Preparation and Characterization of Nickel(II), Palladium(II), and Platinum(II) Complexes Containing (2-Aminoethyl)dimethylphosphine or the Related Didentate Phosphine Ligands

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Here are described several new nickel(II), palladium(II), and platinum(II) complexes of bis(chelate)-type with didentate phosphine ligands having an amino or thioether donor group: $Me_2PCH_2CH_2NH_2$ (edmp), $Ph_2PCH_2CH_2NH_2$ (edpp), $Me_2PCH_2CH_2NMe_2$ (dmedmp), or $Me_2PCH_2CH_2SMe$ (mtdmp). Bis(tetrafluoroborate) salts of $[M(P\text{–}N \text{ or } S)_2]^{2+}$ (M = Ni, Pd, and Pt; (P–N or S)= the ligands above) have been prepared and the geometrical structures determined by NMR spectroscopy. All the palladium(II) complexes prepared in this study are *cis*-isomers, in contrast to the analogous $Me_2PCH_2CH_2S^-$ (dmsp) complex (*trans*-$[Pd(dmsp)_2]$), which indicates that the anionic phosphine-thiolate ligand prefers the *trans* geometry more than the neutral phosphine-amine or -thioether ligand does. The dichloride salts of the bis(edmp) complexes, *cis*-$[M(edmp)_2]Cl_2$ (M=Ni (**4a**), Pd(**5a**), and Pt(**6a**)), and those of the bis(edpp) complexes have been obtained as crystals, while the corresponding salts of dmedmp, mtdmp, and 8-(dimethylphosphino)quinoline complexes can not be isolated due to their oily properties. Further, addition of $LiBF_4$ to a methanolic solution of **4a**, **5a**, or **6a** gives exclusively a precipitate of the chloride tetrafluoroborate salt, *cis*-$[M(edmp)_2]Cl(BF_4)$ (M=Ni (**4c**), Pd(**5c**), or Pt(**6c**)). The crystal structures of **4a**, **5c**, and **6a** determined by X-ray analyses indicate a weak (not strong enough to form a five-coordinated complex) interaction between *cis*-$[M(edmp)_2]^{2+}$ and Cl^- anion. The average M–N bond lengths in **4a**, **5c**, and **6a** are considerably longer than those in the corresponding 1,2-ethanediamine complexes, owing to the strong trans influence of the $-PMe_2$ group in edmp. The order of strength of the trans influence among Ni^{II}, Pd^{II}, and Pt^{II} triad metal series is non-periodical: $Ni^{II} < Pt^{II} < Pd^{II}$. This order is similar to the order among Co^{III}, Rh^{III}, and Ir^{III} triad metal series found in our previous study on *fac*-$[M'(edmp)_3]^{3+}$ ($M' = Co^{III}$, Rh^{III}, and Ir^{III}) complexes.

Hybrid donor-type didentate or polydentate phosphine ligands are currently of interest, because their transition metal complexes have potential for development of novel homogeneous catalysts.[1,2] Further, such unsymmetric ligands often give rise to intriguing stereospecificity in their complexation and reactivities of the resulting complexes. We are interested in syntheses and structures of transition metal complexes with hybrid phosphine ligands having nitrogen or sulfur donor atoms.[3—10] During the studies on palladium(II) complexes, we found that 2-(dimethylphosphino)ethane-1-thiolato (dmsp) gave exclusively *trans*-$[Pd(dmsp)_2]$,[3] while 8-(dimethylphosphino)quinoline (Me_2Pqn) formed only the *cis*-isomer, *cis*-$[Pd(Me_2Pqn)_2](BF_4)_2$,[4] despite the severe steric hindrance due to mutually *cis*-positioned quinolyl donor groups of Me_2Pqn. Two major differences between dmsp and Me_2Pqn are considered as the factors controlling the geometrical structures of the complexes above: (1) the ligating atoms other than phosphorus: P–S type (dmsp) vs. P–N(imine) type (Me_2Pqn) and (2) the charge on the ligands: anionic (dmsp) vs. neutral (Me_2Pqn). In order to elucidate the factor which controls the geometrical structures of bis(hybrid-type didentate phosphine)palladium(II) complexes, we will describe here the preparation and structural characterization of new palladium(II) complexes containing neutral P–N(amine) or P–S(thioether) didentate ligands: (2-aminoethyl)dimethylphosphine (edmp), (2-aminoethyl)diphenylphosphine (edpp), 2-(*N*, *N*-dimethylamino)dimethylphosphinoethane (dmedmp), and 2-(methylthio)dimethylphosphinoethane (mtdmp). Analogous nickel(II) and platinum(II) complexes were also prepared, and the crystal structures of $[M(edmp)_2]^{2+}$ ($M = Ni^{II}$, Pd^{II}, and Pt^{II}) complexes were determined, in order to compare the structural parameters among Ni^{II}, Pd^{II}, and Pt^{II} triad metal complexes. In our previous study on *fac*-$[M'(edmp)_3]^{3+}$ ($M' = Co^{III}$, Rh^{III}, and Ir^{III}) complexes, we found the non-periodical order ($Co^{III} < Ir^{III} < Rh^{III}$) for strength of the trans influence of the $-PMe_2$ group in edmp.[5] In this paper we will show that the non-periodical order also holds in the Ni^{II}, Pd^{II}, and Pt^{II} triad metal series.

Results and Discussion

Preparation of Complexes. In our previous study about palladium(II) complexes of Me_2Pqn, the mono(chelate) four-coordinate square-planar complex, $[PdCl_2(Me_2Pqn)]$, was

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prepared by a reaction of $[PdCl_2(PhCN)_2]$ and Me_2Pqn in a 1 : 1 molar ratio in dichloromethane.[4] The corresponding edmp and edpp complexes, $[PdCl_2(edmp)]$ (**1**) and $[PdCl_2(edpp)]$ (**2**), were prepared by a similar method using edmp and edpp; the complexes were structurally characterized by their infrared spectra. Each spectrum shows two ν(Pd–Cl) stretching bands at 264 and 317 cm^{-1} for **1** and at 269 and 293 cm^{-1} for **2**, which strongly indicates the *cis* configuration in the complexes.[4,11] In this paper we extended the study to nickel(II) complex of edmp. An ethanolic reaction mixture of $NiCl_2 \cdot 6H_2O$ and edmp in a 1 : 1 molar ratio afforded a red solution immediately, and then gave a green precipitate, not of a neutral complex of $[NiCl_2(edmp)]$, but of a complex double salt of *cis*-$[Ni(edmp)_2][NiCl_4]$ (**3**). The crude product of **3** was recrystallized from a mixture of methanol and diethyl ether to deposit greenish columnar hygroscopic crystals. The crystal structure was determined by X-ray analysis (the X-ray structure determination, together with those of the other complexes, will be described collectively in the next section). The red color of the reaction mixture which formed immediately after the addition of edmp is due to $[Ni(edmp)_2]^{2+}$ complex, and thus, it can be stated that nickel(II), as distinct from the palladium(II) and platinum(II) analogs, tends to form a bis(edmp)-type dicationic complex preferentially, rather than forming a neutral dichloro(edmp) complex. When recrystallization of **3** by the above method was repeated several times, a small amount of red prismatic crystals of *cis*-$[Ni(edmp)_2]Cl_2$ (**4a**) was obtained as a by-product, owing to decomposition of $[NiCl_4]^{2-}$ by moisture. The complex chloride **4a** was also structurally characterized by X-ray analysis. It had been obtained in a moderate yield by anion exchange of $[Ni(edmp)_2](BF_4)_2$ (**4b**), which was prepared by a reaction of $Ni(BF_4)_2 \cdot 6H_2O$ and edmp in a 1 : 2 molar ratio in ethanol.

Preparation of bis(edmp)palladium(II) complexes gave somewhat different complex salts from those of the Me_2Pqn complexes. A reaction of $[PdCl_2(PhCN)_2]$ and Me_2Pqn in a 1 : 2 molar ratio in dichloromethane produced a yellow powder of structurally uncharacterized compound, and colorless crystals of *cis*-$[Pd(Me_2Pqn)_2](BF_4)_2$ were isolated from a methanolic solution of the yellow powder by addition of $LiBF_4$.[4] In contrast, from a reaction mixture of $[PdCl_2(PhCN)_2]$ and edmp in a 1 : 2 molar ratio in dichloromethane, a white precipitate was obtained by evaporation of the solvent and treatment of the residue with diethyl ether. Recrystallization of the crude product from a mixture of methanol and diethyl ether deposited pale yellow columnar crystals of *cis*-$[Pd(edmp)_2]Cl_2$ (**5a**). The corresponding platinum(II) complex salt, *cis*-$[Pt(edmp)_2]Cl_2$ (**6a**), was also prepared by a similar method using $[PtCl_2(EtCN)_2]$, and the crystal structure of **6a** was determined by a single-crystal X-ray diffraction method. Complexes **5a** and **6a** are very soluble in methanol, and from the methanolic solutions were afforded colorless crystals of *cis*-$[Pd(edmp)_2]Cl(BF_4)$ (**5c**) and *cis*-$[Pt(edmp)_2]Cl(BF_4)$ (**6c**), respectively, on addition of a saturated methanolic solution of $LiBF_4$. The existence of both chloride and tetrafluoroborate anions in these complex salts was confirmed by elemental analyses and by a single-crystal X-ray structure determination for **5c**. Although the corresponding nickel(II) complex chloride, **4a**, could not be isolated directly from an ethanolic reaction mixture of $NiCl_2 \cdot 6H_2O$ and edmp (1 : 2), orange crystals of the complex chloride tetrafluoroborate salt, *cis*-$[Ni(edmp)_2]Cl(BF_4)$ (**4c**), were obtained on addition of $LiBF_4$.

The precipitation of the complex chloride tetrafluoroborate salt from methanol is specific for the edmp complexes. For instance, the corresponding dmedmp complexes gave the bis(tetrafluoroborate) salt, *cis*-$[Pd(dmedmp)_2](BF_4)_2$ (**7b**), on addition of $LiBF_4$ to a methanolic solution of the reaction product from $[PdCl_2(PhCN)_2]$ and dmedmp (1 : 2), similar to the Me_2Pqn complexes. Also, *cis*-$[M(mtdmp)_2](BF_4)_2$ (M = Ni (**8b**), Pd (**9b**), and Pt (**10b**)) were obtained by a similar preparative procedure with mtdmp ligand. Since the bonding interaction between M (= Ni, Pd, or Pt) and Cl atoms is not strong enough to form a five-coordinate square-pyramidal complex in the crystal structures of **4a**, **5c**, and **6a** (vide infra), the formation of the chloride tetrafluoroborate salts may result from the coordinated amino groups of edmp ligands. In the case of edpp complexes, which have also amino groups coordinated to a metal center, a complex dichloride salt of *cis*-$[M(edpp)_2]Cl_2$ (M = Pd (**11a**) or Pt (**12a**)) was isolated from a reaction mixture of either $[PdCl_2(PhCN)_2]$ or $[PtCl_2(EtCN)_2]$ and edpp (1 : 2) in dichloromethane. However, no pure crystalline products could be obtained on addition of $LiBF_4$ to a methanol solution of **11a** or **12a**; this is probably due to steric mismatch of the edpp complex cation and chloride tetrafluoroborate anions.

The bis(tetrafluoroborate) salts of bis(edmp or edpp)-metal(II) complexes: *cis*-$[Ni(edmp)_2](BF_4)_2$ (**4b**), *cis*-$[Pd(edmp)_2](BF_4)_2$ (**5b**), *cis*-$[Pt(edmp)_2](BF_4)_2$ (**6b**), *cis*-$[Ni(edpp)_2](BF_4)_2$ (**13b**), *cis*-$[Pd(edpp)_2](BF_4)_2$ (**11b**), and the bis(perchlorate) salt of *cis*-$[Pt(edpp)_2](ClO_4)_2$ (**12b′**), were obtained using chloride-free starting materials: $Ni(BF_4)_2 \cdot 6H_2O$, $[Pd(EtCN)_4](BF_4)_2$, and $[Pt(EtCN)_4](BF_4)_2$, respectively. The elemental analyses of the complexes prepared in this study, which fit well with the calculated values, are collected in Table 1.

Crystal Structural Analyses. The crystal structures of **3**, **4a**, **5c**, and **6a** are shown in Figs. 1, 2, 3, and 4, respectively, and selected bond lengths and angles are collected in Table 2. For all the complex cations, the metal center is coordinated by two chelating edmp ligands with *cis* configuration in square-planar geometry. The $[NiCl_4]^{2-}$ anion in **3** has a slightly distorted tetrahedral geometry; the Cl–Ni(2)–Cl bond angles are in the 104.3(1)—117.3(1)° range. Although the Ni(2)–Cl(1) bond length (2.275(2) Å) is slightly longer than the other Ni(2)–Cl lengths, where the Cl(1) atom is placed at the apical position of Ni(1) of the square-planar *cis*-$[Ni(edmp)_2]^{2+}$ complex cation, the distance of Ni(1)···Cl(1) (3.141(2) Å) indicates that there is no bonding interaction between Ni(1) and Cl(1). Also, for **4a**, **5c**, and **6a**, the Cl(1) atom locates at the apical position of the square-planar metal center. The Ni(1)···Cl(1) distance in **4a** (2.841(2) Å) is considerably longer than the Ni–Cl bond

Table 1. Elemental Analyses of the Complexes (Found/% (Calcd/%))

Abbr.	Complex	C	H	N
1	$[PdCl_2(edmp)]$	16.90 (17.01)	4.26 (4.28)	4.59 (4.96)
2	$[PdCl_2(edpp)]$	41.30 (41.36)	3.75 (3.79)	3.35 (3.44)
3	$[Ni(edmp)_2][NiCl_4]$	20.59 (20.47)	5.24 (5.15)	6.10 (5.97)
4a	$[Ni(edmp)_2]Cl_2$	28.24 (28.28)	7.31 (7.12)	7.99 (8.24)
4b	$[Ni(edmp)_2](BF_4)_2$	21.65 (21.70)	5.54 (5.47)	6.12 (6.33)
4c	$[Ni(edmp)_2]Cl(BF_4)$	24.48 (24.56)	6.10 (6.18)	7.31 (7.16)
5a	$[Pd(edmp)_2]Cl_2$	24.70 (24.79)	6.24 (6.24)	7.12 (7.23)
5b	$[Pd(edmp)_2](BF_4)_2$	20.21 (19.60)	5.16 (4.93)	5.71 (5.71)
5c	$[Pd(edmp)_2]Cl(BF_4)$	21.64 (21.89)	5.52 (5.51)	6.27 (6.38)
6a	$[Pt(edmp)_2]Cl_2$	20.14 (20.18)	5.07 (5.08)	5.38 (5.88)
6b	$[Pt(edmp)_2](BF_4)_2$	16.70 (16.60)	4.38 (4.18)	5.07 (4.84)
6c	$[Pt(edmp)_2]Cl(BF_4)$	18.21 (18.21)	4.47 (4.59)	5.22 (5.31)
7b	$[Pd(dmedmp)_2](BF_4)_2$	26.27 (26.38)	6.03 (5.90)	5.02 (5.13)
8b	$[Ni(mtdmp)_2](BF_4)_2$	23.76 (23.80)	5.29 (5.19)	— (—)
9b	$[Pd(mtdmp)_2](BF_4)_2$	21.68 (21.74)	4.77 (4.74)	— (—)
10b	$[Pt(mtdmp)_2](BF_4)_2$	18.88 (18.74)	4.13 (4.09)	— (—)
11a	$[Pd(edpp)_2]Cl_2$	52.83 (52.89)	5.00 (5.07)	4.40 (4.41)
11b	$[Pd(edpp)_2](BF_4)_2$	45.59 (45.60)	4.37 (4.37)	3.80 (3.79)
12a	$[Pt(edpp)_2]Cl_2$	46.35 (46.42)	4.33 (4.45)	3.91 (3.87)
12b′	$[Pt(edpp)_2](ClO_4)_2$	39.60 (39.45)	3.71 (3.78)	3.30 (3.29)
13b	$[Ni(edpp)_2](BF_4)_2$	48.50 (48.68)	4.63 (4.67)	3.98 (4.06)

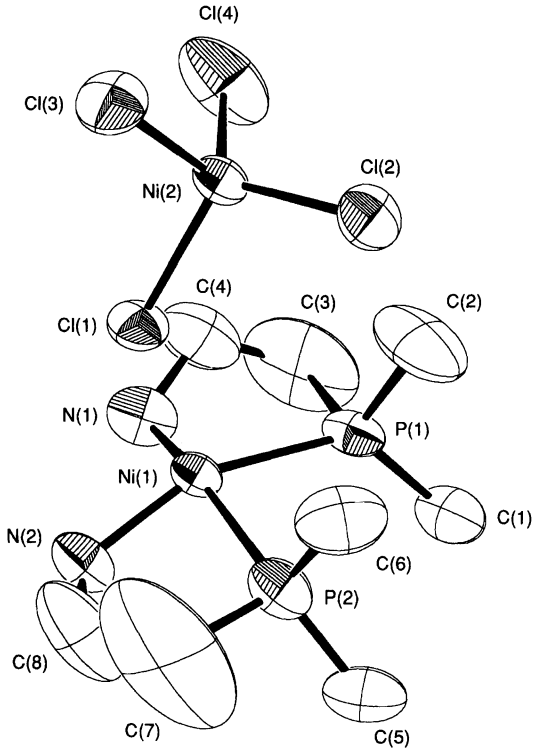

Fig. 1. Perspective drawing of *cis*-$[Ni(edmp)_2][NiCl_4]$.

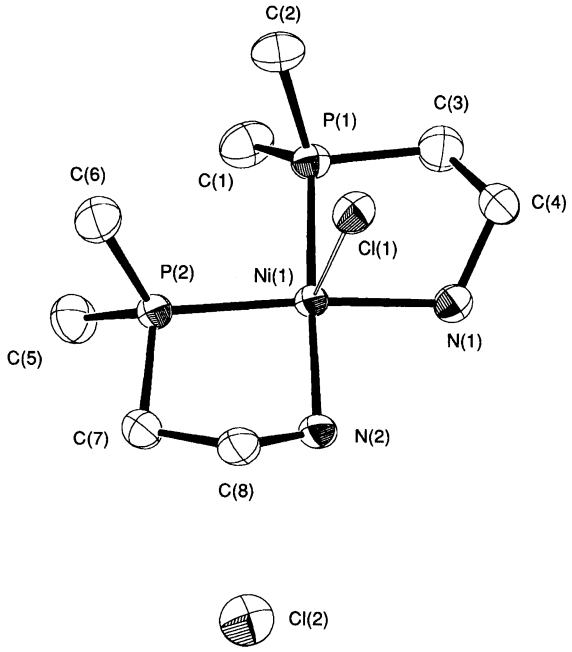

Fig. 2. Perspective drawing of *cis*-$[Ni(edmp)_2]Cl_2$.

lengths in $[NiCl\{rac(P)\text{-}343NPPN\}]PF_6$ (2.629(2) Å)[10] and $[NiCl\{meso(P)\text{-}333NPPN\}]PF_6$ (2.699(7) Å);[12] those have been reported as square-pyramidal five-coordinated complexes. The Pd(1)···Cl(1) distance in **5c** and the Pt(1)···Cl(1) distance in **6a** are 3.156(3) and 3.229(3) Å, respectively. Since these M(1)···Cl(1) distances are far from the sum of ionic radii of $M^{2+}(sp)$ (Ni: 0.63, Pd: 0.78, and Pt: 0.74 Å) and Cl^- (1.67 Å),[13] we conclude that the bonding interaction between the metal center and the apical-positioned Cl^- anion is too weak to form a square-pyramidal five-coordinated complex. However, since the distances are slightly shorter than the sum of the van der Waals radii of M (for Ni: 1.63 Å, Pd: 1.63 Å, and Pt: 1.72 Å) and Cl (1.75 Å),[14] and since crystallization of the chloride tetrafluoroborate salts is specific for these edmp complexes, there might be a certain, but weak, interaction between the complex cation and chloride anion in these crystals. This interaction weakens in the order of $Ni^{II} > Pd^{II} > Pt^{II}$, which is suggested by the

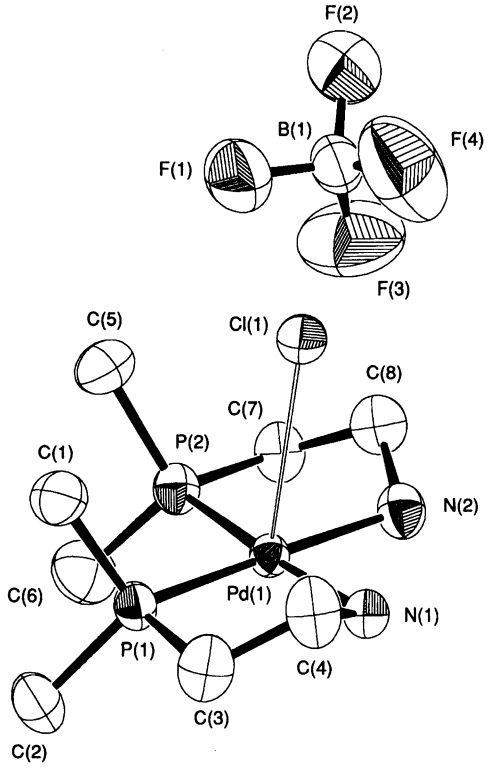

Fig. 3. Perspective drawing of *cis*-$[Pd(edmp)_2]Cl(BF_4)$.

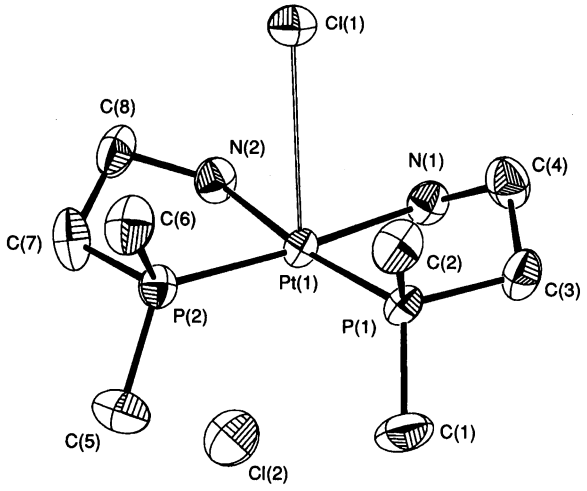

Fig. 4. Perspective drawing of *cis*-$[Pt(edmp)_2]Cl_2$.

difference between the observed M···Cl(1) distance and the sum of ionic radii of M^{2+}(*sp*) and Cl^-: Ni^{II} (Δ = 0.54 Å) < Pd^{II} (Δ = 0.71 Å) < Pt^{II} (Δ = 0.82 Å). Anderson and Cross summarized the isomerization mechanisms of square-planar complexes.[15] The associative pathway is the most probable for the present system. The better affinity of Cl^- ion to *cis*-$[M(edmp)_2]^{2+}$ in the order of $Ni^{II} > Pd^{II} > Pt^{II}$ is consistent with the tendency towards *cis–trans* isomerization rate of square-planar M^{2+} complexes; Ni^{II} complexes isomerize more rapidly than Pd^{II} and Pt^{II} complexes.

The complex cations of *cis*-$[M(edmp)_2]^{2+}$ in **4a** (M = Ni), **5c**, (M=Pd), and **6a** (M = Pt) have a pseudo symmetrical plane, which is perpendicular to the coordination plane. The conformations of two five-membered edmp-chelate rings in each complex are therefore δ and λ. For **3**, owing to the large thermal factors for the ring carbons, the conformation of the chelate ring is uncertain. The structural parameters of *cis*-$[Ni(edmp)_2]^{2+}$ in **3** and **4a** are slightly different from each other: for example, the Ni–P bond lengths in **3** (av 2.148 Å) are slightly shorter, the P–Ni–P bond angle (92.2(1)°) is smaller, and the N–Ni–N bond angle (88.5(3)°) is wider than those in **4a** (av 2.169 Å, 97.10(5)°, and 90.4(2)°, respectively). The origin of these differences is uncertain (they may be due to a crystal packing effect of the different counter anions). Since the *R* value of **3** is worse than that of **4a**, and since the thermal factors of the atoms in **3** are far larger than those in **4a**, we would like to use the structural parameters of **4a** in the following discussion.

The most striking features of the edmp complexes, **4a**, **5c**, and **6a**, are their M–N bond lengths. The M–N bond lengths of **4a** (av 1.973 Å), **5c** (av 2.138 Å), and **6a** (av 2.106 Å) are considerably longer than those of the structure-related 1,2-ethanediamine (en) complexes, $[Ni(en)_2][AgX_2]_2$ (X = Br or I; av. 1.921 Å),[16] $[Pd(en)_2]Cl_2$ (av 2.047 Å),[17] and $[Pt(en)_2]Cl_2$ (av 2.043 Å).[18] (For $[Ni(en)_2]^{2+}$ complex, there is no data available for the simple chloride salt; the Ni–N bond lengths in the related complex dichloride salts are av 1.912 Å for $[Ni(chxn)_2]Cl_2$ (chxn = 1,2-cyclohexanediamine)[19] and av 1.912 Å for $[Ni(en\text{-}Me_4)_2]Cl_2 \cdot H_2O$ (en-Me_4 = 2,3-dimethyl-2,3-diaminobutane).[20]) The elongation is due to the strong trans influence of the $-PMe_2$ group in edmp. The values of elongation of the M–N bond lengths from those of the en complexes are 0.052 Å for Ni^{II}, 0.091 Å for Pd^{II}, and 0.063 Å for Pt^{II}. It is noteworthy that the trans influence of the $-PMe_2$ group on the Pt^{II} complex is weaker than that on the Pd^{II} complex, and the order of the metal ions is $Ni^{II} < Pt^{II} < Pd^{II}$. In a previous study on *fac*-$[M'(edmp)_3]^{3+}$ (M' = Co^{III}, Rh^{III}, and Ir^{III})-type complexes, we found that the order of the trans influence of the $-PMe_2$ group in edmp ($Co^{III} < Ir^{III} < Rh^{III}$) is apparently different from the periodic series.[5] This study shows that the non-periodical order also holds in the Ni^{II}, Pd^{II}, and Pt^{II} triad metal series. The reason why the trans influence of the $-PMe_2$ group shows the non-periodical order remains unknown, and further studies including theoretical ones will be needed.

Structures of the Complexes in Solution. Our main interest in this study is to characterize the geometrical structures (*cis* or *trans*) of the $[Pd(P\text{–}N \text{ or } S)_2]^{2+}$ -type complexes, in order to elucidate the factor which controls the geometrical structure of the complexes. For the three kinds of $[Pd(edmp)_2]^{2+}$ salt (**5a**, **5b**, and **5c**), almost identical ^1H, ^{13}C, and ^{31}P NMR spectra in D_2O (Table 3) were obtained; this suggests that there is no interaction between $[Pd(edmp)_2]^{2+}$ complex cation and Cl^- anion in water. This is also the case for $[Ni(edmp)_2]^{2+}$ (**4a**, **4b**, and **4c**) and $[Pt(edmp)_2]^{2+}$ (**6a**, **6b**, and **6c**) complexes. The NMR spectra of **5a**, **5b**, and **5c** indicate that $[Pd(edmp)_2]^{2+}$ complex exists as the *cis–isomer* in water, as revealed by the crystal structure analysis of **5c**, because the P–CH_3 group gives a filled-in doublet resonance in the ^1H and ^{13}C spectra.[4,21] The ^1H and ^{13}C NMR reso-

Table 2. Selected Bond Lengths and Angles of *cis*-[Ni(edmp)$_2$] [NiCl$_4$] (**3**), *cis*-[Ni(edmp)$_2$]Cl$_2$ (**4a**), *cis*-[Pd(edmp)$_2$]Cl(BF$_4$) (**5c**), and *cis*-[Pt(edmp)$_2$]Cl$_2$ (**6a**)

Compound	**3** (M=Ni)	**4a** (M=Ni)	**5c** (M=Pd)	**6a** (M=Pt)
M(1)–P(1)	2.147(3)	2.171(1)	2.248(3)	2.233(3)
M(1)–P(2)	2.149(3)	2.166(1)	2.243(3)	2.231(2)
M(1)–N(1)	1.972(9)	1.971(4)	2.123(10)	2.110(8)
M(1)–N(2)	1.981(8)	1.975(3)	2.153(10)	2.101(9)
M(2)–Cl(1)	2.275(2)			
M(2)–Cl(2)	2.236(3)			
M(2)–Cl(3)	2.251(3)			
M(2)–Cl(4)	2.247(3)			
M(1)···Cl(1)	3.141(2)	2.841(2)	3.156(3)	3.229(2)
P(1)–M(1)–P(2)	92.2(1)	97.10(5)	99.0(1)	100.8(1)
P(1)–M(1)–N(1)	87.7(2)	86.6(1)	84.5(3)	84.4(4)
P(1)–M(1)–N(2)	174.4(2)	174.9(1)	177.1(3)	173.5(3)
P(2)–M(1)–N(1)	174.3(3)	175.1(1)	176.3(3)	174.8(3)
P(2)–M(1)–N(2)	86.8(3)	85.7(1)	83.9(3)	84.7(3)
N(1)–M(1)–N(2)	88.5(3)	90.4(2)	92.6(4)	90.1(4)

Table 3. ^{1}H, ^{13}C, and ^{31}P NMR Spectral Data of [M(P–N or S)$_2$]X$_2$-Type Complexes[a,b]

Complex	Solvent	^{31}P $\delta\{^1J_{Pt-P}\}$	^{13}C (P–CH$_3$ or –C$_{ipso}$)[c] $\delta[J_{P-C}]\ \{^1J_{Pt-P}\}$	^{1}H (P–CH$_3$) $\delta[J_{P-H}]\ \{^1J_{Pt-P}\}$
4a	D_2O	33.4	12.90 (t) [16.0]	1.64 (t) [5.9]
4b(*trans*)	D_2O	33.4	11.09 (t) [15.9]	1.64 (t) [5.8]
(*cis*)	CD_3NO_2	35.2	d)	1.68 (fd) [12.1]
4c	D_2O	33.8	12.84 (t) [15.9]	1.63 (t) [5.9]
5a	D_2O	33.8	12.06 (fd) [35.9]	1.82 (fd) [11.0]
5b	D_2O	34.3	12.43 (fd) [35.9]	1.78 (fd) [11.0]
5c	D_2O	33.8	12.00 (fd) [35.9]	1.79 (fd) [11.0]
6a	D_2O	14.6{3117}	12.20 (d) [42.1]{65.3}	1.88 (d) [11.7]{40.8}
6b	D_2O	14.0{3123}	11.96 (d) [42.1]{65.3}	1.85 (d) [11.7]{40.9}
6c	D_2O	14.2{3122}	12.02 (d) [42.2]{64.9}	1.86 (d) [11.3]{40.6}
7b	D_2O	31.8	14.16 (fd) [36.6]	1.84 (fd) [10.3]
8b(*trans*)	CD_3NO_2	44.6	11.18 (t) [16.1]	1.84 (t) [5.6]
(*cis*)	CD_3NO_2	46.9	d)	1.88 (fd) [11.2]
9b	CD_3NO_2	46.6	12.74 (fd) [35.0]	1.96 (fd) [10.4]
10b	CD_3NO_2	31.2{2887}	12.64 (d) [40.1]{39.9}	2.01 (d) [11.7]{38.1}
11a	CD_3OH	56.7	125.69 (fd) [56.0]	—
11b	CD_3OH	56.8	125.50 (fd) [56.7]	—
12a	CD_3OH	32.0{3311}	125.34 (fd) [68.4]{50.4}	—
12b′	CD_3NO_2	32.6{3363}	124.94 (fd) [64.9]{51.6}	—
13b	CD_3NO_2	48.4	124.81 (t) [15.9]	—

a) d: doublet, fd: filled-in doublet, t: triplet. b) The remaining data are deposited (Ref. 33). c) The data of P–CH$_3$ are given for edmp, dmedmp, and mtdmp complexes, and those of P–C$_{ipso}$(C$_6$H$_5$) for edpp complexes. d) The *cis*-isomers of **4b** and **8b** were not detected in the ^{13}C NMR spectra, probably due to *cis*→*trans* isomerization reaction and long accumulation time.

nances for P–CH$_3$ of the platinum(II) complexes (**6a**, **6b**, and **6c**) show a doublet signal with ^{195}Pt satellites, and the $^1J_{Pt-P}$ coupling constants observed in their ^{31}P NMR spectra are ca. 3120 Hz; these facts strongly indicate the *cis*(*P*,*P*) configuration in the platinum(II) complexes.[21,22] In contrast, the NMR spectra of the nickel(II) complexes (**4a**, **4b**, and **4c**) are different in pattern from those of the palladium(II) and platinum(II) complexes. The P–CH$_3$ resonances observed in their ^{1}H and ^{13}C NMR spectra in D_2O are a virtually coupled triplet, which gives support to the *trans*(*P*,*P*) geometry, although the single-crystal X-ray analysis of **4a** reveals the structure of *cis*-[Ni(edmp)$_2$]$^{2+}$ in the crystal. This inconsistency between the structures in the crystal and in water can be accounted for by the ^{1}H NMR spectrum of **4b** in CD_3NO_2. The spectrum at room temperature, immediately after the crystal was dissolved, showed a filled-in doublet resonance for P–CH$_3$, indicating the existence of *cis*-[Ni(edmp)$_2$]$^{2+}$ isomer in the solution. However, on heating the solution to 50 °C or on standing for several days at room temperature, the spectrum was changed to that of *trans*-[Ni(edmp)$_2$]$^{2+}$ isomer. The spectral change indicates that there is an isomerization equilibrium between *cis*- and *trans*-[Ni(edmp)$_2$]$^{2+}$ in solution

(the *trans*-isomer is more thermodynamically stable, and the equilibrium is reached very fast in water). The preferential crystallization of *cis*-$[Ni(edmp)_2]^{2+}$ from the equilibrium mixture is probably due to the low solubility of *cis*-isomer.

The dmedmp complex, $[Pd(dmedmp)_2](BF_4)_2$ (**7b**), in D_2O gives a filled-in doublet resonance for P–CH_3 in their ^1H and ^{13}C NMR spectra, suggesting that the complex has *cis* geometry also in water. The edpp complexes, $[Pd(edpp)_2]Cl_2$ (**11a**), $[Pd(edpp)_2](BF_4)_2$ (**11b**), $[Pt(edpp)_2]Cl_2$ (**12a**), and $[Pt(edpp)_2](ClO_4)_2$ (**12b′**), in CD_3OD or CD_3NO_2 are also found to be *cis*-isomers from their ^{13}C and ^{31}P NMR spectra. Further, the mtdmp complexes, $[Pd(mtdmp)_2](BF_4)_2$ (**8b**) and $[Pt(mtdmp)_2](BF_4)_2$ (**9b**), which give a filled-in doublet resonance and a doublet resonance with ^{195}Pt satellites, respectively, for P–CH_3 in their ^1H and ^{13}C NMR spectra and $^1J_{Pt-P} = 2887$ Hz in the ^{31}P NMR spectrum of **9b**, also exist as *cis*-isomers in CD_3NO_2. Therefore, all the palladium(II) complexes investigated in this study are *cis*(*P*,*P*)-isomers.

Conclusion

In the previous[4] and present study, we have prepared palladium(II) complexes containing neutral P–N(amine or imine) or P–S(thioether) hybrid-type phosphine ligands: Me_2Pqn, edmp, edpp, dmedmp, and mtdmp. We have assigned their geometrical structures to *cis*(*P*,*P*)-isomers, in contrast to *trans*(*P*,*P*)-isomer of anionic P–S(thiolate) ligand (dmsp) complex. It is well documented that the strong trans influence of $-PMe_2$ donor group tends preferentially to form the mutually *cis*(*P*,*P*) configuration in the complexes rather than the *trans*(*P*,*P*) one,[5] and this study shows that this is the case for neutral P–N(amine or imine) or P–S(thioether) ligands. The results lead to the conclusion that the origin of the preferential formation of *trans*(*P*,*P*)-isomer for dmsp complex is the anionic nature of the P–S(thiolate) ligand.

The crystal structure analyses of *cis*-$[M(edmp)_2]^{2+}$ (M = Ni^{II} (**4a**), Pd^{II} (**5c**), and Pt^{II} (**6a**)) complexes reveal two interesting features for comparison of the triad metal complexes; (1) there is a weak interaction between $[M(edmp)_2]^{2+}$ and Cl^- anion, and the interaction weakens in the order of $Ni^{II} > Pd^{II} > Pt^{II}$, which would correspond to the tendency towards *cis–trans* isomerization rate for the square-planar complexes. (2) The order of the trans influence of the $-PMe_2$ group in edmp among Ni^{II}, Pd^{II}, and Pt^{II} is apparently different from the periodic order: $Ni^{II} < Pt^{II} < Pd^{II}$, but similar to the order ($Co^{III} < Ir^{III} < Rh^{III}$) found in Co^{III}, Rh^{III}, and Ir^{III} triad metal complexes of *fac*-$[M'(edmp)_3]^{3+}$.

Experimental

All preparative procedures were performed under an atmosphere of nitrogen until air-stable complexes were formed. All solvents used in the preparation of the ligands and complexes were bubbled with nitrogen for 20 min immediately before use. The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Hitachi R-90HS (at 90.02, 22.66, and 36.46 MHz, respectively) or a JEOL GX400 (at 399.8, 100.5, and 161.9 MHz, respectively) spectrometer.

Preparation of the Ligands. The ligands, edmp and edpp, were prepared by methods described previously.[5]

2-(*N*,*N*-Dimethylamino)dimethylphosphinoethane (dmedmp). The ligand was synthesized simultaneously by Field and Luck[23] and by us.[24] The following preparative procedure was, incidentally, almost the same as that of Field and Luck. To a dark-blue liquid ammonia solution (200 cm^3) of sodium metal (2.24 g), which was cooled in a dry ice–acetone bath, was added tetramethyldiphosphane[25] (5.95 g, 48.7 mmol) dropwise with mechanical stirring. The stirring of the resulting green solution was continued for 30 min, and then 2-chloroethyl-*N*,*N*-dimethylamine hydrochloride (7.02 g, 48.7 mmol) was added with three portions to the solution on cooling at −78 °C. When the addition was complete, the color of the mixture disappeared. After stirring for another 1 h at −78 °C, the solvent ammonia was slowly evaporated to dryness by removing the dry ice–acetone bath. The resulting white residue was extracted with diethyl ether (50 $cm^3 \times 3$), the undissolved precipitate was filtered off, and the ethereal extract was evaporated under slightly reduced pressure (note: the boiling point of the desired product is not so high). Pure dmedmp was obtained by careful distillation under reduced pressure (bp 65—68 °C, 4.87 kPa). Yield 3.50 g (27%). ^{31}P NMR ($CDCl_3$) $\delta = -50.6$ (s) (lit,[23] −54.3).

2-(Methylthio)dimethylphosphinoethane (mtdmp). This compound was prepared by a method similar to the above, using (2-chloroethyl)methylsulfide instead of 2-chloroethyl-*N*,*N*-dimethylamine hydrochloride. A colorless oily product was obtained by evaporation of the ethereal extract. The crude product was found to be a mixture of the desired mtdmp and a by-product of 1,2-bis(dimethylphosphino)ethane (20 : 3) by the ^{31}P NMR spectrum. However, since it was difficult to separate the phosphines by distillation, the crude product was used for the preparation of metal complexes without further purification. The isolation and purification were performed through their complex formation. ^{31}P NMR ($CDCl_3$) $\delta = -49.6$ (s); ^{13}C NMR ($CDCl_3$) $\delta = 13.81$ (d, $J = 13.1$ Hz), 15.53 (s), 30.72 (d, $J = 17.3$ Hz), 31.80 (d, $J = 12.4$ Hz).

Preparation of the Complexes. The complexes: $[PdCl_2(PhCN)_2]$,[26] $[Pd(EtCN)_4](BF_4)_2$, $[PtCl_2(EtCN)_2]$, and $[Pt(EtCN)_4](BF_4)_2$[27] were prepared by the literature methods.

[$PdCl_2$(edmp)] (1). A methanolic solution (5 cm^3) of edmp (0.32 g, 3.0 mmol) was added to a dichloromethane solution (20 cm^3) of $[PdCl_2(PhCN)_2]$ (0.73 g, 1.9 mmol) dropwise with stirring to give a yellow precipitate. Stirring was continued for 2 h, and then the volume of the reaction mixture was reduced to ca. 5 cm^3 by evaporation under reduced pressure. Diethyl ether (50 cm^3) was added with vigorous stirring to complete precipitation of the complex. The resulting yellow precipitate was filtered off, washed with diethyl ether (5 $cm^3 \times 2$), and then dried in vacuo. The crude product was dissolved in hot nitromethane (60 °C, 500 cm^3), and the filtered solution was evaporated under reduced pressure to form pale yellow microcrystalline solids. The product was collected by filtration and dried in vacuo. Yield 0.39 g (72%). The complex is only slightly soluble in common organic solvents, except for dimethylsulfoxide.

[$PdCl_2$(edpp)] (2). To an aqueous solution (20 cm^3) of $K_2[PdCl_4]$ (1.31 g, 4.00 mmol) was added an ethanolic solution (4 cm^3) of edpp (917 mg, 4.00 mmol) dropwise with stirring. The mixture was stirred for 1 h, and the resulting yellow precipitate collected by filtration and washed with water (20 $cm^3 \times 2$), ethanol (20 cm^3), and diethyl ether (20 cm^3). The crude product was recrystallized by a similar method to **1**, giving yellow crystals. Yield 1.00 g (61.5%). The complex is hardly soluble in common organic solvents, except for dimethylsulfoxide.

[$Ni(edmp)_2$][$NiCl_4$] (3). To an ethanolic solution (20 cm^3) of $NiCl_2 \cdot 6H_2O$ (0.96 g, 4.0 mmol) was added edmp (0.45 g, 4.3 mmol) dropwise with stirring. A clear red solution was immediately

obtained, and within a few minutes of stirring, green solids were precipitated from the solution. The stirring of the mixture was continued for 1 h, then the precipitate was collected by filtration, washed with diethyl ether (5 $cm^3 \times 2$), and dried in vacuo. The crude product was dissolved in a minimum amount of methanol, and the filtered solution was kept in a desiccator together with diethyl ether to form greenish prismatic crystals. Yield 0.73 g (78%). The complex is soluble in methanol, and highly hygroscopic.

[Ni(edmp)$_2$](BF$_4$)$_2$ (4b). An aqueous solution of Ni(BF$_4$)$_2$ (40 wt%, 1.20 g, 2.1 mmol) was evaporated to dryness under reduced pressure, and the residue was dissolved in ethanol (20 cm^3). To the solution was added edmp (0.54 g, 5.1 mmol) with stirring, giving a yellow precipitate. The mixture was stirred for 1 h, cooled for 3 h in an ice bath, and then filtered. The collected precipitate was washed with ice–cold ethanol (15 cm^3) and diethyl ether (5 $cm^3 \times 2$) and dried in vacuo. The crude product was dissolved in a minimum amount of hot methanol (50 °C), and the filtered solution was allowed to stand in a refrigerator to deposit yellow crystals. Yield 0.74 g (84%). The complex is soluble in water, methanol and nitromethane.

[Ni(edmp)$_2$]Cl$_2$ (4a). An aqueous solution (100 cm^3) of **4b** (0.10 g, 0.30 mmol) was applied on a column (ϕ 2.5 cm× 12 cm) of SP-Sephadex C-25 (Na^+-form), and the adsorbed product was eluted with 0.1 mol dm^{-3} aqueous NaCl solution. A yellow band was eluted and collected. The eluate was evaporated to dryness under reduced pressure, and the residue was extracted with methanol. To desalt from the extract, the methanolic extract was then applied on a column (ϕ 2.5 cm× 20 cm) of Sephadex LH-20. A yellow band eluted was collected, and the eluate was evaporated under reduced pressure to give red microcrystalline solids. Recrystallization from methanol and diethyl ether by a method similar to that for **3** gave red columnar crystals. Yield 0.04 g (40%). The complex is soluble in water and methanol.

[Ni(edmp)$_2$]Cl(BF$_4$) (4c). To a methanolic solution (15 cm^3) of NiCl$_2$·6H$_2$O (0.71 g, 3.0 mmol) was added edmp (0.78 g, 7.4 mmol) dropwise with stirring; the resulting clear red solution was stirred for 3 h. The solution was concentrated to ca. 10 cm^3 under reduced pressure, and an excess amount of saturated methanolic solution of LiBF$_4$ was added with stirring to give an orange precipitate. After stirred for 30 min, the precipitated was filtered off, washed with diethyl ether (5 cm^3), and dried in vacuo. The crude product was dissolved in a minimum amount of hot nitromethane (45 °C), and the filtered solution was allowed to stand in a refrigerator to form orange crystals. Yield 0.32 g (27%). The complex is soluble in water and methanol.

[Pd(edmp)$_2$]Cl$_2$ (5a). To a solution of [PdCl$_2$(PhCN)$_2$] (1.15 g, 3.00 mmol) in dichloromethane (50 cm^3) was added a methanolic solution (7 cm^3) of edmp (0.70 g, 6.7 mmol) dropwise with stirring, giving a clear pale yellow solution. After being stirred for 2 h, the solution was evaporated to ca. 5 cm^3 under reduced pressure, and diethyl ether (50 cm^3) was added with stirring. The resulting white precipitate was filtered off, washed with diethyl ether (5 $cm^3 \times 2$), and dried in vacuo. The crude product was recrystallized from methanol and diethyl ether by a method similar to that for **3**. Yield 1.04 g (89%). The complex is soluble in water and methanol, and highly hygroscopic.

[Pd(edmp)$_2$]Cl(BF$_4$) (5c). The complex **5a** was prepared from 0.77 g (2.0 mmol) of [PdCl$_2$(PhCN)$_2$] and 0.42 g (4.0 mmol) of edmp by the method described above. The crude product was dissolved in methanol (20 cm^3), and to the filtered solution was added an excess amount of saturated methanolic solution of LiBF$_4$ with stirring, giving a white precipitate. The precipitate collected by filtration was recrystallized from 90% ethanol (65 °C) to deposit pale yellow prismatic crystals. Yield 0.75 g (85%). The complex is soluble in water, methanol, and nitromethane.

[Pd(edmp)$_2$](BF$_4$)$_2$ (5b). A solution of [Pd(EtCN)$_4$](BF$_4$)$_2$ in dichloromethane (40 cm^3, 2.0 mmol of Pd) was placed in a Schlenk tube, and deaerated by bubbling with nitrogen for 5 min. To the solution was added a methanolic solution (7 cm^3) of edmp (0.42 g, 4.0 mmol) dropwise with stirring, giving a clear pale yellow solution. After stirring for 2 h, the solution was evaporated to ca. 5 cm^3 under reduced pressure, and diethyl ether (40 cm^3) was added with stirring. The resulting white precipitate was filtered off, washed with diethyl ether (5 $cm^3 \times 2$), and dried in vacuo. The crude product was recrystallized from hot (60 °C) methanol by a method similar to that for **4a**. Yield 0.72 g (74%). The complex is soluble in water, methanol, and nitromethane.

[Pt(edmp)$_2$]Cl$_2$ (6a) and [Pt(edmp)$_2$]Cl(BF$_4$) (6c). These complexes were prepared from [PtCl$_2$(EtCN)$_2$], instead of [PdCl$_2$(PhCN)$_2$] and recrystallized by methods similar to those for **5a** and **5c**, respectively. Yield 73% for **6a** and 43% for **6c**.

[Pt(edmp)$_2$](BF$_4$)$_2$ (6b). The complex was prepared by a method similar to that for **5b** using [Pt(EtCN)$_4$](BF$_4$)$_2$. The crude product was recrystallized from hot (60 °C) methanol. Yield 0.88 g (76%).

The solubility of the platinum(II) complexes are similar to those of the palladium(II) analogs, respectively.

[Pd(dmedmp)$_2$](BF$_4$)$_2$ (7b). To a dichloromethane (10 cm^3) solution of [PdCl$_2$(PhCN)$_2$] (384 mg, 1.00 mmol) was added dmedmp (400 mg, 3.0 mmol) dropwise with stirring, giving a clear yellow solution. The mixture was stirred for 30 min, and then evaporated to nearly dryness under reduced pressure. The residue was mixed with diethyl ether (50 cm^3), and the mixture was stirred vigorously to form a yellow precipitate. The crude product collected by filtration was dissolved in methanol (5 cm^3), and to the filtered solution was added a saturated methanol solution (10 cm^3) of LiBF$_4$. The mixture was allowed to stand in a refrigerator overnight to deposit colorless columnar crystals, which was collected by filtration and dried in vacuo. Yield 171 mg (31%). The complex is soluble in water, methanol, and nitromethane.

[Ni(mtdmp)$_2$](BF$_4$)$_2$ (8b). The complex was prepared from 40 wt% aqueous Ni(BF$_4$)$_2$ solution (3.48 g, 6.00 mmol) and mtdmp (1.65 g, 12.0 mmol) by a method similar to that of **4b**, and recrystallized from a mixture of nitromethane and diethyl ether to give yellow crystals. Yield 2.10 g (69.3%).

[Pd(mtdmp)$_2$](BF$_4$)$_2$ (9b) and [Pt(mtdmp)$_2$](BF$_4$)$_2$ (10b). These complexes were prepared by a method similar to those of **5c** and **6c**, and recrystallized from a mixture of nitromethane and diethyl ether. The obtained colorless crystals were, however, of the complex bis(tetrafluoroborate) salts; these results were confirmed by elemental analyses. Yield 39% for **9b** and 58% for **10b**.

The mtdmp complexes, **8b**, **9b**, and **10b**, are soluble in water, methanol, and nitromethane.

[Pd(edpp)$_2$]Cl$_2$ (11a) and [Pd(edpp)$_2$](BF$_4$)$_2$ (11b). These complexes were prepared by a method similar to those of **5a** and **5c**, respectively, using edpp instead of edmp. The complexes were recrystallized from methanol and diethyl ether to deposit a colorless microcrystalline solid of **11a** in a 77% yield and colorless microcrystalline solids of **11b** in 71%.

[Pt(edpp)$_2$]Cl$_2$ (12a). The complex was prepared from [PtCl$_2$(EtCN)$_2$] and edpp by a similar method to that of **6a**, and recrystallized from hot (60 °C) methanol. Yield 78%.

[Pt(edpp)$_2$](ClO$_4$)$_2$ (12b′). To a solution of [Pt(EtCN)$_4$](BF$_4$)$_2$ in dichloromethane (40 cm^3, 2.0 mmol of Pt) was added a meth-

anolic solution (7 cm^3) of edpp (0.92 g, 4.0 mmol) dropwise with stirring. Stirring was continued for 2 h, and the resulting colorless solution was evaporated to dryness under reduced pressure. The residue was washed with diethyl ether (40 cm^3), and dissolved in a minimum amount of methanol. To the filtered solution was added to an excess amount of saturated methanolic solution of $NaClO_4$, giving a white precipitate. The precipitate was filtered off, washed with diethyl ether (5 $cm^3 \times 2$), and dried in vacuo. Recrystallization was performed from methanol and diethyl ether. Yield 0.77 g (45%).

[Ni(edpp)$_2$](BF$_4$)$_2$ (13b). The nickel(II)-edpp complex was prepared from aqueous $Ni(BF_4)_2$ (40 wt%, 1.16 g, 2.0 mmol) and edpp (0.92 g, 4.0 mmol) by a method similar to that for **4b**, and recrystallized from nitromethane and diethyl ether to form yellow microcrystalline solids. Yield 1.06 g (76%).

The edpp complexes are soluble in methanol and nitromethane.

X-Ray Data Collection. An ethanolic solution of **3** was kept in a desiccator together with diethyl ether, giving greenish columnar crystals of **3** and a small amount of reddish prismatic crystals of **4a**. Colorless columnar crystals of **5c** were grown from a saturated aqueous ethanol (90%) solution at 60 °C by slow cooling. Colorless columnar crystals of **6a** were obtained from a methanol solution by diffusion of vapor of diethyl ether in a desiccator. Because the crystals of **3** and **6a** were highly hygroscopic, a suitable crystal of each complex was sealed in a glass capillary. The non-hygroscopic crystals of **4a** and **5c** were mounted on the top of a glass fiber with epoxy resin. The X-ray intensities were measured at 23 °C with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) on an automated Rigaku four-circle diffractometer AFC-5. The ω–2θ scan technique was employed. Three standard reflections were monitored every 150 reflections. No serious decomposition were found for all crystals. Absorption corrections were made either by empirical method using three sets of Ψ-scan data (for **3**) or by the Gauss numerical integration method[28] (for **4a**, **5c**, and **6a**). The final lattice constants were determined by least-squares treatments using setting angles of 22—25 reflections in the $20 \leq 2\theta \leq 30°$ range. Crystal data are collected in Table 4.

Crystal Structure Analyses. For complex **3**, the positions of Ni, Cl, and P atoms were determined by a direct method using SHELXS-86 program,[29] and the structure was expanded by Fourier synthesis. For complexes **4a** and **5c**, the structures were solved by the usual heavy-atom method. Among 24 hydrogen atoms for each complex, 17 for **3**, 16 for **4a**, and 18 for **5c** were located by Fourier-difference syntheses; the other hydrogen atoms

Table 5. Fractional Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen Atoms for *cis*-[Ni(edmp)$_2$][NiCl$_4$] (**3**)

Atom	*x/a*	*y/b*	*z/c*	B_{eq}[a]/Å^2
Ni(1)	0.39720(4)	0.27112(6)	0.31490(7)	2.7
Ni(2)	0.63561(5)	0.26370(6)	0.59058(8)	3.2
Cl(1)	0.53765(9)	0.3182(2)	0.4214(2)	4.3
Cl(2)	0.6303(1)	0.2866(2)	0.7521(2)	5.1
Cl(3)	0.7251(1)	0.3382(2)	0.6007(2)	5.8
Cl(4)	0.6454(2)	0.1206(2)	0.5465(3)	7.4
P(1)	0.3907(1)	0.1613(1)	0.4297(2)	3.5
P(2)	0.3643(1)	0.3758(1)	0.4110(2)	3.8
N(1)	0.3971(4)	0.1844(4)	0.2220(6)	4.4
N(2)	0.3624(4)	0.3648(5)	0.1955(6)	4.6
C(1)	0.3178(4)	0.1310(6)	0.4423(8)	4.7
C(2)	0.4680(6)	0.1566(9)	0.5807(12)	9.3
C(3)	0.3952(8)	0.0662(6)	0.3402(14)	8.0
C(4)	0.4246(6)	0.0972(7)	0.2769(10)	6.2
C(5)	0.2879(5)	0.3780(6)	0.4200(9)	5.0
C(6)	0.4375(5)	0.4006(8)	0.5634(10)	6.9
C(7)	0.3491(13)	0.4712(7)	0.3150(11)	14.1
C(8)	0.3517(8)	0.4553(7)	0.2190(11)	7.9

a) $B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

Table 4. Crystal Data of *cis*-[Ni(edmp)$_2$][NiCl$_4$] (**3**), *cis*-[Ni(edmp)$_2$]Cl$_2$ (**4a**), *cis*-[Pd(edmp)$_2$]Cl(BF$_4$) (**5c**), and *cis*-[Pt(edmp)$_2$]Cl$_2$ (**6a**)

Compound	**3**	**4a**	**5c**	**6a**
Chemical formula	$C_8H_{24}Cl_4N_2Ni_2P_2$	$C_8H_{24}Cl_2N_2NiP_2$	$C_8H_{24}BClF_4N_2P_2Pd$	$C_8H_{24}Cl_2N_2P_2Pt$
Formula weight	469.43	339.84	439.92	476.23
Temperature/°C	23	23	23	23
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	22.703(3)	6.628(3)	6.825(2)	6.668(2)
b/Å	14.838(2)	14.336(3)	15.682(2)	14.461(2)
c/Å	13.263(3)	16.227(3)	16.941(1)	16.581(4)
β/°	123.168(8)	99.11(2)	99.18(1)	99.57(2)
V/Å^3	3740(1)	1552.4(7)	1742.6(5)	1577.0(6)
Z	8	4	4	4
D_m and D_x/Mg m^{-3}	1.67, 1.67	1.45, 1.45	1.67, 1.68	2.01, 2.01
μ(Mo $K\alpha$)/mm^{-1}	2.76	1.78	1.41	9.42
Transmission factor, *A*	0.874—1.000	0.664—0.769	0.736—0.798	0.090—0.261
Number of reflections measured	5770	4984	5783	5168
Number of unique reflections	3551	3531	3041	2665
Cutoff criteria	$\lvert F_o \rvert > 3\sigma(\lvert F_o \rvert)$	$\lvert F_o \rvert > 3\sigma(\lvert F_o \rvert)$	$\lvert F_o \rvert > 3\sigma(\lvert F_o \rvert)$	$\lvert F_o \rvert > 6\sigma(\lvert F_o \rvert)$
Number of parameters refined	232	201	245	200
R[a]	0.060	0.042	0.071	0.043
R_w[b]	0.063	0.053	0.083	0.052

a) $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. b) $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$. $(w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$.

Table 6. Fractional Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen Atoms for *cis*-[Ni(edmp)$_2$]Cl$_2$ (**4a**)

Atom	*x/a*	*y/b*	*z/c*	B_{eq}[a)]/Å^2
Ni(1)	0.66992(7)	0.83271(3)	0.59473(3)	1.8
Cl(1)	0.2877(2)	0.88745(7)	0.50255(7)	2.6
Cl(2)	1.0752(2)	0.9816(1)	0.80608(9)	3.9
P(1)	0.6740(2)	0.69792(7)	0.53397(7)	2.2
P(2)	0.5513(2)	0.78498(7)	0.70431(6)	2.0
N(1)	0.7943(5)	0.8830(2)	0.5015(2)	2.2
N(2)	0.6928(6)	0.9561(2)	0.6495(2)	2.5
C(1)	0.8221(8)	0.5991(4)	0.5813(4)	3.7
C(2)	0.4285(7)	0.6455(4)	0.4944(3)	3.3
C(3)	0.7931(8)	0.7276(3)	0.4423(3)	3.3
C(4)	0.7444(7)	0.8300(3)	0.4218(3)	2.9
C(5)	0.6966(8)	0.7011(4)	0.7738(3)	3.5
C(6)	0.2889(7)	0.7415(4)	0.6885(3)	3.4
C(7)	0.5507(8)	0.9715(3)	0.7654(3)	2.7
C(8)	0.5325(8)	0.8715(3)	0.7032(3)	2.8

a) $B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

Table 7. Fractional Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen Atoms for *cis*-[Pd(edmp)$_2$]Cl(BF$_4$) (**5c**)

Atom	*x/a*	*y/b*	*z/c*	B_{eq}[a)]/Å^2
Pd(1)	0.70772(11)	0.66456(5)	0.58587(5)	2.4
Cl(1)	0.2888(4)	0.0606(2)	0.4940(2)	3.8
P(1)	0.7082(4)	0.7906(2)	0.5172(2)	2.9
P(2)	0.5952(5)	0.7156(2)	0.6943(2)	3.1
F(1)	0.1011(16)	0.5954(7)	0.6943(2)	8.0
F(2)	−0.0238(16)	0.4815(7)	0.8437(7)	7.8
F(3)	0.2978(17)	0.5071(10)	0.8614(8)	11.4
F(4)	0.1424(25)	0.4641(9)	0.7457(9)	13.1
N(1)	0.8088(14)	0.6079(6)	0.4852(6)	3.3
N(2)	0.7177(15)	0.5421(6)	0.6458(6)	3.6
C(1)	0.4654(18)	0.8358(9)	0.4807(8)	4.4
C(2)	0.8558(22)	0.8833(9)	0.5570(10)	5.5
C(3)	0.8091(22)	0.7551(9)	0.4285(7)	4.4
C(4)	0.7487(21)	0.6588(9)	0.4098(7)	4.3
C(5)	0.3350(19)	0.7521(10)	0.6768(8)	4.4
C(6)	0.7333(23)	0.7996(10)	0.7558(9)	5.2
C(7)	0.6013(20)	0.6176(8)	0.7568(8)	4.0
C(8)	0.5704(20)	0.5377(9)	0.7022(7)	4.0
B(1)	0.1343(25)	0.5103(10)	0.8110(10)	4.5

a) $B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

were not included in the calculation. The observed independent reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the structural calculations. The function, $\Sigma w |F_o| - |F_c|^2$, with $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$ was minimized by block-diagonal least-squares methods using anisotropic and isotropic thermal parameters for all non-hydrogen and hydrogen atoms, respectively, and complex neutral-atom scattering factors.[30] Calculations were carried out on a HITAC M-680 computer using the computational program system UNICS-III.[31]

The structural calculation for **6a** was carried out on a Fujitsu S-4/IX workstation using the Xtal 3.2 software.[32] The structure was solved by the usual heavy-atom method. All non-hydrogen

Table 8. Fractional Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen Atoms for *cis*-[Pt(edmp)$_2$]Cl$_2$ (**6a**)

Atom	*x/a*	*y/b*	*z/c*	U_{eq}[a)]/Å^2
Pt(1)	0.30700(5)	0.32501(2)	0.39833(2)	0.0264(1)
Cl(1)	0.7250(4)	0.3961(2)	0.5077(2)	0.0400(8)
Cl(2)	0.5800(5)	−0.0164(2)	0.3127(2)	0.056(1)
P(1)	0.4417(4)	0.2815(2)	0.2897(2)	0.0309(7)
P(2)	0.3148(4)	0.1917(2)	0.4665(2)	0.0334(8)
N(1)	0.294(1)	0.4570(6)	0.3436(5)	0.034(3)
N(2)	0.196(1)	0.3806(6)	0.4994(5)	0.035(3)
C(1)	0.313(2)	0.1962(9)	0.2217(8)	0.055(4)
C(2)	0.705(2)	0.2429(9)	0.3114(7)	0.047(4)
C(3)	0.441(2)	0.3888(8)	0.2319(7)	0.042(4)
C(4)	0.459(2)	0.4681(7)	0.2932(7)	0.045(4)
C(5)	0.169(2)	0.0911(9)	0.425(1)	0.054(5)
C(6)	0.564(2)	0.1460(9)	0.5050(9)	0.050(4)
C(7)	0.205(2)	0.2259(8)	0.5565(8)	0.049(4)
C(8)	0.257(2)	0.3254(8)	0.5761(7)	0.043(4)

a) $U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

atoms were refined anisotropically, and 18 among 24 hydrogen atoms located by Fourier-difference syntheses were refined isotropically. The other hydrogen atoms were introduced at the theoretical positions and fixed in the refinement. The observed independent reflections with $|F_o| > 6\sigma(|F_o|)$ were used for the structural calculations. The function, $\Sigma w |F_o| - |F_c|^2$, with $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$ was minimized by full-matrix methods using complex neutral-atom scattering factors.[30]

Atomic parameters of **3**, **4a**, **5c**, and **6a** are listed in Tables 5, 6, 7, and 8, respectively.[33]

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