Photochemical Reaction of Tricarbonyl(η-methylcyclopentadienyl)manganese(I), [Mn(CO)$_3$(MeCp)], with 1,1′-Bis(diphenylphosphino)ferrocene, (dppfe), and X-Ray Molecular Structure Analysis of [Mn(CO)(MeCp)(dppfe)]

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Synopsis. Photochemical reaction of MeCpMn(CO)$_3$ with (Ph$_2$PC$_5$H$_4$)$_2$Fe, (dppfe), was conducted in benzene. From the reaction mixture, the title compound [Mn(CO)(MeCp)(dppfe)] was isolated and its molecular structure was solved by X-ray analysis. ν(CO) peak at 1810 cm^{-1} of the title compound was clarified to be originated from the terminal carbonyl. Temperature-dependent ^{1}H NMR spectra were also measured for the title compound.

It is well-established that tricarbonyl(η-cyclopentadienyl)manganese(I), [Mn(CO)$_3$Cp], dissociates CO quite easily upon photolysis to yield CpMn(CO)$_2$, which, on treatment with various nucleophiles to yield CpMn(CO)$_2$L,[1] where L is phosphines, nitriles, alkadienes, and alkynes. However, the reaction with bidentate phosphine ligands has not yet been well-explored except PR$_2$(CH$_2$)$_n$PR$_2$ type ligands (n=1 and 2; R=CH$_3$ and C$_6$H$_5$) to our knowledge.[2] Recently, it was demonstrated that the dppfe-palladium complex, PdCl$_2$(dppfe), exhibits selective catalytic activity toward cross-coupling of Grignard and organozinc reagents.[3] Therefore, the reaction of **dppfe**, which is a new type of enticing bindentate ligand, with tricarbonyl(η-methylcyclopentadienyl)manganese(I)(**1**), which is a cheaper congener of CpMn(CO)$_3$, under UV irradiation was attempted with the hope of obtaining a new bimetallic compound which may exhibit intriguing reactivity.

From the photolysis of **1** with **dppfe** in benzene, two components were isolated by column chromatography. The second component eluted with benzene afforded orange-red crystals **2** by recrystallization from chloroform–hexane, which showed a strong IR peak at 1810 cm^{-1}. This peak is 24 cm^{-1} lower than that of CpMn(CO)(Ph$_2$PCH$_2$CH$_2$PPh$_2$) and 44 cm^{-1} lower than that of CpMn(CO)(Ph$_2$PCH$_2$PPh$_2$).[2] The observation posed some expectation that the CO group in **2** might be located in a bridging or semi-bridging position. ^{1}H NMR spectrum of **2** showed a broad feature in the methyl proton region at room temperature; the observation suggested some kind of dynamic process such as exchange among the conformers. These lines of structural interest motivated us to carry out X-ray molecular structure analysis of **2**.

Figure 1 shows an ORTEP view of the complex **2**, (CH$_3$C$_5$H$_4$)Mn(CO){(C$_6$H$_5$)$_2$PC$_5$H$_4$}$_2$Fe, and the atom numbering system; **dppfe** functions as a bidentate ligand. Important bond lengths and angles are listed in Table 1. The separation between Mn and Fe is 4.231(2)—4.308(2) Å, which is too far to expect any strong interaction between these two metal atoms. The distances between the carbon atom in CO and Fe atom are 3.89(1)—3.91(1) Å. This range of distance falsifies our expectation that the CO group may occupy a bridging position or a semi-bridging position rather than a terminal position. Therefore, occurance of the absorption of the carbonyl group as low as 1810 cm^{-1} for a terminal carbonyl should be originated from the strong electron-donating nature of **dppfe**. Another interesting feature of the structure of **2** is that the methyl substituent in CH$_3$C$_5$H$_4$ group extends to the same direction as that of CO in solid state, that is, the methyl and CO groups form an eclipsed conformation. Two Ph$_2$PC$_5$H$_4$ groups in **dppfe** moiety also compose an eclipsed conformation. Two C$_5$H$_4$ planes in **dppfe** moiety are almost parallel for each other and perpendicular to the C$_5$H$_4$ plane in (CH$_3$C$_5$H$_4$)Mn(CO) moiety. Mn–P distances are in

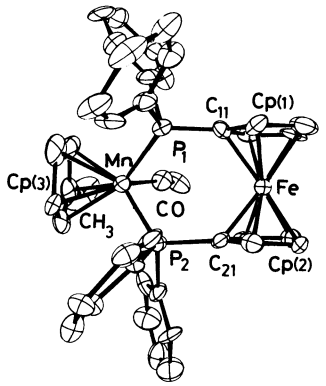


Fig. 1. An ORTEP view of MeCpMn(CO)·dppfe. Thermal elipsoids are drawn at 50% probability level.

Table 1. Important Bond Lengths and Angles

Bond, Angle	Molecule 1	Molecule 2
Mn···Fe	4.308(2) Å	4.231(2) Å
Mn–P$_1$	2.233(3)	2.209(3)
Mn–P$_2$	2.222(3)	2.214(3)
Mn–CO	1.85(1)	1.68(1)
C–O	1.12(2)	1.24(2)
Fe···CO	3.89(1)	3.91(1)
P$_1$–C$_{11}$	1.76(1)	1.94(1)
P$_2$–C$_{21}$	1.85(1)	1.82(1)
Mn···Cp(3) plane	1.80	1.76
Fe···Cp(1) plane	1.60	1.58
Fe···Cp(2) plane	1.70	1.69
CH$_3$–Cp(3)	1.57(3)	1.51(2)
∠P$_1$–Mn–P$_2$	99.5(1)°	98.2(1)°

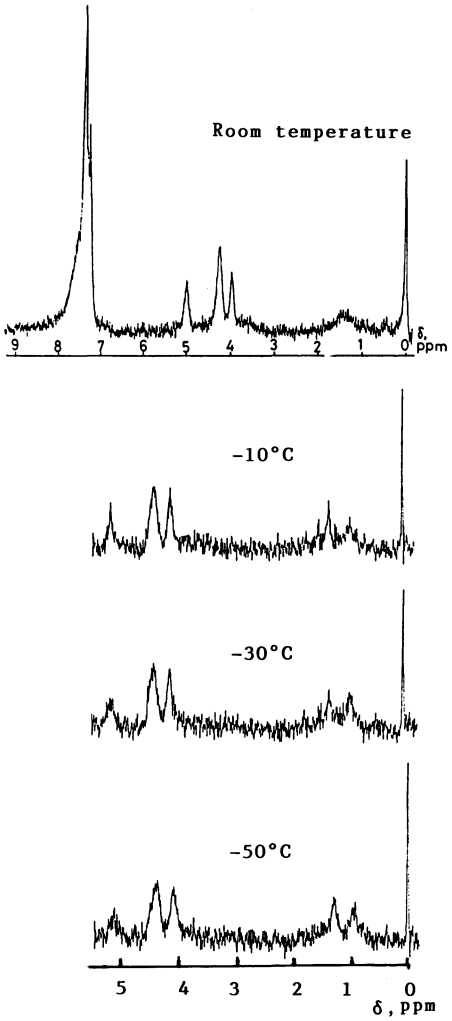
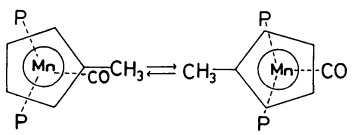


Fig. 2. Temperature-dependent ^{1}H NMR spectra of MeCpMn(CO)·dppfe in $CDCl_3$.

the range of 2.209(3)—2.233(3) Å, which are shorter than Pd-P distances in $PdCl_2$(dppfe) and the bond angle, ∠P-Mn-P, is 99.5(1)—98.2(1)°, which is close to 99.07° for ∠P-Pd-P in $PdCl_2$(dppfe).[3]

Figure 2 shows a temperature-dependent ^{1}H NMR spectra of **2** in $CDCl_3$; the broad feature at around δ 1.4 ppm observed at room temperature splits into two peaks with lowering the temperature. This observation clearly indicates the existence of exchange between two structures. The most plausible explanation for this dynamic process is that **2** exchanges between two conformers in solution such as shown in the Scheme.



Scheme

Experimental

Syntheses. 1.11 g (2 mmol) of **dppfe** and 410 mg (2 mmol) of **1**, which were both purchased from Strem Chemicals, Inc., were dissolved into 75 ml of benzene and this orange solution was photolyzed for 3.5 h under Ar atmosphere with a Riko 100 W high-pressure Hg lamp. The resulting yellow brown precipitate was filtered off and the solvent was vacuum-stripped from the filtrate to leave orange-red semisolid. This semisolid was dissolved into minimum amount of chloroform and was loaded on a Florisil column. First, an orange band was eluted with petroleum ether and then second orange band was eluted with benzene. From the first orange band, yellow microcrystalline product **3** was isolated by recrystallization from dichloromethane–hexane, which showed two strong ν(CO) peaks at 1920 and 1845 cm^{-1} (a Nujol mull). IR data suggest that **dppfe** functions as a monodentate ligand in **3**. 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%. The orange-red product from the benzene eluent was recrystallized from chloroform–hexane to yield orange-red crystals **2** from which a good crystal for X-ray analysis was selected. X-Ray analysis showed that one chloroform molecule is contained for one [$Mn(CO)(CH_3C_5H_4)$(dppfe)] molecule in the crystal of **2**. Anal. Calcd for $FeMnC_{41}H_{35}OP_2\cdot CHCl_3$: C, 60.35; H, 4.34%. Found: C, 60.79; H, 4.45%. IR spectra were measured with a Jasco 701G spectrometer for Nujol mull samples and proton NMR spectra were recorded with a Hitachi-Perkin-Elmer R-20B and R-24A spectrometers (60 MHz) for $CDCl_3$ solutions.

X-Ray Analysis. A single crystal of $Mn(CO)(CH_3C_5H_4)(Ph_2PC_5H_4)_2Fe\cdot CHCl_3$ with approximate dimensions 0.25×0.35×0.60 mm^3 was mounted on a Rigaku AFC-5 diffractometer with graphite monochromatized Mo $K\alpha$ radiation. Crystal data: monoclinic, $P2_1$, a=18.589(3), b=20.574(3), c=9.785(1) Å, β=91.46(1)°, V=3741(1) $Å^3$, Z=4 and μ(Mo $K\alpha$)=10.5 cm^{-1}. The structure was solved by direct method with MULTAN 78 and refined by block-diagonal least-squares method. Two independent molecules of $Mn(CO)(CH_3C_5H_4)(Ph_2PC_5H_4)_2Fe$ and $CHCl_3$ were contained in an asymmetric unit. The final R indices were 0.057 and R_w=0.072 for 100 non-hydrogen atoms with anisotropic temperature factors based on 4838 independent reflections ($2\theta<50°$ and $|F_o|>3\sigma(|F_o|)$), which were collected by 2θ—ω scan method.[4,5] Calculations were made on the HITAC M-200H computer at the Computation Center of the Institute for Molecular Science by use of the Universal Crystallographic Computation Program System, UNICS III.[6]

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4) Chloroform molecules were so severely disordered that it was difficult to locate exact positions of atoms in $CHCl_3$.

5) Tables of atom coordinates, anisotropic thermal parameters, and observed and calculated structure factors are kept in the office of the Chemical Society of Japan (Document No. 8636).

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