$(μ-dppfe) has been provided recently and also the bridging geometry of dppfe (coordination mode **d** in Scheme 1) has been revealed for the first time for $CH_3CCo_3(CO)_7$dppfe by this laboratory.[6b] Thus, it is quite interesting to clarify the factors which primarily affect the coordination mode



Scheme 1.



Scheme 2.



Scheme 3.

of dppfe. Here we report the syntheses, ^{57}Fe-Mössbauer characterization, and the amassed details of the crystal and molecular structure analyses for a series of dppfe complexes[6] in which all the coordination modes **a**—**d** in Scheme 1 are exhibited.

Experimental

General Procedures and Materials. Syntheses and manipulations were made under a nitrogen atmosphere with standard Schlenk-line techniques. All solvents were purified by standard procedures. Photolysis was made with a Riko 100 W high-pressure Hg lamp under an argon atmosphere. 1,1′-bis(diphenylphosphino)ferrocene (dppfe), tricarbonyl (methylcyclopentadienyl)manganese, decacarbonyldimanganese, and octacarbonyldicobalt were purchased from Strem Chemicals and were used as received. $CH_3CCo_3(CO)_9$ was synthesized according to the literature method from $Co_2(CO)_8$.[8] IR spectra were recorded on a JASCO 701G spectrometer. ^{1}H NMR spectra were recorded with Hitachi-Perkin-Elmer R-20B and R-24B spectrometers (60 MHz). ^{31}P NMR spectra were measured on a Varian XL-200 spectrometer operated at 80.984 MHz with Fourier transform mode for the naturally abundant level and were referenced to external H_3PO_4 using a 10 mm o.d. sample tube. A positive chemical shift designates a resonance to a lower field than that of the resonance of the standard. ^{57}Fe-Mössbauer spectra were obtained on about 100 mg of finely powdered crystals contained in a brass holder of 8-mm diameter. The holder was wrapped with Teflon tape and maintained at 80 K through the data collection. The data were accumulated and analyzed by an Elscint AME-50 spectrometer. Isomer shift is referred to iron foil.

(η^5-$CH_3C_5H_4$)Mn(CO)$_2$dppfe (1) and (η^5-$CH_3C_5H_4$)Mn(CO)dppfe (2). A benzene solution (75 mL) of $(CH_3C_5H_4)Mn(CO)_3$ (0.41 g, 2 mmol) and dppfe (1.11 g, 2 mmol) was photolyzed for 3.5 h. The resulting yellow brown precipitate was filtered off and the solvent was partially distilled off from the filtrate at reduced pressure. This concentrated solution was loaded on a Florisil column. A yellow band was eluted with petroleum ether and vacuum-distillation of the solvent left yellow solid. Recrystallization of this solid from dichloromethane–hexane (1 : 10) gave a yellow microcrystalline product **1**. Yield 300 mg (20%). Anal. Calcd for $[Mn(CO)_2(CH_3C_5H_4)(dppfe)]$, $C_{42}H_{35}FeMnO_2P_2$: C, 67.76; H, 4.74%. Found: C, 67.53; H, 4.91%. IR (ν(CO)) (Nujol mull) 1920(s), 1845(s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C) δ=1.6(1H, CH_3), 1.8(2H, CH_3), 4.0(6H, C_5H_4), 4.3(6H, C_5H_4), 7.3(20H, C_6H_5). Then an orange band was eluted with benzene. The orange-red product from the benzene effluent was recrystallized from chloroform–hexane to yield orange-red crystals **2**. Yield 340 mg (30%). Anal. Calcd for $C_{41}H_{35}FeMnOP_2\cdot CHCl_3$: C, 60.35; H, 4.34%. Found: C, 60.79; H, 4.45%. IR (ν(CO)) (Nujol mull) 1810(s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C) δ=1.5(br. 3H, CH_3), 4.1(4H, C_5H_4), 4.4(5H, C_5H_4), 5.1(3H, C_5H_4), 7.4, 7.5(20H, C_6H_5, multiplet). When the photolysis was ceased at 30 min. **1** was preferentially obtained.

[ClMn(CO)$_4$]$_2$(μ-dppfe) (3). A toluene solution (50 mL) of $Mn_2(CO)_{10}$ (300 mg, 0.77 mmol) and dppfe (400 mg, 0.72 mmol) was photolyzed for 1 h under an argon atmosphere. Then 0.7 mL of CCl_4 was added and the mixture was photolyzed for additional 30 min. Pale brown precipitates were removed by filtration and the solvent was distilled off at reduced pressure from the filtrate. The resulting orange solid was recrystallized from CH_2Cl_2–hexane (1 : 5) to afford trigonal pyramidal shaped orange crystals **3**. Yield 120 mg (16%). Anal. Calcd for $C_{42}H_{28}Cl_2FeMn_2O_8P_2\cdot 1/2CH_2Cl_2$: C, 50.96; H, 2.92%. Found: C, 51.06; H, 3.24%. IR (ν(CO))(toluene) 2095(s), 2028(vs), 1960(s), 1919(s) cm^{-1}.

$CH_3CCo_3(CO)_7$dppfe (4). A benzene solution (100 mL) of $CH_3CCo_3(CO)_9$ (**5**) (460 mg, 1 mmol) and dppfe (550 mg, 1 mmol) was heated at 70 °C for half an hour. During this heating, purple color turned to red-brown. The solvent was rotary-evaporated to leave red-brown solid. This solid was dissolved into a minimum amount of THF and the solution was loaded on a silica-gel column (Wako-gel C-200) with an ice-water cooled jacket. Unreacted starting compound (purple band) was eluted with petroleum ether. Then a red-orange band was eluted with hexane–benzene (1 : 1). Solvent was vaccum-stripped from this effluent and the orange-red residue was recrystallized from dichloromethane–hexane (1 : 1) to afford orange-red crystals. Yield 700 mg (73%). Anal. Calcd for $C_{43}H_{31}Co_3FeO_7P_2\cdot CH_2Cl_2$: C, 50.85; H, 3.20%. Good analytical result has not yet been obtained. However, X-ray crystal structure analysis confirmed this composition. IR (ν(CO))(benzene) 2042(vs), 2004(vs), 1984(vs), 1960(s), 1880(w), 1860(s), 1810(s) cm^{-1}. When $C_6H_5CCo_3(CO)_9$ was employed instead of $CH_3CCo_3(CO)_9$, $C_6H_5CCo_3(CO)_7$dppfe (**6**) was obtained by the same procedure of preparation.[6b]

X-Ray Data Collection and Structure Determination. Crystal data for compounds **1**—**4** are given in Table 1. Accurate cell constants were determined by least-squares refinements of a number (36 ($20°<2\theta<30°$), 22 ($15°<2\theta<20°$), 40 ($25°<2\theta<30°$), and 40 ($25°<2\theta<30°$)) of relatively high-angle reflections, for **1**, **2**, **3**, and **4**, respectively on the diffractometer. Reflection data were collected by using a Rigaku AFC-5 and/or AFC-5R four-circle diffractometer (compound **1**, **3**, and **4**) and a MAC MXC^3 diffractometer

Table 1. Crystal Data

Compound	1	2	3	4
Formula	$C_{42}H_{35}FeMnO_2P_2$	$C_{41}H_{35}FeMnOP_2{\cdot}CHCl_3$	$C_{42}H_{28}Cl_2FeMn_2O_8P_2{\cdot}1/2CH_2Cl_2$	$C_{43}H_{31}Co_3FeO_7P_2{\cdot}CH_2Cl_2$
F.W.	744.43	835.79	1001.68	1039.18
Cryst system	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	*Pbcn*	$P2_1/n$	$A2/a$	$P\bar{1}$
a/Å	20.551(3)	18.682(5)	18.978(5)	13.031(2)
b/Å	28.951(5)	20.495(4)	15.293(4)	15.338(2)
c/Å	11.786(1)	9.750(2)	16.513(5)	11.583(2)
α/deg	90	90	90	99.13(2)
β/deg	90	91.24(2)	112.62(2)	98.35(2)
γ/deg	90	90	90	99.64(2)
V/Å^3	7012(2)	3732(1)	4424(2)	2218.1(7)
Z	8	4	4	2
D_{calcd}/g cm^{-3}	1.41	1.48	1.50	1.56
Cryst dimens/mm	0.12×0.30×0.64	0.10×0.25×0.40	0.32×0.57×0.63	0.08×0.26×0.40
μ (Mo $K\alpha$)/cm^{-1}	9.32	10.5	12.1	15.8
Scan type	ω–2θ	ω–2θ	ω–2θ	ω–2θ
Scan range/deg in ω	1.1+0.4tanθ	1.3+0.5tanθ	1.3+0.5tanθ	1.2+0.5tanθ
Scan speed/deg min^{-1}	3	4	2	2
$2\theta_{max}$/deg	50	50	55	55
Data collected	$+h, +k, +l$	$-h, -k, \pm l$	$+h, +k, \pm l$	$\pm h, \pm k, -l$
Unique reflctns	3050	6569	2991	6668
Reflectns with $\|F_o\|>3\sigma(\|F_o\|)$	2639	4219	2575	6098
No. of parameters refined	443	476	275	530
R	0.075	0.084	0.074	0.056
R_w	0.082	0.069	0.105	0.067

Temperature 24°C; Mo $K\alpha$ radiation (λ=0.71073 Å); $R=\Sigma\|\|F_o|-|F_c\|/|F_o|$; $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w(F_o)^2]^{1/2}$ where $w=1/\sigma^2(F)$.

Table 2. Atomic Coordinates and Isotropic Thermal Parameters, B_{eq} (Å^2)

Atom	x	y	z	B_{eq} (Å^2)
	{η^5-($CH_3C_5H_4$)}Mn(CO)$_2$dppfe (**1**)			
Mn	0.4615(1)	0.0689(1)	0.3176(2)	3.5
Fe	0.2974(1)	0.1759(1)	0.4071(1)	3.0
P1	0.4284(2)	0.1354(1)	0.2395(3)	2.9
P2	0.1857(2)	0.1299(1)	0.5919(3)	3.6
C1	0.4622(6)	0.0897(4)	0.4587(11)	4.2
O1	0.4641(5)	0.1015(3)	0.5534(7)	5.7
C2	0.5411(6)	0.0822(4)	0.2913(10)	4.0
O2	0.5971(4)	0.0893(3)	0.2760(8)	5.8
C3(Me1)	0.5550(13)	−0.0166(9)	0.2533(31)	6.6
C4(Me2)	0.4762(15)	0.0128(10)	0.0837(25)	6.5
C5(Cp31)	0.4517(7)	0.0172(5)	0.1886(12)	5.8
C6(Cp32)	0.3885(7)	0.0316(4)	0.2221(12)	5.1
C7(Cp33)	0.3818(7)	0.0210(5)	0.3402(12)	5.4
C8(Cp34)	0.4414(7)	0.0010(5)	0.3767(14)	6.5
C9(Cp35)	0.4847(8)	−0.0022(5)	0.2814(14)	6.6
C10(Cp11)	0.3458(5)	0.1546(4)	0.2643(9)	2.8
C11(Cp12)	0.2925(6)	0.1240(4)	0.2919(9)	3.6
C12(Cp13)	0.2327(6)	0.1510(4)	0.2886(10)	3.6
C13(Cp14)	0.2498(6)	0.1987(5)	0.2632(10)	4.3
C14(Cp15)	0.3197(6)	0.2014(4)	0.2483(10)	3.7
C15(Cp21)	0.2575(6)	0.1633(4)	0.5632(9)	3.2
C16(Cp22)	0.2555(6)	0.2123(4)	0.5362(10)	3.6
C17(Cp23)	0.3231(6)	0.2284(4)	0.5182(10)	4.0
C18(Cp24)	0.3639(6)	0.1888(4)	0.5337(9)	3.7
C19(Cp25)	0.3261(6)	0.1488(4)	0.5612(9)	3.2
C21(Ph111)	0.4783(5)	0.1883(4)	0.2636(10)	3.2
C22(Ph112)	0.4768(6)	0.2247(4)	0.1858(12)	4.7
C23(Ph113)	0.5165(7)	0.2638(5)	0.2054(13)	6.2
C24(Ph114)	0.5557(7)	0.2659(4)	0.3016(13)	5.7
C25(Ph115)	0.5558(6)	0.2301(4)	0.3808(12)	5.0
C26(Ph116)	0.5169(6)	0.1903(4)	0.3609(11)	4.1
C31(Ph121)	0.4301(6)	0.1330(4)	0.0839(9)	2.9
C32(Ph122)	0.3719(6)	0.1318(5)	0.0207(10)	4.1
C33(Ph123)	0.3762(7)	0.1294(5)	−0.1001(11)	5.9
C34(Ph124)	0.4366(8)	0.1277(6)	−0.1515(12)	6.4
C35(Ph125)	0.4946(7)	0.1271(5)	−0.0883(11)	5.4
C36(Ph126)	0.4914(6)	0.1308(5)	0.0281(10)	4.4
C41(Ph211)	0.1817(5)	0.1335(4)	0.7476(10)	2.9
C42(Ph212)	0.1371(6)	0.1046(4)	0.8046(10)	3.9
C43(Ph213)	0.1289(6)	0.1089(5)	0.9230(11)	4.7
C44(Ph214)	0.1643(6)	0.1412(4)	0.9845(11)	4.4
C45(Ph215)	0.2082(7)	0.1705(4)	0.9295(11)	4.8
C46(Ph216)	0.2165(6)	0.1668(4)	0.8072(10)	4.1
C51(Ph221)	0.2128(6)	0.0698(4)	0.5709(10)	3.7
C52(Ph222)	0.2559(7)	0.0479(4)	0.6440(11)	4.3
C53(Ph223)	0.2748(7)	0.0014(5)	0.6218(13)	5.6
C54(Ph224)	0.2486(8)	−0.0213(5)	0.5308(14)	6.8
C55(Ph225)	0.2042(8)	0.0003(5)	0.4570(12)	6.4
C56(Ph226)	0.1843(7)	0.0473(5)	0.4762(11)	5.1
	{η^5-($CH_3C_5H_4$)}Mn(CO)dppfe (**2**)			
Fe	0.24266(6)	0.12403(6)	0.1430(1)	3.21
Mn	0.39348(7)	0.21867(7)	0.4113(1)	3.08
P1	0.2825(1)	0.2514(1)	0.3660(2)	2.91
P2	0.4181(1)	0.1738(1)	0.2109(2)	2.85
C	0.3607(5)	0.1453(5)	0.4754(9)	3.7
O	0.3423(4)	0.0962(3)	0.5278(7)	5.1
C2	0.4849(6)	0.1720(6)	0.690(1)	6.6
C3	0.4676(5)	0.2242(5)	0.584(1)	4.9
C4	0.5053(5)	0.2363(6)	0.461(1)	5.1
C5	0.4732(6)	0.2948(6)	0.396(1)	5.2
C6	0.4183(6)	0.3160(5)	0.485(1)	5.3
C7	0.4144(5)	0.2721(6)	0.598(1)	4.8
C10	0.3507(4)	0.1252(4)	0.1158(9)	3.1
C11	0.3150(4)	0.1347(5)	−0.0137(9)	3.8
C12	0.2680(5)	0.0794(5)	−0.039(1)	4.4
C13	0.2785(5)	0.0352(5)	0.075(1)	4.4
C14	0.3285(4)	0.0630(4)	0.174(1)	3.6
C15	0.2176(4)	0.1943(4)	0.2839(8)	3.0
C16	0.1781(5)	0.2051(5)	0.1554(9)	3.8
C17	0.1354(5)	0.1483(5)	0.127(1)	4.5
C18	0.1488(5)	0.1027(5)	0.237(1)	4.6
C19	0.2000(4)	0.1303(4)	0.3355(9)	3.5
C21	0.2403(4)	0.2722(4)	0.5302(8)	3.0
C22	0.2344(5)	0.3376(4)	0.570(1)	4.4
C23	0.2127(6)	0.3526(5)	0.707(1)	5.2
C24	0.1964(5)	0.3041(6)	0.798(1)	5.4
C25	0.2008(5)	0.2380(6)	0.757(1)	5.1
C26	0.2228(5)	0.2229(5)	0.6234(9)	4.0
C31	0.2608(5)	0.3273(4)	0.2656(8)	3.2
C32	0.3175(5)	0.3615(4)	0.2083(8)	3.9
C33	0.3016(6)	0.4177(5)	0.128(1)	5.1
C34	0.2304(7)	0.4380(5)	0.107(1)	5.8
C35	0.1742(6)	0.4035(5)	0.172(1)	4.9
C36	0.1887(5)	0.3483(4)	0.2514(9)	4.0
C41	0.4891(4)	0.1103(4)	0.2119(9)	3.1
C42	0.5089(5)	0.0816(4)	0.338(1)	4.0
C43	0.5584(5)	0.0293(5)	0.337(1)	4.6
C44	0.5878(5)	0.0077(5)	0.214(1)	5.1
C45	0.5674(5)	0.0372(5)	0.090(1)	5.0
C46	0.5182(5)	0.0883(5)	0.087(1)	4.1
C51	0.4495(4)	0.2310(4)	0.0809(8)	2.7
C52	0.5224(5)	0.2422(4)	0.0619(9)	3.9
C53	0.5443(5)	0.2918(5)	−0.028(1)	4.8
C54	0.4928(6)	0.3301(5)	−0.100(1)	4.5
C55	0.4195(5)	0.3204(4)	−0.0781(9)	3.9
C56	0.3977(4)	0.2709(4)	0.0114(8)	3.3
	{$MnCl(CO)_4$}$_2$(μ-dppfe) (**3**)			
Fe	0.2500(0)	0.0018(1)	0.0000(0)	3.1
Mn	0.3987(1)	−0.1423(1)	0.2981(1)	3.8
Cl	0.3920(2)	−0.2004(2)	0.1619(2)	5.7
P	0.3616(1)	−0.0055(2)	0.2284(1)	3.0
C1	0.4064(5)	−0.1007(7)	0.4088(7)	4.8
C2	0.4246(6)	−0.2521(7)	0.3456(8)	5.5
C3	0.5010(5)	−0.1127(6)	0.3312(7)	4.6
C4	0.2948(5)	−0.1711(7)	0.2716(6)	4.4
O1	0.4132(5)	−0.0773(6)	0.4685(5)	7.5
O2	0.4396(5)	−0.3174(5)	0.3764(7)	8.8
O3	0.5625(4)	−0.0921(5)	0.3555(5)	6.5
O4	0.2367(4)	−0.1899(6)	0.2594(5)	6.6
C5(Cp1)	0.2732(4)	−0.0038(6)	0.1323(5)	3.2
C6(Cp2)	0.2325(5)	0.0767(6)	0.0953(6)	4.0
C7(Cp3)	0.1599(5)	0.0494(8)	0.0282(6)	4.6
C8(Cp4)	0.1570(5)	−0.0443(7)	0.0234(6)	4.0
C9(Cp5)	0.2270(5)	−0.0770(6)	0.0870(5)	3.6
C11(Ph11)	0.4304(5)	0.0543(6)	0.1949(5)	3.4
C12(Ph12)	0.4270(6)	0.1440(6)	0.1862(6)	4.3
C13(Ph13)	0.4792(6)	0.1855(7)	0.1566(7)	5.3
C14(Ph14)	0.5304(6)	0.1366(8)	0.1344(7)	6.0
C15(Ph15)	0.5328(6)	0.0493(8)	0.1419(7)	5.3
C16(Ph16)	0.4830(5)	0.0044(7)	0.1730(6)	4.5
C21(Ph21)	0.3421(5)	0.0693(5)	0.3040(6)	3.4
C22(Ph22)	0.2685(5)	0.0759(6)	0.3029(6)	4.2
C23(Ph23)	0.2581(6)	0.1280(7)	0.3690(7)	5.4
C24(Ph24)	0.3191(7)	0.1687(6)	0.4315(7)	5.2
C25(Ph25)	0.3915(6)	0.1617(6)	0.4330(6)	5.0
C26(Ph26)	0.4060(6)	0.1110(6)	0.3704(6)	4.2

Table 2. (Continued)

Atom	x	y	z	B_{eq} (Å^2)	Atom	x	y	z	B_{eq} (Å^2)
					C15(Cp21)	0.3215(5)	0.1004(4)	−0.0674(6)	2.3
	$CH_3CCo_3(CO)_7$dppfe (**4**)				C16(Cp22)	0.3763(6)	0.0453(4)	−0.1399(6)	3.1
Co1	0.1394(1)	0.3340(1)	−0.0316(1)	2.3	C17(Cp23)	0.2992(6)	−0.0145(4)	−0.2317(6)	3.3
Co2	0.0602(1)	0.2324(1)	0.0921(1)	2.8	C18(Cp24)	0.1941(6)	0.0033(4)	−0.2170(6)	3.3
Co3	0.2579(1)	−0.2784(1)	0.1206(1)	2.3	C19(Cp25)	0.2106(5)	0.0743(4)	−0.1153(6)	2.6
Fe	0.2942(1)	0.1189(1)	−0.2374(1)	2.4	C31(Ph111)	0.1571(5)	0.3831(4)	−0.3079(6)	2.5
P1	0.1428(1)	0.2873(1)	−0.2308(1)	2.3	C32(Ph112)	0.0812(6)	0.4377(5)	−0.3070(6)	3.4
P2	0.3672(1)	0.1812(1)	0.0695(1)	2.3	C33(Ph113)	0.0897(7)	0.5100(5)	−0.3647(7)	4.2
C(ap)	0.1507(5)	0.3481(4)	0.1379(6)	2.5	C34(Ph114)	0.1743(7)	0.5300(5)	−0.4246(7)	4.5
C(Me)	0.1488(6)	0.4295(5)	0.2295(6)	3.6	C35(Ph115)	0.2497(7)	0.4760(5)	−0.4258(7)	4.5
C1	0.1299(5)	0.4467(4)	−0.0317(6)	3.0	C36(Ph116)	0.2423(6)	0.4028(5)	−0.3674(6)	3.5
C21	−0.0167(6)	0.1248(5)	0.0179(7)	3.8	C41(Ph121)	0.0243(5)	0.2134(4)	−0.3212(6)	2.7
C22	−0.0122(6)	0.2562(5)	0.2044(7)	3.6	C42(Ph122)	−0.0239(6)	0.2288(5)	−0.4312(6)	4.0
C3	0.3376(6)	0.3353(5)	0.2540(6)	3.5	C43(Ph123)	−0.1121(7)	0.1661(6)	−0.4989(7)	4.9
C12(b)	−0.0057(5)	0.2854(4)	−0.0483(6)	3.0	C44(Ph124)	−0.1504(6)	0.0903(6)	−0.4583(7)	4.8
C13(b)	0.2941(5)	0.3591(4)	0.0100(6)	2.7	C45(Ph125)	−0.1025(6)	0.0726(5)	−0.3489(7)	4.1
C23(b)	0.1727(6)	0.1854(5)	0.1822(7)	3.5	C46(Ph126)	−0.0159(5)	0.1348(5)	−0.2818(6)	3.3
O1	0.1222(5)	0.5211(3)	−0.0245(5)	5.0	C51(Ph211)	0.3873(5)	0.1052(4)	0.1750(6)	2.8
O21	−0.0739(5)	0.0605(4)	−0.0270(6)	6.1	C52(Ph212)	0.3352(6)	0.0148(5)	0.1484(7)	3.6
O22	−0.0572(5)	0.2709(4)	0.2811(5)	5.9	C53(Ph213)	0.3525(7)	−0.0414(5)	0.2315(8)	4.4
O3	0.3863(5)	0.3723(4)	0.3439(5)	6.3	C54(Ph214)	0.4209(7)	−0.0070(6)	0.3374(7)	5.2
O12(b)	−0.0907(4)	0.2801(4)	−0.0947(5)	4.4	C55(Ph215)	0.4726(7)	0.0834(6)	0.3657(7)	5.0
O13(b)	0.3642(4)	0.4079(3)	−0.0106(5)	3.9	C56(Ph216)	0.4552(6)	0.1401(6)	0.2833(7)	4.1
O23(b)	0.1752(4)	0.1328(4)	0.2430(6)	5.5	C61(Ph221)	0.5063(5)	0.2310(4)	0.0730(6)	2.8
C10(Cp11)	0.2442(5)	0.2301(4)	−0.2809(6)	2.5	C62(Ph222)	0.5413(5)	0.3245(5)	0.1038(7)	3.5
C11(Cp12)	0.2247(6)	0.1595(4)	−0.3866(6)	2.9	C63(Ph223)	0.6507(6)	0.3603(5)	0.1187(8)	4.4
C12(Cp13)	0.3267(6)	0.1390(5)	−0.4013(7)	3.6	C64(Ph224)	0.7214(6)	0.3052(6)	0.0984(8)	4.4
C13(Cp14)	0.4049(6)	0.1943(5)	−0.3090(7)	3.6	C65(Ph225)	0.6883(6)	0.2130(5)	0.0685(8)	4.4
C14(Cp15)	0.3551(5)	0.2515(4)	−0.2334(6)	3.1	C66(Ph226)	0.5802(5)	0.1750(5)	0.0567(7)	3.6

Table 3. Selected Interatomic Distances (Å)

Compound	**1**	**2**	**3**	**4**
M–P	2.242(4)(Mn–P_1)	2.215(2)(Mn–P_1) 2.216(3)(Mn–P_2)	2.361(3)(Mn–P)	2.314(2)(Co_1–P_1) 2.297(2)(Co_2–P_2)
M–CO	1.768(13)(Mn–C_1) 1.709(13)(Mn–C_2)	1.74(1)(Mn–C_1)	1.888(11)(Mn–C_1) 1.839(13)(Mn–C_2) 1.859(11)(Mn–C_3) 1.899(10)(Mn–C_4)	1.752(7)(Co_1–C_1) 1.793(7)(Co_2–C_{21}) 1.743(8)(Co_2–C_{22}) 1.741(6)(Co_4–C_3) 1.882(7)(Co_1–C_{12}(b)) 1.961(6)(Co_1–C_{13}(b)) 2.071(7)(Co_2–C_{12}(b)) 1.977(8)(Co_2–C_{23}(b)) 1.970(7)(Co_3–C_{13}(b)) 1.949(8)(Co_3–C_{23}(b))
C–O	1.168(15)(C_1–O_1) 1.183(16)(C_2–O_2)	1.18(1)(C–O)	1.009(15)(C_1–O_1) 1.106(13)(C_2–O_2) 1.125(12)(C_3–O_3) 1.081(13)(C_4–O_4)	1.153(9)(C_1–O_1) 1.130(8)(C_{21}–O_{21}) 1.148(10)(C_{22}–O_{22}) 1.144(8)(C_3–O_3) 1.143(8)(C_{12}(b)–O_{12}(b)) 1.152(11)(C_{23}(b)–O_{23}(b)) 1.158(8)(C_{13}(b)–O_{13}(b))
Fe–Cp	2.051(11)(Cp_{11}) 2.030(12)(Cp_{12}) 2.059(12)(Cp_{13}) 2.067(13)(Cp_{14}) 2.063(12)(Cp_{15}) 2.047(11)(Cp_{21}) 2.041(12)(Cp_{22}) 2.074(12)(Cp_{23}) 2.057(12)(Cp_{24}) 2.065(11)(Cp_{25})	2.042(8)(C_{10}) 2.074(8)(C_{11}) 2.06(1)(C_{12}) 2.05(1)(C_{13}) 2.051(9)(C_{14}) 2.051(8)(C_{15}) 2.058(9)(C_{16}) 2.068(9)(C_{17}) 2.044(9)(C_{18}) 2.058(9)(C_{19})	2.057(9)(Cp_1) 2.073(10)(Cp_2) 2.069(12)(Cp_3) 2.070(10)(Cp_4) 2.047(10)(Cp_5)	2.035(7)(Cp_{11}) 2.067(7)(Cp_{12}) 2.063(8)(Cp_{13}) 2.049(8)(Cp_{14}) 2.047(7)(Cp_{15}) 2.022(7)(Cp_{21}) 2.037(7)(Cp_{22}) 2.068(7)(Cp_{23}) 2.085(7)(Cp_{24}) 2.039(7)(Cp_{25})

Table 3. (Continued)

Compound	1	2	3	4
P–Cp	1.809(12)(P_1–Cp_{11})	1.854(8)(P_1–C_{15})	1.813(7)(P–Cp_1)	1.817(7)(P_1–Cp_{11})
	1.797(12)(P_2–Cp_{21})	1.841(8)(P_2–C_{10})		1.806(6)(P_2–Cp_{21})
Mn–Cp	2.142(14)(Cp_{31})	2.16(1)(C_3)		
	2.166(14)(Cp_{32})	2.16(1)(C_4)		
	2.163(14)(Cp_{33})	2.16(1)(C_5)		
	2.126(14)(Cp_{34})	2.17(1)(C_6)		
	2.156(15)(Cp_{35})	2.15(1)(C_7)		
Me–Cp in MeCp	1.540(31)(Me_1–Cp_{35})	1.52(2)(C_2–C_3)		
	1.342(33)(Me_2–Cp_{31})			
P–Ph	1.863(12)(P_1–Ph_{111})	1.849(8)(P_1–C_{21})	1.844(9)(P–Ph_{11})	1.834(7)(P_1–Ph_{111})
	1.835(11)(P_1–Ph_{121})	1.876(8)(P_1–C_{31})	1.833(10)(P–Ph_{21})	1.827(6)(P_1–Ph_{121})
	1.839(13)(P_2–Ph_{211})	1.860(8)(P_2–C_{41})		1.840(8)(P_2–Ph_{211})
	1.845(13)(P_2–Ph_{221})	1.830(8)(P_2–C_{51})		1.837(6)(P_2–Ph_{221})
Co–Co				2.479(1)(Co_1–Co_2)
				2.513(1)(Co_2–Co_3)
				2.520(1)(Co_1–Co_3)
C(ap)–Co				1.921(7)(Co_1)
				1.908(6)(Co_2)
				1.911(7)(Co_3)
Me–C(ap)				1.511(9)
Mn–Cl			2.375(4)	
P···P		3.376(3)(P_1–P_2)		4.871(3)(P_1–P_2)
Fe···M	4.700(3)(Fe–Mn)	4.269(2)(Fe–Mn)	5.135(2)(Fe–Mn)	4.667(2)(Fe–Co_1)
				4.598(2)(Fe–Co_3)
Fe···CO		3.904(9)(Fe–C)		

Table 4. Selected Angles (deg)

Compound	1	2	3	4
P–M–P		99.3(12)(P_1-Mn-P_2)		
M–P–Cp	118.8(4)(Mn–P_1–Cp_{11})	119.6(3)(Mn–P_1–C_{15})	116.2(3)(Mn–P–Cp_1)	122.4(2)(Co_1–P_1–Cp_{11})
		121.0(3)(Mn–P_2–C_{10})		116.8(2)(Co_3–P_2–Cp_{21})
P–M–CO	95.5(4)(P_1–Mn–C_1)	89.9(3)(P_1–Mn–C)	94.1(4)(P–Mn–C_1)	99.6(2)(P_1–Co_1–C_1)
	91.3(4)(P_1–Mn–C_2)	92.3(3)(P_2–Mn–C)	176.4(4)(P–Mn–C_2)	93.3(2)(P_1–Co_1–C_{12}(b))
			90.5(4)(P–Mn–C_3)	92.4(2)(P_1–Co_1–C_{13}(b))
			90.3(3)(P–Mn–C_4)	96.7(3)(P_2–Co_3–C_3)
				96.0(2)(P_2–Co_3–C_{13}(b))
				90.3(2)(P_2–Co_3–C_{23}(b))
OC–M–CO	95.0(6)(C_1–Mn–C_2)		89.2(5)(C_1–Mn–C_2)	98.3(3)(C_1–Co_1–C_{12}(b))
			87.1(5)(C_1–Mn–C_3)	94.7(3)(C_1–Co_1–C_{13}(b))
			89.3(5)(C_1–Mn–C_4)	99.4(4)(C_{21}–Co_2–C_{22})
			91.1(5)(C_2–Mn–C_3)	87.6(3)(C_{21}–Co_2–C_{12}(b))
			88.3(5)(C_2–Mn–C_4)	96.2(3)(C_{21}–Co_2–C_{23}(b))
			176.4(5)(C_3–Mn–C_4)	105.5(3)(C_{22}–Co_2–C_{12}(b))
				99.0(4)(C_{22}–Co_2–C_{23}(b))
				102.3(3)(C_3–Co_3–C_{13}(b))
				98.3(3)(C_3–Co_3–C_{23}(b))
				164.7(3)(C_{12}(b)–Co_1–C_{13}(b))
				154.3(3)(C_{12}(b)–Co_2–C_{23}(b))
				157.5(3)(C_{13}(b)–Co_3–C_{23}(b))
M–C–O	176.8(12)(Mn–C–O)	174.5(7)(Mn–C–O)	177.2(11)(Mn–C_1–O_1)	175.6(7)(Co_1–C_1–O_1)
	176.4(11)(Mn–C_2–O_2)		177.7(12)(Mn–C_2–O_2)	173.1(8)(Co_2–C_{21}–O_{21})
			175.8(10)(Mn–C_3–O_3)	177.6(7)(Co_2–C_{22}–O_{22})
			176.9(9)(Mn–C_4–O_4)	177.2(7)(Co_3–C_3–O_3)
Cp–P–Ph	103.9(5)(Cp_{11}–P_1–Ph_{111})	103.4(4)(C_{15}–P_1–C_{21})	104.7(4)(Cp_1–P–Ph_{11})	100.8(3)(Cp_{11}–P_1–Ph_{111})
	101.0(5)(Cp_{11}–P_1–Ph_{121})	99.6(4)(C_{15}–P_1–C_{31})	103.1(4)(Cp_1–P–Ph_{21})	100.3(3)(Cp_{11}–P_1–Ph_{121})
	101.2(5)(Cp_{21}–P_2–Ph_{211})	95.9(4)(C_{10}–P_2–C_{41})		100.4(3)(Cp_{21}–P_2–Ph_{211})
	103.5(6)(Cp_{21}–P_2–Ph_{221})	102.9(4)(C_{10}–P_2–C_{51})		107.9(3)(Cp_{21}–P_2–Ph_{221})
P–Mn–Cl			88.4(1)	
Cl–Mn–CO			177.5(3)(Cl–Mn–C_1)	
			88.3(4)(Cl–Mn–C_2)	
			92.3(4)(Cl–Mn–C_3)	
			91.3(3)(Cl–Mn–C_4)	

(compound **2**) with graphite monochromated Mo $K\alpha$ radiation. Three standard reflections were monitored every 50 reflections. Crystal decomposition during data collection was not observed according to reflections of these standards. No absorption correction was applied for **1**—**4**. The structure was solved by a combination of direct method (MULTAN 78) and standard heavy atom Fourier techniques. The structural refinements were made by block-diagonal least-squared method (compound **1**, **3**, and **4**) and calculations were performed on the computers at the Computation Center of the Institute for Molecular Science by use of the UNICS III program system. The structural refinement of **2** was made by a full-matrix least-squared method on a Sun SPARK 2 work station (Crystan program system provided by MAC Science).[9] Difference Fourier map revealed the presence of severely disordered chloroform molecule for **2**. Disordered dichloromethane molecules are also contained in **3** and **4** respectively. In **3**, the Fe atom and a Cl atom of the dichloromethane were located on the two-fold axis. Hydrogen atoms were not included in calculations for all the compounds, **1**—**4**, because it is not our present purpose to locate the positions of the hydrogen atoms although the location of all the hydrogen atoms permits to reduce the R factor significantly. Final positional and temperature parameters for nonhydrogen atoms are given in Table 2, selected bond lengths and angles are in Table 3 and 4. Complete lists of molecular dimensions, the anisotropic thermal parameters, and the F_o-F_c tables are deposited as Document No. 8996 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Preparation of the Compounds. It is well known that tricarbonyl(η^5-cyclopentadienyl)manganese, [Mn(CO)$_3$Cp], dissociates one CO group quite easily upon photolysis to yield 16 electron [Mn(CO)$_2$Cp], which on treatment with various nucleophiles yields CpMn(CO)$_2$L.[10] As was described in Experimental section, the yield of **1** is greater than that of **2** at the beginning of irradiation. This finding indicates that 16 electron intermediate MeCpMn(CO)$_2$ traps one of the phosphorus atoms in dppfe to afford **1** in which dppfe behaves as a monodentate ligand. Then second CO group is dissociated from **1** upon prolonged irradiation to afford **2** finally.

$$\mathrm{MeCpMn(CO)_3} \xrightarrow{h\nu} \mathrm{MeCpMn(CO)_2} + \mathrm{CO}$$

$$\mathrm{MeCpMn(CO)_2} + \mathrm{dppfe} \longrightarrow \mathrm{MeCpMn(CO)_2dppfe}\ (\mathbf{1})$$

$$\mathrm{MeCpMn(CO)_2dppfe}\ (\mathbf{1}) \xrightarrow{h\nu} \mathrm{MeCpMn(CO)dppfe}\ (\mathbf{2}) + \mathrm{CO}$$

Indeed, photolysis of **1** in benzene yields **2**.

$Mn_2(CO)_{10}$ has two photochemical processes, that is, CO dissociation and the Mn–Mn homolysis.[11] In the present photochemical reaction of $Mn_2(CO)_{10}$ with dppfe, uv spectra are measured to deduce the intermediate formed during the photolysis. The absorption spectrum shows a red shift of the peak at 340 to 370 nm. As the peak at 340 nm is assigned to σ(Mn–Mn)$\rightarrow\sigma^*$(Mn–Mn) transition for $Mn_2(CO)_{10}$,[11] observed peak at 370 nm for an intermediate is assignable to σ(Mn–Mn)$\rightarrow\sigma^*$(Mn–Mn) transition. On the basis of this finding together with the formation of the final product **3**, we surmise that dppfe bridges two manganese atoms with the retention of the Mn–Mn bond at first, and then the Mn–Mn bond is cleaved by CCl_4; we have not so far been successful to confirm the putative dimer [Mn(CO)$_4$]$_2$(μ-dppfe) (**7**), because the intermediate is not so much stable to allow complete characterization.

$$\mathrm{Mn_2(CO)_{10}} + \mathrm{dppfe} \xrightarrow{h\nu} \mathrm{(CO)_4Mn}\overset{\mathrm{P}\frown\mathrm{P}}{\text{——}}\mathrm{Mn(CO)_4}\ (\mathbf{7}) + 2\mathrm{CO}$$

$$\mathrm{(OC)_4Mn}\overset{\mathrm{P}\frown\mathrm{P}}{\text{——}}\mathrm{Mn(CO)_4}\ (\mathbf{7}) \xrightarrow[\mathrm{CCl_4}]{h\nu} \mathrm{ClMn(CO)_4P}\frown\mathrm{PMn(CO)_4Cl} \qquad (3)$$

Thermal reaction of $CH_3CCo_3(CO)_9$ (**5**) with dppfe affords $CH_3CCo_3(CO)_7$dppfe (**4**). The IR spectrum in ν(CO) region indicates that **4** has bridging CO groups. The result is clear contrast to that of the thermal reaction of **5** with bis(diphenylphosphino)methane, dppm; the product of this reaction, $CH_3CCo_3(CO)_7$dppm (**8**), has no bridging carbonyl.[12] Dppfe is bulkier than dppm and this bulkiness may be responsible for induction of terminal carbonyls to bridging positions in **4**.

Structures of 1—4 in the Solid State. Figure 1 shows the molecular structures of the four complexes **1**—**4** studied by X-ray diffraction method. Each complex contains one molecule of dppfe as a ligand. Although dppfe behaves as a monodentate ligand in **1**, dppfe coordinates to metal atoms via the two P atoms in **2**—**4**. As is exhibited in Fig. 1, all four expected coordination modes of dppfe (**a**—**d** in Scheme 1) are demonstrated in **1**—**4**. The rotation of the two cyclopentadienyl rings in dppfe for each complex is shown in Fig. 2 and the exact rotational angle from the complete eclipsed conformation is 128.0(11)° for **1**, 3.1(9)° for **2**, 180° for **3**, and 69.6(6)° for **4** respectively. The approximate conformation of the two cyclopentadienyl rings for **1** is **v** in Scheme 3, that for **2** is **i**, that for **3** is **vi**, and that for **4** is **iii**. The conformation of the two cyclopentadienyl rings in **1** is of interest in that **1** does not take the expected exact staggered conformation **vi** in Scheme 3 as that of free dppfe.[2h] Instead, it takes an intermediate conformation between **iv** and **v**. It may be worthwhile to note that one molecule of [AuCl]$_2$dppfe shows a similar staggered conformation to **v** (rotational angle is 150°), although another independent molecule of this compound in the unit cell exhibited exact staggered conformation **vi** in Scheme 3, in which the Fe atom is on the inversion center.[7] The reason why **1** takes this conformation in the solid state is not clear. High rotational energy barrier about the Cp–Fe–Cp axis may be responsible for this geometry. The P atom

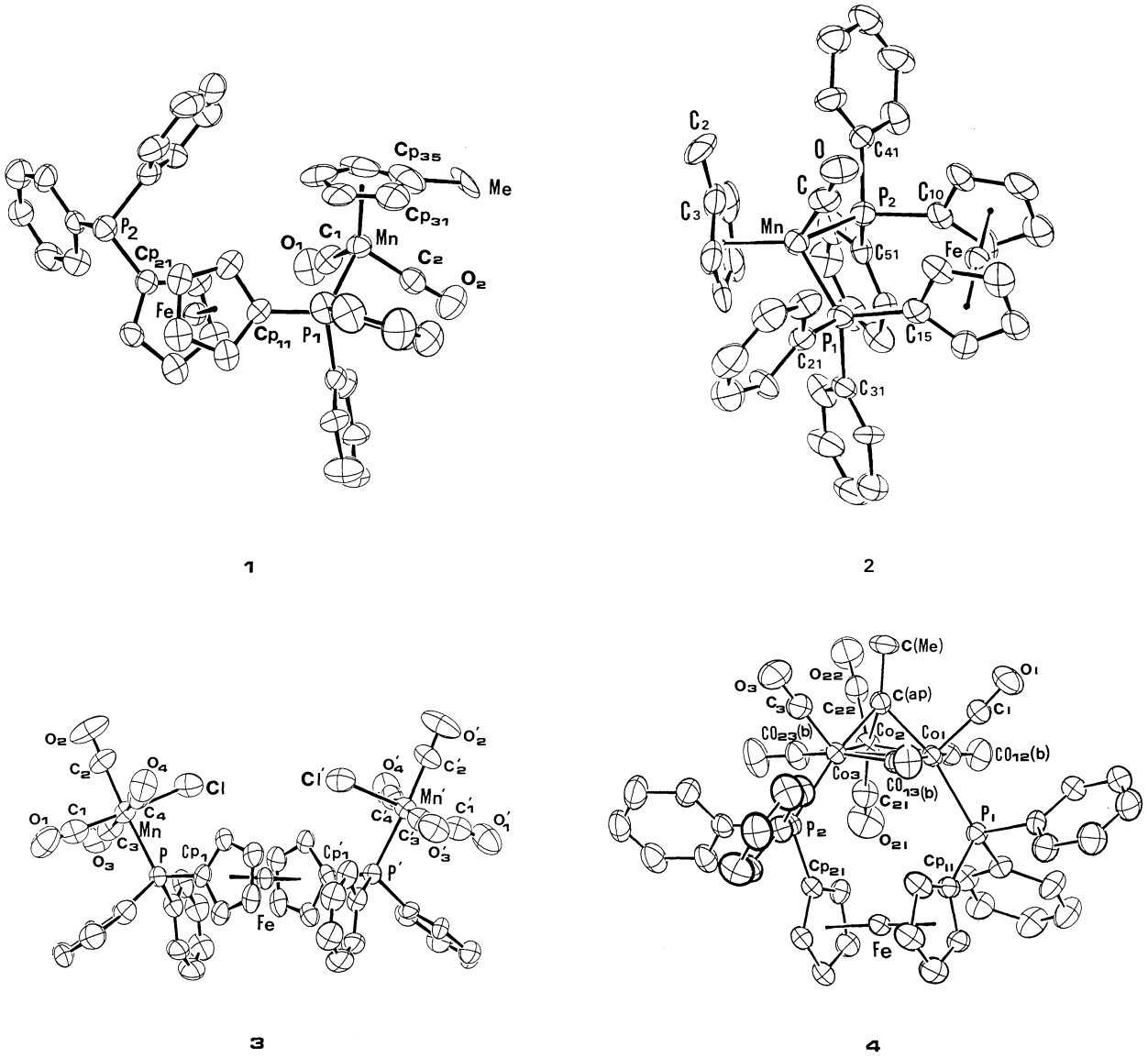


Fig. 1. Molecular Structures and numbering schemes of important atoms for 1: (η^5-$CH_3C_5H_4$)$Mn(CO)_2$dppfe (**1**), 2: (η^5-$CH_3C_5H_4$)Mn(CO)dppfe (**2**), 3: $[MnCl(CO)_4]_2$(μ-dppfe) (**3**), and 4: $CH_3CCo_3(CO)_7$dppfe (**4**). The atoms are represented by 50% probability thermal ellipsoids.

coordinated to the Mn atom is deviated from the cyclopentadienyl ring by 0.21(2) Å and the uncoordinated P atom 0.00(2) Å; this is the only remarkable difference in the structural parameters between the coordinated $Ph_2PC_5H_4$ moiety and the uncoordinated $Ph_2PC_5H_4$ moiety (Table 3 and 4). The tilt angle of the two cyclopentadienyl rings is 2.3(5)° (the P atom is not included to define the least-squared plane of each cyclopentadienyl ring hereafter). The rotational angle 3.1(9)° for **2** are compared to values of 6.5° and 9.0° for analogous NiX_2 complexes[2d,2h] in which dppfe functions as a bidentate chelating ligand. These rotational angles are rather small compared with the observed rotational angles in similar complexes with a chelating dppfe;[2] the largest rotational angle is 41.9° for $Mo(CO)_4$dppfe among so far X-ray structurally determined dppfe complexes[2d] and the rotational angle tends to increase when dppfe coordinates to a larger metal such as Pd and Mo for bidentate chelating mode.[2] The tilt angle of the two cyclopentadienyl rings for **2** is 4.3(6)° and the distance between the two phosphorus atoms is 3.376(3) Å (Table 3). The two cyclopentadienyl rings take exactly staggered conformation (**vi** in Scheme 3) for **3** in which the Fe atom is located on the two-fold axis and each phosphorus atom is bound to a different metal atom. The tilt angle of the two cyclopentadienyl rings is 0° and the two P atoms are slightly displaced from each cyclopentadienyl ring (away from the Fe atom) by 0.22(2) Å (Table 5, Fig. 3). Interesting conformation is revealed in **4**; the two cyclopentadienyl rings exhibit

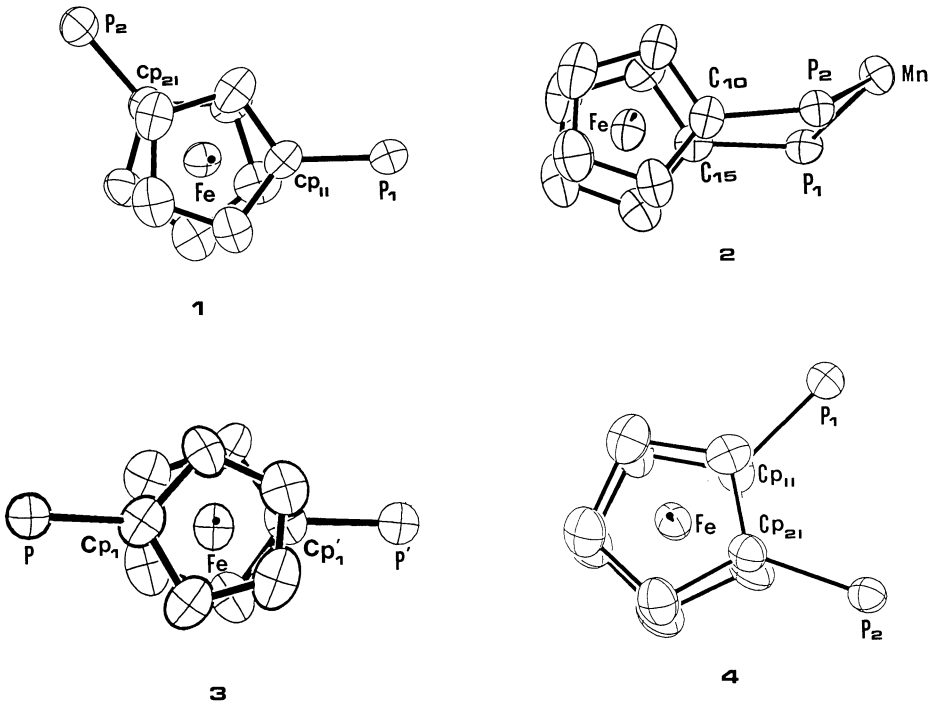


Fig. 2. Rotations of two cyclopentadienyl rings. 1: (η^5-$CH_3C_5H_4$)$Mn(CO)_2$dppfe (**1**), 2: (η^5-$CH_3C_5H_4$)Mn(CO)dppfe (**2**), 3: $[MnCl(CO)_4]_2$(μ-dppfe) (**3**), and 4: $CH_3CCo_3(CO)_7$dppfe (**4**).

Table 5. Distances from the Best Plane (Å)

Compound	1	2	3	4
Fe–Cp(plane)	1.639(6)(Cp_1)	1.647(5)(Cp_1)	1.658(5)	1.648(3)(Cp_1)
	1.643(6)(Cp_2)	1.649(5)(Cp_1)		1.642(3)(Cp_2)
Mn–Cp(plane)	1.778(7)	1.786(6)		
P–Cp(plane)	0.21(2)(P_1)	−0.04(1)(P_1)	0.22(2)	0.15(1)(P_1)
	0.00(2)(P_2)	0.04(1)(P_2)		0.16(1)(P_2)

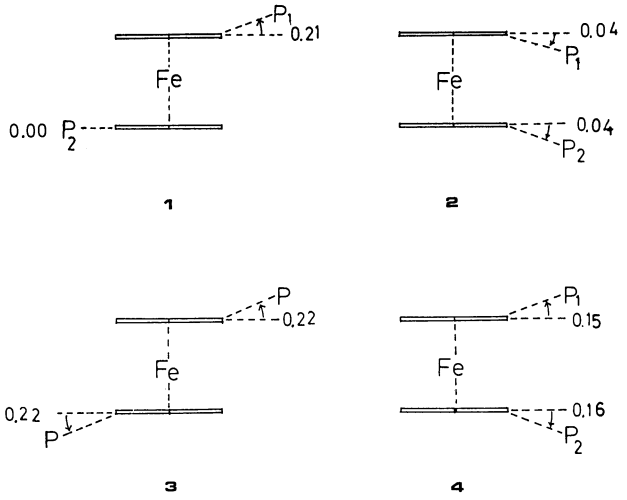


Fig. 3. Schematic representation of the deviation (in Å unit) of P atoms from the least-squares best plane of each cyclopentadienyl ring in compounds **1**—**4**. 1: (η^5-$CH_3C_5H_4$)$Mn(CO)_2$dppfe (**1**), 2: (η^5-$CH_3C_5H_4$)-Mn(CO)dppfe (**2**), 3: $[MnCl(CO)_4]_2$(μ-dppfe) (**3**), 4: $CH_3CCo_3(CO)_7$dppfe (**4**).

rotational angle 69.6(6)° which is quite close to that of the conformation **iii** in Scheme 3, although the tilt angle of the two cyclopentadienyl rings is small (2.3(3)°) and the deviation of each P atom from the cyclopentadienyl ring is also small (0.15(1) and 0.16(1) Å respectively). This large rotational angle makes dppfe possible to bridge the Co–Co bond.

The metal–phosphorus bond length, r(M–P) and the bond angle around the P atom, such as phosphorus–metal–phosphorus bond angle, ∠P–M–P and metal–phosphorus–carbon(cyclopentadienyl), ∠M–P–C are important factors to influence the coordination mode of dppfe. These data are available from Table 4. However, it is difficult to find clear correlation between these data and the coordination modes of dppfe, although metal–phosphorus bond length(s), r(M–P) tends to decrease for these compounds in which the relevant metal atom, M, coordinates to methylcyclopentadienyl ring (compounds **1** and **2**). The distances between the phosphorus atoms and the cyclopentadienyl carbon atoms are not significantly changed by these

coordination modes. Recently it was pointed out that the distances between the Fe atom and the cyclopentadienyl rings are significantly changed depending on the metal coordination geometry of the dppfe complexes.[13] The relevant data listed in Table 5, however, do not indicate any clear correlation between these distances and the conformations of dppfe. The data available from a series of present X-ray structural determinations for **1**—**4** indicate that dppfe can coordinate to metal(s) with various coordination modes such as dppm and dppe (dppe is 1,2-bis(diphenylphosphino)ethane). The versatility and flexibility of dppfe as a ligand toward the metal of the first transition series should be attributed to the rotation rather than the tilt of the two cyclopentadienyl rings and/or deviaton of each P atom from the cyclopentadienyl ring plane. It is interesting to synthesize such a compounds as dppfe bridges a long metal–metal bond and to investigate the structural aspect of dppfe including the rotational angle and the tilt of the two cyclopentadienyl rings.

The most interesting structural feature among the compounds **1**—**4** apart from the structural aspect of the dppfe conformation is demonstrated in **4**; **4** has four terminal carbonyls and three bridging carbonyls, one of which functions as an asymmetric bridging carbonyl (the parent compound **5** possesses nine terminal carbonyls which are classified into two groups, that is, six equatorial carbonyls and three axial carbonyls). In addition, four terminal carbonyls in **4** are at intermediate positions between axial and equatorial carbonyls and/or between apical methyl carbon and equatorial carbonyls; the bond angles ∠C(ap)–Co–L (L=P or terminal carbonyl carbon atom) are close to 180° (166—170°) and/or 90° (92—93°) (Fig. 1(d)). Similar shift is not the case for dppm analogue **8**; seven carbonyls are all at terminal positions with the pristine equatorial-axial conformation.[12] Another fundamental change in the CCo_3 skeleton is the elongation of the Co–Co bonds by dppfe substitution; the Co–Co bonds in **5** are in the range 2.462—2.475 Å[14] and those in **4** are in the range 2.479—2.520 Å. Especially the Co–Co bond which dppfe bridges is elongated (2.520(1) Å, ca. 2.4%). When dppm bridges the Co–Co bond (compound **8**), similar elongation of the Co–Co bond is observed (2.486(21) Å). However, the extent of the elongation is small (ca. 1.0%) and the other two Co–Co bonds are essentially unchanged.[12] Three Co–Co–Co bond angles are very close to 60° (Table 6) and three C(Me)–C(ap)–Co bond angles and three C(ap)–Co bond lengths are also very close for each other in **4**, although the C(ap)–Co bond which is in the opposite side of the dppm-bridged Co–Co bond is significantly elongated and the methyl carbon atom is leaned against the dppm ligand in **8**.[12] The symmetric situation for structural parameters around the apical carbon atom in **4** compared with those of **8** is explained in terms of the relative position of dppfe with respect to the methyl group on the apical carbon atom;

Table 6. Important Bond Angles (deg) in **4**

Co–C(b)–O(b)	149.3(7)(Co_1–C_{12}(b)–O_{12}(b))
	137.2(6)(Co_1–C_{13}(b)–O_{13}(b))
	133.2(6)(Co_2–C_{12}(b)–O_{12}(b))
	135.5(6)(Co_2–C_{23}(b)–O_{23}(b))
	142.0(5)(Co_3–C_{13}(b)–O_{13}(b))
	144.8(6)(Co_3–C_{23}(b)–O_{23}(b))
Co–C(b)–Co	77.5(3)(Co_1–C_{12}(b)–Co_2)
	79.6(3)(Co_2–C_{23}(b)–Co_3)
	79.7(3)(Co_3–C_{13}(b)–Co_1)
C(b)–Co–Co	54.7(2)(C_{12}(b)–Co_1–Co_2)
	47.8(2)(C_{12}(b)–Co_2–Co_1)
	49.7(2)(C_{23}(b)–Co_2–Co_3)
	50.7(2)(C_{23}(b)–Co_3–Co_2)
	50.3(2)(C_{13}(b)–Co_1–Co_3)
	50.0(2)(C_{13}(b)–Co_3–Co_1)
Co–Co–Co	60.34(4)(Co_2–Co_1–Co_3)
	60.65(4)(Co_1–Co_2–Co_3)
	59.01(4)(Co_2–Co_3–Co_1)
C(ap)–Co–Co	49.4(2)(C(ap)–Co_1–Co_2)
	48.7(2)(C(ap)–Co_1–Co_3)
	49.9(2)(C(ap)–Co_2–Co_1)
	48.9(2)(C(ap)–Co_2–Co_3)
	48.8(2)(C(ap)–Co_3–Co_2)
	49.1(2)(C(ap)–Co_3–Co_1)
C(Me)–C(ap)–Co	130.3(5)(Co_1)
	132.0(5)(Co_2)
	130.5(5)(Co_3)
C(ap)–Co–CO	93.2(3)(C(ap)–Co_1–C_1)
	167.4(3)(C(ap)–Co_2–C_{21})
	92.0(3)(C(ap)–Co_2–C_{22})
	93.4(3)(C(ap)–Co_3–C_3)
C(ap)–Co–P	166.4(2)(C(ap)–Co_1–P_1)
	169.9(2)(C(ap)–Co_3–P_2)

dppfe coordinates to two cobalt atoms from almost the opposite side of the Co_3 plane against the methyl group on the apical carbon in **4**, whereas dppm coordinates to two cobalt atoms almost in the same plane of the Co_3 triangle in **8** and thus the distance between the methylene group in dppm and the methyl group on the apical carbon atom is close.[12] The cobalt triangle and three bridging carbonyl carbon atoms are almost in the same plane in **4** (Fig. 4); the largest deviation from the plane is 0.302(8) Å for C(23b). Deviations of the oxygen atoms in these bridging carbonyls are somewhat larger than those of the corresponding carbon atoms (Table 7). The distance between Co(1) and C(12b), 1.882(7) Å, is shorter than that between Co(2) and C(12b), 2.071(7) Å by about 0.19 Å. The bond angle ∠Co(2)–C(12b)–O(12b), 133.2(6)°, is a little bit acuter than that of ∠Co(1)–C(12b)–O(12b), 149.3(6)°. The bridge carbon atoms for other bridging carbonyls are almost equidistant from each component cobalt atom (1.95—1.98 Å). On the other hand, cobalt–carbon–oxygen bond angles, ∠Co–C(b)–O(b), for other bridging carbonyls are not so close. This finding suggests that asymmetric bridging mode for bridging carbonyl, C(12b)O(12b), might be due to crystal packing force to which the bulkiness of dppfe may contribute significantly. However, this assertion is

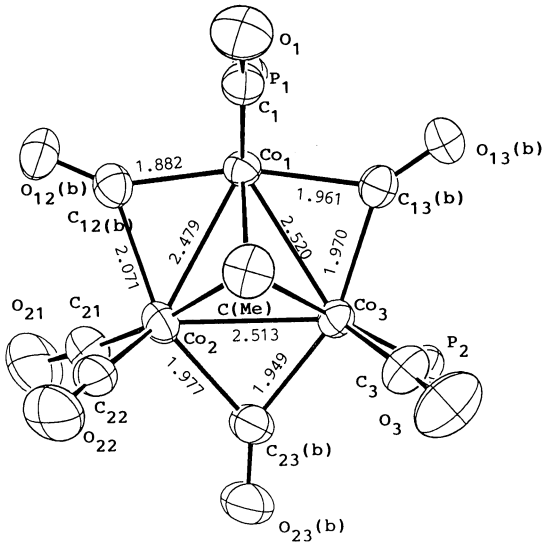


Fig. 4. The vertical view of $CH_3CCo_3(CO)_7$dppfe (**4**) with important bond-length data (Å) from the methyl group. Phenyl groups are omitted for clarity.

Table 7. Deviations (Å) of Each Atom from the Co_3C_3 Least Squares Plane in **4**

Atom					
Co_1	−0.001(1)	$C_{12}(b)$	−0.132(7)	$O_{12}(b)$	−0.203(6)
Co_2	0.006(2)	$C_{13}(b)$	0.007(7)	$O_{13}(b)$	0.153(6)
Co_3	0.002(1)	$C_{23}(b)$	−0.295(8)	$O_{23}(b)$	−0.467(7)

unlikely for following reason. IR spectrum in ν(CO) region for KBr sample of **4** shows three peaks at 1881(w), 1862(s), and 1812(s) cm^{-1} for bridging carbonyls (we presume the asymmetric bridging carbonyl gives rise to the highest energy peak at 1881 cm^{-1} because the bond angle ∠Co–C–O of this CO group is the closest to linear among three bridging carbonyls) and this three peak pattern is manifested even in a benzene solution. Thus, asymmetric coordination mode for C(12b)O(12b) group is due to essential requirement rather than to primitive crystal packing force. Both cobalt atoms, Co(1) and Co(2) satisfy 18 electron rule with an idea that this bridging carbonyl provides one electron to each cobalt atom. The Co(1)–Co(2) bond over which the C(12b)O(12b) bridges is the shortest among the three Co–Co bonds in **4**. This fact may have some connection with the asymmetric coordination mode of C(12b)–O(12b) group.

X-Ray analysis of **1** has shown that the methyl carbon atom in methylcyclopentadienyl group is disordered and occupies two positions with an occupancy factor 0.5 to each site, suggesting that the methylcyclopentadienyl ring can rotate easily about the manganese–methylcyclopentadienyl axis.

As is described in Experimental section, **2** shows a quite low CO stretching frequency (1810 cm^{-1}) as a terminal carbonyl. At first, the occurrence of the CO stretching as low as 1810 cm^{-1} was suspected to indicate any interaction of the CO with the metal atom such as Fe, or **2** was dimeric and the CO interacted with other manganese atom; this suspicion was the motivation to carry out X-ray analysis of **2**.[6a] However, **2** is monomeric, the CO occupies a terminal position, and the Fe–CO distance (3.904(9) Å) is too far to expect strong interaction between the CO and the Fe in dppfe. Thus, the appearance of the CO stretching frequency at 1810 cm^{-1} as a terminal carbonyl should be ascribed to another factor; the CO group extends to the same direction as that of the methyl substituent on the cyclopentadiene ring, that is, eclipsed conformation is exhibited. This conformation suggests that there is some kind of interaction between the CO group and the methyl group. This issue will the discussed in the forthcoming paper.

One of the impetuses behing the syntheses and spectroscopic and electrochemical studies and/or X-ray structure determinations of dppfe metal complexes is to elicit evidence for direct metal-to-iron bonding or interaction in these compounds.[2c,2g,2k,13,15] The closest metal-to-iron distance among the compounds **1**—**4** is 4.269(2) Å for **2** (Table 3). This distance is too far to expect strong metal-to-iron interaction. Evidence for this sort of interaction has not been provided by ^{57}Fe Mössbauer spectroscopy as is mentioned later for **1**—**4**.

^{57}Fe Mössbauer Data. Table 8 shows Mössbauer parameters measured at 80 K together with ^{31}P NMR data for **1**—**4**. Isomer shift data are essentially constant with the change of the metal atom to which dppfe coordinates and/or with the change of coordination mode of dppfe, suggesting that electron density around the Fe atom is not detectably changed by coordination. However, the change of the quadrupole splitting is not negligible. The quadrupole splitting is relatively larger

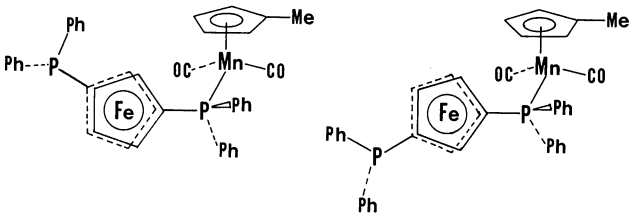
Table 8. ^{57}Fe Mössbauer and ^{31}P NMR Data

Compound	Free dppfe	**1**	**2**	**3**	**4**
^{57}Fe Mössbauer Data (mm/s^{-1})					
Isomer shift	0.51	0.51	0.50	0.52	0.50
Quadrupole splitting	2.30	2.29	2.28	2.35	2.22
^{31}P NMR (δ/ppm)	−17.2	−17.2 (uncoord) 84.7 (coord)	not observed due to exchange	40.3	25.4

for the compounds with large rotational angle such as **1**, **3**, and free dppfe (conformation **iv**, **v**, and **vi** in Scheme 3) than those with small rotational angle such as **2** and **4** (conformation **i** and **iii**). As for the factors which influence the quadrupole splitting, following geometrical and electronical effects should be taken into consideration; (1) ring conformation, (2) ring tilt, (3) iron-to-ring distance, and (4) metal-to-iron bonding or interaction. The fourth factor is not effective for the present series of compounds, because the metal-to-iron separation is too far to expect any strong interaction. The ring tilt angle is in the order **2**>**1**=**4**>**3** and the iron-to-ring distance is in the order **3**>**4**>**2**>**1**. These trends are not in consonant with the trend of the quadrupole splitting, **3**>**1**>**2**>**4**. The observed trend of the quadrupole splitting is, if say, compatible with the trend of the rotational angle of the two cyclopentadienyl rings, alghouth Hillmann and co-workers showed that the Mössbauer parameters have a linear correlation with the iron-to-ring distances for a series of ferrocene derivatives.[16] Recently Silver and co-workers measured ^{57}Fe Mössbauer spectra of a series of metal–dppfe complexes and attempted to correlate Mössbauer parameters with aforementioned these factors. Instead they found that the change in the quadrupole splitting are predominantly a consequence of the structural demands by the metal ion to which dppfe coordinates and cannot be explained by any single factors among them; they found that the compounds with the tetrahedral structure have the tendency to show larger quadrupole splitting than those with the octahedral and/or square planar structures. For a present series of compounds, **3** which possesses octahedral geometry around the manganese atom shows a larger quadrupole splitting than **1** and **2** which have pseudo-tetrahedral structures around the manganese atom. All of these findings indicate that accumulation of data on dppfe–metal complexes is necessary before we draw any conclusive remarks on the Mössbauer parameters for these complexes.

NMR Data. Table 8 shows ^{31}P NMR data. Free dppfe and uncoordinated phosphorus atom in **1** show high-field resonances. When the phosphorus atom coordinates to metal atom, low-filed shift is observed; a sharp signlet is observed at 84.7 ppm for the coordinated phosphorus atom in **1** and a weak broad feature is observed at around 40.3 ppm for **3**. The resonance has eluded observation for **2** at room temperature because of exchange between conformers due to methylcyclopentadienyl rings in solutions (the detail was described in the previous paper).[6a] **4** shows a fairly broad multiplet at 25.4 ppm.

At room temperature, ^{1}H NMR spectrum for **1** shows somewhat broad two triplets at 1.9 and 2.3 ppm (it is difficult to read the coupling constants with ^{31}P from a room temperature spectrum because each triplet is not well resolved) due to the methyl group in MeCp of **1**. Existence of two methyl signals indicates that there are



Scheme 4.

two conformers such as shown in Scheme 4 and exchange between these two conformers is restricted even at this temperature; rotational energy barrier for this exchange is supposed to be rather high owing to interference of the bulky phenyl groups with the methylcyclopentadienyl group.

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