CHEMISTRY LETTERS, pp. 2037-2040, 1989.

Various Coordination Modes of 1,1'-Bis(diphenylphosphino)ferrocene, dppfe, with Metals. Syntheses and X-Ray Structural Characterization of Metal Carbonyl Complexes of dppfe, $MeCCo_3(CO)_7$dppfe and $[ClMn(CO)_4]_2$dppfe

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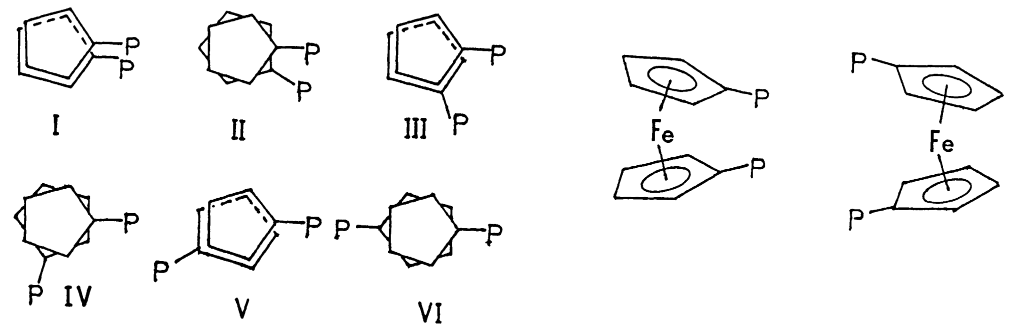
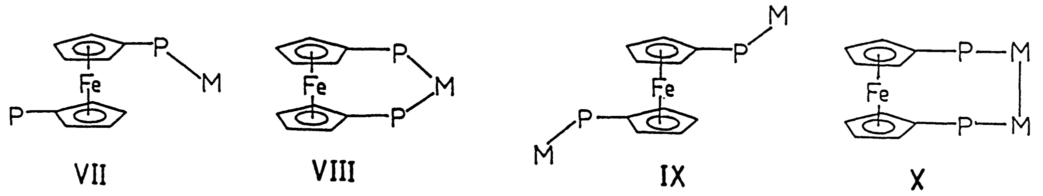
Thermal reaction of $MeCCo_3(CO)_9$ with dppfe has afforded $MeCCo_3(CO)_7$-dppfe (**2**), where three terminal carbonyls shift to bridging positions and dppfe functions as a bridging ligand. Photochemical reaction of $Mn_2(CO)_{10}$ with dppfe followed by further photolysis with CCl_4 has yielded $[ClMn(CO)_4]_2$dppfe (**3**). Two new types of coordination mode of dppfe as a bidentate ligand have been demonstrated by X-ray molecular analyses of **2** and **3** instead of a chelational type of coordination.

The chemistry of transition metal complexes of ferrocene-bridged bis(tertiary phosphine) such as 1,1'-bis(diphenylphosphino)ferrocene, dppfe, has attracted interest for a past decade predominantly from their catalytic properties.[1-6] We have, however, noticed potential idiosyncrasy of dppfe which should be displayed upon complexation with metals; dppfe possesses two freedoms to adjust the coordination mode to metals and/or to minimize the straint which should be imposed on dppfe in complexation to metals, that is, the rotation around the Cp-Fe-Cp axis and the tilt of the two Cp rings (Scheme 1). With these freedoms, dppfe can adjust its bite angle and/or distance between two metal atoms which dppfe bridges. Scheme 2 depicts possible coordination mode of dppfe with metal(s). We have already demonstrated two coordination modes, **VII** and **VIII** for two photochemical products of $MeCpMn(CO)_3$ with dppfe;[7] in MeCpMn(CO)dppfe, dppfe shows the coordination mode of **VIII** in Scheme 2 and takes a completely eclipsped conformation (I in Scheme 1) with two Cp rings almost parallel to each other. So far, only chelating mode of coordination has been reported for dppfe complexes with Pd,[8] Pt,[9] Ni, Mo, and Rh[10] to our knowledge. In the present study, we would like to report the structures of two new complexes where the other coordination modes **IX** and **X** than **VII** and **VIII** are exhibited.



Rotation around the Cp-Fe-Cp axis Tilt of two Cp rings

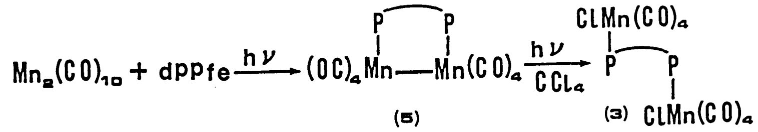
Scheme 1.



Scheme 2.

Thermal reaction of $MeCCo_3(CO)_9$ (**1**) with dppfe (1:1 mole ratio) in C_6H_6 gave an orange solution. The product $MeCCo_3(CO)_7$dppfe (**2**) obtained from the orange solution was purified by column chromatography (silica-gel, eluted with benzene) and recrystallization from CH_2Cl_2-C_6H_6 in a form of orange, air-stable plate crystals with 54% yield. The molecular structure of **2** (Fig. 1)† shows that dppfe bridges one of the Co-Co bond (coordination mode **X** in Scheme 2). As is shown in Fig. 1, two Cp rings take the conformation **III** in Scheme 1 and are parallel to each other. Upon complexation with dppfe, three terminal carbonyls in **1** move to bridging positions and four terminal carbonyls shift to intermediate terminal positions between axial and equatorial carbonyls and/or between apical methyl carbon and equatorial carbonyls in **1**.11) These shifts are marked contrast to the reaction of **1** with $Ph_2PCH_2PPh_2$ (dppm); in this reaction, $MeCCo_3(CO)_7$dppm (**4**) is obtained with retention of the original carbonyl conformation by replacing two equatorial carbonyls with dppm.12) Presumably four bulky phenyl groups prohibit to retain original axial-equatorial carbonyl conformation in **2**. Another interesting finding for **2** is that the Co-Co bond bridged by dppfe is significantly elongated although dppm does not beget such elongation in **4**; the Co-Co bond bridged by dppfe in **2** is 2.520(1) Å and the Co-Co bond bridged by dppm in **4** is 2.486(1) Å12) whereas the averaged Co-Co bond length in **1** is 2.467 Å.11)

Photochemical reaction of $Mn_2(CO)_{10}$ with dppfe in toluene (1:1 mole ratio) followed by further photolysis together with equimolar amount of CCl_4 gave orange crystals after recrystallization from CH_2Cl_2-hexane. The molecular structure analysis of this product (**3**) has revealed that dppfe functions as a bridging ligand (Fig. 2)[‡] (coordination mode **IX** in Scheme 2); two Cp rings take the conformation **VI** in Scheme 1. In due course of photochemical reaction of $Mn_2(CO)_{10}$ with dppfe, the absorption spectrum shows a red shift of the peak at 340 nm to 370 nm. As these peaks are assignable to $\sigma(Mn-Mn) \rightarrow \sigma^*(Mn-Mn)$ transitions, the original photochemical product of $Mn_2(CO)_{10}$ with dppfe is strongly suggested to be $Mn_2(CO)_8(\mu$-dppfe) (**5**) before addition of CCl_4; in **5**, dppfe functions as a bridging ligand between two Mn atoms (coordination mode **X** in Scheme 2). The overall photochemical reaction pathway is depicted in Scheme 3. Although exact Mn-Mn distance in **5** is not known from the absorption spectrum, the Mn-Mn distance is supposed to be ≈2.90 Å on the basis of X-ray molecular structure analysis of $Mn_2(CO)_5(dppm)_2$(2.934(6) Å)[13] and of $Mn_2(CO)_{10}$ (2.923(3) Å).[14] Thus, dppfe serves not only as a chelating ligand, but also as a compliant and versatile bridging ligand over wide range of metal-metal bond and X-ray molecular structure analysis for **5** is awaited as early as possible to know what conformation dppfe takes as a bridging ligand over a long metal-metal bond.



Scheme 3.

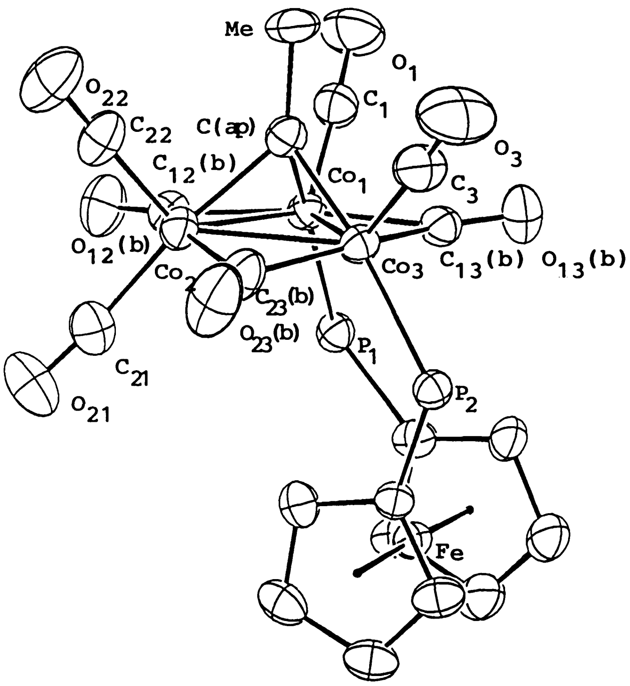
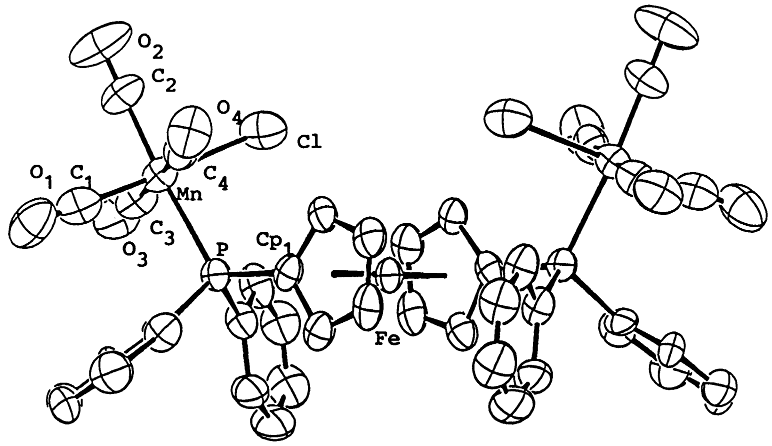


Fig. 1. Phenyl groups are omitted for clarity.

[†] **Crystal data for 3:** triclinic, $P\bar{1}$, $a = 13.031(2)$, $b = 15.338(2)$, $C = 11.583(2)$ Å, $\alpha = 99.13(2)$, $\beta = 98.35(2)$, $\gamma = 99.64(2)°$, $U = 2218.1(7)$ Å^3, $Z = 2$, $D_c = 1.42$ g cm^{-3}, μ(Mo-K_α) = 15.8 cm^{-1}, Rigaku AFC5R (Mo-K_α), 6098 reflections with $|F_o| > 3\sigma(|F_o|)$, R = 5.55% **Selected Bond Length(Å):** Co_1-Co_2= 2.479(1), Co_2-Co_3= 2.513(1), Co_1-Co_3= 2.520(1), Co_1-P_1= 2.314(2), Co_3-P_2= 2.297(2), Co_2-C_{12}(b)= 2.071(7), Co_1-C_{12}(b)= 1.882(7), C(ap)-C(Me)= 1.511(10) **Selected Bond Angle(°):** Co_2-Co_1-Co_3= 60.34(4), Co_1-Co_2-Co_3= 60.54(4), Co_2-Co_3-Co_1= 59.01(4), P_1-Co_1-Co_3= 118.7(6), P_2-Co_3-Co_1= 122.63(6), Co_1-C_{12}(b)-O_{12}(b)=149.3(6), Co_2-C_{12}(b)-O_{12}(b)=133.2(6)



Selected Bond Length(Å): Mn-P= 2.364(4), Mn-Cl= 2.347(6), $Mn-C_1$= 1.91(2), $Mn-C_2$= 1.83(2), $Mn-C_3$= 1.87(2), $Mn-C_4$= 1.90(1) $P-Cp_1$= 1.82(1), Fe-Cp(av)= 2.07 **Selected Bond Angle(°):** Cl-Mn-P= 89.0(2), $Mn-P-Cp_1$= 115.1(5), $P-Mn-C_1$= 92.2(5), $P-Mn-C_2$= 177.4(6), $P-Mn-C_3$= 89.6(6), $P-Mn-C_4$=90.3(3)

Fig. 2. Fe is located on the two-fold axis.

‡**Crystal data for 3:** monoclinic, space group A2/a, a = 18.978(5), b = 15.293(4), c = 16.513(5) Å, β = 112.62(2)°, U = 4423.9(2) $Å^3$, Z = 4, D_c = 1.42 g cm^{-3}, μ(Mo-K_α) = 12.1 cm^{-1}. Rigaku AFC5(Mo-K_α), 2575 reflections with $|F_o| > 3\sigma(|F_o|)$, R = 7.42%.

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(Received August 2, 1989)