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Preparation, crystal structures and spectroscopic properties of novel $[M^{III}Cl_{3-n}(P)_{3+n}]^{n+}$ (M = Co, Rh; n = 0, 1, 2 or 3) series of complexes containing tripodal tridentate phosphine, 1,1,1-tris(dimethylphosphinomethyl)ethane

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Abstract

Cobalt(III) and rhodium(III) complexes of the series of $[M^{III}Cl_{3-n}(P)_{3+n}]^{n+}$ (M = Co or Rh; n = 0, 1, 2 or 3) have been prepared with the use of 1,1,1-tris(dimethylphosphinomethyl)ethane (tdmme) and mono- or didentate phosphines. The single-crystal X-ray analyses of both series of complexes revealed that the M–P and M–Cl bond lengths were dependent primarily on the strong *trans* influence of the phosphines, and secondarily on the steric congestion around the metal center resulting from the coordination of several phosphine groups. In fact, the M–P(tdmme) bonds became longer in the order of [MCl₃(tdmme)] < [MCl₂(tdmme)-(PMe₃)]⁺ < [MCl(tdmme)(dmpe)]²⁺ (dmpe = 1,2-bis(dimethylphosphino)ethane) < [M(tdmme)₂]³⁺ for both Co^{III} and Rh^{III} series of complexes, while the M–Cl bond lengths were shortened in this order (except for [M(tdmme)₂]³⁺). Such a steric congestion around the metal center can also account for the structural and spectroscopic characteristics of the series of complexes, [MCl(tdmme)(dmpm)]²⁺ (dmpm = bis(dimethylphosphino)methane, dmpp = 1,3-bis(dimethylphosphino)propane). The X-ray analysis for [CoCl(tdmme)(dmpm or dmpe)](BF₄)₂ showed that all Co–P bonds in the dmpm complex were shorter by 0.03–0.04 Å than those in the dmpe complex. Furthermore, the first d–d transition energy of the Co^{III} complexes and the ¹J_{Rh-P(tdmme)} coupling constants observed for the Rh^{III} complexes indicated an unusual order in the coordination bond strengths of the didentate diphosphines, i.e., dmpm > dmpe > dmpp.

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1. Introduction

In relation to the efficient catalytic abilities of rhodium-phosphine complexes for, e.g., (asymmetric) hydrogenation or hydroformylation of alkenes, not only the coordinatively unsaturated rhodium(I) complexes but also the octahedral 18-electron rhodium(III)-phosphine complexes have been investigated extensively [1]. However, there have been surprisingly few studies on the rhodium(III) complexes containing more than four phosphino donor groups. For instance, tris(didentate diphosphine)rhodium(III) complexes, [Rh(dmpm or dmpe)₃]³⁺ (dmpm = Me₂PCH₂PMe₂; dmpe = Me₂PCH₂-CH₂PMe₂), have recently been reported for the first time as [Rh^{III}(P)₆]³⁺-type complexes [2], although their

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crystal structures have not yet been determined. For the analogous $[Co^{III}(P)_{6]}^{3+}$ -type complexes, $[Co(dmpe \text{ or } o-Me_2PC_6H_4PMe_2)_3]^{3+}$ and $[Co(tdmme)_2]^{3+}$ {tdmme = MeC(CH₂PMe₂)₃} have been prepared [3–5], and the crystal structure of $[Co(tdmme)_2][Co(CN)_6]$. nH_2O has been analyzed by X-ray [5].¹ The cyclotriphosphate (P₃³⁻) or cyclothiadiphosphate (P₂S²⁻) complexes of $[M^{III}(tdpme)(\eta^3-P_3 \text{ or } \eta^3-P_2S)]^{(0 \text{ or } +)}$ {M = Co, Rh; tdpme = MeC(CH₂PPh₂)₃} [6] and a few other $[M^{III}(P)_6]^{n+}$ -type complexes prepared by oxidative addition of white phosphorus (P₄) [7] have also been described, but there have been no studies concerning the $[M^{III}Cl(P)_5]^{2+}$ -type complexes to our best knowledge.

Since most of the phosphines used in the preparation of their metal complexes have bulky substituents on P atom(s), the steric congestion arising from their substituents might become severe to prevent aggregation of more than four phosphino donor groups on a metal center. However, we expected from our previous studies [5,8,9] that "M^{III}(tdmme)" fragment should be a good candidate for preparation of the series of complexes, such as [M^{III}Cl₃(tdmme)], [M^{III}Cl₂(tdmme)- (P)]⁺, $[M^{III}Cl(tdmme)(P-P)]^{2+}$, and $[M^{III}(tdmme)_2]^{3+}$, because the dimethyl-substituted tripodal tridentate phosphine, tdmme, is sterically as compact as to incorporate some other phosphine donors in the metal coordination sphere. In this article, we deal with the preparation, crystal structures, and spectroscopic properties of the above mentioned series of Rh^{III} and Co^{III} complexes (Scheme 1), through the reactions of [MCl₃(tdmme)] and either a monodentate P-ligand {PMe_nPh_{3-n} or P(OMe)_nPh_{3-n}}, a didentate diphosphine {dmpm, dmpe or dmpp (=Me₂PCH₂CH₂CH₂-PMe₂)}, or a tripodal triphosphine (tdmme).

2. Experimental

2.1. Materials and spectroscopic measurements

The phosphines, tdmme [10] and dmpp [11], were prepared according to the literature methods, and the other P-ligands were purchased from Aldrich or Strem Chemicals, Inc. The complexes, [CoCl₃(tdmme)] (1) [5] and $[RhX_3(tdmme)] \{X = Cl (2), Br (2') \text{ or } I (2'')\} [9], were$ prepared by the methods described previously. All reactions involving free P-ligands were handled under a dinitrogen atmosphere using Schlenk techniques. All of the solvents used for the preparation of phosphines and their complexes were deaerated with dinitrogen for 20 min immediately before use. The ${}^{1}H$, ${}^{13}C{}^{1}H$, ${}^{31}P{}^{1}H$ and ${}^{59}Co{}^{1}H$ NMR spectra were recorded at 30 °C on a JEOL GSX-400, EX270, or Lambda 500 spectrometer using tetramethylsilane as an internal reference for ¹H and ¹³C and 85% H₃PO₄ as an external reference for ³¹P NMR spectra. The ⁵⁹Co NMR chemical shifts were reported in reference to the signal of $K_3[Co(CN)_6]$ in D₂O. The UV-vis absorption spectra were recorded on a Perkin-Elmer Lambda 19 spectrophotometer at ambient temperature.

2.2. Preparation of complexes

2.2.1. $[MCl_2(tdmme)(P)]BF_4$ (M = Co or Rh)

To a suspension of $[CoCl_3(tdmme)]$ (1; 462 mg, 1.16 mmol) in methanol (5 cm³) was added a toluene solution of PMe₃ (1.0 M, 1.0 cm³) dropwise with stirring. The mixture was stirred at ambient temperature for 30 min and filtered to remove unreacted Co^{III} complex. To the red orange filtrate was added a methanol solution (2 cm³) of LiBF₄ (284 mg, 3.03 mmol); an orange precipitate formed was collected by filtration. The crude product was recrystallized from hot methanol to deposit red plate crystals of $[CoCl_2(tdmme)(PMe_3)]BF_4$ (3). Yield: 446 mg (70% based on Co). *Anal.* Calc. for C₁₄H₃₆BCl₂CoF₄P₄: C, 30.86; H, 6.66. Found: C, 30.79; H, 6.57%. The following Co^{III} and Rh^{III}

¹ The revision of the X-ray analysis for this compound has previously been reported briefly in [21]; CCDC deposition No. 176058.

complexes were prepared by a similar method, using (a methanol solution of) the respective P-ligand instead of a toluene solution of PMe₃ and/or [RhCl₃(tdmme)] (2) instead of 1. $[CoCl_2(tdmme)] P(OMe)_3$ BF₄ (4): red microcrystalline solid. Yield: 50%. Anal. Calc. for C₁₄H₃₆BCl₂CoF₄O₃P₄: C, 28.36; H, 6.12. Found: C, 28.37; H, 6.05%. [CoCl₂(tdmme)(PMe₂Ph)]BF₄ (5): red-purple prismatic crystals. Yield: 77%. Anal. Calc. for C₁₉H₃₈BCl₂CoF₄P₄: C, 37.59; H, 6.31. Found: C, 37.46; H, 6.29%. [RhCl₂(tdmme)(PMe₃)]BF₄ (6): colorless prismatic crystals. Yield: 71%. Anal. Calc. for C₁₄H₃₆BCl₂F₄P₄Rh: C, 28.55; H, 6.16. Found: C, 28.56; H, 6.09%. [RhCl₂(tdmme){ $P(OMe)_3$ }]BF₄ (7): colorless microcrystalline solid. Yield: 55%. Anal. Calc. for C₁₄H₃₆BCl₂F₄O₃P₄Rh: C, 26.40; H, 5.70. Found: C, 26.58; H, 5.59%. [RhCl₂(tdmme)(PMe₂Ph)]BF₄ (8): colorless prismatic crystals. Yield: 62%. Anal. Calc. for $C_{19}H_{38}BCl_2F_4P_4Rh$: C, 34.57; H, 5.96. Found: C, 34.58; H, 6.00%. [RhCl₂(tdmme){P(OMe)₂Ph}]BF₄ (9): colorless microcrystalline solid. Yield: 71%. Anal. Calc. for C₁₉H₃₈BCl₂F₄O₂P₄Rh: C, 33.41; H, 5.61. Found: C, 33.22; H, 5.58%.

2.2.2. $[CoCl(tdmme)(P-P)](BF_4)_2$

To a red suspension of 1 (614 mg, 1.47 mmol) in methanol (10 cm³) was added dmpm (200 mg, 1.47 mmol) dropwise with stirring. The mixture turned immediately to a clear red orange solution. After stirring at room temperature for 4 h, the solution was evaporated to dryness under reduced pressure. The residue was vigorously washed with diethyl ether (50 cm^3) and dissolved in a minimum amount of methanol. To the filtered solution was added a methanol solution of LiBF₄ (750 mg, 8.00 mmol) with stirring. The resulting orange yellow precipitate was collected by filtration. The crude product was recrystallized by diffusion of dichloromethane vapor into an acetonitrile solution, affording orange prismatic crystals of $[CoCl(tdmme)(dmpm)](BF_4)_2$. H₂O (10 · H₂O). Yield: 849 mg (88%). Anal. Calc. for C₁₆H₄₃B₂ClCoF₈OP₅: C, 28.50; H, 6.43. Found: C, 28.54; H, 6.36%. The corresponding dmpe and dmpp complexes were prepared by an analogous method described above. $[CoCl(tdmme)(dmpe)](BF_4)_2 \cdot CH_3CN$ (11 · AN): orange prismatic crystals. Yield: 70%. Anal. Calc. for $C_{19}H_{46}B_2ClCoF_8NP_5$: C, 32.08; H, 6.52; N, 1.97. Found: C, 31.56; H, 6.49; N, 1.44%. [CoCl(tdmme)(dmpp)](BF₄)₂ · CH₃CN (12 · AN): orange needle crystals. Yield: 57%. Anal. Calc. for C₂₀H₄₈B₂-ClCoF₈NP₅: C, 33.11; H, 6.67; N, 1.93. Found: C, 32.84; H, 6.62; N, 2.20%.

2.2.3. $[RhCl(tdmme)(dmpm)](BF_4)_2$

A mixture of complex 2 (678 mg, 1.45 mmol) and dmpm (200 mg, 1.47 mmol) in methanol (10 cm³) was refluxed for 20 h, affording a clear pale yellow solution. After cooling to room temperature, the solution was

evaporated to dryness under reduced pressure. The residue was vigorously washed with diethyl ether (50 cm³) and extracted with a minimum amount of methanol. A methanol solution of LiBF₄ (750 mg, 8.00 mmol) was added with stirring to the extract to give a white precipitate. The crude product was recrystallized by diffusion of dichloromethane vapor into an acetonitrile solution, depositing colorless microcrystalline solids of [RhCl(tdmme)(dmpm)](BF₄)₂ (**13**). Yield: 80%. *Anal.* Calc. for C₁₆H₄₁B₂ClF₈P₅Rh: C, 27.44; H, 5.90. Found: C, 27.44; H, 5.87%.

2.2.4. $[Rh(Cl \text{ or } Br)(tdmme)(dmpe \text{ or } dmpp)](BF_4)_2$

These complexes were prepared by a similar method that for complex 13 using dmpe or dmpp to and/or [RhBr₃(tdmme)] (2'). [RhCl(tdmme)(dmpe)]- $(BF_4)_2 \cdot CH_3CN$ (14 · AN): colorless prismatic crystals. Yield: 82%. Anal. Calc. for $C_{19}H_{46}B_2ClF_8NP_5Rh$: C, 30.21; H, 6.14, N, 1.85. Found: C, 29.91; H, 6.04; N, 1.84%. [RhCl(tdmme)(dmpp)](BF₄)₂ · CH₃CN (15 · AN): colorless needle crystals. Yield: 74%. Anal. Calc. for C₂₀H₄₈B₂ClCoF₈NP₅Rh: C, 31.10; H, 6.26; N, 1.81. Found: C, 30.97; H, 6.29; N, 1.74%. [RhBr(tdmme)(dmpe)](BF₄)₂ (14'): colorless crystals. Yield: 79%. Anal. Calc. for C₁₇H₄₃B₂BrF₈P₅Rh: C, 26.16; H, 5.71. Found (after drying completely in vacuo): C, 26.16; H, 5.61%. [RhBr(tdmme)(dmpp)](BF₄)₂ (15'): colorless microcrystalline solids. Yield: 51%. Anal. Calc. for C₁₈H₄₅B₂-BrF₈P₅Rh: C, 27.98; H, 5.88. Found (after drying completely in vacuo): C, 27.98; H, 5.88%.

2.2.5. [RhI(tdmme)(dmpe or dmpp)] $I_2 \cdot H_2O$

To a methanol suspension (5 cm³) of [RhI₃(tdmme)] (258 mg, 0.351 mmol) was added a methanol (0.6 cm³) solution of dmpe (60 mg, 0.40 mmol) dropwise with stirring. The mixture was refluxed under a nitrogen atmosphere for 20 h and cooled to room temperature. The resulting yellow precipitate was collected by filtration. The crude product was recrystallized from hot methanol, affording yellow plate crystals of [RhI(tdmme)(dmpe)]-I₂ · H₂O (14" · H₂O): Yield: 51%. *Anal.* Calc. for C₁₇H₄₅I₃OP₅Rh: C, 22.59; H, 5.02. Found: C, 22.58; H, 4.91%. [RhI(tdmme)(dmpp)]I₂ · H₂O (15" · H₂O): yellow crystals. Yield: 61%. *Anal.* Calc. for C₁₈H₄₇I₃OP₅Rh: C, 23.55; H, 5.16. Found: C, 23.47; H, 5.04%.

2.2.6. $[Rh(tdmme)_2](BF_4)_3 \cdot NaBF_4(17')$

To an aqueous solution (10 cm³) of [Rh(tdmme)₂-(μ -OH)₃](BF₄)₃ [9] (542 mg, 0.496 mmol) were added tetrafluoroboric acid (42%, 311 mg, 1.487 mmol) and tdmme (250 mg, 0.991 mmol), and the mixture was refluxed for 20 h. After cooling the reaction mixture to ambient temperature, excess NaBF₄ (solid) was added with vigorous stirring, affording a white precipitate. The crude product was filtered off and recrystallized from acetonitrile/dichloromethane/diethyl ether to give colorless microcrystals. Yield: 50%. Anal. Calc. for C_{22} - $H_{54}B_4F_{16}NaP_6Rh$: C, 27.03; H, 5.57. Found: C, 27.33; H, 5.61%.

2.2.7. $[Rh(tdmme)_2][Co(CN)_6] \cdot 4H_2O(17 \cdot 4H_2O)$

Compound 17' was dissolved in water and the solution was layered on an aqueous solution of $K_3[Co(CN)_6]$. The mixture was allowed to stand at ambient temperature for several days, depositing colorless prismatic crystals in a nearly quantitative yield. *Anal.* Calc. for $C_{28}H_{54}CoN_6P_6Rh$: C, 40.89; H, 6.62; N, 10.22. Found (after drying completely in vacuo): C, 40.08; H, 6.30; N, 10.21%.

2.3. Crystallography

2.3.1. $17 \cdot 4H_2O$ and re-analysis of $16 \cdot 4H_2O$ (see footnote 1)

A colorless prismatic crystal of $17 \cdot 4H_2O$ was sealed in a glass capillary tube. The X-ray diffraction data were measured at 23(2) °C with a graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) on a Rigaku AFC-5R diffractometer. Final lattice constants were determined by the least-squares treatment using the setting angles of 25 reflections in the range of $22 \leq 2\theta \leq 30^{\circ}$. Three standard reflections were monitored every 150, showing no serious decomposition. The intensities in a (+h, +k, +l) octant up to $2\theta \leq 60^{\circ}$ were collected and absorption corrections were made by the numerical integration method [12a]. The observed independent reflections with $F_{\rm o} \ge 3\sigma(F_{\rm o})$ were used for the structural calculation. Systematic absences indicated the space group *Pmab* or $P2_1ab$ and the structure was successfully solved based on the former space group by the direct method using SHELXS-86 program [13a]. In an asymmetric unit there were two halves of Rh(tdmme)₂ and two halves of $Co(CN)_6$ moieties, as well as three and two halves of O atoms for water molecules. The Rh(A), Rh(B), Co(C), and Co(D) atoms were located at the site symmetries of 2, m., $\bar{1}$, and m., respectively. The function, $\sum w \|F_0\| - \|F_c\|^2$ with $w^{-1} = \sigma^2 (|F_0|) + (0.015|F_0|)^2$, was minimized on F using anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were not included in the calculations. All calculations were carried out on a Fujitsu IX-4 workstation using the Xtal-3.2 software package [14a].

This result for $17 \cdot 4H_2O$ prompted us to re-analyze the crystal structure of the analogous Co^{III} complex, $16 \cdot nH_2O$, because these complexes were most likely isomorphic to each other, but the Co^{III} complex was previously analyzed based on the corresponding noncentrosymmetric space group, *Pca2*₁. The diffraction data that were corrected for absorption effects were provided by Prof. S. Ohba (Keio University). We have re-analyzed the crystal structure, based on the space group of *Pcam*, by a similar method to that for $17 \cdot 4H_2O$; the number of water molecules of hydration was revised to be 4, which was consistent with the analytical data [5].

2.3.2. The others

The X-ray diffraction data of **3** and **10** · 2H₂O were measured at 23(2) °C on a Rigaku R-axis rapid imaging plate detector equipped with a graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Each crystal of **3** (red plate) or **10** · 2H₂O (yellow plate) was glued on the top of a glass fiber and used for the diffraction study. A total of 44 images with the oscillation angle of $\omega = 5^{\circ}$ were collected with two different goniometer settings ($8 \le 2\theta \le 55^{\circ}$). Data were processed by the Process-Auto program [15] and the lattice parameters were determined by the least-squares treatment using the setting angles of all observed reflections. Empirical absorption corrections were applied by the multi-scan method [12b].

For the crystals of $6 \cdot 2\text{MeOH}$, $8 \cdot \text{H}_2\text{O}$, $11 \cdot \text{AN}$, $14 \cdot \text{AN}$, and $14' \cdot \text{AN}$, the X-ray diffraction experiments were performed on a Rigaku AFC-5R diffractometer (λ (Mo K α) = 0.71073 Å) at 23(2) °C. Each crystal suitable for the X-ray study was sealed in a glass capillary tube and used for the collection of the diffraction data ($2\theta \leq 60^\circ$). Final lattice constants were determined by the least-squares treatment using the setting angles of 25 reflections in the range of $22 \leq 2\theta \leq 30^\circ$. Three standard reflections were monitored every 150 and no serious decomposition was observed except for $11 \cdot \text{AN}$, for which ($|F_0|_{\text{final}}/|F_0|_{\text{initial}} = 0.899$) a linear decay correction was made. Absorption corrections were made

Table 1

Crystal data for [Rh(tdmme)₂][Co(CN)₆] · 4H₂O (17 · 4H₂O)

	20 (11 11220)
Formula	C28H62CoN6O4P6Rh
Formula weight	894.52
T (K)	296(2)
Crystal color, shape	colorless, plate
Crystal size (mm)	$0.40 \times 0.20 \times 0.10$
Crystal system	orthorhombic
Space group	Pmab
Ζ	8
a (Å)	23.713(2)
b (Å)	31.756(4)
<i>c</i> (Å)	10.571(2)
$V(\text{\AA}^3)$	7960(3)
$D_{\rm calc} ({\rm Mg}{\rm m}^{-3})$	1.49
<i>F</i> (000)	3727
μ (Mo K α) (mm ⁻¹)	1.11
T_{\min}, T_{\max}	0.809, 0.906
Number of measured/observed ^a reflections	11885/3808
Number of parameters	480
R^{b}	0.081
R_w^{c}	0.075

^a $F_{\rm o} > 3\sigma(F_{\rm o})$.

^b $R = \sum ||F_o| - |F_c|| / \sum |F_o|.$

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

Table 2				
Crystal	data	for	comp	lexes

Complex	3	6 · 2MeOH	$\pmb{8}\cdot H_2O$	$10\cdot 2\mathrm{H_2O}$	$11 \cdot AN$	$14 \cdot AN$	14' · AN
Formula	$C_{14}H_{36}BCl_2CoF_4P_4$	$C_{16}H_{44}BCl_2F_4O_2P_4Rh$	C19H40BCl2F4OP4Rh	$C_{16}H_{45}B_2ClCoF_8O_2P_5$	C19H46B2ClCoF8NP5	C19H46B2ClF8NP5Rh	C ₁₉ H ₄₆ B ₂ BrF ₈ NP ₅ Rh
Formula weight	544.95	653.01	669.01	692.37	711.42	755.40	799.86
T (K)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)
Crystal color, shape	red, plate	colorless, plate	colorless, column	yellow, plate	orange, block	colorless, prism	colorless, prism
Crystal size (mm)	$0.40 \times 0.40 \times 0.10$	$0.50 \times 0.30 \times 0.20$	$0.46 \times 0.26 \times 0.26$	$0.10\times0.10\times0.05$	$0.40 \times 0.35 \times 0.35$	$0.40 \times 0.30 \times 0.30$	$0.50 \times 0.40 \times 0.25$
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$Pna2_1$	$P2_{1}/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_{1}/c$
Ζ	4	4	4	4	4	4	4
a (Å)	18.582(7)	12.824(2)	9.255(2)	10.234(6)	11.017(2)	11.022(3)	11.028(2)
b (Å)	11.314(5)	13.158(2)	21.597(3)	21.318(10)	17.564(2)	17.681(5)	17.532(2)
c (Å)	11.563(4)	17.402(2)	14.408(2)	13.914(6)	17.356(2)	17.449(3)	17.605(2)
β (°)	90	96.75(1)	95.38(1)	99.11(4)	108.03(1)	107.83(1)	107.190(8)
$V(Å^3)$	2431(2)	2916.0(7)	2867.1(7)	2977(2)	3193.4(7)	3237(1)	3251.7(7)
$D_{\rm calc}~({\rm Mg~m}^{-3})$	1.489	1.487	1.550	1.534	1.480	1.550	1.634
<i>F</i> (000)	1128	1344	1368	1432	1472	1544	1616
μ (Mo K α) (mm ⁻¹)	1.218	1.024	1.043	0.993	0.931	0.916	2.058
R _{int}	0.043	0.009	0.030	0.064	0.012	0.013	0.016
T_{\min}, T_{\max}	0.642, 0.888	0.628, 0.921	0.646, 0.773	0.907, 0.952	0.707, 0.737	0.711, 0.771	0.426, 0.627
Reflection/parameter ratio	5560/236	8502/274	8343/290	6848/317	9314/336	9442/336	9483/335
$R_1 [F_{\alpha}^2 > 2\sigma(F_{\alpha}^2)]$	0.033	0.041	0.044	0.063	0.047	0.041	0.041
wR_2 (all reflections)	0.077	0.123	0.191	0.196	0.131	0.112	0.116
Goodness-of-fit	0.961	1.017	1.066	1.003	1.019	1.028	1.002

either by the numerical integration method [12c] or by an empirical method based on three sets of Ψ -scan data [12d].

The data reduction and the following structural calculation were performed using the CrystalStructure software package [14b]. The structures were solved by the direct method with the siR-92 program [13b] and refined on F^2 with all independent reflections using the SHELXL-97 program [13c]. All non-hydrogen atoms were refined anisotropically, and H atoms (except for the water molecules of $10 \cdot 2H_2O$) were introduced at the theoretically calculated positions and treated with riding models.

Crystal data of $17 \cdot 4H_2O$ and the others are collected in Tables 1 and 2.

3. Results and discussion

3.1. Preparation of complexes

The [CoCl₃(tdmme)] (1) complex was obtained by a stoichiometric reaction of *trans*-[CoCl₂(py)₄]Cl and tdmme in dry pyridine at room temperature [5]. When the reaction mixture was refluxed for a while, red complex 1 disproportionated to yield yellow [Co(tdmme)₂]³⁺ and the original green *trans*-[CoCl₂(py)₄]⁺ complexes, which were successfully separated by the cation-exchange chromatography. The bis(tdmme) complex, [Co(tdmme)₂]³⁺, was also prepared quantitatively by a reaction of 1 with an equimolar tdmme in methanol, and isolated as the BF₄⁻ (16') or [Co^{III}(CN)₆]³⁻ (16) salt [5]. In contrast, the corresponding Rh^{III} complex, [RhCl₃(tdmme)] (2), was thermally stable and no disproportionation reaction was observed [9].

When (a toluene solution of) PMe₃ was added to a red suspension of complex 1 in methanol, the reaction mixture gave immediately a clear red orange solution, from which red crystals of [CoCl₂(tdmme)(PMe₃)]BF₄ (3) were isolated by addition of LiBF₄. The analogous P(OMe)₃ and PMe₂Ph complexes, [CoCl₂(tdmme)- $\{P(OMe)_3 \text{ or } PMe_2Ph\}]BF_4$ (4 or 5), were prepared in the same manner and isolated as red crystals. The corresponding Rh^{III} complexes, [RhCl₂(tdmme){PMe₃, $P(OMe)_3$, PMe_2Ph or $P(OMe)_2Ph$ BF₄ (6–9), were obtained also from the mixture of complex 2 and the respective P-ligand. The crystal structures of 3, $6 \cdot 2$ MeOH and $8 \cdot H_2$ O were determined by the X-ray analyses, which revealed the structures of the monomeric [M^{III}Cl₂(tdmme)(P)]⁺-type complex cations. The structures of the cationic part of $R\bar{h}^{III}$ complexes in $6 \cdot 2$ MeOH and $8 \cdot H_2$ O are shown in Fig. 1. On the other hand, a similar reaction of complex 1 or 2 with PPh_3 in methanol did not take place; the dissolution of trichloro complex was not observed upon addition of PPh₃ (for complex 2, even when the mixture was refluxed). With PMePh₂ or P(OMe)Ph₂, the complex 1

or **2** reacted to produce a clear (pale) yellow solution. However, it was not possible to isolate the desired complex, $[MCl_2(tdmme){PMePh_2 \text{ or } P(OMe)Ph_2}]^+$, due probably to the dissociation equilibrium of the P-ligand in solution. In fact, the ³¹P NMR spectra (in CD₃CN) of the reaction product showed resonances corresponding to the $[MCl_2(tdmme){PMePh_2 \text{ or } P(OMe)Ph_2}]^+$ and $[MCl_2(tdmme)(CD_3CN)]^+$ complexes. It should be noted that the difficulty of isolation and the probable thermal instability of the PPh₃, PMePh₂ and P(OMe)Ph₂ complexes seem to originate from the steric bulkiness of the P-ligands, being irrelevant to the electronic properties such as σ -donor/ π -acceptor abilities of the Pligands.

The reactions of complex 1 with didentate dimethylsubstituted phosphines (dmpm, dmpe or dmpp) at ambient temperature gave novel $[CoCl(P)_5]^{2+}$ -type complexes, which were isolated in high yields as yellow crystals of [CoCl(tdmme)(dmpm, dmpe or dmpp)](BF₄)₂ (10, 11 or 12). The crystal structures of $10 \cdot H_2O$ and 11 · AN were determined by the X-ray analyses, and the molecular structures of the cationic complexes, [CoCl(tdmme)(dmpm or dmpe)]²⁺, are illustrated in Fig. 2. It was shown that dmpm and dmpe ligands formed a four- and a five-membered chelated ring, respectively, in the complexes. For preparation of the analogous Rh^{III} complexes, an elevated reaction temperature was required to complete the reaction. In fact, although a mixture of complex 2 and an equimolar amount of dmpm at room temperature afforded a clear pale yellow solution, it contained several different species as confirmed by ³¹P NMR spectroscopy. However, refluxing the reaction mixture for 20 h, followed by addition of LiBF₄, afforded the colorless crystals of $[RhCl(tdmme)(dmpm)](BF_4)_2$ (13) in a nearly quantitative yield. Analogous [RhCl(tdmme)(dmpe or dmpp)]- $(BF_4)_2 \cdot CH_3CN$ (14 · AN or 15 · AN) complexes were prepared in the same manner with the respective didentate diphosphines. In addition, the corresponding bromo (14' or 15') and iodo $(14'' \cdot H_2O \text{ or } 15'' \cdot H_2O)$ complexes were synthesized from [RhBr₃(tdmme)] (2') and $[RhI_3(tdmme)]$ (2"), respectively, in high yields. The crystal structures of the dmpe complexes, $14 \cdot AN$ and $14' \cdot AN$, were also determined.

Although the formation of $[Co(tdmme)_2]^{3+}$ was thermodynamically favorable as described above, the analogous Rh^{III} complex, $[Rh(tdmme)_2]^{3+}$, was found to be less easy to synthesize because of the kinetic robustness of the Rh–Cl bond. Reaction of complex **2** with an equimolar tdmme in methanol at room temperature immediately gave a clear pale yellow solution, from which colorless needle crystals were obtained by addition of LiBF₄, followed by recrystallization from acetonitrile/ methanol. The elemental analysis of this product indicated the composition of Rh(tdmme)_2HCl(BF₄)₃(H₂O)₂ (Found: C, 27.89; H, 6.36%. C₂₂H₅₉B₃ClF₁₂O₂P₆Rh



Fig. 1. ORTEPs (30% probability level) of the cationic parts in (a) $6 \cdot 2$ MeOH and (b) $8 \cdot H_2$ O (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°) are: (a) Rh-P1 2.3454(9), Rh-P2 2.2865(9), Rh-P3 2.2721(8), Rh-P4 2.4221(10), Rh-Cl1 2.4213(9), Rh-Cl2 2.4214(9), P1-Rh-P2 87.56(3), P1-Rh-P3 88.02(3), P2-Rh-P3 87.82(3), P1-Rh-P4 169.77(3), P2-Rh-P4 102.02(3), P3-Rh-P4 95.84(3), Cl1-Rh-Cl2 87.50(4), P2-Rh-Cl1 174.61(4), P3-Rh-Cl2 176.91(3), P4-Rh-Cl1 82.51(4), P4-Rh-Cl2 86.62(3); (b) Rh-P1 2.344(1), Rh-P2 2.271(1), Rh-P3 2.282(1), Rh-P4 2.423(1), Rh-Cl1 2.417(1), Rh-Cl2 2.441(1), P1-Rh-P2 87.89(5), P1-Rh-P3 88.20(4), P2-Rh-P3 86.66(4), P1-Rh-P4 167.70(4), P2-Rh-P4 97.67(4), P3-Rh-P4 97.67(4), Cl1-Rh-Cl2 89.94(5), P2-Rh-Cl1 176.56(4), P3-Rh-Cl2 176.22(4), P4-Rh-Cl1 84.26(4), P4-Rh-Cl2 80.75(4).

requires C, 28.09; H, 6.32%.), and the ³¹P NMR spectrum (in CD₃CN) suggested the existence of $[RhCl(tdmme-\kappa^3 P, P', P'')(tdmme-\kappa^2 P, P')]^{2+}$ complex cation. These facts imply that the last Cl ligand does not tend to dissociate from the Rh^{III} center, even when the reaction mixture was refluxed for several hours. The desired $[Rh(tdmme)_2]^{3+}$ complex was, therefore, prepared from the Cl-free starting material, $[Rh(tdmme)_2(\mu-OH)_3](BF_4)_3$. The tris(aqua) complex of $[Rh(tdmme)-(H_2O)_3]^{3+}$ was prepared in situ by a reaction of $[{Rh(tdmme)}_2 - (\mu-OH)_3](BF_4)_3$ and HBF₄ in water [9], and the reaction with an equimolar amount of tdmme afforded colorless microcrystalline solid of $[Rh(tdmme)_2](BF_4)_3$ (17'). The structure of the cationic



Fig. 2. ORTEPs (30% probability level, hydrogen atoms omitted) of the cationic parts in (a) $10 \cdot H_2O$ and (b) $11 \cdot AN$. Selected bond lengths (Å) and angles (°) are: (a) Co-P1 2.242(2), Co-P2 2.251(2), Co-P3 2.219(2), Co-P4 2.287(2), Co-P5 2.295(2), Co-Cl1 2.282(2), P1-Co-P2 89.09(5), P1-Co-P3 88.62(5), P2-Co-P3 87.23(6), P4-Co-P5 72.38(5), P1-Co-P4 167.63(5), P2-Co-P4 100.97(5), P3-Co-P4 98.96(5), P1-Co-P5 96.47(6), P2-Co-P5 168.43(5), P3-Co-P5 102.99(6), P3-Co-Cl1 174.98(5), P4-Co-Cl1 81.98(5), P5-Co-Cl1 82.01(6); (b) Co-P1 2.2797(9), Co-P2 2.2754(9), Co-P3 2.2520(8), Co-P4 2.3233(9), Co-P5 2.3345(8), Co-Cl1 2.2852(8), P1-Co-P2 87.86(3), P1-Co-P3 86.90(3), P2-Co-P3 86.75(3), P4-Co-P5 83.62(3), P1-Co-P4 169.74(3), P2-Co-P4 92.32(3), P3-Co-P4 103.36(3), P1-Co-P5 95.44(3), P2-Co-P5 174.37(3), P3-Co-P5 97.96(3), P3-Co-Cl1 174.39(3), P4-Co-Cl1 81.44(3), P5-Co-Cl1 85.38(3).

part of $[Rh^{III}(tdmme-\kappa^3 P, P', P'')_2]^{3+}$ (Fig. 3) was obtained by X-ray analysis of the $[Co(CN)_6]^{3-}$ salt, $[Rh(tdmme)_2][Co(CN)_6] \cdot 4H_2O(17 \cdot 4H_2O).$

3.2. Crystal structures

In this study, the crystal structures of Co^{III}-PMe₃ complex (3), Rh^{III} –PMe₃ and PMe₂Ph complexes (6 and 8), Co^{III}-dmpm and dmpe complexes (10 and 11), Rh^{III}-dmpe complexes (14 and 14'), and Rh^{III}-(tdmme)₂ complex (17) were determined. All of these analyses revealed the mononuclear structures of $[M^{III}Cl_2(P)_4]^+$, $[M^{III}Cl(P)_5]^{2+}$ or $[M^{III}(P)_6]^{3+}$ -type complex cations (Figs. 1-3). The bite angles of tdmme ligands were varied in the typical range for the tripodal phosphines: 83– 89° (Table 3). Three arms (C2–Cn+2–Pn–M; n = 1, 2 or 3) of the tripod were screwed in the same direction, as



Fig. 3. ORTEP (50% probability level) of one of the crystallographically independent cationic complexes in $17 \cdot 4H_2O$.

observed for the trichloro complexes 1 and 2 [8,9]. Hence, each complex cation was inherently chiral, although all complexes formed as racemic crystals.

The coordination bond lengths in $[M^{III}Cl_2(tdmme)-(P)]^+$ and $[M^{III}Cl(tdmme)(P-P)]^{2+}$ -type complexes clearly indicated the elongation of the M–P(tdmme) bonds due to the strong *trans* influence of the phosphines (P or P–P ligands). As listed in Table 3, the M–P bond *trans* to PMe₃ was longer than that *trans* to Cl by 0.04 Å in the Co^{III} complex (3) or by 0.065 Å in the Rh^{III} complex (8). In the dmpe complexes (11 and 14), such an elongation of the M–P bond was as much as 0.03 Å (for Co^{III})

Table 3

C	omparison	of	(averaged)	bond	lengths	: (A	.) and	l angle	s (°)	of	the	compl	exes
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or 0.05 Å (for Rh^{III}). Hence, it can be stated that the M–P(tdmme) bond lengths in the $[M^{III}Cl_{3-n}(P)_{3+n}]^{n+}$ -series of complexes were governed primarily by the *trans* influence of the *trans*-positioned ligand.

For the Rh^{III}–PMe₃ and PMe₂Ph complexes (6 and 8), the P1-Rh-P4(PMe₃ or PMe₂Ph) bond angles were 169.77(3)° for 6 and 167.70(4)° for 8, while the P2-Rh-P4 and P3-Rh-P4 angles were relatively larger than the right angle (95.8–103.1°). These deviations from the regular octahedron were attributable to the steric interaction between tdmme and PMe₃/PMe₂Ph. Although sterically more bulky PMe₂Ph was expected to induce larger distortion of the coordination geometry from the regular octahedron, the structural parameters around the Rh^{III} center, including the Rh-P4 bond length, were similar to each other for both PMe₂Ph and PMe₃ complexes. For instance, although the phenyl group of the PMe₂Ph complex (8) was located close to P3 atom of tdmme, the P3-Rh-P4 angle (103.01(4)°) was similar to the corresponding angle of the PMe₃ complex (6, P2-Rh-P4: $102.02(3)^{\circ}$; it seems that similarity of these structures originates from the conformation for the phenyl ring that is located to minimize the steric interaction with tdmme (Fig. 1(b)). However, the analogous PMePh₂, P(OMe)Ph₂ and PPh₃ complexes seem to be thermodynamically unstable, since (at least two) phenyl substituents on the P-ligands cannot avoid the steric hindrance of the tdmme moiety in these complexes.

Complex	1	3	10	11	16
Number of Cl ligands	Cl ₃	Cl_2	Cl	Cl	
P-ligand		(PMe ₃)	(dmpm)	(dmpe)	(tdmme)
Co–Cl					
(trans P)	2.323(3)	2.287(1)	2.282(2)	2.2852(8)	
Co–P(tdmme)					
(trans Cl)	2.203(2)	2.216(1)	2.219(2)	2.252(1)	
(trans P)		2.256(1)	2.247(2)	2.278(1)	2.331(4)
Co–P(P-ligand)					
(trans tdmme)		2.329(1)	2.289(2)	2.329(1)	
P–Co–P(tdmme)	89.57(4)	88.22(4)	88.31(5)	87.17(3)	84.8(1)
(bite angle of tdmme)					
P-Co-P(dmpm or dmpe)			72.38(5)	83.62(3)	
(bite angle of dmpm or dmpe)					
Complex	2	6	8	14	17
Number of Cl ligands	Cl ₃	Cl_2	Cl_2	Cl	
P-ligand		(PMe ₃)	(PMe ₂ Ph)	(dmpe)	(tdmme)
Rh–Cl					
(trans P)	2.444(3)	2.421(1)	2.429(1)	2.410(1)	
Rh–P(tdmme)					
(trans Cl)	2.253(2)	2.279(1)	2.277(1)	2.303(1)	
(trans P)		2.345(1)	2.342(1)	2.352(1)	2.402(6)
Rh–P(P-ligand)					
(trans tdmme)		2.422(1)	2.423(1)	2.404(1)	
P–Co–P(tdmme)	89.1(1)	87.80(3)	87.58(4)	86.66(4)	84.2(2)
(bite angle of tdmme)					
P-Rh-P(dmpe)				82.35(3)	
(bite angle of dmpe)					

In the dmpm complex (10), the four-membered chelate ring formed by dmpm is not planar; the P4-C14-P5 plane was bent from the P4–Co–P5 plane by $17.0(2)^{\circ}$ to avoid the steric repulsion between the methyl substituents of dmpm and tdmme (Fig. 2(a)). For the Co^{III}-dmpe complex (11), the five-membered ring formed by the chelation of dmpe had a typical skew conformation; the five-membered chelate ring was in the δ configuration for the complex having a λ -screwed tdmme. The molecular modeling study indicates that this configurational set for the combination of tdmme/ dmpe ligands is the most favorable to avoid the steric interaction between the methyl substituents. We have also analyzed the two Rh^{III}-dmpe complexes (14 · AN and $14' \cdot AN$), which were isomorphous to $11 \cdot AN$, and found the same configurational set, $\delta(dmpe)$ - $\lambda(tdmme)/\lambda(dmpe)\delta(tdmme)$, for the complex cations. For both complexes of 10 and 11, the Co–P1 and Co– P2 bonds were longer by ca. 0.025 Å than the Co-P3 bond due to the trans influence of the P-P (dmpm or dmpe) ligand. It should also be noted that both types of Co-P(tdmme) bonds in the dmpe complex (11) were longer by ca. 0.03 Å than those in the dmpm complex (10) (Table 3). Furthermore, the Co-P(dmpe: i.e., P4 or P5) bonds in 11 (2.3233(9) and 2.3345(8) Å) were remarkably longer than the Co-P(dmpm: P4 or P5) bonds in 10 (2.287(2) and 2.295(2) Å). Since the bite angle (P4-Co-P5) of dmpm is considerably small $(72.38(5)^{\circ}$ in **10**) as compared to that of dmpe $(83.62(3)^{\circ} \text{ in } 11)$, it is expected that a larger steric interaction between dmpe and tdmme induces the longer Co-P(tdmme or dmpe) bonds in 11. By the same reason, the Co-P(dmpe) bonds in 11 were much longer than the Co-P bond lengths in *trans*- $[CoCl_2(dmpe)_2]ClO_4$ (av. 2.260(1) Å) [16]. Moreover, the Co-P(dmpm) bonds in 10 were longer than the mutually trans Co-P bonds in $[Co(Me_2dtc)(dmpm)_2](BF_4)_2$ (Me_2dtc = N,N-dimethyldithiocarbamate; 2.222(5)-2.264(5) Å) [17], indicating that steric congestion around Co^{III} center affected the elongation of the Co-P coordination bonds.

The complex cation of $[Rh^{III}(tdmme)_2]^{3+}$ in 17 exhibited much longer Rh–P(tdmme) bonds (av. 2.402(6) Å) compared with complexes 2, 8, and 14. It seems that the steric congestion, which depends on the number of coordinated phosphine groups, is important to account for the Rh–P bond lengths, although the elongation of Rh–P bonds is primarily governed by the strong trans influence of phosphines. The order of the M^{III}-P(tdmme) bond lengths, $[M^{III}Cl_3(P)_3] < [M^{III}Cl_2(P)_4]^+ < [M^{III}Cl(P)_5]^{2+} < [M^{III}(P)_6]^{3+}$ in both Co^{III} and Rh^{III} complexes (Table 3), can be explained on this basis. On the other hand, the M^{III}–Cl bonds in the series of complexes were gradually shortened as the number of the phosphine donor groups increased: 1 (av. 2.323(3) \dot{A} > 3 (av. 2.287(1) \dot{A}) > 11 (2.2852(8) \dot{A}) for Co^{III} and **2** (av. 2.444(3) Å) > **6** (av. 2.421(1) Å) > **14** (2.410(1) Å)

Fig. 4. UV-vis absorption spectra of (a) [CoCl₃(tdmme)] (-·-·-) in dichloromethane, $[CoCl_2(tdmme)(PMe_2Ph)]^+$ (----), $[CoCl_1(tdmme)(dmpe)]^{2+}$ (----), and $[Co(tdmme)_2]^{3+}$ (----); (b) $[CoCl(tdmme)(dmpm)]^{2+}$ (----), $[CoCl(tdmme)(dmpe)]^{2+}$ (----), and $[CoCl(tdmme)(dmpp)]^{2+}$ (----) in acetonitrile at ambient temperature.

 σ / cm^{-1}

30

35

40x10³

25

for Rh^{III}. This order is consistent with the inertness of the Rh^{III}–Cl bonds in the series of complexes.

3.3. Absorption spectra

15

20

The trichloro complex [CoCl₃(tdmme)] (1) showed the first d-d transition band at 20120 cm⁻¹ ($\varepsilon = 1350$ $mol^{-1} dm^3 cm^{-1}$). With this value and the corresponding first d–d transition energies for [Co- $(NH_3)_3(tdmme)]^{3+}$ and $[Co(CN)_3(tdmme)]$, the complex of $[Co(tdmme)_2]^{3+}$ was expected to exhibit the first d-d band at ca. 27000-30000 cm⁻¹. However, the first d-d transition band of complex 16' was observed at 23920 cm^{-1} ($\varepsilon = 891 mol^{-1} dm^3 cm^{-1}$). It seems that this remarkable weakening of the ligand-field strength of tdmme was caused by the strong mutual trans influence of tdmme [5] and the severe steric congestion around the Co^{III} center. In this study, we have prepared the $[Co^{III}Cl_2(tdmme)(P)]^+$ and $[Co^{III}Cl(tdmme)(P-P)]^{2+}$ type complexes, and compared the absorption spectra,



(a)

3

especially the first d-d transition energy, of the $[Co^{III}Cl_{3-n}(P)_{3+n}]^{n+}$ series of complexes (Fig. 4(a)).

The simplest estimation, on the basis of Yamatera rule [18] with the assumption of equal ligand-field strengths for PMe₃/PMe₂Ph, dmpm/dmpe/dmpp and tdmme, would predict that the first d-d transition band was split into two components at 20100 and 22000 cm^{-1} for [Co^{III}Cl₂(tdmme)(P)]⁺, and at 22000 and 23900 cm^{-1} for $[Co^{III}Cl(tdmme)(P-P)]^{2+}$. In fact, the complex of cis-[Co^{III}Cl₂(dmpe)₂]⁺, which has the same cis- $[Co^{III}Cl_2(P)_4]^+$ chromophere as $[Co^{III}Cl_2(tdmme)(P)]^+$, exhibited two absorption bands at 19500 ($\varepsilon = 250$) and 22470 cm⁻¹ ($\varepsilon = 417 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) corresponding to the predicted splitting components of the first d-d band [19]. However, the [Co^{III}Cl₂(tdmme)(P)]⁺-type complexes examined in this study did not show an explicit splitting of the first d-d band; the PMe₃ complex (3) gave a broad absorption band centered at 21 350 cm⁻ $(\varepsilon = 1000 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1})$ accompanied by a shoulder around 20000 cm⁻¹. The P(OMe)₃ and PMe₂Ph complexes (4 and 5) exhibited a similar broad d-d transition band centered at 21880 ($\varepsilon = 795$) and 21560 cm⁻¹ $(\varepsilon = 1050 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1})$, respectively.

The complex, $[CoCl(tdmme)(dmpe)](BF_4)_2$ (11), showed an absorption band at 21690 cm⁻¹ ($\varepsilon = 437$ $mol^{-1} dm^3 cm^{-1}$), which may correspond to the one $(a^{1}E_{g} \leftarrow {}^{1}A_{1g})$ of the splitting components of the first d-d transition bands. Although the other component $({}^{1}A_{2g} \leftarrow {}^{1}A_{1g})$ was expected to be located at 23900 cm⁻¹ or at positions higher in energy, any explicit absorption band corresponding to this component was not observed in this region. Interestingly, while the dmpp complex (12) exhibited the corresponding d-d transition band at 21 320 cm⁻¹ ($\varepsilon = 562 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$), analogous dmpm complex (10) exhibited such a band at a higher energy region, 22880 cm⁻¹ ($\varepsilon = 575 \text{ mol}^{-1}$ $dm^3 cm^{-1}$) (Fig. 4(b)). This order of d-d transition energy, dmpp < dmpe < dmpm, is unusual, since dmpm ligand that forms a four-membered chelate ring is expected to have a weaker interaction with the central metal ion. In fact, the d-d transition energy was shifted in the order of dmpp < dmpe > dmpm for the series of $[Co^{III}(Me_2dtc)_2(P-P)]^+$ and $[Co^{III}(Me_2dtc)(P-P)_2]^{2+}$ complexes; this order was also confirmed by the AOM analysis [17]. As seen in the crystal structures, the bite angles of dmpm and dmpe ligands were within the ordinary range for the Co^{III} complexes [17], while the Co-P bond lengths of dmpm complex 10 were shorter by 0.03-0.04 Å than those of dmpe complex 11. This is due to the steric congestion around the Co^{III} center. This seems to be the reason why the unusual order of the d-d transition energy was observed for the series of complexes with didentate P-P ligands.

For the Rh^{III} series of complexes, the same tendency of their d–d transition bands was observed, although the

d–d transition energies of the Rh^{III} complexes were shifted to higher energy region, resulting in obscuration by overlapping the intense charge-transfer bands.

3.4. ⁵⁹Co NMR spectra

It has been well established that the ⁵⁹Co NMR chemical shift, δ ⁽⁵⁹Co), correlates well to the reciprocal ${}^{1}T_{1g} \leftarrow {}^{1}A_{1g}$ (the first d-d) transition energy of the complex [20]. The [Co(dmpe)₃](BF₄)₃ complex was reported to exhibit the ⁵⁹Co NMR resonance at the very high-field region (δ (⁵⁹Co) = -2530) [3], while the ⁵⁹Co NMR spectrum of the analogous $[Co(P)_6]^{3+}$ -type complex of [Co- $(tdmme)_2$ (BF₄)₃ (16') showed its resonance at δ (⁵⁹Co) = + 180. The first d-d transition band of complex 16' was observed at markedly lower energy region (23920 cm^{-1}) than that of $[Co(dmpe)_3](BF_4)_3$ (26 300 cm⁻¹), which correlates well with the δ (⁵⁹Co) values for these complexes. Furthermore, the $[Co(P)_3(S)_3]^{3+}$ -type complex, [Co- $(tdmme)(ttcn)](BF_4)_3$ (ttcn = 1,4,7-trithiacyclononane), showed the first d–d transition band at 24600 cm⁻¹ [21]; the ⁵⁹Co NMR signal observed at δ (⁵⁹Co) = -200 is well accommodated with this simple relation.

The ⁵⁹Co NMR signals for the [CoCl(tdmme)(P– P)]²⁺-type complexes (10–12) were observed at δ (⁵⁹Co) = +710, +770, and +1330 for P–P = dmpm (10), dmpe (11), and dmpp (12), respectively. Although the absorption band appeared in the visible region originates from the splitting (a¹E_g \leftarrow ¹A_{1g}) component of the first d–d transition band, the order of the observed transition energy was consistent with that of the δ (⁵⁹Co) values; the ligand-field strength of dmpe in complex 11 was weaker than that of dmpm in 10 due to the steric congestion around the Co^{III} center.

The ⁵⁹Co NMR resonances of the $[CoCl_2-(tdmme)(P)]^{2+}$ -type complexes were observed at much lower-field region; $\delta(^{59}Co) = +2040$ for the PMe₃ complex (**3**), +1710 for the P(OMe)₃ complex (**4**), and +2220 for the PMe₂Ph complex (**5**), although the corresponding absorption band maxima were observed in a similar energy region to those of $[CoCl(tdmme)-(P-P)]^{2+}$ -type complexes. The $\delta(^{59}Co)$ values of these complexes indicated that the ligand-field strength of P(OMe)₃ on Co^{III} ion was larger than that of PMe₃ [22], while it was obscured in their absorption spectra.

3.5. ³¹P NMR spectra

The ³¹P NMR spectral data for the Rh^{III} complexes are listed in Table 4. In this series of complexes, clear tendencies in the chemical shifts, $\delta(^{31}P)$, and/or the coupling constants, ¹J_{Rh-P} or ²J_{P-P}, were observed. The trichloro complex of [RhCl₃(tdmme)] (**2**) showed a doublet resonance at δ 18.6 with ¹J_{Rh-P} = 100.8 Hz. For the

Table 4 ³¹P NMR data for the Rh^{III} complexes (chemical shift from 85% H₃PO₄ in δ -scale; *J* in Hz)

\searrow	D	#	P-ligand	$\delta(\mathbf{P}) \left[J_{\mathbf{Rh}-\mathbf{P}} \right]$					
P	CI Rh CI CI	2		18.6 [100.8]					
	+	#	P-ligand	$\delta(\mathbf{P}_{\mathrm{A}}) \left[J_{\mathrm{Rh-PA}}\right]$	$\delta(\mathbf{P}_{\mathbf{B}}) \left[J_{\mathbf{R}\mathbf{h}-\mathbf{P}\mathbf{B}} \right]$	$\delta(\mathbf{P}_{\mathrm{C}}) \left[J_{\mathrm{Rh-PC}} \right]$	$(J_{\mathrm{PA-PB}})$	$(J_{\text{PA-PC}})$	$(J_{\text{PB-PC}})$
	Pc	6	PMe ₃	0.43 [76.3]	13.56 [101.1]	-10.94 [83.7]	(34.9)	(429.3)	(18.4)
	/.0	7	$P(OMe)_3$	-1.19 [74.7]	15.74 [99.1]	97.36 [143.4]	(35.1)	(665.3)	(22.9)
		8	PMe ₂ Ph	2.19 [77.2]	12.04 [103.0]	-6.97 [80.9]	(36.8)	(430.2)	(14.7)
	CI	9	P(OMe) ₂ Ph	1.30 [74.2]	14.95 [100.3]	131.81 [122.4]	(35.7)	(584.2)	(16.5)
CI		-	PMePh ₂	6.16 [79.8]	9.75 [101.8]	-0.97 [82.5]	(35.7)	(431.7)	(16.5)
	2+	#	P—P	$\delta(\mathbf{P}_{\mathrm{A}}) \left[J_{\mathrm{Rh-PA}}\right]$	$\delta(\mathbf{P}_{\mathrm{B}}) \left[J_{\mathrm{Rh-PB}} \right]$	$\delta(\mathbf{P}_{\mathrm{C}}) \left[J_{\mathrm{Rh-PC}}\right]$	$(J_{\mathrm{PA-PB}})$	$(J_{\rm PA-PC})$	$(J_{\text{PB-PC}})$
	ZPc.	13	dmpm	-0.23 [77.2]	11.08 [102.0]	-34.66 [69.9]	(42.3)	(342.9)	(19.3)
	$\langle \rangle$	14	dmpe	-7.34 [75.3]	6.51 [100.2]	33.27 [80.2]	(36.4)	(312.2)	(17.7)
P _A	P _C	15	dmpp	-6.37 [74.1]	4.74 [98.9]	-16.61 [78.5]	(36.6)	(315.6)	(17.9)
Р	3+	#		$\delta(\mathbf{P}) \left[J_{\mathbf{R}\mathbf{h}-\mathbf{P}} \right]$					
P RK	P P	17		-14.02 [73.2]					

[RhCl₂- (tdmme)(P)]⁺- and [RhCl(tdmme)(P-P)]²⁺-type complexes, there are two kinds of chemically non-equivalent P atoms of tdmme; one (P_A) is *trans* to P (of the phosphines) and the other (P_B) is *trans* to Cl. The resonance due to the P_B atom provides the ${}^{1}J_{Rh-PB}$ values nearly equal to 100 Hz for all complexes, while the ${}^{1}J_{Rh-PA}$ values were remarkably smaller (73-80 Hz), which seems to originate from the mutual trans influence as observed in cis-[RhCl₂(dmpe or dmpp)₂]⁺ [11]. Since the Rh–P bond lengths became longer in the order [RhCl₃(tdmme)] < $[RhCl_2(tdmme)(P)]^+ < [RhCl(tdmme)(P-P)]^{2+} < [Rh(td-P)]^{2+} < [Rh(td-P)]^{2+}$ mme)₂]³⁺, the ${}^{1}J_{Rh-P}$ coupling constant is expected to decrease in this order, although the difference in ${}^{1}J_{Rh-P}$ values for this series of complexes was too small to be discussed. On the other hand, the chemical shifts of the P atoms on tdmme, $\delta(^{31}P_A)$ and $\delta(^{31}P_B)$, exhibited gradual shifts toward the higher-field region in the above order; i.e., $\delta({}^{31}P_{\rm B})$: [RhCl₃(tdmme)] (18.6) > [RhCl₂(tdmme)(P)]⁺ $\begin{array}{l} (\text{from } 9-16) > [\text{RhCl}(\text{tdmme})(\text{P-P})]^{2+} & (\text{from } 4.5-11); \\ \delta(^{31}\text{P}_{\text{A}}): [\text{RhCl}_2(\text{tdmme})(\text{P})]^+ & (\text{from } -1.2 \text{ to } 6) > [\text{RhCl}_2(\text{tdmme})(\text{P-P})]^{2+} & (\text{from } -7.5 \text{ to } 0) > [\text{Rh}(\text{tdmme})_2]^{3+} \end{array}$ (-14.0).

For the $[RhCl(tdmme)(P-P)]^{2+}$ -series complexes, the chemical shifts and the coupling constants were found to be dependent on the chelate ring size formed by the

P–P ligands. Both $\delta({}^{31}P_A)$ and $\delta({}^{31}P_B)$ values exhibited higher-field shifts in the order of dmpm < dmpe < dmpp. Moreover, both ${}^{1}J_{Rh-PA}$ and ${}^{1}J_{Rh-PB}$ constants became smaller in this order (Table 4). These observations are consistent with the order of the Rh–P bond strengths; dmpm > dmpe > dmpp, that is governed by the steric congestion around the metal center (vide infra). On the contrary, both the chemical shift, $\delta({}^{31}P_C)$, and the ${}^{1}J_{Rh-PC}$ coupling constant of the P–P ligand decreased in the order of dmpe (δ 33.3, J = 80.2 Hz) > dmpp (δ –16.6, J = 78.5 Hz) >> dmpm (δ –34.7, J = 69.9 Hz), which is consistent with the chelate ring size effect [23] observed for the other series of complexes with P–P ligands.

4. Conclusion

In this study, the cobalt(III) and rhodium(III) complexes of the series of $[M^{III}Cl_3(P)_3]$, $[M^{III}Cl_2(P)_4]^+$, $[M^{III}Cl(P)_5]^{2+}$, and $[M^{III}(P)_6]^{3+}$ have been completed with the use of tripodal tridentate phosphine, 1,1,1-tris(dimethylphoshinomethyl)ethane (tdmme), as a common ligand. The single-crystal X-ray analyses of both series of complexes revealed that the M–P and M–Cl bond lengths were dependent primarily on the strong (mutual)

trans influence of the phosphines; the steric congestion around the metal center as a function of the number of the coordinated phosphine donor groups is the secondary important factor. The M-P(tdmme) bonds were found to become longer in the order of [MCl₃(tdmme)] < [MCl₂- $(tdmme)(PMe_3)]^+ < [MCl(tdmme)(dmpe)]^{2+} < [M(tdm-me)_2]^{3+}$ for both Co^{III} and Rh^{III} series of complexes, while the M-Cl bonds were compressed in this order. This secondary steric effect, congestion around the metal center, is also related to the structural and spectroscopic properties of the series of [MCl(tdmme)(dmpm, dmpe or dmpp)]²⁺ complexes. The X-ray analysis for [CoCl(tdmme)(dmpm or dmpe)](BF₄)₂ showed that all Co–P bonds in the dmpm complex were shorter by 0.03–0.04 Å than those in the dmpe complex. The first d-d transition energy of this series of Co^{III} complexes and the ${}^{1}J_{Rh-P(tdmme)}$ coupling constants observed for the series of Rh^{III} complexes exhibited an unusual order of the coordination bond strengths in the diphosphine complexes: dmpm > dmpe > dmpp. This order seems to have resulted from the steric requirement of the didentate ligands; the four-membered chelate ring formed by dmpm is the most compact and provides the most effective interaction with the central metal ions.

The steric requirement of the incorporated P-ligand seems to be an important factor to determine the thermal stability/the formation constant of the series of $[M^{III}Cl_2(tdmme)(P)]^+$ -type complexes. Although the P(OMe)₃ and P(OMe)₂Ph ligands are weak σ -donors, these ligands formed stable $[M^{III}Cl_2(tdmme)(P)]^+$ -type complexes, while it was not possible to isolate the corresponding complexes with PMePh₂ and PPh₃ as thermally stable products because of the larger steric bulk compared with those for P(OMe)₃ and P(OMe)₂Ph.

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Appendix A. Supporting information

Crystallographic data for complexes **3**, **6** · 2MeOH, **8** · H₂O, **10** · 2H₂O, **11** · AN, **14** · AN, **14** ' · AN and **17** · 4H₂O have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 260076–260083, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2005.02.008.

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