Syntheses and X-Ray Crystal Structures of Platinum(II) Complexes Bearing Two and Three Phosphorus-Bridged [1]Ferrocenophanes, *cis*-$[PtCl_2(fcpp)_2]$ and $[PtCl(fcpp)_3]BF_4$

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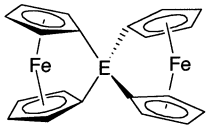
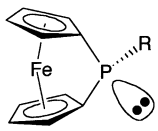
Platinum complexes having two and three (1,1'-ferrocenediyl)phenylphosphine (fcpp) groups, *cis*-$[PtCl_2(fcpp)_2]$ and $[PtCl(fcpp)_3]BF_4$, were prepared and their molecular structures were determined by X-ray analysis.

Ring-opening polymerization of strained [1]ferrocenophanes represents a well-established route to high molecular-weight poly(ferrocenes).[1] Most of the starting monomers for such polymerization have a single [1]ferrocenophane unit. Recently, Manners et al. reported the molecular structure of spirocyclic silicon- and germanium-bridged [1]ferrocenophanes **1** and **2**,[2] which have two [1]ferrocenophane units per one monomer. Since a monomer having several [1]ferrocenophane units is a possible cross-linking agent for poly(ferrocenes), it is meaningful to develop a simple and versatile method for the preparation of such a monomer.



1, E=Si; **2**, E=Ge



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On the other hand, phosphorus-bridged [1]ferrocenophane **3** is also known to undergo a similar ring-opening polymerization.[3] In addition, since **3** has lone pair electrons on the bridging phosphorus atom, it acts as a ligand for a metal complex. Several examples of metal complexes bearing one **3** unit as a ligand have been reported,[4–6] but a metal complex with two or three **3** units has not been reported,[7] though it is considered to be readily obtained by a usual ligand-substitution reaction. Here, we report the preparation and molecular structures of platinum complexes with two or three phosphorus-bridged [1]ferrocenophane units.

Two equivalents of (1,1'-ferrocenediyl)phenylphosphine (**3** with R=Ph), abbreviated as fcpp,[8] reacted with *cis*-$[PtCl_2(PhCN)_2]$ to give a platinum complex *cis*-$[PtCl_2(fcpp)_2]$ **4** in a good yield.[9] The $^{31}P\{^1H\}$ NMR spectrum of **4** thus obtained showed a singlet at 18.0 ppm accompanied with satellites due to a coupling with ^{195}Pt, $^1J_{PtP}$ = 3638 Hz. The $^1J_{PtP}$ over 3500 Hz is characteristic of a cis configuration, while a trans isomer generally has $^1J_{PtP}$ around 2500 Hz.[10]

To prepare a platinum complex with three fcpp units, $AgBF_4$ was added to a CH_2Cl_2 solution of **4** in the presence of fcpp. The $^{31}P\{^1H\}$ NMR spectrum of the solution showed a triplet and a doublet with a 1 : 2 intensity ratio, indicating the formation of the expected $[PtCl(fcpp)_3](BF_4)$ **5**.[11] The triplet at 9.5 ppm with a satellite, $^1J_{PtP}$ = 3537 Hz, was assigned to the fcpp ligand trans to a remaining Cl ligand and a doublet at 31.4 ppm with a satellite, $^1J_{PtP}$ = 2459 Hz, to the two fcpp ligands cis to Cl. Preparation of the further-substituted complex, $[Pt(fcpp)_4](BF_4)_2$, was attempted by using excess $AgBF_4$ and fcpp, but the replacement of the last Cl ligand did not take place, probably due to the steric hindrance of the three bulky fcpp ligands coordinating to the Pt center.

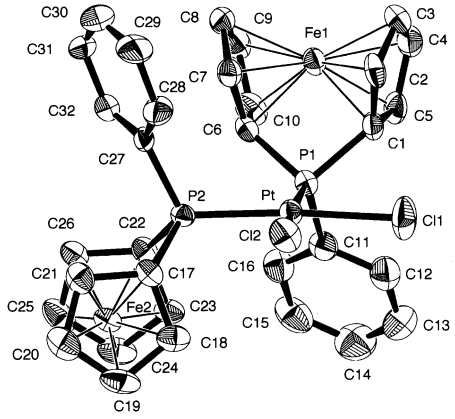

Figure 1. Molecular structure of **4**. Selected bond lengths(Å) and angles(deg): Pt-Cl1, 2.344(2); Pt-Cl2, 2.364(2); Pt-P1, 2.227(2); Pt-P2, 2.237(2); P1-C1, 1.832(9); P1-C6, 1.830(8); P1-C11, 1.816(9); P2-C17, 1.805(8); P2-C22, 1.830(8); P2-C27, 1.820(8); Cl1-Pt-Cl2, 88.11(9); P1-Pt-P2, 97.11(7); Cl1-Pt-P1, 86.73(9); Cl2-Pt-P2, 88.35(8); Cl1-Pt-P2, 174.89(8); Cl2-Pt-P1, 172.90(8); C1-P1-C6, 93.2(4); C17-P2-C22, 94.6(4).

The molecular structure of **4** is shown in Figure 1,[12] where two Cl and two fcpp ligands coordinate to the Pt center to form a square-planar geometry with a cis configuration. Two ferrocene units are each located above or below the square-planar coordination plane to avoid the steric congestion.

The molecular structure of **5** is shown in Figure 2,[13] which indicates that one of the two Cl's in **4** has been replaced with fcpp. The three ferrocene units adopt a below-above-below arrangement similar to that shown in Figure 1. There are two types of Pt–P bonds in **5**, i.e., Pt–P bonds mutually trans (Pt–P1 and Pt–P3) and that trans to the Cl (Pt–P2). The average of the former two bond lengths (2.330(2) Å) is significantly larger than the latter (2.239(2) Å) because of the usual trans influence, which may also explain the difference between the observed coupling constants $^1J_{PtP1\text{ or }P3}$ and $^1J_{PtP2}$ mentioned above.

The structural data of some strained phosphorus-bridged [1]ferrocenophanes coordinating to a metal fragment are summarized in Table 1 for **4** and **5** as well as for related phosphorus-bridged [1]ferrocenophanes.[14] The definitions of α and β are given elsewhere.[3c] The ring tilt angle α's of the fcpp ligands attached to metal fragments are all comparable to that of the free ligand, indicating that the strain of the [1]ferrocenophane unit is almost intact upon the coordination. The Fe–P distances of **4** and **5** become shorter than that of the free fcpp, which may come from a weak interaction between a vacant σ* orbital of the bridging phosphorus and a filled d orbital of the

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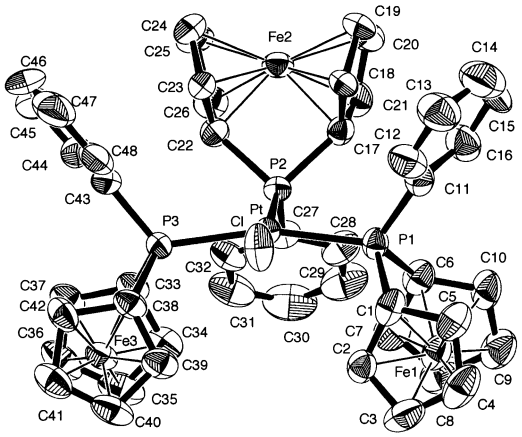

Figure 2. Molecular structure of **5**. Selected bond lengths(Å) and angles(deg): Pt-Cl1, 2.332(2); Pt-P1, 2.320(2); Pt-P2, 2.239(2); Pt-P3, 2.340(2); P1-C1, 1.816(7); P1-C6, 1.828(7); P1-C11, 1.804(7); P2-C17, 1.834(7); P2-C22, 1.832(7); P2-C27, 1.800(7); P3-C33, 1.826(7); P3-C38, 1.817(7); P3-C43, 1.796(8); Cl1-Pt-P1, 86.15(6); Cl1-Pt-P2, 165.40(7); Cl1-Pt-P3, 86.80(6); P1-Pt-P2, 94.42(6); P1-Pt-P3, 164.63(7); P2-Pt-P3, 95.83(6); C1-P1-C6, 95.3(3); C17-P2-C22, 94.6(3); C33-P3-C38, 94.4(3).

Table 1. Selected structural data for fcpp ligands

		P-Fe Distance/Å	ring tilt, α/deg	β/deg
fcpp[a]		2.774(1)	26.9	32.3
[Cp(CO)FeH(fcpp)][b]		2.731(2)	25.4	33.9
$[Cp(CO)_2Fe(fcpp)]^+$ [c]		2.693(2)	25.4	34.6
4[d]	fcpp1	2.718(3)	26.5	33.5
	fcpp2	2.701(2)	26.1	34.2
5[d]	fcpp1	2.690(2)	25.5	34.6
	fcpp2	2.693(2)	25.2	34.8
	fcpp3	2.688(2)	26.3	34.0

[a]Ref. 14. [b]Ref. 5. [c]Ref. 6. [d]This work.

iron, as discussed previously.[6] The interaction is considered to be enhanced when the phosphorus atom coordinates to an electron-withdrawing metal fragment.

Recently, we found that two neutral complexes having one fcpp unit, $[MnCp(CO)_2(fcpp)]$ and $[W(CO)_5(fcpp)]$, successfully polymerize upon UV irradiation in THF or acetonitrile.[15] Thus, a similar photolysis was carried out for the neutral **4**. Upon irradiation of **4** for 1 h, a brown precipitate was formed and a $^{31}P\{^1H\}$ NMR spectrum of the supernatant solution showed complete disappearance of the signal due to the starting **4**. Unfortunately, owing to very low solubility of the precipitate, detailed spectroscopic characterization is difficult at present, but elemental analyses indicate that a formula of the product is close to that of **4**. We consider that the product is a poly-**4** having a cross-linked structure which is responsible for the low solubility. Reactivity of **5** is now under investigation.

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7 Preparation of $[PdCl_2(\mathbf{3})_2]$ was briefly described as unpublished results in Ref. 5, p. 880.

8 fcpp was prepared according to the methods described in Ref 3c.

9 Reactions were carried out under an N_2 atmosphere. *cis*-$[PtCl_2(NCPh)_2]$ (266 mg, 0.564 mmol), fcpp (347 mg, 1.188 mmol), and CH_2Cl_2 (15 mL) were put in Schlenk tube, and the solution was stirred for 30 min. After the volume of the solution was reduced to ca. 5 mL, hexane (20 mL) was added to complete precipitation. The product was washed twice with hexane (10 mL), and dried in vaccuo. *cis*-$[PtCl_2(fcpp)_2]$ (**4**) was obtained as a monosolvate of CH_2Cl_2. Yield: 388 mg (97%). ^1H NMR (300 MHz, $CDCl_3$) δ 4.18 (br, 2H, Fc), 4.37 (br, 4H, Fc), 4.61 (br, 2H, Fc), 7.43 (m, 2H, Ph), 7.54 (m, 1H, Ph), 7.95, (m, 2H, Ph). Anal. Found: C, 42.30; H, 2.76 %. Calcd for $C_{33}H_{28}Cl_4Fe_2P_2Pt$: C, 42.39; H, 3.02 %.

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11 **4** (312 mg, 0.333 mmol), fcpp (107 mg, 0.366 mmol), and CH_2Cl_2 (40 mL) were put in a Schlenk tube. To the solution thus obtained was added excess $AgBF_4$ (136 mg, 0.699 mmol). The suspension was stirred for 30 min, and then the precipitate was filtered off. The volume of the filtrate was reduced to ca. 10 mL, and then hexane (20 mL) was added slowly. The precipitate was collected by filtration, washed twice with hexane (10 mL), and dried in vaccuo. Yield: 398 mg (93%). ^1H NMR (300 MHz, $CDCl_3$) δ 3.86 (br, 2H, Fc),4.08 (br, 2H, Fc), 4.12 (br, 2H, Fc), 4.18 (br, 2H, Fc), 4.45 (br, 2H, Fc), 4.51 (br, 2H, Fc), 4.70 (br, 6H, Fc),4.76 (br, 4H, Fc), 4.94 (br, 2H, Fc), 7.32 (m, 1H, Ph), 7.45 (m, 4H, Ph), 7.57, (m, 4H, Ph), 7.78 (m, 2H, Ph), 7.94, (m, 4H, Ph). Anal. Found: C, 46.95; H, 3.22 %. Calcd for a partial solvate, $C_{48}H_{39}BClF_4Fe_3P_3Pt\cdot(CH_2Cl_2)_{0.6}$: C, 46.90; H, 3.26 %.

12 Crystal data for **4**: dark red crystals, monoclinic, space group $P2_1/n$ (No. 14), formula $C_{33}H_{28}Cl_4Fe_2P_2Pt$, formula weight 935.13; a = 18.576(3), b = 17.409(3), c = 9.888(2) Å, β = 96.13(1)°, V = 3179.3(8) Å^3; Z = 4, D_{calc} = 1.954 g cm^{-3}, R = 0.039, R_w = 0.046 for 4479 reflections with $|F_o| > 3\sigma(Fo)$, 377 parameters, GOF = 1.07.

13 Crystal data for **5**: dark red crystals, monoclinic, space group $P2_1/n$ (No. 14), formula $C_{49}H_{41}BCl_3F_4Fe_3P_3Pt$, formula weight 1278.58; a = 20.133(3), b = 14.540(2), c = 17.319(3) Å, β = 110.08(1)°, V = 4761(1) Å^3; Z = 4, D_{calc} = 1.783 g cm^{-3}, R = 0.037, R_w = 0.047 for 5526 reflections with $|F_o| > 3\sigma(Fo)$, 578 parameters, GOF = 1.14.

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