Synthesis, Crystal Structures and Spectroscopic Properties of *cis*- and *trans*-[$RhCl_2L_2$]$^+$ [L = 1,3-bis(dimethylphosphino)propane or 1,2-bis(dimethylphosphino)ethane (dmpe)]: Reinvestigation of the dmpe Complexes‡

Takayoshi Suzuki,*,†,[a] Kiyoshi Isobe[b] and Kazuo Kashiwabara[c]
[a] *Institute for Molecular Science, Myodaiji, Okazaki 444, Japan*
[b] *Department of Material Science, Faculty of Science, Osaka City University, Sugimoto, Sumiyoshi, Osaka 558, Japan*
[c] *Department of Chemistry, Faculty of Science, Nagoya University, Furo-cho, Chikusa, Nagoya 464–01, Japan*

Two pairs of geometrical isomers, *cis*- and *trans*-[$RhCl_2L_2$]$^+$ [L = 1,3-bis(dimethylphosphino)propane or 1,2-bis(dimethylphosphino)ethane], have been synthesized and their structures and spectroscopic properties investigated. The previous characterization of the dmpe complexes made by other workers was found to be erroneous. A convenient method of preparation and separation of the complexes into isomers has been found. The geometrical structures of the isomers have been confirmed by ^1H, ^{13}C and ^{31}P NMR spectroscopy and by single-crystal X-ray structure determinations. The Rh–Cl bond lengths in the *cis* complexes are considerably longer than those in the corresponding *trans* isomers, and the Rh–P bonds *trans* to Cl in the *cis* isomers are relatively shorter than those of mutually *trans* phosphine ligands in both the *cis*- and *trans*-isomers, exhibiting a strong *trans* influence of the dimethylphosphino group. The ^1H, ^{13}C and ^{31}P NMR spectra of the complexes were found to be consistent with the structures found by single-crystal X-ray analyses, and the chemical shifts (δ_P) and coupling constants [^1J(RhP) and ^2J(PP)] correspond well with the structural parameters (Rh–P bond length and P–Rh–P angle). The electronic spectra and isomerization reactions of the complexes were also determined.

In previous papers,[1–4] we have examined the structural and spectroscopic properties of cobalt(III) complexes with didentate phosphine ligands in terms of the sizes of the chelate rings formed by the ligands. In this study, we extend the study to rhodium(III) complexes. A large number of rhodium(III) complexes with various kinds of phosphine ligands are known,[5,6] but surprisingly few studies have been made on the complexes of methyl-substituted didentate phosphine ligands, $Me_2P(CH_2)_nPMe_2$ (n = 1–3).[7–10] Here, we describe the synthesis and characterization of a new pair of geometrical isomers, *cis*- and *trans*-[$RhCl_2(dmpp)_2$]$^+$ [*cis*-**1** and *trans*-**1**, dmpp = 1,3-bis(dimethylphosphino)propane], and compare their properties with those of the corresponding dmpe [1,2-bis(dimethylphosphino)ethane] complexes.

The isomeric pair of dmpe complexes, *cis*- and *trans*-[$RhCl_2(dmpe)_2$]$^+$ (*cis*- and *trans*-**2**), was first reported by Butter and Chatt[7] in 1970, and their paper has been quoted in many reviews.[5,11] Although they mentioned in the paper that 'the configurations assigned mainly on the basis of electronic spectra must be accepted with caution,' no report had been published on the re-examination of the synthesis and characterization of the complexes until 1989. Simonsen *et al.*[8] determined the crystal structure of *trans*-[$RhCl_2(dmpe)_2$]CF_3SO_3 *trans*-**2d**, and also reported that 'a similar reaction to that of Butter and Chatt yielded only the *trans* isomer, no fraction indicative of the other isomer being obtained in column chromatography'.[8] In this study, we have succeeded in preparing both geometrical isomers of the dmpe complex using *trans*-[$RhCl_2(py)_4$]$Cl{\cdot}5H_2O$ (py = pyridine) as starting material and acetonitrile as solvent, and characterized their structures by NMR spectroscopy and X-ray analysis. The previous characterizations made by Butter and Chatt[7] have been found to be erroneous. The reason why the *cis* isomer of the dmpe complex (*cis*-**2**) is difficult to prepare and isolate is also discussed.

Results and Discussion

Preparations.—cis- and trans-[$RhCl_2(dmpp)_2$]$^+$ **1**. The complex *cis*-[$RhCl_2(dmpp)_2$]Cl *cis*-**1a** was obtained as a white precipitate by the reaction of *trans*-[$RhCl_2(py)_4$]$Cl{\cdot}5H_2O$ with dmpp in acetonitrile. The yellow filtrate of the reaction mixture contained a small amount of *cis*- and *trans*-**1a**, which was confirmed by NMR spectroscopy, and was subjected to column chromatography to separate the isomers. Both isomers can be purified as their hexafluorophosphate salts (**1b**) by recrystallization. The *cis*-**1b** isomer is readily soluble in acetonitrile, moderately in methanol and hardly in water, and can be crystallized from hot methanol as colourless prisms. On the other hand, *trans*-**1b** is poorly soluble in methanol, and was crystallized from a mixture of acetonitrile and water as yellow prisms.

Pure crystals of *cis*- and *trans*-**1b**, respectively, can also be obtained from the yellow filtrate in moderate yield by successive recrystallization without using column chromatography. The mixture of *cis*- and *trans*-**1b**, which is obtained by addition of NH_4PF_6 to the filtrate, is recrystallized successively from methanol to form pure colourless crystals of *cis*-**1b**. Pure yellow crystals of *trans*-**1b** are obtained by recrystallization of the yellow residue from a mixture of acetonitrile and water.

In the case of the synthesis utilizing $RhCl_3{\cdot}3H_2O$ as a source of rhodium(III), its reaction with dmpp in acetonitrile needs a

---

† *Present address:* Department of Chemistry, Faculty of Science, Osaka University, Toyonaka 560, Japan.

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

longer time, owing to the insolubility of $RhCl_3 \cdot 3H_2O$ in acetonitrile. This causes a lower yield of the *cis* isomer and a higher one of the *trans* isomer.

cis- and trans-$[RhCl_2(dmpe)_2]^+$ **2**. Using a similar preparative method to that of **1** the corresponding dmpe complexes were obtained. The reaction of *trans*-$[RhCl_2(py)_4]Cl \cdot 5H_2O$ with dmpe in acetonitrile gives a pale yellow precipitate of *cis*-$[RhCl_2(dmpe)_2]Cl$ *cis*-**2a**. The crude product, which is contaminated with a small amount of the *trans*-isomer *trans*-**2a** and unreacted starting pyridine complex, can be purified as the hexafluorophosphate salt *cis*-**2b**. Recrystallization from hot methanol gives pure crystals of *cis*-**2b** as colourless needles, although the isolated yield is relatively low compared to that of the corresponding dmpp complex. The low yield of *cis*-**2b** is due to its fair solubility in acetonitrile. In order to separate the PF_6 salts of the isomers, successive recrystallization from methanol is performed in the dark, since the *cis* isomer is easily isomerized to the *trans* isomer on exposure to visible light. A small quantity of both pure colourless crystals (*cis*-**2b**) and pure yellow crystals (*trans*-**2b**) can be obtained, owing to the small difference in their solubilities in methanol. When the recrystallization is performed under visible light, pure yellow crystals of *trans*-**2b** are obtained in good yield without any difficulty, but *cis*-**2b** is not isolated.

For separation of the isomers, cation-exchange column chromatography was also attempted. Our results are the same as those of Simonsen *et al.*,[8] no band other than a yellow one of *trans*-**2** being observed. However, from the NMR spectra we find that the eluates before and after the yellow band, and even the methanol washings of the unmoved materials on the top of column resin, contain *cis*-**2a**, that is, *cis*-**2** adheres to the column resin. Also, the *cis–trans* isomerization reaction may make the chromatographic separation difficult. The separation with SP-Sephadex is not effective for the isolation of *cis*-**2**, but is acceptable for that of *trans*-**2**.

As shown later, the electronic spectra of *cis*- and *trans*-**2** are different from those reported by Butter and Chatt,[7] who assigned the geometrical structures on the basis of the electronic spectra. They also described the solubilities of their compounds in several solvents, but some of them are completely different from our observation, for example, our *cis*- and *trans*-**2a** complexes are very soluble in water, whereas their compounds were insoluble. Moreover, they mentioned that no interconversion between *cis* and *trans* isomers were observed in the normal course of handling, however, we found that *cis*-**2** is easily isomerized to *trans*-**2** on exposure to visible light. Unfortunately, we could not produce the compounds using their methods, and hence, could not characterize their compounds.

The complex *cis*-**2b** gave needle-shaped crystals which were not good enough for a single-crystal X-ray diffraction study, but the perchlorate salt (*cis*-**2c**), obtained from *cis*-**2a** and $LiClO_4$ in methanol, forms prismatic crystals suitable for an X-ray study. The ^{31}P NMR spectrum of *cis*-**2c** is almost identical to that of *cis*-**2b**, indicating the existence of the same complex cation in both salts. Since *cis*-**2c** is *highly explosive*, further characterization such as elemental analysis and measurement of the infrared spectrum has not been performed.

Molecular Structures.—The geometrical structures of *cis*-**1b**, *trans*-**1b** and *cis*-**2c** were determined by single-crystal X-ray diffraction. Perspective drawings of the complex cations of *cis*-**1**, *trans*-**1** and *cis*-**2** are shown in Figs. 1–3, respectively. In *trans*-**1** (Fig. 2), there is a crystallographic C_2 axis which bisects the $P(1)–Rh–P(1^I)$ and $P(2)–Rh–P(2^I)$ angles. Selected bond lengths and angles are listed in Table 1, together with those of *trans*-**2d**[8] and the analogous arsine complexes *cis*-$[RhCl_2(dmap)_2]X$ [*cis*-**3b** X = PF_6 or *cis*-**3d** X = CF_3SO_3, dmap = 1,3-bis(dimethylarsino)propane] and *trans*-$[RhCl_2(dmap)_2]ClO_4$ *trans*-**3c**.[12]

The Rh–Cl and Rh–P bond lengths in the complexes can be discussed in relation to the strong *trans* influence of the dimethylphosphino group. The Rh–Cl bond lengths in *cis*-**1** (average 2.428 Å) are considerably elongated by the *trans*-positioned PMe_2 groups, compared to those in *trans*-**1** (average 2.359 Å). On the other hand, the lengths of the mutually *trans* Rh–P bonds in *cis*-**1** [Rh–P(2) and Rh–P(3); average 2.382 Å] and in *trans*-**1** (average 2.364 Å) are longer by 0.06–0.09 Å than those of Rh–P(1) and Rh–P(4) in *cis*-**1** (average 2.301 Å) which are *trans* to the chloride ligands. The elongation of Rh–Cl and Rh–P bonds due to the strong *trans* influence of the PMe_2 group is also found in the dmpe complexes, the degrees of elongation being similar or a little less than those in the dmpp complexes. The Rh–Cl bonds in *cis*-**2** (average 2.417 Å) are elongated by 0.06 Å as compared to those in *trans*-**2** (average 2.358 Å), and the mutually *trans* Rh–P bonds in *cis*-**2** (average 2.344 Å) and in *trans*-**2** (average 2.337 Å) are longer by 0.04–0.065 Å than Rh–P(1) and Rh–P(4) in *cis*-**2** (average 2.291 Å). By comparison of the structural parameters of *cis*-**1** and -**2** and *trans*-**1** and -**2** with those of the analogous arsine complexes, *cis*- and *trans*-**3**, it can be concluded that the *trans* influence of the $AsMe_2$ group is not so strong as that of PMe_2. The elongation of the Rh–Cl (0.02–0.04 Å) and Rh–As bonds (0.04–0.07 Å) due

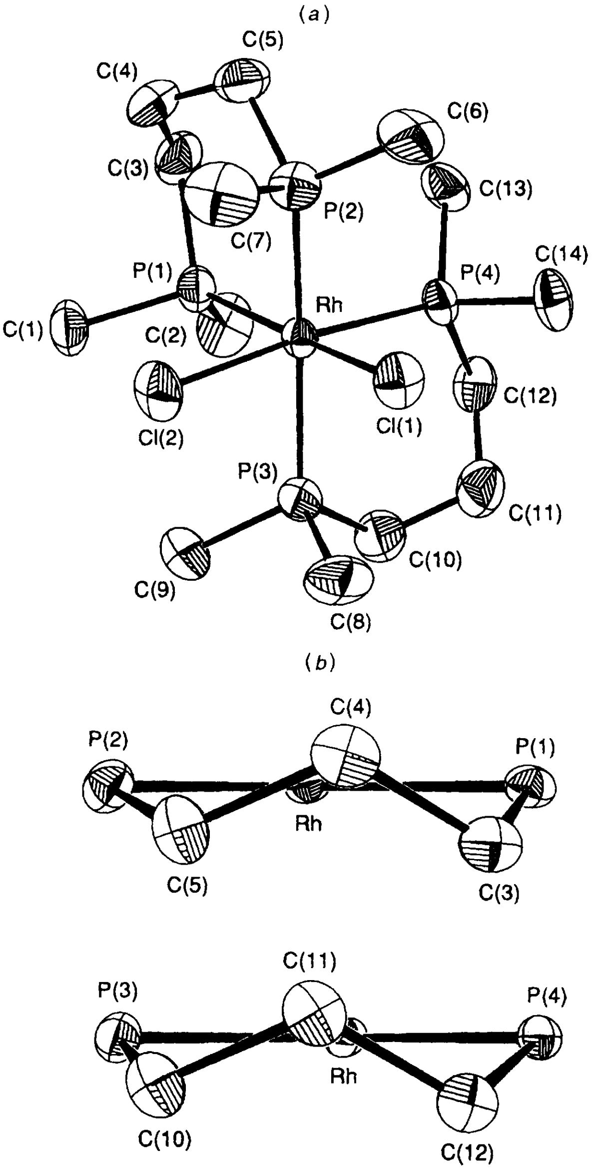

Fig. 1 (*a*) Perspective drawing of the cationic complex *cis*-**1** in *cis*-$[RhCl_2(dmpp)_2]PF_6$ with atom numbering scheme. (*b*) Edge-on views of the six-membered dmpp chelate rings in *cis*-**1**

Table 1 Selected bond lengths (Å) and angles (°) for *cis*-**1b**, *trans*-**1b**, *cis*-**2c**, *trans*-**2d**,[a] *cis*-**3b**,[b] *cis*-**3d**[b] and *trans*-**3c**[c]

	cis-**1b**	*trans*-**1b**	*cis*-**2c**	*trans*-**2d**	*cis*-**3b**	*cis*-**3d**	*trans*-**3c**
Rh–Cl(1)	2.420(2)	2.359(1)	2.399(4)	2.359(2)	2.386(7)	2.406(11)	2.366(4)
Rh–Cl(2)	2.436(2)	—	2.437(5)	2.357(2)	2.372(9)	2.383(13)	2.352(3)
Rh–P(1)[As(1)]	2.302(2)	2.363(1)	2.296(5)	2.335(1)	2.385(3)	2.387(4)	2.454(4)
Rh–P(2)[As(2)]	2.376(3)	2.364(1)	2.337(5)	2.341(2)	2.370(4)	2.367(5)	2.442(4)
Rh–P(3)[As(3)]	2.387(3)	—	2.351(5)	2.335(1)	2.345(4)	2.441(10)	2.442(4)
Rh–P(4)[As(4)]	2.299(2)	—	2.286(4)	2.337(2)	2.486(6)	2.389(10)	2.447(4)
Cl(1)–Rh–Cl(2)	86.76(8)	180	87.8(2)	179.8(1)	88.5(3)	90.3(4)	177.7(1)
P(1)–Rh–P(2)	93.67(9)	88.36(4)	84.6(2)	84.0(1)			
As(1)–Rh–As(4)					90.2(2)	92.3(3)	89.1(1)
P(3)–Rh–P(4)	93.18(9)	—	85.6(2)	84.4(1)			
As(2)–Rh–As(3)					93.9(1)	91.5(3)	89.9(1)

[a] Ref. 8. [b] Ref. 12.

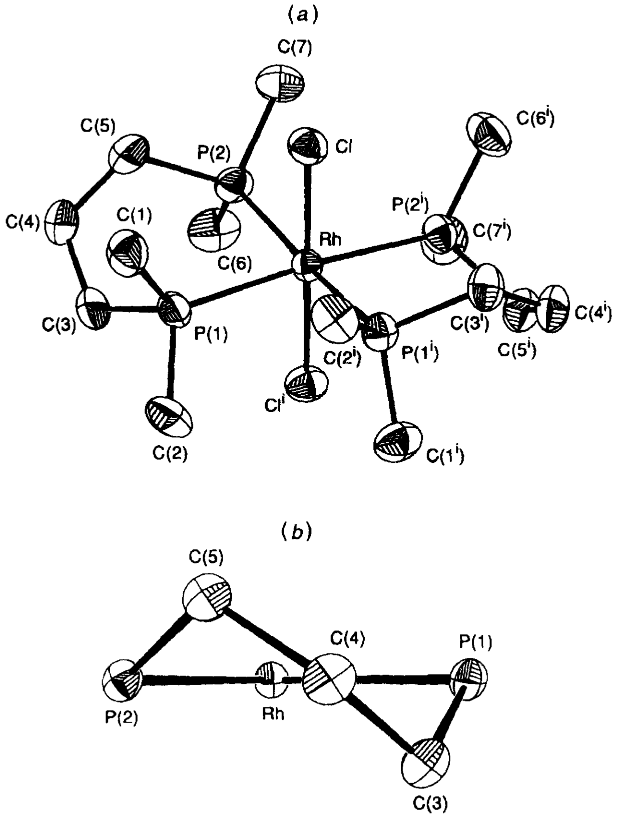

Fig. 2 (*a*) Perspective drawing of the cationic complex *trans*-**1** in *trans*-[RhCl$_2$(dmpp)$_2$]PF$_6$ with atom numbering scheme. (*b*) Edge-on view of the six-membered dmpp chelate ring in *trans*-**1**

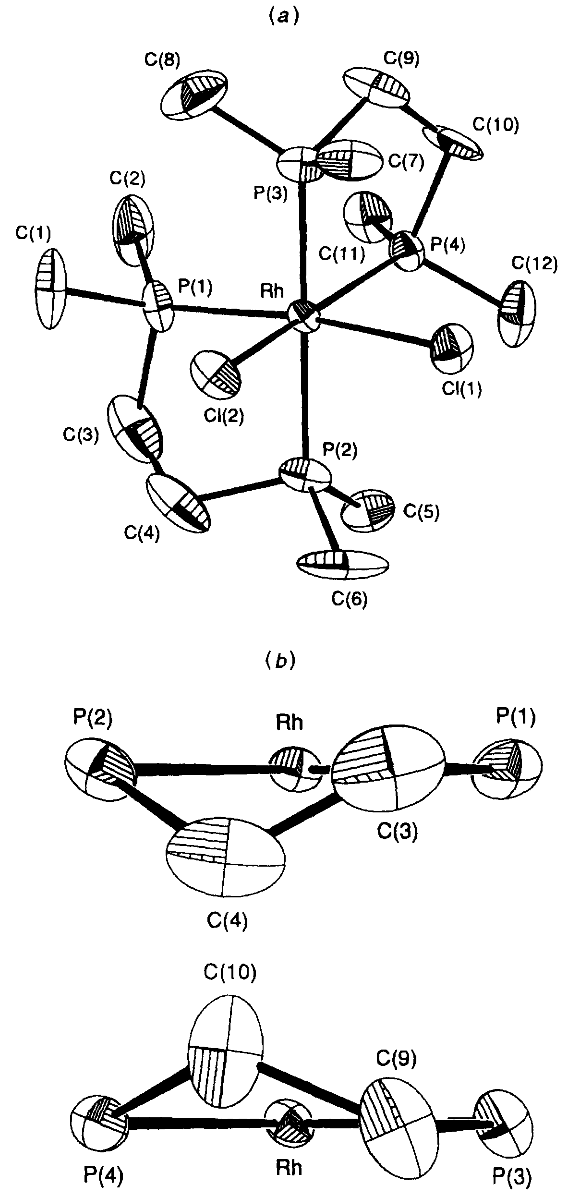

Fig. 3 (*a*) Perspective drawing of the cationic complex *cis*-**2** in *cis*-[RhCl$_2$(dmpe)$_2$]ClO$_4$ with atom numbering scheme. (*b*) Edge-on views of the five-membered dmpe chelate rings in *cis*-**2**

to the *trans* influence of the AsMe$_2$ group in dmap is relatively small compared to that of the corresponding dmpp complexes. The rhodium(III) centre has a stronger affinity for the PMe$_2$ than for the AsMe$_2$ groups,[12] and the order of *trans* influence towards the rhodium(III) centre is concluded to be as follows: AsMe$_2$ $\leqslant$ PMe$_2$ (dmpe) $\leqslant$ PMe$_2$ (dmpp).

As shown in Fig. 3(*b*), large thermal ellipsoids are found for the dmpe ligand in *cis*- and *trans*-**2**,[8] suggesting positional disorders for the atoms. The five-membered ring formed by chelation of dmpe to the rhodium(III) centre cannot take a stable conformation owing to the small bite angle of rhodium(III), whereas the six-membered chelated ring of dmpp takes an ideal chair or a skew conformation [Fig. 1(*b*) and Fig. 2(*b*)]. In fact, the bite angle of the dmpp ligand is larger and closer to 90° than that of dmpe. It is notable that the bite angle of dmpp in *cis*-**1** is relatively larger than that in *trans*-**1**. The tendency to enlarge the bite angle in the *cis*-isomer is also found in the analogous arsine complexes, *cis*- and *trans*-**3**.[12] In the dmpp complexes the conformations of six-membered chelate rings are different from each other: a chair for *cis*-**1** and a skew for *trans*-**1**. However, all the six-membered rings formed by chelation of dmap in *cis*- and *trans*-**3** are in a chair conformation, and hence there seems to be no relationship between the bite angle and the conformation of the rings. The smaller bite angles in the *trans* isomer may be affected by the interligand steric hindrance due to the PMe_2 ($AsMe_2$) groups, which is not present in the *cis* isomer.

NMR Spectra.—The geometrical structures of the complexes prepared in this study are also assigned on the basis of their NMR spectra (Table 2). The ^{31}P NMR spectrum of *trans*-**1b** in CD_3CN is a doublet signal at δ −8.62 accompanied by ^1J(RhP) 79.3 Hz. In contrast, *cis*-**1b** in CD_3CN gives two types of doublet of triplet signals at δ −13.29 and 3.15. The higher-field resonance is due to the mutually *trans* phosphorus atoms, since the coupling constant to rhodium [^1J(RhP) 79.4 Hz] is as small as that of the *trans* isomer, while the lower-field resonance, having a relatively large coupling constant [^1J(RhP) 103.7 Hz], is assigned to the phosphorus atoms *trans* to the chloride ligand. A similarly large ^1J(RhP) value is found for [$RhCl_3$(tmpme)] [tmpme = $Me_3C(CH_2PMe_2)_3$ ^1J(RhP) 100.8 Hz in CD_3CN].[13] The ^{31}P NMR spectra of *cis*- and *trans*-**2b** in CD_3CN have a similar pattern to those of the corresponding dmpp complexes, although all the resonances are shifted to lower field by 40–60 ppm. This is the so-called effect of 'ring contribution', which is defined in Garrou's review in detail.[14] It has been shown that the phosphorus atom in a five-membered chelate ring gives a lower field resonance, 30–60 ppm (the shift value being dependent on the metal ions), than that in the corresponding six-membered chelate ring.[14]

The ^1J(RhP) coupling constants in these complexes correspond well to the Rh–P bond lengths found by X-ray analyses. As described above, the ^1J(RhP) value for the mutually *trans* phosphorus atoms is smaller than that for the phosphorus atoms *trans* to the chloride ligands in the *cis* isomers, which corresponds to the length of the Rh–P bond. The dmpp complexes (*cis*- and *trans*-**1**) give slightly smaller ^1J(RhP) values than the dmpe complexes (*cis*- and *trans*-**2**) (Table 2). From X-ray structural data, the Rh–P bond lengths in the dmpp complexes are slightly longer than those in the dmpe complexes (Table 1), so that it is obvious that the difference in ^1J(RhP) values corresponds to the difference in the bond lengths. In contrast, the ^2J(PP) value in *cis*-**2** is relatively small compared to that in *cis*-**1**, which might be influenced by the P–Rh–P bond angles. The bite angles of dmpp in *cis*-**1** are larger and closer to 90° than those of dmpe in *cis*-**2**, and hence, the ideal octahedral co-ordination geometry around the rhodium(III) may give an effective coupling between mutually *cis* phosphorus atoms.

The ^1H and ^{13}C NMR spectra also show characteristics of their structures (Table 2). The *trans* isomers, which ideally have a D_{2h} symmetry in solution because of rapid puckering of the chelate rings on the NMR time-scale, give only one kind of P–Me resonance in their ^1H and ^{13}C NMR spectra, and two and one signals appear in the CH_2 region for *trans*-**1b** and *trans*-**2b**, respectively. On the other hand, the *cis* isomers give a much more complicated ^1H NMR spectrum, which is similar in pattern to the corresponding cobalt(III) complexes.[1] In the ^{13}C NMR spectra of the *cis* isomers four kinds of multiplet signals due to P–Me are found, as expected by the ideal C_2 symmetry of the complex cations, and three and two peaks appear in the CH_2 region for *cis*-**1b** and *cis*-**2b**, respectively.

Electronic Spectra and cis–trans *Isomerization.*—Fig. 4 shows the electronic spectra of *cis*- and *trans*-[$RhCl_2L_2$]PF_6 (L = dmpp or dmpe) in acetonitrile, and the spectroscopic data are given in Table 3 together with those of the analogous cobalt(III) and/or arsine (dmap) complexes in methanol.[1,12,15] The spectrum of *trans*-**2b** in acetonitrile is almost identical to that of

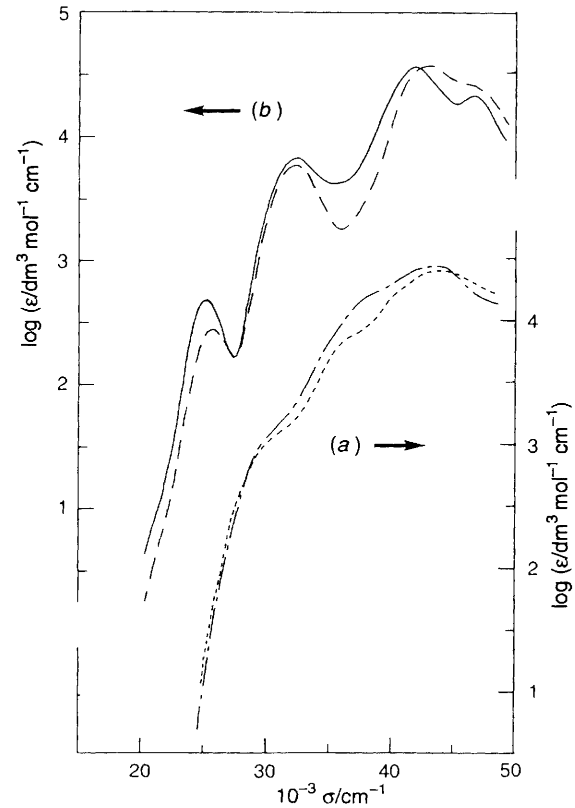

Fig. 4 Electronic spectra of (*a*) *cis*-[$RhCl_2L_2$]PF_6 [L = dmpp, *cis*-**1b** (— · —); L = dmpe, *cis*-**2b** (· · · · ·)] and (*b*) *trans*-[$RhCl_2L_2$]PF_6 [L = dmpp, *trans*-**1b** (—); L = dmpe, *trans*-**2b** (– – – –)] in acetonitrile at room temperature

Table 2 NMR data for the complexes in CD_3CN at room temperature *

Complex	^{31}P-{^1H} (δ)	^{13}C-{^1H} (δ)	^1H (δ)
cis-**1b**	−13.29 (79.4) [*trans*-P], 3.15 (103.7) [*trans*-Cl], {27.5}	10.5, 11.5, 14.2, 16.0 [P–Me], 23.9, 26.6 [P–CH_2], 14.7 [CH_2]	1.64–1.74 [m, 6 H, P–Me], 1.99–2.41 [m, 2 H, P–CH_2], 1.76–1.87 [m, 1 H, CH_2]
trans-**1b**	−8.62 (79.3)	7.8 [P–Me], 19.2 [P–CH_2], 13.8 [CH_2]	1.56 [m, 6 H, P–Me], 2.30 [m, 2 H, P–CH_2], 2.01 [t, 1 H, CH_2]
cis-**2b**	44.24 (83.1) [*trans*-P], 47.38 (109.6) [*trans*-Cl], {15.7}	7.9, 10.7, 13.1, 13.7 [P–Me], 21.5, 29.6 [P–CH_2]	1.65–1.80 [m, 3 H, P–Me], 1.97–2.41 [m, 1 H, P–CH_2]
trans-**2b**	37.19 (81.2)	10.6 [P–Me], 27.9 [P–CH_2]	1.61 [m, 3 H, P–Me], 2.07 [m, 1 H, P–CH_2]

* (^1J(RhP)/Hz), [Assignment], {^2J(PP)/Hz}.

Table 3 Electronic spectral data[a]

Complex	Solvent	10^{-3} σ/cm^{-1} (log ε/dm^3 mol^{-1} cm^{-1})
cis-**1b**	MeCN	30.4 (sh) (3.10), 38.9 (sh) (4.24), 42.0 (sh) (4.43), 43.77 (4.46)
trans-**1b**	MeCN	25.26 (2.66), 32.32 (3.82), 41.67 (4.56), 46.57 (4.32)
cis-**2b**	MeCN	30.9 (sh) (3.06), 37.0 (sh) (3.90), 43.62 (4.45)
trans-**2b**	MeCN	25.79 (2.43), 32.40 (3.79), 43.10 (4.61), 46.6 (sh) (4.59)
trans-**2d**[b]	MeOH	25.9 (2.42), 32.6 (3.78), 43.0 (4.61), 46 (sh) (4.4)
cis-[CoCl$_2$(dmpp)$_2$]ClO$_4$[c]	MeOH	19.5 (sh) (2.5), 21.01 (2.62), 25.0 (sh) (3.1)
trans-[CoCl$_2$(dmpp)$_2$]ClO$_4$[c]	MeOH	16.66 (2.19), 26.50 (3.50), 33.50 (4.34), 40.30 (4.06)
cis-[CoCl$_2$(dmpe)$_2$]ClO$_4$[c]	MeOH	19.7 (sh) (2.5), 22.30 (2.69), 26.60 (3.06)
trans-[CoCl$_2$(dmpe)$_2$]ClO$_4$[c]	MeOH	17.30 (1.92), 26.10 (3.70), 35.40 (4.35), 40.50 (4.16)
cis-**3b**[d]	MeOH	28.5 (sh) (3.25), 34.7 (4.27), 40.3 (4.41), 47 (sh) (4.1)
trans-**3d**[d]	MeOH	23.9 (2.56), 32 (sh) (4.0), 36.5 (4.52), 44.3 (4.18)
cis-[CoCl$_2$(dmap)$_2$]ClO$_4$[e]	MeOH	17 (sh) (2.60), 18.7 (2.74), 22.5 (sh) (3.01), 27.4 (4.13), 31.9 (4.11), 35 (sh) (3.98), 40 (sh) (3.97)
trans-[CoCl$_2$(dmap)$_2$]ClO$_4$[e]	MeOH	15.7 (2.11), 25.0 (3.77), 29.6 (4.31), 39.1 (3.94)

[a] sh = Shoulder. [b] Ref. 8. [c] Ref. 1. [d] Ref. 12. [e] Ref. 15.

trans-**2d** in methanol,[8] suggesting that the difference in counter anion or solvent does not have a significant effect on the electronic spectra. The spectral data for *cis*- and *trans*-**2** are different from those reported by Butter and Chatt.[7] From our characterization by X-ray analyses combined with NMR and electronic spectroscopy, we believe that the previous characterization made by Butter and Chatt is erroneous.

The spectra of the rhodium(III) and cobalt(III) complexes[1] are similar in pattern, although all of the bands of the rhodium(III) complexes are shifted toward higher energy than those of the corresponding cobalt(III) complexes. In the spectra of *cis*-**1** and *cis*-**2**, the d–d absorption bands, which are clearly observed for the cobalt(III) complexes around 19 000–23 000 cm^{-1}, appear as an obscure shoulder at *ca.* 30 000 cm^{-1}, since the bands are overlapped by intense charge-transfer bands. Compared to the spectra of the *trans* isomers of the dmpp and dmpe complexes [Fig. 4(*b*) and ref. 1], the I_a components of the d–d bands {16 660 cm^{-1} for *trans*-[CoCl$_2$(dmpp)$_2$]ClO$_4$ and 17 300 cm^{-1} for *trans*-[CoCl$_2$(dmpe)$_2$]ClO$_4$; 25 260 cm^{-1} for *trans*-**1b** and 25 790 cm^{-1} for *trans*-**2b**} are slightly shifted toward lower energy in the dmpp complexes than those in the dmpe complexes for both cobalt(III) and rhodium(III). The dmpp ligand gives a weaker ligand field than dmpe, corresponding with the longer Rh–P bond lengths in *trans*-**1b** than those in *trans*-**2d**. Comparison of the I_a component of the first d–d band between dmpp and dmap complexes (Table 3) shows a clear difference: the dmap complex gives its component at lower energy than the dmpp complex does. Therefore, the spectrochemical series for the ligands can be determined as dmpe > dmpp $\gg$ dmap.[16] It is noteworthy that the order is different from that of the *trans* influence for these ligands: dmpp $\geqslant$ dmpe $\gg$ dmap.

There are three charge-transfer bands for the *trans* isomers of [MCl$_2$L$_2$]$^+$ [M = Co^{III} or Rh^{III}, L = dmpp, dmpe or dmap, Fig. 4(*b*) and Table 3]. The second charge-transfer bands of the dmpe complexes of both Co^{III} and Rh^{III} are slightly more blue-shifted than those of the corresponding dmpp complexes, while the bands of the dmap complexes are relatively red-shifted. On the other hand, the other two charge-transfer bands remain unshifted when the ligand is changed from dmpp to dmpe or dmap. Thus, the second bands can be assigned to the M(Rh^{III} or Co^{III})–(P or As) charge-transfer band, and the other two bands to M–Cl charge-transfer bands. The assignment is consistent with previous studies.[1,8,12,15] In contrast, assignments of charge-transfer bands for the *cis* isomers [Fig. 4(*a*)] are unclear, since the effects of mutually *trans* ligands in the complexes are averaged owing to the lower symmetry.

The rhodium(III) complexes prepared in this study are stable in acetonitrile in the dark even at elevated temperatures (50 °C), while *cis*-[CoCl$_2$L$_2$]$^+$ (L = dmpp or dmpe) isomerizes rapidly to the *trans* isomer.[1] When an acetonitrile solution of *cis*-**2** is irradiated with visible light the absorption spectrum gradually changes as shown in Fig. 5. Three isosbestic points are found at 370, 342 and 293 nm, and the final spectrum is identical with that of *trans*-**2**. This observation indicates that the *cis* isomer isomerizes to the *trans* isomer, and no reverse reaction occurs. In contrast, *cis*-**1** is stable on irradiation with visible light, the spectrum being unchanged after 2 weeks under the conditions where *cis*-**1** isomerizes completely within 2 h. The stability of *cis*-**1** to isomerization is rather unexpected, since in the case of cobalt(III) complexes the corresponding dmpp complex isomerizes (thermally[1] and photochemically[2]) more rapidly than the dmpe complex. The reason for the extreme stability of *cis*-**1** towards photoisomerization and the mechanism of the isomerization are unknown at present. We can conclude that the photoisomerization reaction causes some difficulties in the preparation and isolation of the *cis*-**2** complex.

Experimental

Phosphine ligands were handled under an atmosphere of argon until they formed air-stable rhodium(III) complexes. All solvents used were bubbled with argon for 20 min immediately before use. The ligand dmpe was purchased from Aldrich, and dmpp was prepared according to the literature.[17] The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded at 23 °C on a JEOL GX400 (at 399.8, 100.5 and 161.9 MHz, respectively) spectrometer. Tetramethylsilane was used as an internal reference for ^{1}H and ^{13}C NMR, and 85% H$_3$PO$_4$ as an external reference for ^{31}P NMR spectra. Infrared spectra were obtained on a Perkin-Elmer System 2000 FT-IR spectrophotometer by the Nujol mull method using polyethylene film. Electronic spectra were measured at room temperature on a Hitachi U-3410 spectrophotometer. Qualitative irradiation with visible light was performed with a tungsten light (Ushio, model UI-501C) and Pyrex-glass filter.

CAUTION.—The perchlorate salts of rhodium(III)–phosphine complexes are potentially explosive and should be handled carefully.

Complex Preparation.—trans-*Dichlorotetrakis(pyridine)-rhodium*(III) *chloride pentahydrate*. The complex was prepared by a modification of the literature procedure.[18] Pyridine (12 cm^3) was added with stirring to an aqueous solution (62 cm^3) of RhCl$_3$·3H$_2$O (8.40 g, 31.9 mmol), and the mixture refluxed for 5 h. The mixture was allowed to cool in a refrigerator overnight, and the resulting yellow precipitate filtered off, washed with ice-cold water (60 cm^3) and dried *in vacuo*. The crude precipitate was recrystallized from boiling water (250 cm^3), giving yellow plate crystals of *trans*-[RhCl$_2$(py)$_4$]Cl·5H$_2$O. The crystals were collected by filtration and dried in air (15.18 g, 77.3%) (Found: C, 38.10; H, 5.05; N, 8.90. C$_{20}$H$_{30}$Cl$_3$N$_4$O$_5$Rh requires C, 39.00; H, 4.90; N, 9.10%).

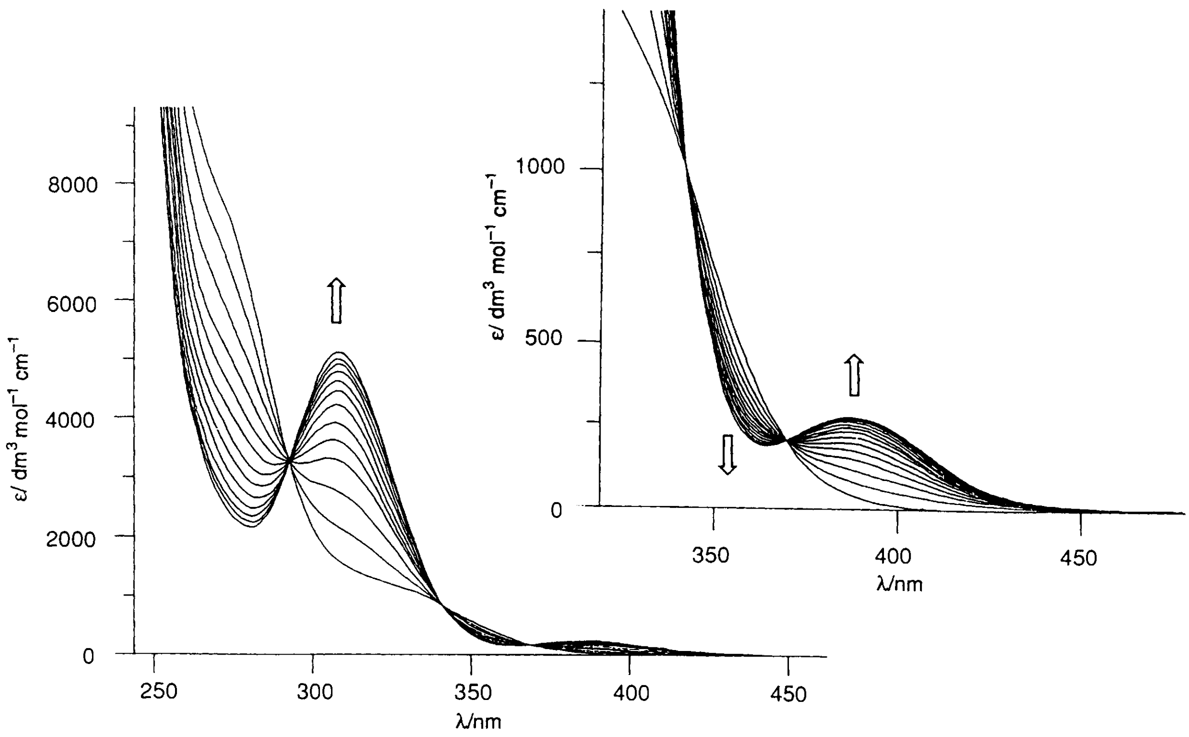

Fig. 5 Change in electronic spectrum of *cis*-**2b** in acetonitrile on irradiation with visible light (the result is qualitative)

cis- *and* trans-*Bis*[1,3-*bis*(*dimethylphosphino*)*propane*]*dichlororhodium*(III) *hexafluorophosphate*, *cis- and trans*-**1b**. A solution of dmpp (0.62 g, 3.78 mmol) in acetonitrile (2 cm^3) was added dropwise with stirring to a yellow suspension of *trans*-[RhCl$_2$(py)$_4$]Cl·5H$_2$O (1.06 g, 1.71 mmol) in acetonitrile (5 cm^3), and the mixture refluxed for 7 h. After cooling to room temperature, the resulting white precipitate was filtered off, washed twice with acetonitrile (2 cm^3) and diethyl ether (30 cm^3), and dried *in vacuo*. The crude product (*cis*-**1a**) was dissolved in methanol (10 cm^3), undissolved impurities removed by filtration, and a saturated methanol solution of NH$_4$PF$_6$ (1 cm^3) added with stirring. The colourless microcrystals obtained were filtered off and recrystallized from hot methanol to give colourless *crystals* of *cis*-**1b**. Further crystals were obtained from the filtrate of the reaction mixture and the acetonitrile washings of the crude precipitate. They were combined and evaporated under reduced pressure, giving a yellow oily residue. The residue was washed twice with diethyl ether (30 cm^3) and dissolved in methanol (4 cm^3). To the filtered solution was added a saturated methanol solution of NH$_4$PF$_6$ (1 cm^3) with stirring. Pale yellow precipitates of a mixture of *cis*- and *trans*-**1b** were formed, which were collected by filtration and dried *in vacuo*. The precipitates were mixed with hot methanol (60 °C, 40 cm^3) to extract *cis*-**1b**. Yellow *trans*-**1b** remained in the undissolved residue. The extract was allowed to stand in a refrigerator for 2 d, giving colourless crystals of *cis*-**1b** (total 589 mg, 53.2%) (Found: C, 25.90; H, 5.25. C$_{14}$H$_{36}$Cl$_2$F$_6$P$_5$Rh requires C, 26.00; H, 5.60%). $\tilde{\nu}_{max}$/cm^{-1} (Nujol): 671m, 647s, 639vs, 558vs, 395vs, 345m, 314m, 295s, 273s, 244s and 213m. A suitable crystal for X-ray analysis was obtained by recrystallization from methanol.

The *trans*-**1b** complex, which remained as an undissolved precipitate after extraction of *cis*-**1b**, was recrystallized from acetonitrile–water (*ca.* 15 cm^3, 1:1 v/v) to form yellow prismatic *crystals* (60 mg, 5.4%) (Found: C, 25.90; H, 5.20. C$_{14}$H$_{36}$Cl$_2$F$_6$P$_5$Rh requires C, 26.00; H, 5.60%). $\tilde{\nu}_{max}$/cm^{-1} (Nujol): 666s, 653m, 557vs, 514vs, 359vs, 352s, 279w and 250vs. The crystals were suitable for X-ray analysis.

A similar reaction using RhCl$_3$·3H$_2$O instead of *trans*-[RhCl$_2$(py)$_4$]Cl·5H$_2$O, which needed a longer reaction time (24 h), gave a lower yield of *cis*-**1b** (30.5%) and a higher one of *trans*-**1b** (24.7%).

Chromatographic separation of cis- and trans-**1**. The aqueous (50 cm^3) solution of a mixture of *cis*- and *trans*-**1a** in the above preparation was applied to a column (3 cm × 20 cm) of SP-Sephadex C-25 (Na$^+$ form), and the adsorbed product was eluted with 0.05 mol dm^{-3} aqueous NaCl solution. Two bands were observed: a faster moving yellow band of *trans*-**1a** and a slower moving ivory band of *cis*-**1a**. Each eluate was evaporated to dryness under reduced pressure and the residue extracted with ethanol (*ca.* 50 cm^3). The extract was evaporated to dryness under reduced pressure and the residue dissolved in methanol (10 cm^3). A saturated methanol solution of NH$_4$PF$_6$ (1 cm^3) was added to the solution, giving a precipitate of the PF$_6$ salt. The crude product was recrystallized by the above method to form pure colourless crystals of *cis*-**1b** or yellow ones of *trans*-**1b**.

cis-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*dichlororhodium*(III) *hexafluorophosphate and perchlorate*, *cis*-**2b** *and* -**2c**. A solution of dmpe (0.55 g, 3.67 mmol) in acetonitrile (2 cm^3) was added dropwise with stirring to a suspension of *trans*-[RhCl$_2$(py)$_4$]Cl·5H$_2$O (802 mg, 1.30 mmol) in acetonitrile (10 cm^3), and the mixture refluxed for 1 h. After cooling in an ice bath for 30 min, the resulting pale yellow precipitate was filtered off, washed with acetonitrile (5 cm^3 × 2) and diethyl ether (50 cm^3), and then dried *in vacuo*. The crude product (*cis*-**2a**) was dissolved in methanol (5 cm^3) and undissolved impurities removed by filtration. To the filtrate was added a saturated methanol solution of NH$_4$PF$_6$ (1 cm^3) with stirring. The resulting white precipitate was filtered off and dried *in vacuo*. Recrystallization of the crude product from hot methanol (60 °C, 30 cm^3) gave colourless needle-shaped *crystals* of *cis*-**2b** (241 mg, 29.9%) (Found: C, 23.05; H, 4.90. C$_{12}$H$_{32}$Cl$_2$F$_6$P$_5$Rh requires C, 23.30; H, 5.20%). $\tilde{\nu}_{max}$/cm^{-1} (Nujol): 656s, 558vs, 455s, 363s and 257s (br).

The perchlorate salt (*cis*-**2c**) was prepared by a similar method using LiClO$_4$ instead of NH$_4$PF$_6$, and obtained as colourless prismatic crystals suitable for X-ray analysis by

Table 4 Crystallographic data for *cis*-**1b**, *trans*-**1b** and *cis*-**2c**

	cis-**1a**	*trans*-**1a**	*cis*-**2c**
Formula	$C_{14}H_{36}Cl_2F_6P_5Rh$	$C_{14}H_{36}Cl_2F_6P_5Rh$	$C_{12}H_{32}Cl_3O_4P_4Rh$
M	647.11	647.11	604.52
Crystal size/mm	0.2 × 0.2 × 0.3	0.15 × 0.15 × 0.22	0.1 × 0.1 × 0.2
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2/n$	*Pccn*
Z	2	2	8
a/Å	11.653(4)	11.561(2)	17.305(2)
b/Å	13.886(2)	9.429(3)	18.374(2)
c/Å	8.144(2)	11.649(1)	14.569(2)
α/°	93.48(2)	90	90
β/°	90.20(3)	93.273(9)	90
γ/°	81.90(2)	90	90
U/Å^3	1302.2(6)	1267.8(5)	4632.4(9)
D_c/Mg m^{-3}	1.65	1.70	1.65
$F(000)$	656	656	2336
μ(Mo-Kα)/mm^{-1}	1.21	1.24	1.36
Transmission factor	0.718–0.803	0.833–0.855	0.953–1.000
No. of observed reflections [$\lvert F_o\rvert > 5\sigma(\lvert F_o\rvert)$]	3029	2707	1688
R, R' *	0.050, 0.060	0.041, 0.052	0.062, 0.062

* $R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$. $R' = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}$ [$w^{-1} = \sigma^2(\lvert F_o\rvert) + (0.015\lvert F_o\rvert)^2$].

Table 5 Fractional atomic coordinates for *cis*-[$RhCl_2(dmpp)_2$]PF_6 *cis*-**1b**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Rh	0.731 36(6)	0.756 61(5)	0.875 95(7)
Cl(1)	0.652 7(2)	0.889 3(2)	1.067 5(3)
Cl(2)	0.778 7(2)	0.661 9(2)	1.115 3(3)
P(1)	0.795 9(2)	0.621 5(2)	0.706 0(3)
P(2)	0.537 0(2)	0.720 8(2)	0.883 1(3)
P(3)	0.920 0(2)	0.798 4(2)	0.923 5(3)
P(4)	0.696 1(2)	0.858 7(2)	0.663 9(3)
P(5)	1.227 1(2)	0.764 1(2)	0.405 9(3)
F(1)	1.218 4(7)	0.707 3(6)	0.565 9(9)
F(2)	1.357 2(6)	0.758 6(9)	0.422(1)
F(3)	1.244 7(9)	0.670 6(5)	0.289(1)
F(4)	1.093 7(6)	0.768 7(9)	0.387(1)
F(5)	1.208(1)	0.859 0(6)	0.513(1)
F(6)	1.233 1(6)	0.820 1(5)	0.243 8(8)
C(1)	0.873(1)	0.518 6(7)	0.810(1)
C(2)	0.896(1)	0.634 8(9)	0.540(1)
C(3)	0.686(1)	0.561 2(7)	0.594(1)
C(4)	0.586(1)	0.539 4(8)	0.701(1)
C(5)	0.494 9(9)	0.626 4(8)	0.733(2)
C(6)	0.420(1)	0.821(1)	0.862(2)
C(7)	0.506(1)	0.677(1)	0.080(2)
C(8)	0.922(1)	0.878(1)	0.109(1)
C(9)	1.038(1)	0.700 9(9)	0.955(2)
C(10)	0.987(1)	0.863 5(9)	0.769(2)
C(11)	0.905(1)	0.941 7(8)	0.688(1)
C(12)	0.824 0(9)	0.897 5(7)	0.568(1)
C(13)	0.621(1)	0.815 4(9)	0.486(1)
C(14)	0.608(1)	0.977 1(8)	0.718(2)

recrystallization from methanol. Since the perchlorate salt is highly explosive elemental analysis and IR measurement were not performed.

trans-*Bis*[1,2-bis(*dimethylphosphino*)*ethane*]*dichlororhodium*(III) *hexafluorophosphate*, *trans*-**2b**. In the above preparation the filtrate and acetonitrile washings contained a mixture of *cis*- and *trans*-**2a**. The filtrate and washings were combined and evaporated to dryness under reduced pressure. The resulting yellow solid was washed with diethyl ether (50 cm^3 × 2) and dissolved in methanol (10 cm^3). To the filtered solution was added a saturated methanol solution of NH_4PF_6 (2 cm^3) with stirring; the resulting yellow precipitates were filtered off and dried *in vacuo*. The crude products were recrystallized from methanol, giving a mixture of colourless needle-shaped crystals of *cis*-**2b** and yellow prisms of *trans*-**2b** (the mixture 384 mg, 47.7%). By successive recrystallization of the mixture from methanol in the dark it was possible to separate the isomers, but the loss of the *cis* isomer during recrystallization was relatively large, owing to a small difference in solubility of the isomers. When the successive recrystallization was performed under visible light, pure yellow crystals of *trans*-**2b** were formed nearly quantitatively.

For isolation of *trans*-**2b**, cation-exchange column chromatography was effective. A mixture of *cis*- and *trans*-**2a** which was obtained in the above preparation, was dissolved in water (200 cm^3), and undissolved impurities filtered off. The filtrate was applied to a column (3 cm × 20 cm) of SP-Sephadex C-25 (Na^+ form), and the adsorbed product was eluted with 0.05 mol dm^{-3} aqueous NaCl solution. Only one yellow band was eluted, similar to the observation by Simonsen *et al.*[8] The eluate was evaporated to dryness under reduced pressure, and the residue was extracted with ethanol (*ca.* 50 cm^3). The extract was evaporated to dryness under reduced pressure, and the residue dissolved in methanol (10 cm^3). A saturated methanol solution of NH_4PF_6 was added to the solution giving a yellow precipitate. The crude product was recrystallized from a mixture of water–acetonitrile (30 cm^3, 3 : 1 v/v), giving yellow prismatic *crystals* of *trans*-**2b** (Found: C, 23.20; H, 4.85. $C_{12}H_{32}Cl_2F_6P_5Rh$ requires C, 23.30; H, 5.20%). $\tilde{\nu}_{max}$/cm^{-1} (Nujol): 652s, 557vs, 452s, 362s, 309s, 289m, 262vs and 234m.

X-Ray Analysis.—The X-ray intensities were measured at 23 °C with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) on an automated Rigaku four-circle diffractometer AFC-5 or AFC-5R. The θ–2θ scan technique was employed. Final lattice parameters were determined by least-squares treatment using setting angles of 25 reflections in the range $20 \leqslant 2\theta \leqslant 30°$. Three standard reflections were monitored every 150 reflections and showed no serious decomposition [$\lvert F_o\rvert/(\lvert F_o\rvert)_{initial} > 97\%$]. The intensities were corrected for Lorentz and polarization effects, and absorption corrections were made by either the Gauss numerical integration method[19] (*cis*- and *trans*-**1b**) or the empirical ψ-scan method[20] (*cis*-**2c**). Crystal data are summarized in Table 4.

The structures were solved by the usual heavy-atom method. The space group of *cis*-**2c** was uniquely determined as *Pccn* by systematic absences, and those of *cis*- and *trans*-**1b** were assumed as centrosymmetric groups, $P\bar{1}$ and $P2/n$, respectively, the assumption resulting in a reasonable solution. In *trans*-**1b**, the rhodium atom and the P(3), F(1) and F(2) atoms of the hexafluorophosphate anion were located on a crystallographic

Table 6 Fractional atomic coordinates for *trans*-[$RhCl_2(dmpp)_2$]PF_6 *trans*-**1b**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Rh	0.25	0.018 73(4)	0.75
Cl	0.045 65(9)	0.018 4(1)	0.733 6(1)
P(1)	0.242 7(1)	0.192 9(1)	0.603 87(9)
P(2)	0.265 6(1)	−0.155 4(1)	0.605 67(9)
P(3)	−0.25	0.484 5(3)	0.75
F(1)	−0.25	0.642 8(8)	0.75
F(2)	−0.25	0.326 5(8)	0.75
F(3)	−0.275(1)	0.482 6(7)	0.624 6(5)
F(4)	−0.134(1)	0.485(1)	0.724(2)
C(1)	0.377 6(5)	0.276 4(7)	0.568 5(6)
C(2)	0.143 5(5)	0.340 4(6)	0.624 7(5)
C(3)	0.181 5(5)	0.121 2(6)	0.468 2(4)
C(4)	0.260 6(5)	0.020 1(6)	0.404 9(4)
C(5)	0.333 4(4)	−0.084 5(6)	0.480 3(4)
C(6)	0.132 9(5)	−0.239 2(6)	0.547 3(6)
C(7)	0.362 6(5)	−0.303 1(6)	0.642 4(5)

Table 7 Fractional atomic coordinates for *cis*-[$RhCl_2(dmpe)_2$]ClO_4 *cis*-**2c**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Rh	0.466 69(8)	0.356 71(6)	0.790 70(9)
Cl(1)	0.491 7(3)	0.372 5(3)	0.951 5(3)
Cl(2)	0.422 4(3)	0.234 0(2)	0.826 2(4)
Cl(3)	0.296 0(4)	0.563 6(3)	0.519 8(4)
P(1)	0.452 7(3)	0.328 0(3)	0.638 3(4)
P(2)	0.591 5(3)	0.308 0(3)	0.773 5(4)
P(3)	0.340 5(3)	0.397 5(3)	0.815 6(4)
P(4)	0.498 6(3)	0.477 2(2)	0.782 5(3)
O(1)	0.328(1)	0.531(1)	0.444(1)
O(2)	0.253(1)	0.619(1)	0.492(1)
O(3)	0.349(2)	0.587(1)	0.578(2)
O(4)	0.257(2)	0.511(1)	0.563(2)
C(1)	0.382(2)	0.258(2)	0.610(2)
C(2)	0.439(3)	0.393(2)	0.548(2)
C(3)	0.548(2)	0.285(2)	0.600(3)
C(4)	0.584(2)	0.248(2)	0.674(2)
C(5)	0.675(1)	0.363(2)	0.752(2)
C(6)	0.623(2)	0.248(2)	0.865(3)
C(7)	0.300(1)	0.371(1)	0.927(2)
C(8)	0.262(2)	0.376(2)	0.741(3)
C(9)	0.342(2)	0.495(1)	0.812(2)
C(10)	0.418(2)	0.525(1)	0.837(2)
C(11)	0.514(2)	0.524(1)	0.676(2)
C(12)	0.580(2)	0.509(2)	0.847(2)

two-fold axis, and therefore, an asymmetric part contains half of the complex cation and half of the hexafluorophosphate anion. All hydrogen atoms, which were located either by Fourier-difference syntheses or theoretical calculations, are included in the structural calculation. The function, $\Sigma w||F_o| - |F_c||^2$, with $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$ was minimized by a full-matrix method using anisotropic and isotropic thermal parameters for all non-hydrogen and hydrogen atoms, respectively. Complex neutral-atom scattering factors[21] were used. Final Fourier-difference syntheses were featureless. All the calculations were carried out on a Fujitsu IX-4 workstation using the Xtal3.2 software package.[22] The atomic parameters of *cis*-**1b**, *trans*-**1b** and *cis*-**2c** are listed in Tables 5–7, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 06453048 from the Ministry of Education, Science and Culture.

References

1 T. Ohishi, K. Kashiwabara and J. Fujita, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 575.
2 K. Oguni, T. Ohishi, M. Kita, K. Kashiwabara and J. Fujita, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 588.
3 M. Kita, A. Okuyama, K. Kashiwabara and J. Fujita, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1994.
4 T. Ohishi, K. Kashiwabara, J. Fujita, S. Ohba, T. Ishii and Y. Saito, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 385.
5 F. H. Jardine and P. S. Sheridan, *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 4, ch. 48.
6 H. A. Mayer and W. C. Kaska, *Chem. Rev.*, 1994, **94**, 1239.
7 S. A. Butter and J. Chatt, *J. Chem. Soc. A*, 1970, 1411.
8 K. P. Simonsen, N. Suzuki, M. Hamada, M. Kojima, S. Ohba, Y. Saito and J. Fujita, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 3790.
9 T. B. Marder, W. C. Fultz, J. C. Calabrese, R. L. Harlow and D. Milstein, *J. Chem. Soc., Chem. Commun.*, 1987, 1543.
10 A. P. Ginsberg, W. E. Lindsell, C. R. Sprinkle, K. W. West and R. L. Cohen, *Inorg. Chem.*, 1982, **21**, 3666.
11 *Dictionary of Inorganic Compounds*, eds. J. Macintyre, F. M. Daniel and V. H. Spirling, Chapman and Hall, London, 1992.
12 K. Simonsen, M. Hamada, N. Suzuki, M. Kojima, S. Ohba, F. Galsbøl, Y. Saito and J. Fujita, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 2904.
13 T. Suzuki, unpublished work.
14 P. E. Garrou, *Chem. Rev.*, 1981, **81**, 229.
15 K. Iwata, M. Kojima and J. Fujita, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 3003.
16 Y. Shimura, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 693.
17 J. C. Cloyd, jun., and D. W. Meek, *Inorg. Chem.*, 1972, **6**, 480.
18 R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1964, 1224, and refs. therein.
19 W. R. Busing and H. A. Levy, *Acta Crystallogr.*, 1957, **10**, 180.
20 K. Watenpaugh and J. Stewart, ABSCAL, Scale Diffractometer Intensity Data in Xtal3.2 Programme System (ref. 22).
21 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
22 S. R. Hall, H. D. Flack and J. M. Stewart, Xtal3.2, Programme for Crystal Structure Analysis, Universities of Western Australia, Geneva and Maryland, 1992.

Received 18*th May* 1995; *Paper* 5/03178H