Bull. Chem. Soc. Jpn., ***75***, *1547–1552 (2002)*

Interaction Modes with a Halide Anion of Metal Centers of Edge-Sharing Dinuclear Complexes Bearing a Bent Form

Tsutomu Mizuta, Koji Nakayama, Shizuka Aoki, and Katsuhiko Miyoshi*

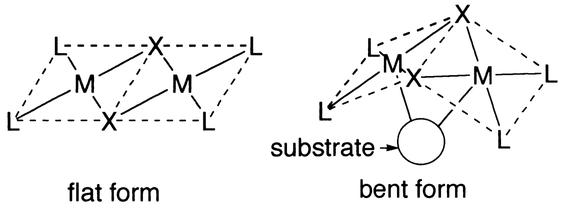
Department of Chemistry, Graduate School of Science, Hiroshima University,
1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526

(Received January 30, 2002)

Two types of diphosphido ligands, mpe and ppe (mpe = $MePCH_2CH_2PMe^{2-}$ and ppe = $PhPCH_2CH_2PPh^{2-}$), were used as a bridging unit in the edge-sharing bis-squareplanar complexes, $[\{Pt(dppe)\}_2(\mu\text{-mpe or }\mu\text{-ppe})]Cl_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$), which were prepared by the reaction of $[Pt(dppe)(H_2mpe\text{ or }H_2ppe)]Cl_2$ with $[PtCl_2(dppe)]$ in the presence of Na_2CO_3. X-ray crystal structure analyses were performed for the following diplatinum complexes: $[\{Pt(dppe)\}_2(\mu\text{-mpe})]X_2$ (X = Cl^- and I^-) and $[\{Pt(dppe)\}_2(\mu\text{-ppe})]X_2$ (X = Cl^- and $BArf^-$), and their palladium analogs: $[\{Pd(dppe)\}_2(\mu\text{-ppe})]X_2$ (X = I^- and $BArf^-$) ($BArf^-$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion). Regarding an M_2P_6 core framework, all of the dinuclear complexes in the above six crystals adopted a common bent form reported previously. It is only in $[\{Pd(dppe)\}_2(\mu\text{-ppe})]^{2+}$ that a chloride or iodide anion is incorporated into a "pocket" located under the bent bis-squareplanes to allow the two metal centers to interact simultaneously with the halide anion. The factors responsible for the above interaction mode are discussed.

The edge-sharing bis-squareplanar framework is a common structure for the complexes having a general formula $L_2M(\mu\text{-}X)_2ML_2$ (M = d^8 transition metal; X = halide anion, RO^-, S^{2-}, RS^-, and R_2P^-).[1–3] The molecular structures of such complexes are classified into either a flat form or a bent form (Scheme 1). Of these two forms, the bent one is interesting, particularly because axial orbitals of the two metals are in close proximity under the hinged planes and are expected to interact simultaneously with a substrate bound to the dinuclear complex.[4] Such an interaction is expected to play an important role in a bimetallic activation reaction. In addition, the bent form has attracted considerable interest from a theoretical point of view, since the factors responsible for the bent structure adopted by a particular dinuclear complex have not been completely understood.[1–3, 5–7]

Although both flat and bent forms often occur for dinuclear complexes having the general formula $L_2M(\mu\text{-}X)_2ML_2$ (X = halide anion, RO^-, S^{2-}, RS^-),[1] most of the diphosphido-bridged analogs (X = R_2P^-) are regarded as a flat form,[8–18] two limited exceptions being $(dppe)Rh(\mu\text{-}PPh_2)_2Rh(dppe)$ and $MePt(\mu\text{-cypp})_2PtMe$.[19] Since the examples of the bent diphosphido dinuclear complexes reported so far are limited to these two Rh(I) and Pt(II) complexes,[20–22] it is worth preparing a bent diphosphido complex intentionally to search for the factors responsible for the bent structure. Recently, we reported dipalladium complexes $[\{Pd(dppe)\}_2(\mu\text{-mpe or }\mu\text{-ppe})]Cl_2$ (mpe = $MePCH_2CH_2PMe^{2-}$, ppe = $PhPCH_2CH_2PPh^{2-}$), in which two phosphorus atoms of mpe and ppe are linked with a CH_2CH_2 chain. The X-ray crystal structures of these two complexes showed that the two squareplanes are enforced to adopt the bent form.[23] In this report, a similar method to achieve the bent form was applied to the preparation of the corresponding diplatinum complexes.



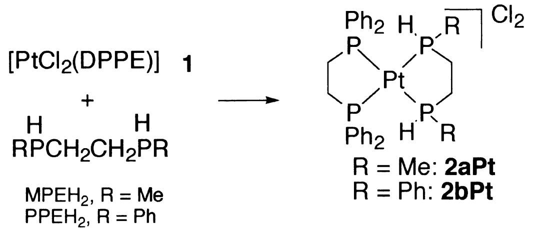
Scheme 1.

In addition, we previously observed that a chloride counter anion in a crystal of $[\{Pd(dppe)\}_2(\mu\text{-ppe})]Cl_2$ is located under the hinged plane, and simultaneously interacts with the two palladium centers in such a manner as shown in the right-hand figure of Scheme 1. Since such a bifurcated interaction mode is not only unprecedented, but also important as a multisite interaction model for the activation of an organic substrate, it is of interest whether the platinum analogs adopt a similar interaction mode or not.

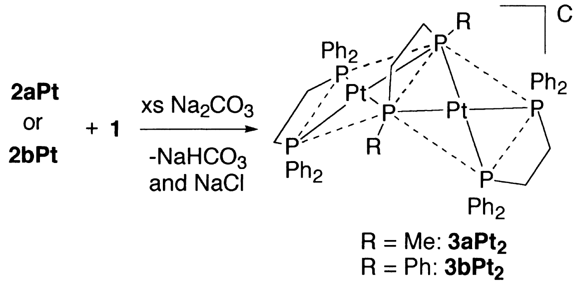
Results and Discussion

Preparation of $[\{Pt(dppe)\}_2(\mu\text{-mpe})]Cl_2$. The bridging ligands were prepared as a protonated form, $RHPCH_2CH_2PHR$ (H_2mpe, R = Me; H_2ppe, R = Ph), according to literature methods.[24–26] Thus-obtained H_2mpe and H_2ppe were a mixture of diastereomers due to two chiral phosphorus centers, and were used without separation, because the phosphorus centers of mpe and ppe bridges were deprotonated in the final products to no longer be asymmetric.

The dinuclear platinum complexes were prepared in a manner similar to those reported for the corresponding dipalladium complexes, $[\{Pd(dppe)\}_2(\mu\text{-mpe or }\mu\text{-ppe})]Cl_2$, (Eqs. 1 and 2).[23]



(1)



(2)

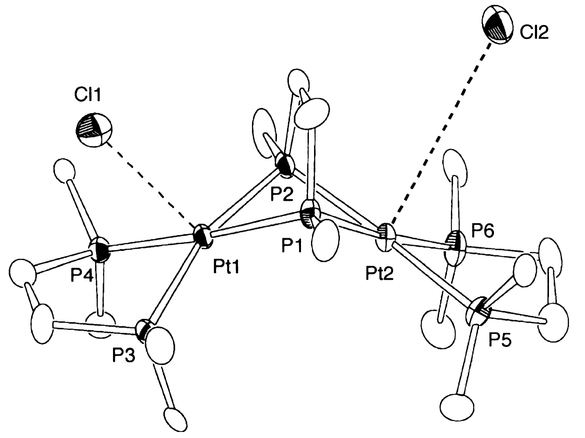


Fig. 1. Molecular structure of **3aPt₂**. The thermal ellipsoids are drawn at 50% probability level. Only ipso-carbons of the phenyl groups are drawn for clarity.

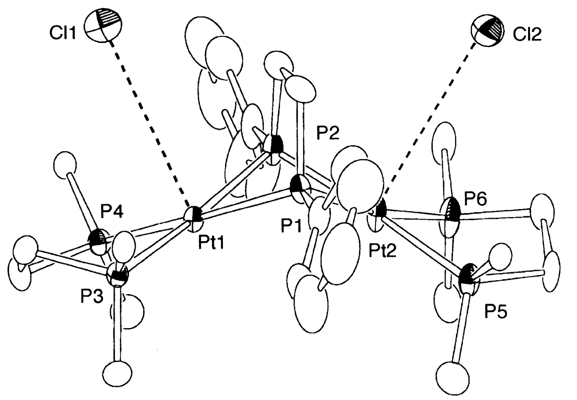


Fig. 2. Molecular structure of **3bPt₂**. The thermal ellipsoids are drawn at 50% probability level. Only ipso-carbons are drawn for the phenyl groups of dppe.

First, the bridging ligand, H_2mpe, was reacted with [$PtCl_2$(dppe)] (**1**) in CH_2Cl_2 to give [Pt(dppe)(H_2mpe)] (**2aPt**) as a mixture of two diastereomers due to the H_2mpe ligand. The $^{31}P\{^1H\}$ NMR spectrum of **2aPt** showed four sets of doublets of multiplets at 9.7, 11.3, 44.9, and 45.7 ppm. Two signals at a lower field are assigned to dppe, and thus the other two are to H_2mpe. The signals at 11.3 and 44.9 ppm are of slightly greater intensity than those at 9.7 and 45.7 ppm, owing to the presence of major and minor diastereomeric isomers. The thus-obtained **2aPt** was allowed to react with another equivalent of **1** in the presence of Na_2CO_3, which traps HCl formed by the metathesis of a P–H bond of **2aPt** with a Cl–Pt bond of **1**. A thus-formed dinuclear complex had the formula [{Pt(dppe)}$_2$(μ-mpe)]Cl_2 (**3aPt₂**), and showed two complicated $^{31}P\{^1H\}$ signals at -32.0 and 44.9 ppm. The former was assigned to the mpe bridge and the latter to dppe. The complicated coupling pattern was, however, successfully reproduced by an NMR simulation, assuming a coupling pattern similar to that reported for [{Pt(dppe)}$_2$(μ-PPh_2)$_2$]Cl_2 by Dixon et al.[27] (see supplementary materials).

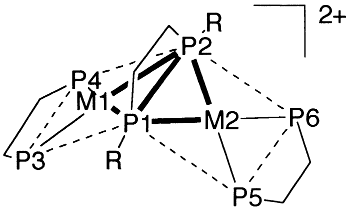
Preparation of [{Pt(dppe)}$_2$(μ-ppe)]Cl_2. [{Pt(dppe)}$_2$(μ-ppe)]Cl_2 (**3bPt₂**) was prepared in a manner similar to that described above (Eqs. 1 and 2). A notable difference with regard to the preparation is that the major/minor ratio of the diastereomeric isomers is much greater for [Pt(dppe)(H_2ppe)]Cl_2 (**2bPt**) than for **2aPt**, probably because a bulky Ph group of H_2ppe induces a greater difference in the steric stability between the major and minor diastereomeric isomers than does a Me group of H_2mpe. Both isomers of **2bPt** were successfully converted to a single final product, **3bPt₂**. The $^{31}P\{^1H\}$ NMR spectrum of **3bPt₂** showed multiplets for ppe and dppe at -35.5 and 45.7 ppm, respectively. The coupling pattern of these signals was also reproduced by a simulation.

Crystal Structures of Dinuclear Complexes. The molecular structures of **3aPt₂** and **3bPt₂** are shown in Figs. 1 and 2, respectively. Selected bond distances and angles are listed in Table 1, which includes those for the dipalladium analogs reported previously and for some iodide and $BArf^-$ salts ($BArf^-$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion). The latter two salts were prepared by the metathesis of the corresponding chloride salt with KI or NaBArf, respectively. All dinuclear complexes analyzed in this study adopted the bent form, as expected. Here, we define the bent angle as a dihedral angle of two triangular planes formed by P1–P2–M1 and P1–P2–M2 (Scheme 2). The bent angles given in Table 1 are in a narrow range of 117.8–127.4°, whereas a wide variety of bent angles (110–180°) have been reported for complexes having the general formula $L_2M(\mu\text{-}X)_2ML_2$.[1–3] The narrow range of the bent angle indicates that an M–(μ-$RPCH_2CH_2PR$)–M core is rigid irrespective of the R group (Me or Ph) on the phosphido centers and of counter anions (chloride, iodide, or BArf). Based on a smaller ionic radius of Pt^{2+}, 0.74 Å, than that of Pd^{2+}, 0.78 Å,[28] the M–P bonds of the diplatinum complexes are expected to be slightly shorter than those of the corresponding palladium complexes. However, the M–P distances given in Table 1 do not indicate such an expected tendency. Similarly, when the structural data are compared between the mpe and ppe complexes, almost comparable M–P(bridge) distances are observed for the μ-mpe and μ-ppe bridges. A similar invariability for the bite angles, P1–M–P2, of the mpe and ppe complexes is also found through the complexes listed in Table 1; the averaged bite angles are 69.2 and 68.7°, respectively. The structural invariability described in this section has a significant meaning in the following discussion on the inter-

Table 1. Averages of the Geometrical Parameters for the Dinuclear Complexes

Entry	Complex	M–P distances/Å		Bite angles/deg		Bent angle/deg
		Bridge	Terminal	Bridge	dppe	
1	$[\{Pd(dppe)\}_2(\mu\text{-mpe})]Cl_2$	2.339	2.316	69.25	83.29	118.3
2	$[\{Pt(dppe)\}_2(\mu\text{-mpe})]Cl_2$	2.318	2.313	69.0	82.2	122.3
3	$[\{Pt(dppe)\}_2(\mu\text{-mpe})]I_2$ [a)]	2.334	2.290	69.4	85.7	120.4
4	$[\{Pt(dppe)\}_2(\mu\text{-mpe})]I_2$ [a)]	2.348	2.304	68.9	85.0	124.8
5	$[\{Pd(dppe)\}_2(\mu\text{-ppe})]Cl_2$ [a)]	2.343	2.312	67.79	84.89	127.4
6	$[\{Pd(dppe)\}_2(\mu\text{-ppe})]Cl_2$ [a)]	2.347	2.312	67.69	85.47	124.5
7	$[\{Pd(dppe)\}_2(\mu\text{-ppe})]I_2$	2.341	2.332	68.40	83.67	120.2
8	$[\{Pd(dppe)\}_2(\mu\text{-ppe})]BArf_2$	2.344	2.328	69.88	84.59	117.8
9	$[\{Pt(dppe)\}_2(\mu\text{-ppe})]Cl_2$	2.344	2.305	68.86	83.73	123.9
10	$[\{Pt(dppe)\}_2(\mu\text{-ppe})]BArf_2$	2.349	2.315	69.78	84.71	120.0

a) Two independent molecules are present in an asymmetric unit.



Scheme 2.

action modes of these dinuclear complexes with halide anions.

Interaction with Halide Anions. We previously reported the bifurcated chloride-palladium interaction found in a crystal of $[\{Pd(dppe)\}_2(\mu\text{-ppe})]Cl_2$.[23] A similar interaction mode was also observed for its iodide salt analyzed in this study, as shown in Fig. 3. On the other hand, as shown in Figs. 1 and 2, the chloride anions in **3aPt₂** and **3bPt₂** interact with the platinum centers not in the bifurcated fashion, but in a 1:1 fashion. Here, the interaction modes found are summarized in Table 2. "Roof" means a mode in which a halide ion is located above a bent framework, like a gable roof (Figs. 1 and 2), whereas "pocket" means a mode in which a halide ion is located in a space like a pocket under a bent structure, as shown in Fig. 3. Table 2 indicates that the "pocket" mode is adopted by the chloride salts of $[\{Pd(dppe)\}_2(\mu\text{-ppe})]^{2+}$ (entries 5 and 6),[23] and by its iodide salt (entry 7). All other halide salts adopt the "roof" mode. Thus, it is only in the ppe–Pd combination that a halide anion is accommodated into the "pocket". Since the geometrical parameters in Table 1 are almost constant irrespective of the bridge-type (mpe or ppe) and of the metal ions (Pd^{2+} or Pt^{2+}), it is surprising that interaction modes found in the crystals showed contrasting differences.

As described in the previous section, no appreciable geometrical difference was observed, not only between the palladium and platinum complexes, but also between the mpe and ppe complexes. Thus, as far as the geometrical parameters of the $M_2P_6^{2+}$ core are concerned, we can not find any factor responsible for a "pocket" interaction mode observed only for the ppe–Pd complex. Another possible steric factor is a disposition of a number of bulky phenyl groups around the $M_2P_6^{2+}$ core. Since the steric bulkiness of the mpe bridge is smaller than that of the ppe bridge, it is considered feasible to replace the ppe bridge in the ppe–Pd complex with the mpe bridge with the overall conformations intact. In other words, at least from a steric point of view, it is possible for the mpe complex to adopt the "pocket" interaction mode. However, since such an interaction mode was not actually observed for the mpe complexes, we have to search for factors other than steric ones responsible for the "pocket" interaction modes found for $[\{Pd(dppe)\}_2(\mu\text{-ppe})]^{2+}$.

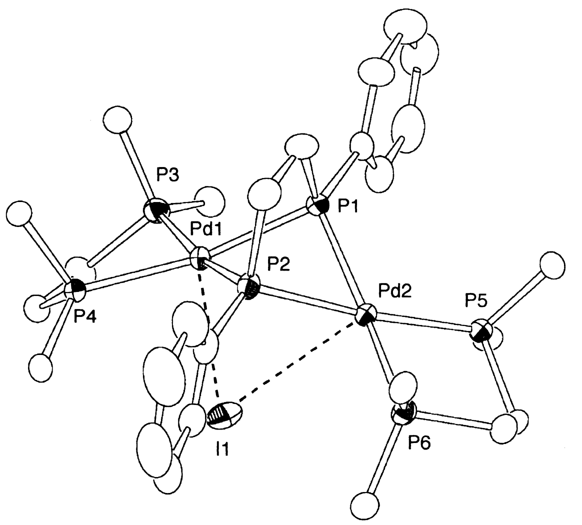


Fig. 3. Molecular structure of $[\{Pd(dppe)\}_2(\mu\text{-ppe})]I_2$. The thermal ellipsoids are drawn at 50% probability level. Only ipso-carbons are drawn for the phenyl groups of dppe.

Next, let us discuss the electronic factors. It is generally recognized that Lewis acidity of a Pd^{2+} complex is stronger than that of a Pt^{2+} analog.[29] This factor makes the halide–palladium interaction stronger than the halide–platinum interaction. The second electronic factor is the ability of the phosphido ligand to donate its lone-pair electrons to the metal center. The phenyl group is an electron-withdrawing group, whereas the methyl group is an electron-donating group, which means that mpe can donate electron density more than does ppe, leading to a reduction of the Lewis acidity at the metal centers. Thus, the ppe complex interacts with a halide anion more strongly than does the mpe complex.

The "pocket" is sterically unfavorable for the interaction with the halide anion, since the "pocket" is more congested than the "roof", owing to the four phenyl groups surrounding

Table 2. Interaction Modes of the Dinuclear Complexes with Halide Ions

Entry	Complex	Mode	M–X distances/Å			
1	$[\{Pd(dppe)\}_2(\mu\text{-mpe})]Cl_2$	roof	Pd1–Cl1	3.268(6)	Pd2–Cl2	4.421(7)
2	$[\{Pt(dppe)\}_2(\mu\text{-mpe})]Cl_2$	roof	Pt1–Cl1	3.354(5)	Pt2–Cl2	4.428(5)
3	$[\{Pt(dppe)\}_2(\mu\text{-mpe})]I_2$ [a)]	roof	Pt1–I3	5.041(1)	Pt2–I1	5.463(1)
4	$[\{Pt(dppe)\}_2(\mu\text{-mpe})]I_2$ [a)]	roof	Pt4–I2	5.226(1)		
5	$[\{Pd(dppe)\}_2(\mu\text{-ppe})]Cl_2$ [a)]	pocket	Pd1–Cl1	3.102(2)	Pd2–Cl1	2.981(7)
6	$[\{Pd(dppe)\}_2(\mu\text{-ppe})]Cl_2$ [a)]	pocket	Pd3–Cl2	3.063(2)	Pd4–Cl2	2.963(7)
7	$[\{Pd(dppe)\}_2(\mu\text{-ppe})]I_2$	pocket	Pd1–I1	3.1540(2)	Pd2–Cl1	4.0220(3)
8	$[\{Pd(dppe)\}_2(\mu\text{-ppe})]BArf_2$	—				
9	$[\{Pt(dppe)\}_2(\mu\text{-ppe})]Cl_2$	roof	Pt1–Cl1	3.994(2)	Pt2–Cl2	4.182(3)
10	$[\{Pt(dppe)\}_2(\mu\text{-ppe})]BArf_2$	—				

a) Two independent molecules are present in an asymmetric unit.

it. However, the bifurcated interaction itself is considered to be stronger than the usual 1:1 interaction in the "roof" mode. Thus, if the metal-halide interaction becomes strong enough to overcome the steric congestion, the counter ion prefers the "pocket" mode. We consider that, of the four combinations (mpe–Pt, mpe–Pd, ppe–Pt, and ppe–Pd), only the ppe–Pd combination satisfies the requirements for the bifurcated interaction as described above. Actually, M–X distances of the "pocket" interaction modes in Table 2 (entries 5–7) are smaller than those of the "roof" interaction modes.

Experimental

General Remarks. All reactions were carried out under an atmosphere of dry nitrogen using Schlenk tube techniques. All solvents were purified by distillation: CH_2Cl_2 was distilled from P_2O_5, and Et_2O and THF were distilled from sodium metal. These were stored under an N_2 atmosphere. $[MCl_2(dppe)]$ (M = Pd, Pt) was prepared from $[MCl_2(cod)]$[30] and dppe. H_2ppe was prepared according to a literature method.[24,25] H_2mpe was also prepared by the reported method, and used as a ca. 0.16 M THF solution.[26] NaBArf was prepared according to a method modified by Brookhart et al.[31]

^1H, ^{13}C, and ^{31}P NMR spectra were measured on JEOL LA-300 and -500 spectrometers. ^1H and ^{13}C NMR chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$) and were referenced internally with respect to the residual solvent peak. ^{31}P NMR data were referred to 85% H_3PO_4 as an external standard and simulated with the gNMR software.[32] Elemental analyses of the dinuclear complexes were tried, but did not give satisfactory results, because it was unsuccessful to separate a trace amount of the starting material from the product.

$[Pt(dppe)(H_2mpe)]Cl_2$, 2aPt. $[PtCl_2(dppe)]$ (664 mg, 1.00 mmol) was suspended in CH_2Cl_2 (50 mL), to which a 0.16 M THF solution of H_2mpe was added until the disappearance of $[PtCl_2(dppe)]$ was confirmed by the ^{31}P NMR spectra. The total amount of H_2mpe added was 6.3 mL (1.00 mmol). After the solvent was completely removed under reduced pressure, the residue was redissolved into 40 mL of CH_2Cl_2, and then 100 mL of Et_2O was added to precipitate **2aPt**. The precipitate was collected by decantation, washed twice with 10 mL of Et_2O, and then dried in vacuo to give 769 mg of **2aPt** (0.98 mmol, 98 %). ^1H NMR(300 MHz, $CDCl_3$) δ 1.32 and 1.59 (m, 6H, CH_3), 2.3–2.8 (8H, CH_2), 5.31 and 5.96 (d, $^1J_{P\text{–}H}$ = 405.7 and 469.0 Hz, respectively, 2H, P–H), 7.47–7.55 and 7.86–8.01 (Ph, 20H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 6.1–7.0 (m, CH_3), 22.6–24.1 (m, CH_2), 30.1–31.6 (m, CH_2), 125.2–127.9 (m, *i*-Ph), 132.3–132.6 (m, Ph), 133.1 (d, $J_{C\text{–}P}$ = 11.8 Hz, J_{C-Pt} = 17.3 Hz, Ph), 133.7 (d, $J_{C\text{–}P}$ = 11.8 Hz, $J_{C\text{–}Pt}$ = 19.8 Hz, Ph), 134.1 (d, $J_{C\text{–}P}$ = 9.9 Hz, $J_{C\text{–}Pt}$ = 21.1 Hz, Ph), 134.7 (d, $J_{C\text{–}P}$ = 12.4 Hz, $J_{C\text{–}Pt}$ = 19.9 Hz, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 9.7 (m, $J_{C\text{–}Pt}$ = 2506 Hz, H_2mpe), 45.7 (m, $J_{P\text{–}Pt}$ = 2464 Hz, dppe); the other isomer, 11.3 (m, $J_{P\text{–}Pt}$ = 2517 Hz, H_2mpe), 44.9 (m, $J_{P\text{–}Pt}$ = 2459 Hz, dppe).

$[Pt(dppe)(H_2ppe)]Cl_2$, 2bPt. To $[PtCl_2(dppe)]$ (94 mg, 0.14 mmol) in CH_2Cl_2 (7 mL) was added H_2ppe (33 μL, 0.14 mmol). After stirring the solution for 30 min, the solvent was completely removed under reduced pressure. The residue was redissolved into 1.5 mL of CH_2Cl_2, and then 28 mL of Et_2O was added to precipitate **2bPt**. The precipitate was collected by decantation, and washed twice with 3 mL of Et_2O. After a work up, **2bPt** was obtained as a white powder (117 mg, 91%). ^1H NMR (300 MHz, $CDCl_3$) δ 2.29 (br, 2H, CH_2), 2.5–3.0 (br, 5H, CH_2), 3.0–3.5 (br, 1H, CH_2), 7.62 (d, $^1J_{P\text{–}H}$ = 426.6 Hz, 2H, P–H), 7.01 (t, $J_{H\text{–}H}$ = 6.7 Hz, Ph), 7.16 (t, $J_{H\text{–}H}$ = 7.0 Hz, Ph), 7.23–8.00 (m, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 24.5 (m, CH_2), 26.6 (m, CH_2), 30.5 (m, CH_2), 31.5 (m, CH_2), 123.8 (d, $J_{C\text{–}P}$ = 55.8 Hz, $J_{C\text{–}Pt}$ = 28.5 Hz, Ph), 124.2 (d, $J_{C\text{–}P}$ = 57.0 Hz, $J_{C\text{–}Pt}$ = 28.7 Hz, Ph), 126.7 (d, $J_{C\text{–}P}$ = 56.5 Hz, $J_{C\text{–}Pt}$ = 34.7 Hz, Ph), 128.4 (d, $J_{C\text{–}P}$ = 11.2 Hz, Ph), 129.0 (d, $J_{C\text{–}P}$ = 11.8 Hz, Ph), 129.3 (d, $J_{C\text{–}P}$ = 11.8 Hz, Ph), 131.3 NMR (s, Ph), 131.8 (m, Ph), 132.1 (s, Ph), 132.2 (s, Ph), 131.3 (m, Ph), 133.0–135.0 (m, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 26.7 (m, $J_{P\text{–}Pt}$ = 2423 Hz, H_2ppe), 46.3 (m, $J_{P\text{–}Pt}$ = 2519 Hz, dppe); the other isomer, 28.1 (m, $J_{P\text{–}Pt}$ = 2468 Hz, H_2ppe), 45.2 (m, $J_{P\text{–}Pt}$ = 2510 Hz, dppe).

$[\{Pt(dppe)\}_2(\mu\text{-mpe})]Cl_2$, 3aPt$_2$. **2aPt** (173 mg, 0.220 mmol) was suspended in 7 mL of CH_2Cl_2, to which Na_2CO_3 (696 mg, 6.56 mmol) and $[PtCl_2(dppe)]$ (146 mg, 0.220 mmol) in 20 mL of CH_2Cl_2 were added. The mixture was vigorously stirred over night. After filtration, the volume of the filtrate was reduced to 2 mL, and then 15 mL of Et_2O was added to precipitate **3aPt$_2$**. After a yellow powder was collected by decantation, it was washed with 5 mL of Et_2O three times, and then dried in vacuo to give 261 mg of **3aPt$_2$** (0.190 mmol, 86 %). ^1H NMR (300 MHz, $CDCl_3$) δ 0.63 (br, 6H, CH_3), 2.66 (br, 8H, CH_2), 2.99 (br, 4H, CH_2), 7.3–7.4 (m, Ph, 8H), 7.4–7.6 (m, Ph, 32H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 3.5 (br, CH_3), 29.2–30.4 (m, CH_2), 127.5 (d, $J_{C\text{–}P}$ = 43.5 Hz, Ph), 128.2 (d, $J_{C\text{–}P}$ = 40.4 Hz, Ph), 129.7 (d, $J_{C\text{–}P}$ = 10.5 Hz, Ph), 129.9 (d, $J_{C\text{–}P}$ = 10.0 Hz, Ph), 132.0 (s, Ph), 132.4 (s, Ph), 132.8 (d, $J_{C\text{–}P}$ = 12.4 Hz, Ph), 133.1 (d, $J_{C\text{–}P}$ = 12.4 Hz, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −32.0 (m, $J_{P\text{–}Pt}$ = 1518 Hz, mpe), 44.9 (m, $J_{P\text{–}Pt}$ = 2373 Hz, dppe).

$[\{Pt(dppe)\}_2(\mu\text{-ppe})]Cl_2$, 3bPt$_2$. The procedure for preparing

3bPt$_2$ was similar to that for **3a**. The quantities used were as follows: **2bPt** (107 mg, 0.118 mmol), Na_2CO_3 (376 mg, 3.55 mmol) and [$PtCl_2$(dppe)] (78mg, 0.118 mmol). 156 mg of **3bPt$_2$** (0.104 mmol, 88%) was obtained. ^{1}H NMR(300 MHz, $CDCl_3$) δ 2.30 (m, 8H, CH_2), 3.37 (br, 4H, CH_2), 6.33 (m, Ph, 8H), 7.08 (m, Ph, 8H), 7.20 (m, Ph, 8H), 7.28 (m, Ph, 8H), 7.6–7.8 (m, Ph, 18H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 25.3 (m, CH_2), 31.3 (dd, $J_{C\text{–}P}$ = 12.4 and 36.6 Hz,CH_2), 125.1 (d, $J_{C\text{–}P}$ = 55.8 Hz, Ph), 127.9 (d, $J_{C\text{–}P}$ = 50.9 Hz, Ph), 128.0 (d, $J_{C\text{–}P}$ = 10.6 Hz, Ph), 129.3 (d, $J_{C\text{–}P}$ = 11.2 Hz, Ph), 129.5 (s, Ph), 129.8 (d, $J_{C\text{–}P}$ = 11.2 Hz, Ph), 130.4 (br, Ph), 131.6 (s, Ph), 131.8 (d, $J_{C\text{–}P}$ = 11.8 Hz, Ph), 132.8 (s, Ph), 133.7 (d, $J_{C\text{–}P}$ = 12.4 Hz, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$) δ −35.5 (m, $J_{P\text{–}Pt}$ = 1544 Hz, ppe), 45.7 (m, $J_{P\text{–}Pt}$ = 2454 Hz, dppe).

BArf Salts of the Dinuclear Complexes. **3bPt$_2$** and **3bPd$_2$** were converted to their BArf salts in a similar manner. To a solution of **3bPd$_2$** (266 mg, 0.201 mmol) in 10 mL of CH_2Cl_2 were added NaBArf (356 mg, 0.402 mmol) in 25 mL of CH_2Cl_2. After stirring for 3 h, the precipitate was removed by filtration, and the solvent was removed under reduced pressure to give [{Pd(dppe)}$_2$(μ-ppe)](BArf)$_2$ (523 mg, 0.177 mmol, 88%).

[{Pt(dppe)}$_2$(μ-ppe)](BArf)$_2$ was obtained from **3bPt$_2$** (244 mg, 0.163 mmol) and NaBArf (288 mg, 0.326 mmol). The yield was 511 mg (0.162 mmol, 99%).

Iodide Salts of the Dinuclear Complexes. All of the iodide salts given in Table 1 were prepared in a similar manner. A typical procedure is as follows. A large excess of potassium iodide (221 mg, 1.332 mmol) was added to a solution of **3aPt$_2$** (50 mg, 0.036 mmol) in 2 mL of CH_2Cl_2. After stirring for 4 h, the precipitate was removed by filtration, and the solvent was removed under reduced pressure to give [{Pt(dppe)}$_2$(μ-mpe)]I$_2$ in a quantitative yield.

X-ray Crystallography. Suitable crystals of the dinuclear complexes were mounted on a glassfiber. All measurements were made on a Mac Science DIP2030 imaging plate area detector at 200 K to prevent efflorescence due to a loss of solvents in the crystals. The crystal-to-detector distance was 100 mm, and read-out was performed in the 0.10 mm pixel mode for the 300 mm detector in diameter. The reflection data were collected to a maximum 2θ value of 55.8°. The cell parameters and intensities for the reflection were estimated by program packages of MacDENZO.[33] The structures were solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms, except for the disordered groups, were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were included, but not refined. All calculations were performed with the teXsan crystallographic software package of Molecular Structure Corporation.[34]

The following are notable comments concerning structure analyses (Table 3) for the respective crystals. For **3aPt$_2$**, an asymmetric unit consists of **3aPt$_2$** and one 1,2-dichloroethane molecule. For the iodide derivative of **3aPt$_2$**, an asymmetric unit consists of two dinuclear complexes, four iodide ions, and seven chloroform molecules. Two of the seven chloroform molecules were treated as molecules having a half occupancy, and four molecules were treated as a rigid molecule. Regarding **3bPd$_2$**, one phenyl group of the terminal dppe ligand was treated as a disordered group. An iodide derivative of **3bPd$_2$** incorporates one chloroform molecule per one dinuclear complex. The dinuclear complex in the two BArf salts lies on a crystallographic two-fold axis, and thus half of the molecular structure was treated as an independent unit. Several CF_3 groups of the BArf anion are considerably disordered, but only one set of CF_3 group could be treated as a group having two orientations.

This work was partly supported by Grants-in-Aid for Scientific Research (Nos. 12640540 and 13640560) from the Ministry of Education, Science, Sports and Culture. Some measurement of NMR spectra was made using JEOL LA-500 at the Instrument Center for Chemical Analysis, Hiroshima University.

Supporting Information Available:

Observed and simulated ^{31}P{^{1}H} NMR spectra (5 pages), and CIF data for the six crystals are deposited as Document No. 75034 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Table 3. Crystal and Structure Refinement Data

	[{Pt(dppe)}$_2$-(μ-mpe)]Cl$_2$	[{Pt(dppe)}$_2$-(μ-mpe)]I$_2$	[{Pd(dppe)}$_2$-(μ-ppe)]I$_2$	[{Pd(dppe)}$_2$-(μ-ppe)]BArf$_2$	[{Pt(dppe)}$_2$-(μ-ppe)]Cl$_2$	[{Pt(dppe)}$_2$-(μ-ppe)]BArf$_2$
Formula	$C_{56}H_{58}Cl_2P_6Pt_2\cdot C_2H_4Cl_2$	$C_{56}H_{58}Cl_2P_6Pt_2\cdot 3CHCl_3$	$C_{66}H_{62}I_2P_6Pd_2\cdot CHCl_3$	$C_{130}H_{86}F_{48}B_2P_6Pd_2\cdot CH_2Cl_2$	$C_{66}H_{62}Cl_2P_6Pt_2\cdot 2CHCl_3$	$C_{130}H_{86}F_{48}B_2P_6Pd_2\cdot 2CHCl_3$
Fw	1476.96	1082.63	1627.05	3065.23	1979.66	3397.44
a /Å	22.2340(3)	16.2220(3)	17.4610(2)	21.7190(2)	15.3100(3)	21.8180(2)
b /Å	22.7530(4)	19.3190(3)	13.7760(1)	23.0260(2)	19.2190(2)	23.0570(1)
c /Å	11.4130(1)	24.4330(3)	27.6000(3)	29.8980(2)	16.0041(2)	29.8280(2)
α /deg		85.501(1)			95.830(1)	
β /deg		84.647(1)	95.192(1)	110.289(1)	60.221(1)	110.169(1)
γ /deg		82.800(1)			107.825(1)	
V /Å^3	5773.7(1)	7546.3(2)	6611.7(1)	14024.3(2)	3883.9(1)	14085.1(2)
Space Group	$Pna2_1$ (No. 33)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	C2/c (No. 15)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
Z	4	4	4	4	2	4
μ (Mo-$K\alpha$)/cm^{-1}	52.09	82.40	17.84	4.73	42.28	22.69
T /K	200	200	200	200	200	200
No. of rflns						
Measured	6989	26267	15461	15579	16434	16505
Obsd($I > 3.00\sigma(I)$)	6596	18246	13622	13962	11536	15224
R	0.047	0.063	0.032	0.080	0.045	0.078
Rw	0.055	0.101	0.053	0.149	0.076	0.149

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 184411–184416 for **3aPt$_2$**, **3bPt$_2$**, [{Pt(dppe)}$_2$(μ-mpe)]I$_2$, [{Pd(dppe)}$_2$(μ-ppe)]I$_2$, [{Pd(dppe)}$_2$(μ-ppe)]BArf$_2$, and [{Pt(dppe)}$_2$(μ-ppe)]BArf$_2$, respectively.

References

1 G. Aullón, G. Ujaque, A. Lledós, S. Alvarez, and P. Alemany, *Inorg. Chem.*, **37**, 804 (1998).

2 G. Aullón, G. Ujaque, A. Lledós, and S. Alvarez, *Chem. Eur. J.*, **5**, 1391 (1999).

3 G. Aullón, A. Lledós, and S. Alvarez, *Inorg. Chem.*, **39**, 906 (2000).

4 E. Sappa, A. Tiripicchio, A. J. Carty, and G. E. Toogood, *Prog. Inorg. Chem.*, **35**, 437 (1987).

5 G. Aullón, P. Alemany, and S. Alvarez, *J. Organomet. Chem.*, **478**, 75 (1994).

6 M. Capdevila, W. Clegg, P. Gouzález-Duarte, A. Jarid, A. Lledós, *Inorg. Chem.*, **35**, 490 (1996).

7 S. Sakaki, S. Yamaguchi, Y. Musashi, and M. Sugimoto, *J. Organomet. Chem.*, **675**, 173 (2001).

8 A. J. Carty, S. A. MacLaughlin, and D. Nucciarone, "Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis" ed by J. G. Verkade and L. D. Quin, VCH: Deerfield Beach, FL, (1987), pp. 559–619; R. A. Jones, T. C. Wright, J. L. Atwood, and W. E. Hunter, *Organometallics*, **2**, 470 (1983); A. J. Carty, F. Hartstock, and N. J. Taylor, *Inorg. Chem.*, **21**, 1349 (1982).

9 R. Glaser, D. J. Kountz, J. C. Gallucci, and D. W. Meek, *Inorg. Chim. Acta*, **77**, L207 (1983).

10 R. Glaser, D. J. Kountz, R. D. Waid, J. C. Gallucci, and D. W. Meek, *J. Am. Chem. Soc.*, **106**, 6324 (1984).

11 P. Look, R. Schmutzler, R. Goodfellow, M. Murray, and D. Schomburg, *Polyhedron*, **7**, 505 (1988).

12 I. P. Parkin, A. M. Z. Slawin, D. J. Williams, and D. J. Woollins, *Inorg. Chim. Acta*, **172**, 159 (1990).

13 T. Gebauer, G. Frenzen, and K. Dehnicke, *Z. Naturforsch.*, *Teil B*, **47**, 1505 (1992).

14 D. Fenske, B. Maczek, and K. Maczek, *Z. Anorg. Allg. Chem.*, **623**, 1113 (1997).

15 J. Fornies, C. Fortuno, R. Navarro, F. Martinez, and A. J. Welch, *J. Organomet. Chem.*, **394**, 643 (1990).

16 G. Bekiaris, G. V. Rochenthaler, and U. Behrens, *Z. Anorg. Allg. Chem.*, **618**, 153 (1992).

17 E. Alonso, J. Fornies, C. Fortuno, and M. Tomas, *J. Chem. Soc., Dalton Trans.*, **1995**, 3777.

18 I. V. Kourkine, M. B. Chapman, D. S. Glueck, K. Eichele, R. E. Wasylishen, G. P. A. Yap, L. M. Liable-Sands, and A. L. Rheingold, *Inorg. Chem.*, **35**, 1478 (1996).

19 dppe = 1,2-bis(diphenylphosphino)ethane, cypp = [(3-dicyclohexylphosphino)-propyl]phenylphosphido: Cy$_2$PCH$_2$CH$_2$CH$_2$PPh$^-$.

20 W. C. Fultz, A. L. Rheingold, P. E. Kreter, and D. W. Meek, *Inorg. Chem.*, **22**, 860 (1983).

21 R. Uriarte, T. J. Mazanec, K. D. Tau, and D. W. Meek, *Inorg. Chem.*, **19**, 79 (1980).

22 D. W. Meek, R. Waid, K. D. Tau, R. M. Kirchner, and C. N. Morimoto, *Inorg. Chim. Acta*, **64**, L221 (1982).

23 T. Mizuta, S. Aoki, K. Nakayama, and K. Miyoshi, *Inorg. Chem.*, **38**, 4361 (1999).

24 B. R. Kimpton, W. McFarlane, A. S. Muir, and P. G. Patel, *Polyhedron*, **20**, 2525 (1993).

25 A. Airey, G. F. Swiegers, A. C. Willis, and B. Wild, *Inorg. Chem.*, **36**, 1588 (1997).

26 M. Baacke, O. Stelzer, and V. Wray, *Chem. Ber.*, **113**, 1356 (1980).

27 J. B. Brandon and K. B. Dixson, *Can. J. Chem.*, **59**, 1188 (1981).

28 R. D. Shanon, *Acta Crystallogr.* Sect.A, **32**, 751 (1976).

29 D. M. P. Mingos, "Essential Trends in Inorganic Chemistry," Oxford University Press, New York (1998), pp. 361–373.

30 D. Drew and J. R. Doyle, *Inorg. Synth.*, **13**, 52 (1972).

31 M. Brookhart, G. Grant, and A. F. Volpe, Jr., *Organometallics*, **11**, 3920 (1992)

32 gNMR: P. H. M. Budzelaar, "Simulation of One-Dimensional NMR Spectra, Version 4.0" Charwell Scientific Publishing Ltd. Oxford, UK, (1993).

33 MacDENZO: D. Gewirth, (with the cooperation of the program authors Z. Otwinowski and W. Minor), in "The MacDenzo Manual-A Description of the Programs DENZO, XDISPLAYF, and SCALEPACK," Yale University, New Haven, CT (1995).

34 "teXsan: Single Crystal Structure Analysis Software, Version 1.6," Molecular Structure Corporation, The Woodlands, TX (1993).