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Preparation and characterization of pentamethylcyclopentadienylrhodium(III) and iridium(III), and (arene)ruthenium(II) complexes of 1,8-bis(diphenylphosphinomethyl)naphthalene

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Abstract

1,8-Bis(diphenylphosphinomethyl)naphthalene (1,8-dpmn) reacted with $[(arene)RuCl_2]_2$ (**1**) or $[Cp^*MCl_2]_2$ (**2**: M = Rh; **3**: M = Ir) to generate the corresponding diphosphine-bridged complexes, $[\{(arene)RuCl_2\}_2(1,8\text{-dpmp-}P,P')]$ (**4**) (arene = *p*-cymene (**a**), 1,2,3-$Me_3C_6H_3$ (**b**), 1,2,3,4-$Me_4C_6H_2$ (**d**), 1,2,3,5-$Me_4C_6H_2$ (**d**), C_6Me_6 (**e**)) or $[(Cp^*MCl_2)_2(1,8\text{-dpmp-}P,P')]$ (**5**: M = Rh; **6**: M = Ir). Homonuclear complexes $[\{(p\text{-cymene})RuCl_2\}(1,8\text{-dpmp-}P,P')\{(arene)RuCl_2\}]$ **7ab** and **7ad** bearing different arene groups were prepared by the reactions of **1a** with **1b** (or **1d**). They existed as two isomers in solution. Reactions of **2** with **1** or **3** gave heteronuclear complexes $[(Cp^*RhCl_2)(1,8\text{-dpmp-}P,P')\ \{(arene)RuCl_2\}]$ (**8**) and $[(Cp^*RhCl_2)(1,8\text{-dpmp-}P,P')(Cp^*IrCl_2)]$ (**10**). The heteronuclear complexes of iridium–ruthenium **9** were generated from **1** to **2**. Complexes **1**, **2** and **3** reacted with 1,8-dpmp in the presence of AgOTf to give the cationic complexes, $[(arene)RuCl(1,8\text{-dpmp-}P,P')](OTf)$ (**11**) or $[Cp^*MCl(1,8\text{-dpmp-}P,P')](OTf)$ (**12**: M = Rh; **13**: M = Ir) that showed the presence of isomers in solution. They were treated with Ag(OTf) to afford the Cl-bridged complexes, $[\{(p\text{-cymene})Ru(\mu\text{-Cl})\}_2(1,8\text{-dpmp-}P,P')](OTf)_2$ (**15a**) or $[\{Cp^*M(\mu\text{-Cl})\}_2(1,8\text{-dpmp-}P,P')](OTf)_2$ (**16**: M = Rh; **17**: M = Ir). Complexes **16** and **17** cleaved the Cl-bridges with xylyl or mesityl isocyanide to generate the dimeric isocyanide complexes $[\{Cp^*MCl(RNC)\}_2(1,8\text{-dpmp-}P,P')](OTf)_2$ (**18**: M = Rh; **19**: M = Ir). X-ray analyses of **5**, **8b**, **10**, **11a**, **12**, **15a** and **18b** were performed.

Keywords: Rh and Ir complexes; 1,8-Bis(diphenylphosphinomethyl)naphthalene; Pentamethylcyclopentadienyl group

1. Introduction

1,8-Diorganophosphino-substituted naphthalenes and their derivative are interested in the structures and properties. Recently, the chemistry has been developed by Schmutzler et al. [1]. Since 1,8-bis(diphenylphosphino)naphthalene (1,8-dppn) and 1,8-bis(dimethylphosphino)naphthalene have the P···P distance of 3.052 and 3.070 Å (and 3.036 Å), respectively, well within the sum of the van der Waals radii (3.80 Å) [1a,2,3], they are very rigid in its manner of coordination because of the direct binding of the phosphorus atom to the naphthalene ring, and forms chelated complexes [1d,1f,2]. They are assumed to have potential significance in metal-assisted reactions, since they are members of a class of bidentate ligands with a rigid C_3-backbone [4]. 1,8-Bis(diphenylphosphinomethyl)-naphthalene (1,8-dpmn) generated from the introduction of a methylene group between the naphthalene ring and phosphorus atom is less rigid than 1,8-dppn and its derivatives, and has the potential of various coordination modes except chelation. It is assumed to be the potential ligand of catalytic reactions by transition-metal complexes. There are few examples of metal complexes bearing 1,8-dpmn ligand. Recently, Tin et al. reported the preparation of $RuH_2(CO)(PPh_3)(1,8\text{-dpmn})$ with a chelate structure [5]. We reported that the reactions of $[M_2(CNR)_6](PF_6)_2$ (M = Pd, Pt) with 1,8-dpmn generated dinuclear palladium and platinum complexes, $[M_2(RNC)_4(1,8\text{-dpmn-}P,P')](PF_6)_2$ and

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$[M_2(RNC)_2(1,8\text{-dpmn-}P,P')_2](PF_6)_2$ (M = Pd, Pt) [6]. These complexes have chelated structures. We report here the reactions of 1,8-dpmn with bis[dichloro(pentamethylcyclopentadienyl)rhodium(III) (or iridium(III))] or bis[dichloro(arene)ruthenium(II)] to form complexes bearing chelation and μ-coordination of 1,8-dpmn ligand.

2. Experimental

All reactions were carried out under nitrogen atmosphere. 1,8-dpmn [6], isocyanides [7], $[Cp^*MCl_2]_2$ [8,9] (**1**: M = Rh, **2**: Ir; $Cp^* = C_5Me_5$) and $[(arene)RuCl_2]_2$ (**3**) [10] (**a**: *p*-cymene; **b**: 1,2,3-$Me_3C_6H_3$; **c**: 1,2,3,4-$Me_4C_6H_2$; **d**: 1,2,3,4-$Me_4C_6H_2$; **e**: C_6Me_6) were prepared according to the literature. Dichloromethane was distilled over CaH_2 and diethyl ether was distilled over $LiAlH_4$. The IR spectra measured on an FT/IR-5300. NMR spectroscopy was carried out on Bruker AC250. The ^1H NMR spectra were measured at 250 MHz and $^{31}P\{^1H\}$ NMR spectra were measured at 101 MHz using 85% H_3PO_4 as an external reference.

2.1. Preparation of dinuclear complexes

2.1.1. [{(*p*-Cymene)$RuCl_2$}$_2$(μ-1,8-dpmn)] (**4a**)

A mixture of [(*p*-cymene)$RuCl_2$]$_2$ (160.7 mg, 0.262 mmol) and 1,8-dpmn (145.5 mg, 0.277 mmol) was stirred in CH_2Cl_2 (15 ml) at room temperature (r.t.) for 24 h. The solution was concentrated and diethylether was added, giving reddish brown crystals of **4a** (253.2 mg, 84.7%). UV–Vis (CH_2Cl_2): λ_{max} 371, 310(sh) nm. ^1H NMR ($CDCl_3$): δ 1.01 (d, $J_{HH} = 7.0$ Hz, Me_2C, 12H), 1.75 (s, Me, 6H), 2.52 (sep. $J_{HH} = 7.0$ Hz, CH, 2H), 4.77 (d, $^2J_{PH} = 9.5$ Hz, PCH_2, 4H), 5.17 (d, $J_{HH} = 6.0$ Hz, 2,6- or 3,5-C_6H, 4H), 5.33 (d, $J_{HH} = 6.0$ Hz, 2,6- or 3,5-C_6H, 4H), 5.30 (s, CH_2Cl_2), 6.56–7.43 (m, ArH). $^{31}P\{^1H\}$ NMR($CDCl_3$): δ 31.4 (s). Calc. for $C_{56}H_{58}P_2Cl_4Ru_2\cdot 1.5CH_2Cl_2$: C, 54.62; H, 4.86. Found: C, 54.95; H, 4.92%. The following complexes were prepared according to a procedure similar to **4a**. [{(1,2,3-$Me_3C_6H_3$)$RuCl_2$}$_2$(μ-1,8-dpmn)] (**4b**) (reddish brown, 60.0%): UV–Vis (CH_2Cl_2): λ_{max} 370, 300(sh) nm. ^1H NMR ($CDCl_3$): δ 1.94 (s, 1,3-Me, 12H), 2.11 (d, $J_{PH} = 2.5$ Hz, 2-Me, 6H), 4.31 (d, $J_{HH} = 3.0$ Hz, 4,6-C_6H, 4H), 4.73 (d, $^2J_{PH} = 9.0$ Hz, PCH_2, 4H), 5.29 (s, CH_2Cl_2), 6.63 (t, $J_{HH} = 3.0$ Hz, 5-C_6H, 2H), 6.5–7.4 (m, ArH, 26H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 36.7 (s). Calc. for $C_{54}H_{54}P_2Cl_4Ru_2\cdot CH_2Cl_2$: C, 55.33; H, 4.73. Found: C, 55.29; H, 4.73%.

[(1,2,3,4-$Me_4C_6H_2$)$RuCl_2$}$_2$(μ-1,8-dpmn)] (**4c**) (reddish brown, 39.4%): UV–Vis (CH_2Cl_2): λ_{max} 371, 310(sh) nm. ^1H NMR ($CDCl_3$): δ 1.67 (s, 1,4- or 2,3-Me, 12H), 2.10 (d, $J_{PH} = 2.3$Hz, 1,4- or 2,3-Me, 12H), 4.26 (d, $J_{PH} = 3.0$ Hz, 5,6-C_6H), 4.71 (d, $^2J_{PH} = 9.5$ Hz, PCH_2, 4H), 6.6–7.4 (m, ArH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 35.9(s). Calc. for $C_{56}H_{58}P_2Cl_4Ru_2\cdot 0.5CH_2Cl_2$: C, 57.54; H, 5.04. Found: C, 57.77; H, 5.09%.

[(1,2,3,5-$Me_4C_6H_2$)$RuCl_2$}(μ-1,8-dpmn)] (**4d**) (orange, 43.7%): UV–Vis (CH_2Cl_2): λ_{max} 372, approximately 310(sh) nm. ^1H NMR ($CDCl_3$): δ 1.48 (s, 5-Me, 6H), 1.87 (s, 1- and 3-Me, 12H), 1.96 (s, 2-Me, 6H), 4.34 (s, 4- and 6-C_6H, 4H), 4.50 (d, $J_{PH} = 10.0$ Hz, PCH_2, 4H), 5.29 (s, CH_2Cl_2), 6.4–7.4 (m, ArH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 34.6(s). Calc. for $C_{56}H_{58}P_2Cl_4Ru_2\cdot CH_2Cl_2$: C, 56.03 H, 4.95. Found: C, 55.38; H, 5.01%.

[{(C_6Me_6)$RuCl_2$}$_2$(μ-1,8-dpmn)] (**4e**) (reddish brown, 44.3%): UV–Vis (CH_2Cl_2): λ_{max} 374, 310 (sh) nm. ^1H NMR ($CDCl_3$): δ 1.67 (s, Me, 32H), 4.14 (d, $J_{PH} = 8.0$ Hz, PCH_2, 4H), 5.29 (s, CH_2Cl_2), 6.4–7.4 (m, ArH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 35.1(s). Calc. for $C_{60}H_{66}P_2Cl_4Ru_2\cdot 0.25CH_2Cl_2$: C, 59.59; H, 5.52. Found: C, 59.48; H, 5.73%.

[(Cp^*RhCl_2)$_2$(μ-1,8-dpmn)] (**5**) (orange, 84.3%): UV–Vis (CH_2Cl_2): λ_{max} 415 nm. ^1H NMR ($CDCl_3$): δ 1.27 (d, $J_{PH} = 3.5$ Hz, Cp*, 30H), 4.63 (b, PCH_2, 4H), 6.9–7.2 (m, ArH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 37.9 (d, $J_{RhP} = 141$ Hz). Calc. for $C_{56}H_{60}P_2Cl_4Rh_2\cdot 2CH_2Cl_2$: C, 53.08 H, 4.91. Found: C, 53.36; H, 5.14%.

[(Cp^*IrCl_2)$_2$(μ-1,8-dpmn)] (**6**) (orange, 84.6%): UV–Vis (CH_2Cl_2): λ_{max} 319 nm. ^1H NMR ($CDCl_3$): δ 1.28 (d, $J_{PH} = 2.5$ Hz, Cp*, 30H), 4.68 (b, PCH_2, 4H), 6.4–7.6 (m, ArH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 5.3 (s). Calc. for $C_{56}H_{60}P_2Cl_4Ir_2\cdot CH_2Cl_2$: C, 48.69 H, 4.44. Found: C, 48.52; H, 4.53%.

2.1.2. [{(*p*-Cymene)$RuCl_2$}{(1,2,3-$Me_3C_6H_3$)$RuCl_2$}(μ-1,8-dpmn)] (**7ab**) (brown, 37.9%)

To a mixture of [(*p*-cymene) $RuCl_2$]$_2$ (**1a**) (31.0 mg, 0.051 mmol) and [(1,2,3-$Me_3C_6H_3$)$RuCl_2$]$_2$ (**1b**) (33.5 mg, 0.057 mmol) in CH_2Cl_2 (20 ml) and acetone (20 ml) was added 1,8-dpmp (58.5 mg, 0.112 mmol) at r.t. and stirred over night. After the solution was concentrated to approximately 3 ml, diethylether was added to give brown crystals of **7ab** (43.1 mg, 37.9%). UV–Vis (CH_2Cl_2): λ_{max} 371, 300(sh) nm. ^1H NMR ($CDCl_3$): δ 0.96 (d, $J_{HH} = 5.5$ Hz, i-Pr)*[a], 0.99 (d, $J_{HH} = 5.5$ Hz, i-Pr)*[b], 1.74 (s, p-Me, 3H), 1.93 (s, 1- and 3-Me, 6H), 2.08 (d, $J_{PH} = 2.5$ Hz, 2-Me, 3H), 2.49 (c, C*H*, 1H)*[a,b], 4.30 (d, $J_{HH} = 5.0$ Hz, 5-C_6H, 1H)*[a], 4.34 (d, $J_{HH} = 5.0$ Hz, 5-C_6H, 1H)*[b], ca. 4.73 (c, 4- and 6-C_6H, and PCH_2, 4H), 5.09 (d, $J_{HH} = 6.5$ Hz, 2,6- or 3,5-C_6H, 2H)*[a], 5.12 (d, $J_{HH} = 6.5$ Hz, 2,6- or 3,5-C6*H*, 4H)*[b], 5.27 (d, $J_{HH} = 6.5$ Hz, 2,6- or 3,5-C_6H, 2H)*[a], 5.31 (d, $J_{HH} = 6.5$ Hz, 2,6- or 3,5-C6*H*, 4H)*[b], 6.56–7.43 (m, ArH, 26H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.5 (s, (*p*-cymene)RuP)*[a], 32.2 (s, (*p*-cymene)RuP)*[b], 36.2 (s, (1,2,3-Me_3-C_6H_3)Ru*P*)*[a], 38.8 (s, (1,2,3-$Me_3C_6H_3$)Ru*P*)*[b]. Isomer ratio: A/B = 1.3. Calc. for $C_{55}H_{56}P_2Cl_4Ru_2$: C, 58.83; H, 5.03. Found: C, 59.08; H, 5.01%.

[{(*p*-Cymene)$RuCl_2$}{(1,2,3,5-$Me_4C_6H_2$)$RuCl_2$}(μ-1,8-dpmn)] (**7ad**) (brown, 59.3%). UV–Vis (CH_2Cl_2): λ_{max} 375, ca. 310(sh) nm. ^{1}H NMR ($CDCl_3$): δ 0.95 (d, $J_{HH}=7.0$ Hz, i-Pr, 6H)*[a], 0.98 (d, $J_{HH}=7.0$ Hz, i-Pr, 6H)*[b], 1.49 (s, 5-Me, 3H)*[a], 1.53 (s, 5-Me, 3H)*[b], 1.73 (s, *p*-Me of *p*-cymene, 3H)*[a], 1.74 (s, *p*-Me of *p*-cymene, 3H)*[b], 1.86 (s, 1- and 3-Me, 6H)*[a], 1.94 (s, 1- and 3-Me, 6H)*[b], 2.50 (c, C*H*, 1H), 4.33 (s, 4- and 6-H, 2H), 4.55 (d, $J_{PH}=10$ Hz, PCH_2, 2H)*[a], 4.73 (d, $J_{HH}=5.0$ Hz, C_6H_4, 2H)*[a], 5.13 (d, $J_{PH}=6.0$ Hz, PCH_2, 2H)*[b], 6.45–7.40 (m, ArH, 26H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 31.2, 31.5 (s, (*p*-cymene)RuP), 35.8 (s, (1,2,3,5-$Me_4C_6H_2$)RuP). Isomer ratio: A/B = 1.8. Calc. for $C_{56}H_{58}P_2Cl_4Ru_2\cdot CH_2Cl_2$: C, 56.03; H, 4.95. Found: C, 56.44; H, 5.24%.

[{(*p*-Cymene)$RuCl_2$}(μ-1,8-dpmn)(Cp*$RhCl_2$)] (**8a**) (brown, 51.7%). UV–Vis (CH_2Cl_2): λ_{max} 395, ca. 340(sh) nm. FAB mass (*m*/*z*): 1105 [(*M*-Cl-1)$^+$]. ^{1}H NMR ($CDCl_3$): δ 0.96 (d, $J_{HH}=7.0$ Hz, i-Pr, 6H)*[a], 0.98 (d, $J_{HH}=7.0$ Hz, i-Pr, 6H)*[b], 1.29 (d, $J_{PH}=4.0$ Hz, Cp*, 15H)*[a,b], 1.73 (s, *p*-Me, 3H)*[a], 1.74 (s, *p*-Me, 3H)*[b], 2.50 (c, C*H*, 1H), 4.57 (d, $J_{HH}=9.0$ Hz, *p*-cymene, 2H)*[a], 4.74 (d, $J_{PH}=9.0$ Hz, PCH_2, 2H)*[a], 4.98 (d, $J_{HH}=9.0$ Hz, *p*-cymene, 2H)*[b], 5.14 (d, $J_{PH}=4.5$ Hz, PCH_2, 2H)*[b], 5.29 (s, CH_2Cl_2), 5.32 (d, $J_{HH}=5.0$ Hz, *p*-cymene, 2H)*[a], 5.42 (d, $J_{HH}=5.0$ Hz, *p*-cymene, 2H)*[b], 6.45–7.70 (m, ArH, 26H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 31.2, 31.5 (s, *p*-cymeneRu), 35.8 (d, $J_{RhP}=142.0$ Hz, RhP). Isomer ratio: A/B = 1.8. Calc. for $C_{56}H_{59}P_2Cl_4RuRh\cdot 1.5CH_2Cl_2$: C, 54.50; H, 4.93. Found: C, 54.67; H, 5.28%.

[{1,2,3-$Me_3C_6H_3$$RuCl_2$}(μ-1,8-dpmn)(Cp*$RhCl_2$)] (**8b**) (yellow, 38.7%). UV–Vis (CH_2Cl_2): λ_{max} 395, ca. 340(sh) nm. ^{1}H NMR ($CDCl_3$): δ 1.28 (d, $J_{RhH}=4.0$ Hz, Cp*, 15H)*[a,b], 1.91 (s, 1- and 3-Me, 6H)*[a], 1.92 (s, 1- and 3-Me, 6H)*[b], 2.06 (d, $J_{PH}=3.0$ Hz, 2-Me, 3H)*[a], 2.09 (d, $J_{PH}=3.0$ Hz, 2-Me, 3H)*[a], 4.29 (d, $J_{HH}=5.0$ Hz, 4,6-Me, 6H)*[a], 4.36 (d, $J_{HH}=5.0$ Hz, 4- and 6-Me, 6H)*[b], 4.60 (d, $J_{PH}=4.0$ Hz, PCH_2, 2H), 4.69 (d, $J_{HH}=$ 4.0 Hz, PCH_2, 2H), 5.92 (t, $J_{HH}=5.0$ Hz, 5-C_6H, 1H), 6.45–7.50 (m, ArH, 26H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 36.7, 36.8 (s, (*p*-cymene)RuP), 39.3 (d, $J_{RhP}=143.0$ Hz, Cp*RhP). Isomer ratio: A/B = 1.2. Calc. for $C_{55}H_{57}P_2Cl_4RuRh$: C, 58.68; H, 5.10. Found: C, 58.83; H, 5.16%.

[(1,2,3,4-$Me_4C_6H_2$)$RuCl_2$}(μ-1,8-dpmn)(Cp*$RhCl_2$)] (**8c**) (reddish brown, 73.4%): UV–Vis (CH_2Cl_2): λ_{max} 394 nm. ^{1}H NMR ($CDCl_3$): δ 1.28 (d, $J_{PH}=4.0$ Hz, Cp*, 15H), 1.62 (s, 1- and 4-Me, 6H)*[a], 1.64 (s, 1- and 4-MeC_6, 6H)*[b], 2.05 (d, $J_{PH}=2.5$Hz, 2- and 3-MeC_6, 6H), 4.24 (d, $J_{PH}=3.0$ Hz, PCH_2, 4H), 4.36 (d, $J_{PH}=3.0$ Hz, PCH_2, 4H), 4.54 (d, $J_{PH}=9.0$ Hz, C_6H, 2H), 4.93 (d, $J_{PH}=9.0$ Hz, C_6H, 2H), 5.29 (s, CH_2Cl_2), 6.4–7.5 (m, ArH, 26H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 33.6 (s, RuP), 35.9 (s, RuP), 39.3 (d, $J_{RhP}=143.0$ Hz, RhP). Isomer ratio: A/B = 3.1. Calc. for $C_{56}H_{59}P_2Cl_4RuRh\cdot CH_2Cl_2$: C, 55.90 H, 5.02. Found: C, 55.52; H, 4.98%.

[{(*p*-Cymene)$RuCl_2$}(μ-1,8-dpmn)(Cp*$IrCl_2$)] (**9a**) (orange, 58.5%). UV–Vis (CH_2Cl_2): λ_{max} 320 nm. FAB mass (*m*/*z*): 1194 [(M-Cl)$^+$]. ^{1}H NMR ($CDCl_3$): δ 0.96 (d, $J_{HH}=7.0$ Hz, i-Pr, 6H)*[a], 0.98 (d, $J_{HH}=7.0$ Hz, i-Pr, 6H)*[b], 1.29 (d, $J_{PH}=2.5$ Hz, Cp*, 15H), 1.56 (s, p-Me, 3H), 2.51 (c, C*H*, 2H), 4.58 (d, $J_{HH}=9.0$ Hz, *p*-cymene, 2H)*[a], 4.74 (d, $J_{HH}=9.0$ Hz, *p*-cymene, 2H)*[a], 5.01 (d, $J_{PH}=9.0$ Hz, PCH_2, 2H)*[b], 5.14 (d, $J_{PH}=6.5$ Hz, PCH_2, 2H)*[b], 5.31 (d, $J_{HH}=5.0$ Hz, *p*-cymene, 2H)*[a], 5.38 (d, $J_{HH}=5.5$ Hz, *p*-cymene, 2H)*[b], 6.45–7.70 (m, ArH, 26H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 31.3, 31.5 (s, *p*-cymeneRu), 6.8 (s, Cp*IrP). Isomer ratio: A/B = 3.1. Calc. for $C_{56}H_{59}P_2Cl_4RuIr$: C, 54.72; H, 4.84. Found: C, 54.48; H, 5.17%.

[{1,2,3-$Me_3C_6H_3$}$RuCl_2$}(μ-1,8-dpmn)(Cp*$IrCl_2$)] (**9b**) (orange, 66.8%). UV–Vis (CH_2Cl_2): λ_{max} approximately 360 (sh), 311 nm. ^{1}H NMR (CD_2Cl_2): δ 1.25 (d, $J_{PH}=2.5$ Hz, Cp*, 15H)*[a], 1.26 (d, $J_{PH}=2.5$ Hz, Cp*, 15H)*[b], 1.90 (s, 1- and 3-Me, 6H)*[a], 1.91 (s, 1- and 3-Me, 6H)*[b], 2.07 (d, $J_{PH}=2.5$Hz, 2-Me, 3H)*[a], 2.08 (d, $J_{PH}=2.5$ Hz, 2-Me, 3H)*[b], 4.25–5.4 (m, 4-, 5-, 6-C_6H, and PCH_2), 5.29 (s, CH_2Cl_2), 6.5–7.4 (m, ArH, 26H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 5.7, 6.5 (s, Cp*IrP), 34.5, 35.5 (s, RuP). Isomer ratio: A/B = 4.7. Calc. for $C_{55}H_{57}P_2Cl_4RuIr\cdot 0.5CH_2Cl_2$: C, 53.01; H, 4.65. Found: C, 52.76; H, 4.72%.

[(Cp*$RhCl_2$)(μ-1,8-dpmn)(Cp*$IrCl_2$)] (**10**) (reddish brown, 91.7%). UV–Vis (CH_2Cl_2): λ_{max} 394, ca. 310(sh) nm. ^{1}H NMR ($CDCl_3$): δ 1.26 (d, $J_{PH}=2.5$ Hz, Cp*Ir, 15H), 1.27 (d, $J_{PH}=3.5$ Hz, Cp*Rh, 15H), 4.65 (b, PCH_2, 4H), 5.30 (s, CH_2Cl_2), 6.4–7.4 (m, ArH, 26H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 5.23 (s, Cp*IrP), 37.9 (d, $J_{RhH}=142.0$ Hz). Calc. for $C_{56}H_{60}P_2Cl_4RhIr\cdot 1.5CH_2Cl_2$: C, 50.80 H, 4.67. Found: C, 50.92; H, 4.23%.

2.2. Preparation of cationic complexes

2.2.1. [{(p-Cymene)RuCl(1,8-dpmn)}(OTf) (11a)

A solution of [(*p*-cymene)$RuCl_2$]$_2$ (72.2 mg, 0.118 mmol) in CH_2Cl_2 (15 ml) and acetone (5 ml) was stirred at r.t. for 10 min. Ag(OTf) (70.2 mg, 0.273 mmol) was added to the solution and then 1,8-dpmn (125.6 mg, 0.239 mmol) was added. After 5 h, the solvent was removed and the residue was extracted with CH_2Cl_2, followed by filtration through the glass filter (G4). The CH_2Cl_2 was concentrated and diethylether was added, giving yellow crystals of **11a** (105.2 mg, 47.2%). UV–Vis (CH_2Cl_2): λ_{max} 360 nm. ^{1}H NMR ($CDCl_3$): δ 0.80 (d, $J_{HH}=6.5$ Hz, Me_2C, 6H)*[a], 0.82 (d, $J_{HH}=6.5$ Hz, i-Pr, 6H)*[b], 1.61 (s, Me, 3H)*[a+b], 2.20 (sep. $J_{HH}=6.5$ Hz, CH, 1H)*[b], 2.45 (sep. $J_{HH}=6.5$ Hz, CH, 1H)*[a], 5.01 (d, $^2J_{PH}=9.5$ Hz, PCH_2, 2H), 5.15–5.85 (c, C_6H_4, 4H), 5.30 (s, CH_2Cl_2), 6.8–8.0 (m, ArH, 10H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 31.4 (s)*[a], 39.0 (s)*[b]. Isomer ratio: C/D = 2.

Calc. for $C_{47}H_{44}P_2ClSO_3F_3Ru\cdot 0.25CH_2Cl_2$: C, 58.77; H, 4.65. Found: C, 58.93; H, 4.56%.

The following cationic complexes were prepared according to a procedure similar to **11a**.

2.2.2. [(1,2,3-$Me_3C_6H_3$)RuCl(1,8-dpmn)](PF_6) (**11b**)

Reddish brown complex **11b** (66.6 mg, 76.2%) was obtained from [(1,2,3-$Me_3C_6H_3$)$RuCl_2$]$_2$ (54.9 mg, 0.094 mmol), Ag(OTf) (56.5 mg, 0.220 mmol) and 1,8-dpmn (106.1 mg, 0.202 mmol). UV–Vis (CH_2Cl_2): λ_{max} 360, 302 nm. ^{1}H NMR ($CDCl_3$): δ 1.43 (s, 1,3-MeC_4, 3H)*[a], 1.47 (s, 1,3-MeC_4, 3H)*[b], 2.15 (s, 2-MeC_6, 3H)*[a + b], 4.02 (b, PCH_2, 2H)*[a or b], 4.84 (b, PCH_2, 2H)*[a or b], 5.28 (s, CH_2Cl_2), 6.4–7.8 (m, ArH, 26H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 32.0 (s)*[a], 38.8 (s)*[b]. Isomer ratio: C/D = 50. Calc. for $C_{46}H_{42}P_2ClSO_3F_3Ru\cdot CH_2Cl_2$: C, 55.60; H, 4.37. Found: C, 55.20; H, 4.33%.

2.2.3. [Cp*RhCl(1,8-dpmn)](OTf) (**12**)

Yellow complex **12** (142.3 mg, 64.2%) was obtained from [Cp*$RhCl_2$]$_2$ (72.6 mg, 0.117 mmol), Ag(OTf) (70.2 mg, 0.273 mmol) and 1,8-dpmn (124.6 mg, 0.238 mmol). UV–Vis (CH_2Cl_2): λ_{max} 363 nm. ^{1}H NMR ($CDCl_3$): δ 1.04 (t, J_{PH} = 3.5 Hz, 15H)*[a], 1.05 (t, J_{PH} = 3.5 Hz, 15H)*[b], 4.09 (b, PCH_2, 2H)*[a or b], 4.93 (b, PCH_2, 2H)*[a or b], 5.28 (s, CH_2Cl_2), 6.4–7.8 (m, ArH, 26H), Isomer ratio: C/D = 8 (at r.t.), C/D = 50 (at −40 °C). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.1 (d, J_{RhP} = 137 Hz)*[a], 37.3 (d, J_{RhP} = 137 Hz)*[b]. Calc. for $C_{47}H_{45}P_2ClSO_3F_3Rh\cdot 0.5CH_2Cl_2$: C, 57.65; H, 4.68. Found: C, 57.79; H, 4.80%.

2.2.4. [Cp*IrCl(1,8-dpmn)](OTf) (**13**)

Yellow complex **13** (47.3 mg, 68.3%) was obtained from [Cp*$IrCl_2$]$_2$ (53.2 mg, 0.067 mmol), Ag(OTf) (45.0 mg, 0.175 mmol) and 1,8-dpmn (72.3 mg, 0.140 mmol). UV–Vis (CH_2Cl_2): λ_{max} 303 nm. ^{1}H NMR ($CDCl_3$): δ 1.03 (t, J_{PH} = 3.5 Hz, 15H)*[a], 1.04 (t, J_{PH} = 3.5 Hz, 15H)*[b], 4.41 (b, PCH_2, 4H)*[a or b], 5.0 (b, PCH_2, 4H)*[a or b], 5.30 (b, CH_2Cl_2), 6.4–7.9 (m, ArH, 26H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −8.2 (s)*[a], 1.46 (s)*[b]. Isomer ratio: C/D = 4. Calc. for $C_{47}H_{45}P_2ClSO_3F_3Ir\ 2CH_2Cl_2$: C, 51.41; H, 4.22. Found: C, 51.42; H, 4.17%.

2.2.5. [Cp*Rh(1,8-dpmn)(MesNC)](OTf)$_2$ (**14**)

After a solution of **12** (53.9 mg, 0.057 mmol) and AgOTf (15.6 mg, 0.061 mmol) in CH_2Cl_2 (15 ml) and acetone (5 ml) was stirred for 10 min at r.t., mesityl isocyanide (14.3 mg, 0.094 mmol) was added. After 5 h, the work-up similar to **11a** gave pale yellow crystals of **14** (31.0 mg, 45.2%). IR (Nujol): 2141 cm^{-1}. UV–Vis (CH_2Cl_2): λ_{max} 302 nm. ^{1}H NMR ($CDCl_3$): δ 1.44 (t, J_{PH} = 3.5 Hz, 15H), 1.93 (s, *o*-Me, 6H), 2.39 (s, *p*-Me, 3H), 4.19 (b, PCH_2, 4H), 6.4–7.9 (m, ArH, 28H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 41.9 (d, J_{RhH} = 122 Hz). Calc. for $C_{58}H_{66}NP_2S_2O_6F_6Rh$: C, 57.76; H, 4.68; N, 1.16. Found: C, 57.11; H, 4.67;N, 1.32%.

2.3. Preparation of Cl-bridged complexes

2.3.1. [{(*p*-Cymene)RuCl}$_2$(μ-1,8-dpmn)](OTf)$_2$ (**15a**)

To a solution of **4a** (221.8 mg, 0.195 mmol) in CH_2Cl_2 (15 ml) and acetone (5 ml) was added stirred at r.t. for 10 min. Ag(OTf) (70.2 mg, 0.273 mmol) was added Ag(OTf) (116.8 mg, 0.455 mmol) at r.t.. After stirring for 1 h, the solvent was removed and the residue was extracted with CH_2Cl_2, followed by filtration through the glass filter (G4). The CH_2Cl_2 was concentrated and diethylether was added, giving brown crystals of **15a** (163.3 mg, 61.4%). FAB mass (*m*/*z*): 1214 ([{*M*+CF_3SO_3)}+l], 1067 (*M*+l) (for *M* = a cationic part). UV–Vis (CH_2Cl_2): λ_{max} 384, 306 nm. ^{1}H NMR ($CDCl_3$): δ 1.27 (d, J_{HH} = 6.0 Hz, Me_2C, 6H), 1.60 (s, Me, 3H), 2.63 (sep. J_{HH} = 6.0 Hz, CH, 1H), 4.15 (d, $^2J_{PH}$ = 9.4 Hz, PCH_2, 2H), 5.30 (s, CH_2Cl_2), 5.81, (b, C_6H_4, 4H), 6.8–8.0 (m, ArH, 26H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.6 (s). Calc. for $C_{58}H_{58}P_2Cl_2O_6F_6Ru_2\cdot CH_2Cl_2$: C, 49.95; H, 4.23. Found: C, 49.65; H, 4.23%.

The following Cl-bridged complexes were prepared according to a procedure similar to **15a**.

2.3.2. [{Cp*RhCl}$_2$(μ-1,8-dpmn)](OTf)$_2$ (**16**)

Reddish brown complex **16** (54.6 mg, 51.9%) was obtained from **5** (87.8 mg, 0.077 mmol) and Ag(OTf) (45.6 mg, 0.177 mmol). UV–Vis (CH_2Cl_2): λ_{max} 399 nm. ^{1}H NMR (CD_2Cl_2): δ 1.40 (d, J_{PH} = 3.5 Hz, 15H)*[a], 1.41 (d, J_{PH} = 3.3 Hz, 15H)*[b], 4.0 (b, PCH_2, 4H)*[a or b], 6.4–7.9 (m, ArH, 26H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 34.4 (d, J_{RhH} = 152 Hz)*[b], 36.5 (d, J_{RhH} = 148 Hz)*[a]. Calc. for $C_{58}H_{60}P_2Cl_2S_2O_6F_6Rh_2\cdot 1.5CH_2Cl_2$: C, 47.73; H, 4.24. Found; C, 47.76; H, 4.38%.

2.3.3. [{Cp*IrCl}$_2$(μ-1,8-dpmn)](OTf)$_2$ (**17**)

Yellow complex **17** (23.7 mg, 22.0%) was obtained from **6** (221.8 mg, 0.195 mmol) and Ag(OTf) (116.8 mg, 0.455 mmol). UV–Vis (CH_2Cl_2): λ_{max} 314 nm. ^{1}H NMR (CD_2Cl_2): δ 1.22 (d, J_{PH} = 2.0 Hz, 30H), 4.63 (b, PCH_2, 4H), 6.4–7.9 (m, ArH, 26H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 13.1 (s). Calc. for $C_{58}H_{58}P_2Cl_2S_2O_6F_6Ir_2\cdot CH_2Cl_2$; C, 43.38; H, 3.83. Found: C, 43.74; H, 3.89%.

2.3.4. [{Cp*RhCl(MesNC)}$_2$(μ-1,8-dpmn)](OTf)$_2$ (**18b**)

A mixture of **16** (32.7 mg, 0.031 mml) and mesityl isocyanide (MesNC) (13.4 mg, 0.092 mmol) was stirred at r.t. After 5 h, the solution was concentrated and diethyl ether was added, giving yellow crystals of **18b** (16.7 mg, 32.3%). IR (Nujol): 2164 cm^{-1}. UV–Vis (CH_2Cl_2): λ_{max} 350 nm. ^{1}H NMR ($CDCl_3$): δ 1.32 (d, J_m = 3.5 Hz, 30H), 2.46 (s, *p*-Me, 6H), 2.51 (s, *o*-Me,

12H), 4.25 (b, PCH_2, 2H), 4.57 (b, PCH_2, 2H), 6.4–7.7 (m, ArH, 30H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 42.6 (d. $J_{RhP} = 126$ Hz)). Calc. for $C_{76}H_{82}N_2P_2Cl_2S_2O_6F_6Rh_2$: C, 56.43; H, 4.98; N, 1.69. Found: C, 56.15; H, 5.01; N, 1.64%.

2.3.5. [{Cp*RhCl(XylNC)}$_2$(μ-1,8-dpmn)](OTf)$_2$ (**18a**)

Yellow complex **18a** (13.5 mg, 28.8%) was obtained from **16** (39.3 mg, 0.029 mmol) and xylyl isocyanide (10.7 mg, 0.082 mmol). IR (Nujol): 2162 cm^{-1}. UV–Vis (CH_2Cl_2): λ_{max} 350 nm. ^1H NMR ($CDCl_3$): δ 1.34 (d, $J_{PH} = 3.5$ Hz, 30H), 2.34 (s, *o*-Me, 12H), 4.31 (b, PCH_2, 2H), 4.92 (b, PCH_2, 2H), 6.4–7.7 (m, ArH, 32H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 42.7 (d. $J_{RhP} = 126$ Hz). Calc. for $C_{76}H_{78}N_2P_2Cl_2S_2O_6F_6Rh_2 \cdot 0.5CH_2Cl_2$: C, 54.86; H, 4.75; N, 1.67. Found: C, 54.93; H, 4.81; N, 1.71%.

2.3.6. [{Cp*IrCl(XylNC)}$_2$(μ-1,8-dpmn)](OTf)$_2$ (**19a**)

This yellow complex (15.7 mg, 41.3%) was obtained from **17** (32.5 mg, 0.021 mmol) and xylyl isocyanide (6.4 mg, 0.049 mmol). IR (Nujol): 2155 cm^{-1}. UV–Vis (CH_2Cl_2): λ_{max} approximately 320(sh) nm. ^1H NMR ($CDCl_3$): δ 1.38 (d, $J_{PH} = 2.5$ Hz, 30H), 2.43 (s, *o*-Me, 12H), 4.45 (b, PCH_2, 2H), 4.65 (b, PCH_2, 2H), 6.4–7.6 (m, ArH, 32H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 6.9 (s). Calc. for $C_{76}H_{78}N_2P_2Cl_2S_2O_6F_6Ir_2$: C, 50.41; H, 4.34; N, 1.55. Found: C, 50.17; H, 4.47; N, 1.37%.

2.3.7. [{Cp*IrCl(MesNC)}$_2$(μ-1,8-dpmn)](OTf)$_2$ (**19b**)

This yellow complex (10.2 mg, 28.0%) was obtained from **17** (32.5 mg, 0.021 mmol) and xylyl isocyanide (mg, 0.049 mmol). IR (Nujol): 2155 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.37 (d, $J_{PH} = 2.5$ Hz, 30H), 2.41 (s, *o*-Me, 12H), 2.44 (s, *p*-Me, 6H), 4.42 (b, PCH_2) 2H), 4.62 (b, PCH_2, 2H), 6.4–7.7 (m, ArH, 32H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 6.8 (s). Calc. for $C_{78}H_{82}N_2P_2Cl_2S_2O_6F_6Ir_2$: C, 50.95; H, 4.49; N, 1.52. Found: C, 50.66; H, 4.48; N, 1.68%.

2.4. Data collection

Complexes, **5**, **8b**, **10**, **11a**, **12**, **15a** and **18b**, were recrystallized from CH_2Cl_2/ether. Cell constants were determined from 20 reflections on Rigaku four-circle automated diffractometer AFC5S. Data collections were carried out by a Rigaku AFC5S refractometer at 27 °C except −50 °C for **10**. The crystal parameters along with data collections are summarized in Table 1. Intensities were measured by the $2\theta-\omega$ scan method using Mo Kα radiation ($\lambda = 0.71069$ Å). Throughout the data collection the intensities of the three standard reflections were measured every 200 reflections as a check of the stability of the crystals and no decay was observed. Intensities were corrected for Lorentz and polarization effects. The absorption correction was made with the ψ scan method. Atomic scattering factors were taken from Cromer and Waber the usual tabulation [11]. Anomalous dispersion effects were included in Fcalc [12]; the values of $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [13]. All calculations were performed using the TEXSAN crystallographic software package [14].

2.5. Determination of the structures

The structures were solved by Patterson methods. The positions of nonhydrogen atoms of complexes except a carbon atom in **11a** were refined with anisotropic thermal parameters by using full-matrix least-squares methods. All hydrogen atoms were calculated at the ideal positions with the C–H distance of 0.95 Å and not refined.

3. Results and discussion

3.1. Dinuclear complexes

3.1.1. Homonuclear complexes

When 1,8-dpmn was treated with an equivalent of [(η^6-arene) $RuCl_2$]$_2$ (**1**) (**a**: *p*-cymene, **b**: 1,2,3-$Me_3C_6H_3$, **c**: 1,2,3,4-$Me_4C_6H_2$, **d**: 1,2,3,5-$Me_4C_6H_2$, **e**: C_6Me_6) or [Cp*MCl_2]$_2$ (**2**: M = Rh, **3**: Ir; Cp* = C_5Me_5) at room temperature, the Cl bridges cleave readily to give the dinuclear complexes, [{(η^6-arene)$RuCl_2$}$_2$(μ-1,8-dpmn-*P*,*P*′)] (**4**) or [(Cp*MCl_2)$_2$(μ-1,8-dpmn-*P*,*P*′)] (**5**: M = Rh, **6**: Ir) (Scheme 1). X-ray analysis of **5** revealed that the Rh atom was surrounded by two Cl atoms and Cp* ligand, and each Cp*$RhCl_2$ moiety was connected by a μ-1,8-dpmp ligand (Fig. 1). Similar type of structures are assumed for **4** and **6**. The ^1H NMR spectra of **4**, **5**, and **6** are in good agreement with the structure in the solid state. In the $^{31}P\{^1H\}$ NMR spectra, the chemical shifts appeared at δ approximately 35 for **4**, δ 37.5 for **5**, and δ 5.3 for **6**, respectively (Fig. 2).

In an attempt to isolate mononuclear complex (arene)$RuCl_2$(1,8-dpmp-*P*), the reaction of **1a** with 1,8-dpmp was carried out in a 1:2 molar ratio, but was unsuccessful to produce **4a** as only isolabe complex (Schemes 2 and 3).

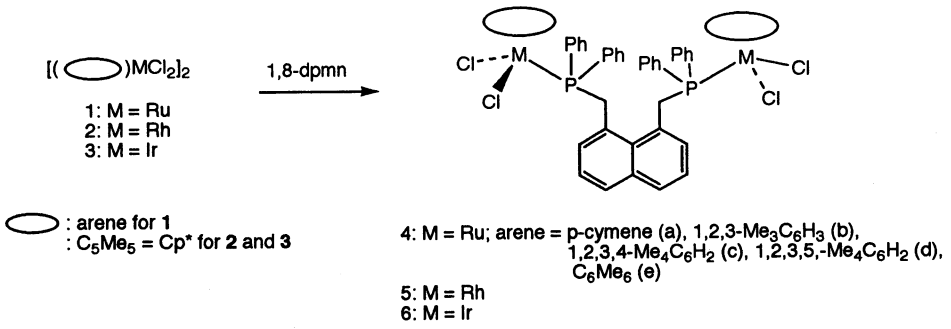
3.1.2. Homonuclear complexes with different arene groups

When **1a** and **1b** (or **1d**) were treated with 2 equiv. of 1,8-dpmp at room temperature, brown complexes, formulated as [{(*p*-cymene)$RuCl_2$} (μ-1,8-dpmn-*P*,*P*′){(arene)$RuCl_2$}] (**7ab**: arene = 1,2,3-$Me_3C_6H_3$; **7ad**: arene = 1,2,3,5-$Me_4C_6H_2$) were obtained selec-

Table 1
Crystal data of [(Cp*RhCl$_2$)$_2$(μ-1,8-dpmp-*P*,*P*′)] (**5**), [(Cp*RhCl$_2$)(μ-1,8-dpmp-*P*,*P*′){(*p*-cymene)RuCl$_2$}] (**8b**), [(Cp*RhCl$_2$)(μ-1,8-dpmp-*P*,*P*′)(Cp*IrCl$_2$] (**10**), [{(*p*-cymene)RuCl}(l,8-dpmp-*P*,*P*′)](OTf) (**11a**), [Cp*RhCI(1,8-dpmp-*P*,*P*′)](OTf) (**12**), [{(*p*-cymene)Ru(μ-Cl)}$_2$(μ-1,8-dpmp-*P*,*P*′)](OTf)$_2$ (**15a**), [{Cp*RhCl(MesNC)}$_2$(μ-1,8-dpmp-*P*,*P*′)](OTf)$_2$ (**18b**)

Compound	**5**	**8b**	**10**	**11a**	**12**	**15a**	**18**
Formula	$C_{56}H_{62}OP_2Cl_4Rh_2$	$C_{55}H_{57}P_2Cl_4RuRh$	$C_{59}H_{66}P_2Cl_{10}IrRh$	$C_{47}H_{44}O_3SP_2ClF_3Ru$	$C_{47}H_{45}O_3SP_2ClF_3Rh$	$C_{58}H_{58}O_6S_2P_2Cl_2F_6Ru_2$	$C_{78}H_{82}O_6S_2P_2Cl_2F_6Rh_2$
Molecular weight	1160.68	1125.79	1486.77	944.36	917.23	1364.20	1674.30
Color	orange	yellow	red	yellow	yellow	brown	yellow
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$(No 14)	$P2_1/c$ (No 14)	$P2_1/c$ (No 14)	$P2_1/c$ (No 14)	$P\bar{1}$ (No2)	$C2/c$ (No15)	$P2_1/n$ (No 14)
Lattice parameters							
a (Å)	15.157(5)	11.548(7)	15.130(2)	11.608(6)	14.104(6)	24.213(9)	16.482(2)
b (Å)	14.886(6)	19.67(1)	14.931(4)	29.285(4)	14.663(5)	17.410(8)	27.511(3)
c (Å)	27.144(6)	21.817(7)	27.141(2)	12.869(5)	11863(4)	16.899(7)	17.346(2)
α (°)	90.0	90.0	90.0	90.0	96.19(3)	90.0	90.0
β (°)	97.47(2)	90.96(4)	96.437(10)	100.23(3)	105.84(4)	125.08(2)	99.37(1)
γ (°)	90.0	90.0	90.0	90.0	107.73(3)	90.0	90.0
V (Å^3)	6072(3)	4955(3)	6092(1)	4304(2)	2198(1)	5830(4)	7760(1)
Z	4	4	4	4	2	4	4
D_{calc} (g cm^{-3})	1.269	1.509	1.621	1.457	1.431	1.552	1.433
μ (cm^{-1})	8.04	9.54	29.86	6.03	6.21	8.04	6.55
Scan rate (° per min)	8	8	16	8	16	8	8
Number of reflections ($\theta < 50°$)	11127	8731	13996	7588	7740	5127	13670
Number of data used	4581 ($I > 3.0\sigma(I)$)	3903 ($I > 2.5\sigma(I)$)	10821 ($I > 3.0\sigma(I)$)	7588	7740	3036 ($I > 2.0\sigma(I)$)	13670
Number of variables	586	568	636	513	523	353	901
R; R_w	0.090; 0.132 [a]	0.118; 0.180 [b]	0.051; 0.081 [a]	0.169; 0.215 [b]	0.121; 0.193 [b]	0.137; 0.181 [b]	0.112; 0.160 [b]
R_1 (reflections)	0.090(4581)	0.065 (3903)	0.051 (10821)	0.066 (3903)	0.061 (6011)	0.070(3036)	0.056 (10317)
GOF [c]	1.81	1.42	1.82	1.22	1.87	1.37	1.31

[a] $R = R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ ($w = 1/\sigma^2(F_o)$).
[b] $R = \Sigma(F_o^2-F_c^2)/\Sigma F_o^2$ and $R_w = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}(w = 1/\sigma^2(F_o))$. $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ for $I > 2.0\sigma(I)$.
[c] GOF $= [\Sigma w(|F_o|-|F_c|)^2/(N_{obs}-N_{parm})]^{1/2}$.



Scheme 1. Reaction of 1,8-dpmp with $[(arene)RuCl_2]_2$ or $[Cp^*MCl_2]_2$ (M = Rh, Ir).

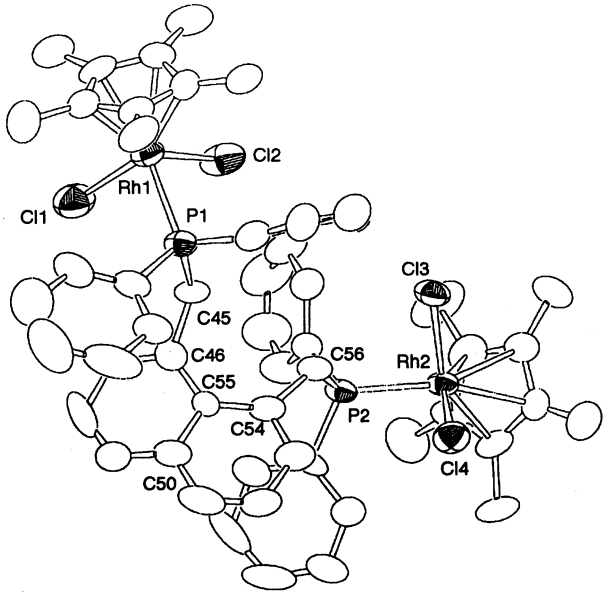


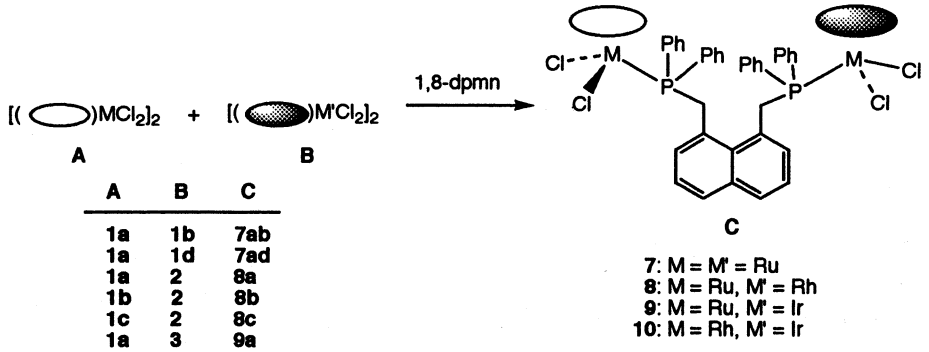
Fig. 1. Molecular structure of $[(Cp^*RhCl_2)_2(\mu\text{–}1,8\text{-dpmp-}P,P')]$ (**5**).

tively. In the ^1H NMR spectra, the methyl resonances for *i*-propyl group were observed as two sets of doublets, suggesting the presence of isomers. In fact, the $^{31}P\{^1H\}$ NMR spectrum of **7ab** showed two sets of singlets for the P atoms connected by the (*p*-cymene)Ru and $(1,2,3\text{-}Me_3C_6H_3)Ru$ groups, respectively; the resonances at δ 31.5 and 32.2 were assigned to the former, and the resonances at δ 36.2 and 38.8 were assigned to the latter on the basis of comparison with the chemical shift values of **1a** and **1b**. The $^{31}P\{^1H\}$ NMR spectrum of **7ad** showed two singlets for the P atom connected by the (*p*-cymene)Ru group, whereas it showed only one singlet at δ 35.8 for another P atom, probably being due to an accidental degeneracy of chemical shifts. Two conformational structures are assumed for the isomers as depicted in Fig. 2; (A) each metal moeity lies on the opposite side through the naphthalene framework and (B) a metal moiety lies on the same side as another metal one. The conformer A, confirmed by X-ray analysis, is sterically more stable than the conformer B. Thus, the isomer ratios A/B derived from the NMR spectra are 1.3 for **7ab** and 1.8 for **7ad**, respectively.

Reactions of **1a** with **1e** gave only **4a** and **4e** bearing the same arenes ring without formation of the complex with different arene rings. There is no information to control the reaction path.

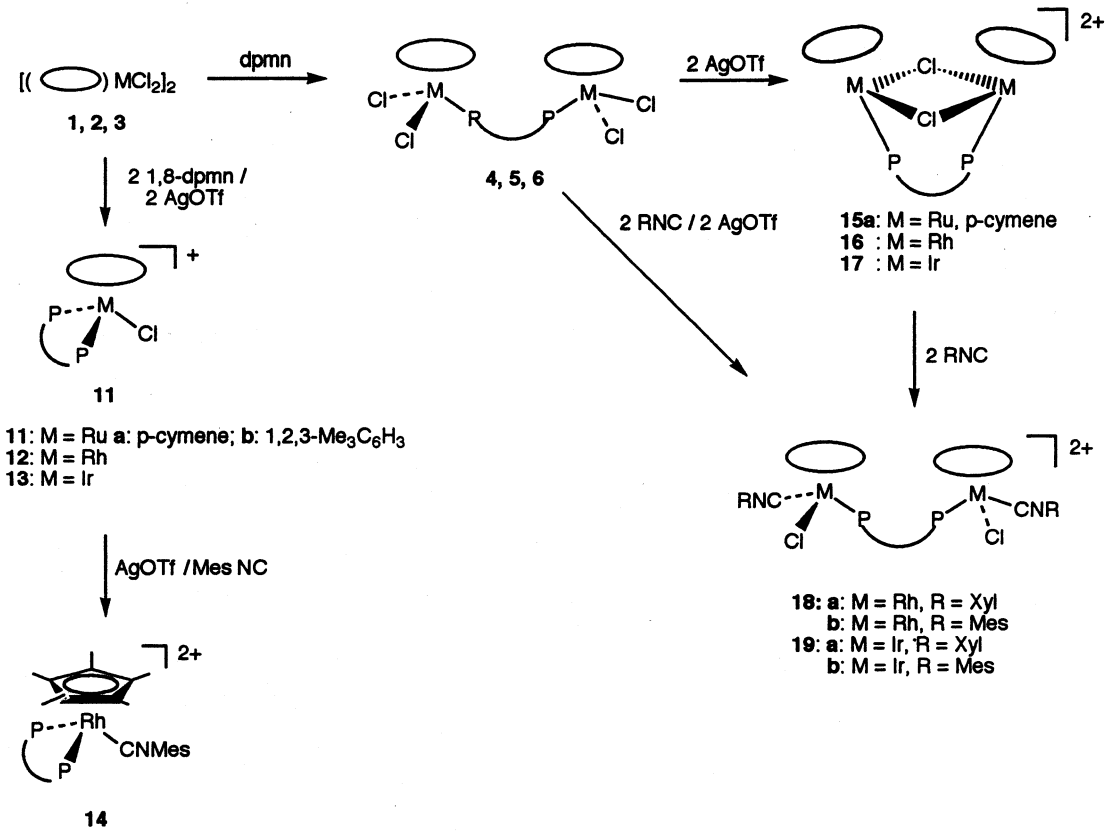
3.1.3. Heteronuclear complexes

Reactions of **2** with **1a**, **1b** or **1e** were carried out in the presence of 1,8-dpmp giving the heteronuclear complexes $[(Cp^*RhCl_2)(\mu\text{-}1,8\text{-dpmn-}P,P')$ $\{(arene)RuCl_2\}]$ (arene = *p*-cymene (**8a**), $1,2,3\text{-}Me_3C_6H_3$ (**8b**); $1,2,3,4\text{-}Me_4C_6H_2$ (**8c**)) bearing Rh(III) and Ru(II) atoms. Heteronuclear complexes bearing Ir(III) and



A	B	C
1a	1b	7ab
1a	1d	7ad
1a	2	8a
1b	2	8b
1c	2	8c
1a	3	9a
1b	3	9b
2	3	10

Scheme 2. Preparation of homonuclear complexes bearing different arene rings and heteronuclear complexes.



Scheme 3. Preparation of ionic complexes (P⌒P = 1,8-dpmn-*P*,*P*′).

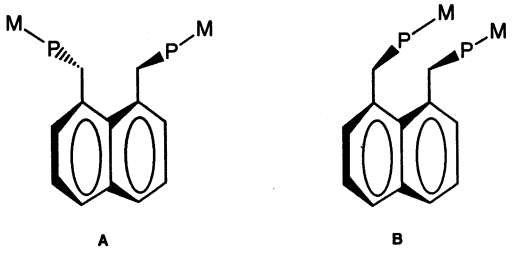


Fig. 2. Conformation of coordinated 1,8-dpmp in dimeric complexes.

Ru(II) atoms, and Ir(III) and Rh(III) atoms, [(Cp*$IrCl_2$)(μ-1,8-dpmn-*P*,*P*′){(arene)$RuCl_2$}] (arene = *p*-cymene (**9a**), 1,2,3-$Me_3C_6H_3$ (**9b**) and [(Cp*$RhCl_2$)(μ-1,8-dpmn-*P*,*P*′)(Cp*$IrCl_2$)] **10** were also generated from the corresponding complexes. It was confirmed by X-ray analyses of **8b** and **10** that the molecular structures are fundamentally similar to that for **5** (Figs. 3 and 4), Thus, complex **9** is assumed to have a structure similar to **10**.

In the ^{1}H NMR spectra, complexes **8** and **9** showed the presence of isomers in solution, whereas **10** has similar structure in solution and the solid state. For example, the ^{1}H NMR spectrum of **9b** in CD_2Cl_2 showed two doublets at δ 1.25 and 1.26 due to Cp* protons, two doublets at δ 1.90 and 1.91 due to 1- and 3-methyl protons on the arene ring and two doublets at δ 2.07 and 2.08 due to 2-methyl protons on the arene ring.

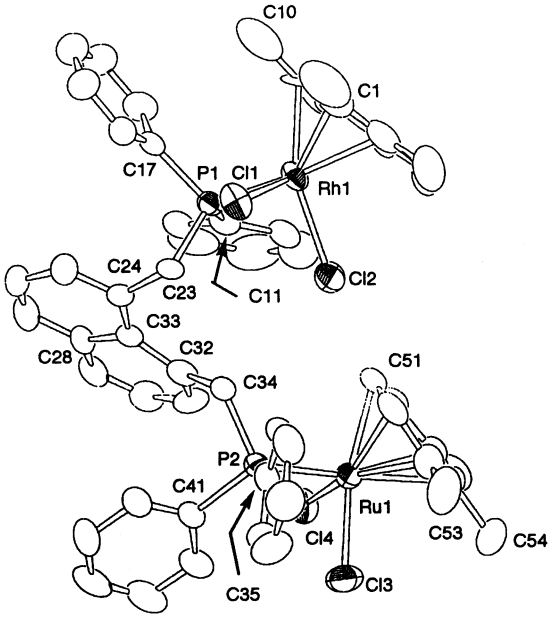


Fig. 3. Molecular structure of [(Cp*$RhCl_2$)(μ-1,8-dpmp){(1,2,3-Me_3-C_6H_3)$RuCl_2$}] (**8b**).

In the ^{31}P{^{1}H} NMR spectrum, four singlets appeared at δ 5.67, 6.54, 34.5 and 35.5. The two singlets at δ 5.67 and 6.54 are due to the P atom connected by the Ir atom, and two singlets at δ 34.5 and 35.5 are due to the

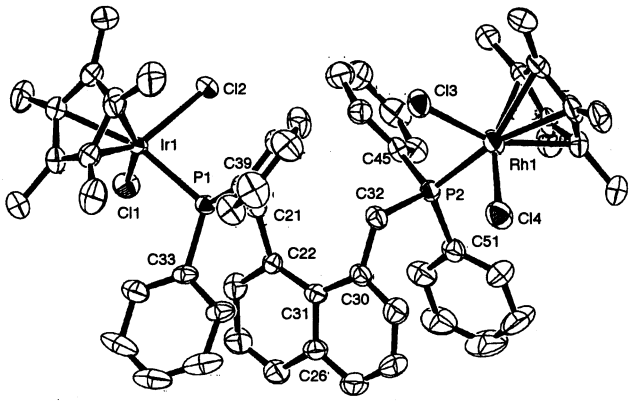


Fig. 4. Molecular structure of $[(Cp^*RhCl_2)(\mu\text{-}1,8\text{-dpmp})(Cp^*IrCl_2)]$ (**10**).

P atom connected by Ru atom on the basis of the chemical shift values of **4b** and **6**. The isomer ratio A/B is 4.7. Based on NMR spectra, the apparent isomer ratios A/B are estimated as 1.8 for **8a**, 1.2 for **8b**, 6.5 for **8c**, and 3.1 for **9a**, respectively.

3.2. Ionic complexes

Reactions of **1a** or **1b** with 2 equiv. of 1,8-dpmn were carried out in the presence of AgOTf, giving the ionic complexes, [(arene)RuCl(1,8-dpmn-*P*,*P*′)](OTf) (**11**) (arene = *p*-cymene (**a**); 1,2,3-Me_3CeH_3 (**b**)). The similar type of rhodium and iridium complexes, [Cp*MCl(1,8-dpmn-*P*,*P*′)] (OTf) (**12**: M = Rh; **13**: M = Ir) were obtained from the reactions of **2** or **3** with 1,8-dpmn. The presence of isomers was observed by the ^1H and $^{31}P\{^1H\}$ NMR spectra. The $^{31}P\{^1H\}$ NMR spectrum of **12** in a mixture of CD_2Cl_2 and CD_3COCD_3 (1:1) showed two doublets at δ 33.4 and 39.1 in an intensity ratio of 1:8 at room temperature. The isomer ratio decreased with cooling and was approximately 1:50 at −45 °C.

In order to examine the detailed structure, X-ray analyses of **11a** and **12** were performed (Figs. 5 and 6). The Cl atom and the naphthalene ring lie on the same side of the P_2C_2 plane and then the Cl atom points towards the centroid of the naphthalene ring as depicted in Fig. 7 (isomer C). Another isomer (D) is assumed that the Cl atom locates on the opposite side as the naphthalene ring. This conformation (D) is assumed to be more unstable than C, since it has steric repulsion between the phenyl rings and the Cl atom. Therefore, the isomer C is assignable to the complex having the structure confirmed by X-ray analyses. Based on the $^{31}P\{^1H\}$ NMR spectra, the apparent isomer ratios C/D in $CDCl_3$ are 2 for **11a**, 50 for **11b** and 4 for **13**, respectively.

When **12** was treated with mesityl isocyanide in the presence of Ag(OTf), pale yellow complex [Cp*Rh(1,8-dpmn-*P*,*P*′)(MesNC)](OTf) (**14**) was generated. No isomers were observed from the NMR spectroscopy.

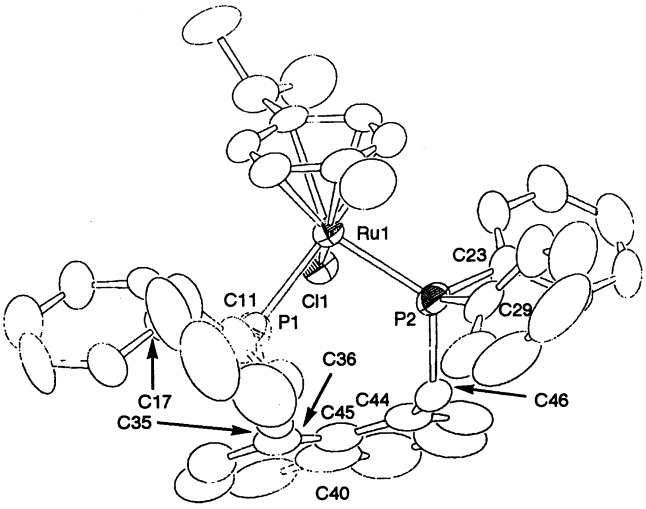


Fig. 5. Molecular structure of [(*p*-cymene)RuCl(μ-1,8-dpmp-*P*,*P*)](OTf) (**11a**).

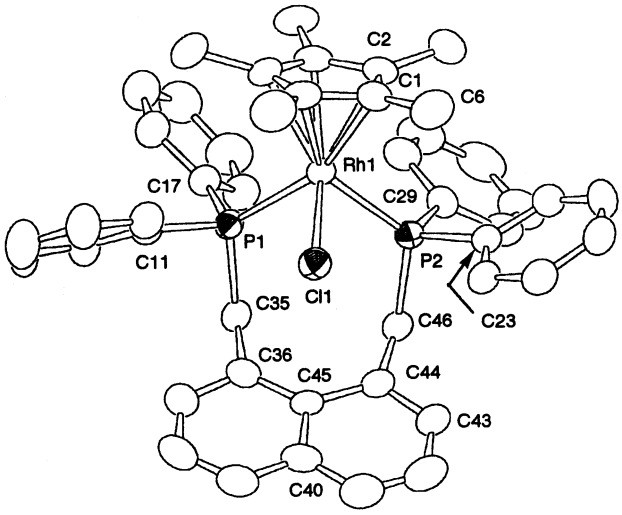


Fig. 6. Molecular structure of [Cp*RhCl(μ-1,8-dpmp-*P*,*P*′)](OTf) (**12**).

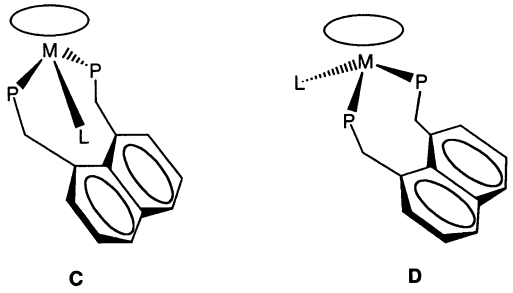


Fig. 7. Conformers of ionic complexes **11**,**12**, **13**.and **14**.

The conformer C is assumed to be superior to D by the steric demand of the bulky isocyanide ligand.

Dimeric complex **4a** was treated with 2 equiv. of AgOTf, giving the brown complex formulated as [{η^6-*p*-

cymene)RuCl}$_2$(μ-1,8-dpmn)](OTf)$_2$ (**15a**). In the FAB MS, the ion fragments centered around *m/z* 1214 and 1067 were estimated to be the $[M+TfO+l]^+$ and $[M+l]^+$ (M = cationic part), respectively. The ^{1}H NMR spectrum showed a doublet at δ 1.27, a singlet at δ 2.01 and a septet at δ 2.63 due to methyl protons of isopropyl group, methyl protons and methine proton, respectively. In the ^{31}P{^{1}H} NMR spectrum a singlet appeared at δ 23.6. The spectroscopic data suggested the Cl-bridged structure. The X-ray analysis supported the proposed structure (Fig. 8). The similar type of rhodium and iridium complexes, [(Cp*MCl)$_2$(1,8-dpmn-*P*,*P*′)](OTf)$_2$ (**16**: M = Rh; 17: M = Ir), were generated by the reactions of **5** or **6** with Ag(OTf).

Complexes **16** and **17** reacted readily with isocyanide to give the isocyanide complexes [{Cp*MCl(RHC)}$_2$-(1,8-dpmn-*P*,*P*′)](OTf)$_2$ (**18a**: M = Rh, R = Xyl; **18b**: M = Rh, R = Mes; **19a**: M = Ir, R = Xyl; **19b**: M = Ir, R = Mes). Complex **19a** was prepared by the direct reaction of [Cp*IrCl$_2$(XylNC)] with 0.5 equiv. of 1,8-dpmn in the presence of 2 equiv. of Ag(OTf). The ^{1}H NMR spectra showed a set of resonances for isocyanide and arene ring, suggesting a symmetric structure. The X-ray analysis of **18b** also confirmed the proposed structure (Fig. 9).

3.3. Molecular structures

Detailed discussion of distances and angles is avoided here because of the low accuracy of the X-ray data, especially the C–C bond lengths, for **5**, **8b**, and **15b**, but the tables of selected bond lengths and angles are given.

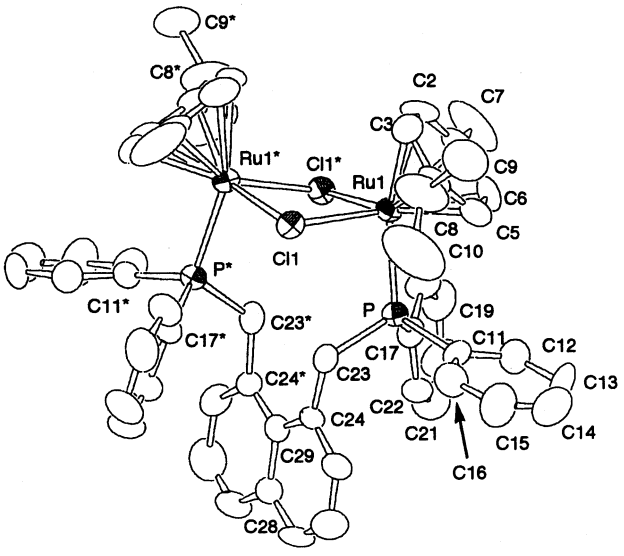


Fig. 8. Molecular structure of [{(*p*-cymene)Ru(μ-Cl)}$_2$(μ-1,8-dpmp-*P*,*P*′)](OTf)$_2$ (**15a**).

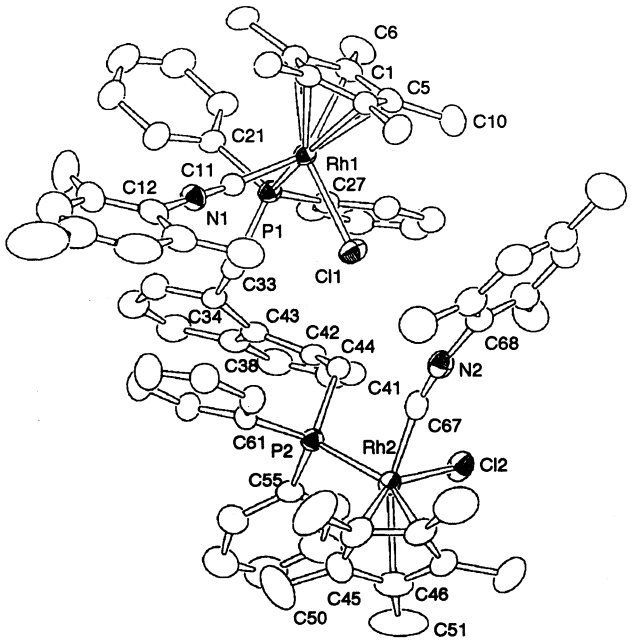


Fig. 9. Molecular structure of [{Cp*RhCl(MesNC)}$_2$(μ-1,8-dpmp-*P*,*P*′)](OTf)$_2$ (**18b**).

3.3.1. Structure of *5*

A perspective drawing of **5** with an atomic numbering scheme is given in Fig. 1, and selected bond lengths and angles are listed in Table 2. The molecule has a dimeric structure connected by a μ-1,8-dpmp ligand, and the rhodium atoms are surrounded by two Cl atoms and a P atom. The Cp*Rh moiety occupies each side of the naphthalene ring and the Rh(l)···Rh(2) and P(l)···P(2) distances are separated by 8.91 and 5.82 Å, respectively. The closest Cl(2) and Cl(3) separation is 5.72 Å. The X–Rh–Y angles around the Rh atoms are in the range from 86 to 93°. The average Rh–Cl and Rh–P bond lengths are 2.406 and 2.332 Å, respectively.

3.3.2. Structure of *8b*

A perspective drawing of **8b** with an atomic numbering scheme is given in Fig. 3, and selected bond lengths and angles are listed in Table 3. The molecule has a dimeric structure connected by a μ-1,8-dpmp ligand, and the rhodium atoms are surrounded by two Cl atoms and a P atom. The Cp*RhCl$_2$ and (1,2,3-Me$_3$C$_6$H$_3$)RuCl$_2$ moieties mutually lies on the both sides of the naphthalene ring. The Rh(1)···Ru(1) and P(1)···P(2) distances are separated by 7.34 and 5.95 Å, respectively. The former is approximately 1.5 Å shorter than that of the parent complex **5c** and the latter is approximately 0.1 Å longer. The closest Cl(2)···Cl(3) and Cl(2)···Cl(4) separations are 6.97 Å, approximately 1.0 Å longer than that found in **5c.** The X–Rh–Y angles around the Rh atoms are in the range from 86 to 94°, and those around the Ru atoms are in the range from 85 to 94°. The average Rh–Cl bond length of 2.395 Å and the Rh–

Table 2
Selected bond lengths (Å) and angles (°) of [(Cp*$RhCl_2$)$_2$(1,8-dpmn-P,P^1)] **5**

Bond lengths					
Rh(1)–Cl(1)	2.400(6)	Rh(1)–Cl(2)	2.409(6)	Rh(1)–P(1)	2.332(5)
Rh(2)–Cl(3)	2.412(5)	Rh(2)–Cl(4)	2.404(6)	Rh(2)–P(2)	2.331(5)
P(1)–C(45)	1.85(2)	P(2)–C(56)	1.86(2)	C(45)–C(46)	1.54(3)
C(54)–C(56)	1.56(2)				
Rh(1)···Rh(2)	8.91	P(1)···P(2)	5.82	Cl(1)···Cl(3)	8.41
C1(1)···C1(4)	10.22	Cl(2)···Cl(3)	5.72	C(2)···Cl(4)	8.38
Bond angles					
Cl(1)–Rh(1)–Cl2	93.1(2)	Cl(1)–Rh(1)–P(1)	89.4(2)	Cl(2)–Rh(1)–P(1)	86.4(2)
Rh(1)–P(1)–C(45)	109.5(7)	P(1)–C(45)–C(46)	114.0(1)	Rh(2)–P(2)–C(56)	111.6(6)
P(2)–C(56)–C(54)	115.0(1)				

Table 3
Selected bond lengths (Å) and angles (°) of [(Cp*$RhCl_2$)(1,8-dpmn-P,P'){(1,2,3-$Me_3C_6H_3$)$RuCl_2$}] (**8b**)

Bond lengths					
Rh(1)–Cl(1)	2.381(4)	Rh(1)–Cl(2)	2.407(4)	Ru(1)–P(1)	2.349(4)
Ru(1)–Cl(3)	2.397(4)	Ru(1)–Cl(4)	2.412(4)	Ru(1)–P(2)	2.356(4)
P(1)–C(23)	1.87(1)	P(2)–C(34)	1.86(1)	C(23)–C(24)	1.52(2)
C(32)–C(34)	1.49(2)				
Rh(1)···Ru(1)	7.34	P(1)···P(2)	5.95	Cl(1)···Cl(3)	9.58
Cl(1)···Cl(4)	9.69	Cl(2)···C1(3)	6.97	C(2)···Cl(4)	6.97
Bond angles					
Cl(1)–Rh(1)–Cl(2)	89.4(2)	Cl(1)–Rh(1)–P(1)	86.5(1)	Cl(2)–Rh(1)–P(1)	89.6(1)
Rh(1)–P(1)–C(23)	113.1(5)	P(1)–C(23)–C(24)	116.2(10)	Cl(3)–Ru(1)–Cl(4)	89.6(2)
Cl(3)–Ru(1)–P(2)	84.9(1)	Cl(4)–Ru(1)–P(2)	93.9(1)	Ru(1)–P(2)–C(34)	116.5(5)
P(2)–C(34)–C(32)	117.4(9)				

Table 4
Selected bond lengths (Å) and angles (°) of [(Cp*$RhCl_2$)(1,8-dpmn-P,P')(Cp*$IrCl_2$)] (**10**)

Bond lengths					
M(1)–Cl(1)	2.405(1)	M(1)–Cl(2)	2.414(1)	M(1)–P(1)	2.316(1)
M(2)–Cl(3)	2.410(1)	M(2)–Cl(4)	2.411(2)	M(2)–P(2)	2.317(1)
P(1)–C(21)	1.879(5)	P(2)–C(32)	1.886(1)	C(21)–C(22)	1.524(7)
C(30)–C(32)	1.503(7)				
Bond angles					
Cl(1)–M(1)–Cl(2)	91.54(1)	Cl(1)–M(1)–P(1)	89.01(5)	Cl(2)–M(1)–P(1)	85.31(4)
Cl(3)–M(2)–Cl(4)	92.36(6)	Cl(3)–M(2)–P(2)	85.55(5)	Cl(4)–M(1)–P(2)	88.53(5)
M(1)–P(1)–C(21)	112.2(2)	P(1)–C(21)–C(22)	114.8(3)	M(2)–P(2)–C(32)	111.4(2)
P(2)–C(32)–C(30)	115.5(4)				

Table 5
Selected bond lengths (Å) and angles (°) of [(p-cymene)RuCl (1,8-dpmn-P,P')](OTf) (**11a**)

Bond lengths					
Ru(1)–Cl(1)	2.388(2)	Ru(1)–P(1)	2.355(3)	Ru(1)–P(2)	2.342(2)
P(1)–C(35)	1.849(9)	P(2)–C(46)	1.869(9)	C(35)–C(36)	1.52(1)
C(44)–C(46)	1.51(1)				
Bond angles					
Cl(1)–Ru(1)–P(1)	88.12(9)	Cl(1)–Ru(1)–P(2)	83.99(8)	P(1)–Ru(1)–P(2)	94.60(9)
Ru(1)–P(1)–C(35)	123.5(3)	P(1)–C(35)–C(36)	117.2(6)	C(35)–C(36)–C(45)	126.9(9)
C(36)–C(45)–C(44)	126.7(9)	C(45)–C(44)–C(46)	126.6(9)	Ru(1)–P(2)–C(46)	122.0(3)
P(2)–C(46)–C(44)	119.0(6)				

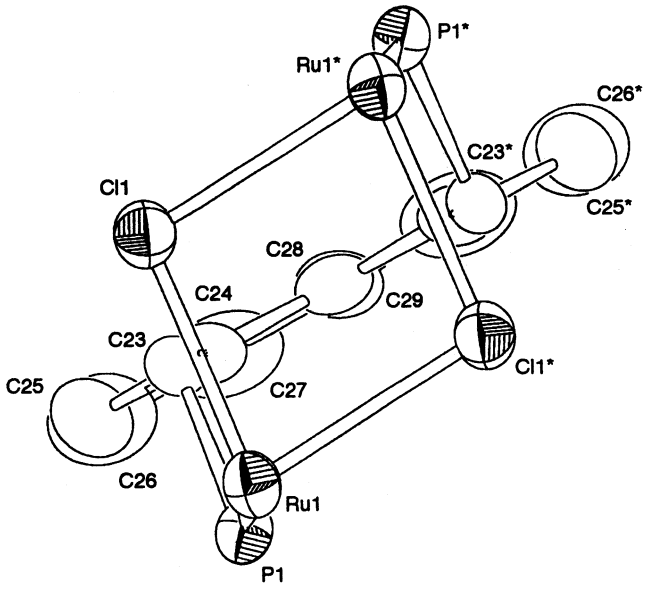


Fig. 10. Framework of [{Ru(μ-Cl)}$_2$(μ-1,8-dpmn-*P*,*P*′)] in **15a**.

P length of 2.332 Å is not significantly different from the Ru–Cl one of 2.405 Å and the Ru–P length of 2.354 Å, respectively.

3.3.3. Structures of *10*

A perspective drawing of **10** with an atomic numbering scheme is given in Fig. 4, and selected bond lengths and angles are listed in Table 4. Compound **10** was analyzed as a structure that two metal atoms have a Rh/Ir occupancy of 0.5. The structure is fundamentally similar to that for **5** or **8b**. Two metals are separated by 8.90 Å, compared with the Rh···Rh separation in **5**. The average metal–Cl and metal–P bond lengths are 2.410 Å and 2.316 Å, respectively, compared with those found in **5**.

3.3.4. Structure of *11a* and *12*

Perspective drawings with the atomic numbering schemes are given in Figs. 5 and 6, and selected bond lengths and angles are listed in Tables 5 and 6. The average lengths of the Ru–P and Rh–P bond are 2.349 and 2.348 Å, respectively, compared with those found in the neutral complexes. The P–Ru–P bite angles are 94.60(9)° for **11a** and 96.04(5)° for **12**, compared with those of [MCl_2(1,8-dpmn)] (M = Pd, Pt), [M_2(1,8-dpmn)(MesNC)$_4$](PF_6)$_2$ (M = Pd, Pt), [Pd_2(1,8-dpmn)$_2$(MesNC)$_2$](PF_6)$_2$ and RuH_2(CO)(PPh_3)(1,8-dpmn).

3.3.5. Structure of *15a*

A perspective drawing with an atomic numbering scheme is given in Fig. 8, and selected bond lengths and angles are listed in Table 7. The molecule has crystallographic twofold symmetry and sits astride a twofold axis making one-half of the complex unique. The complex cation consists of two ruthenium atoms bridged by two Cl atoms and a 1,8-dpmp ligand with Ru···Ru* separation of 3.71 Å and Cl···Cl* separation of 3.14 Å. These separations are compared with those (Rh···Rh = 3.68 Å and Cl···Cl = 3.28 Å) found in tetranuclear complex [{Cp*Rh(μ-Cl)}$_4$(pyrazine)$_2$](OTf)$_4$ [15]. One methyl-carbon atom of the isopropyl group lies above the benzene ring plane and a similar behavior is observed in **11a**, whereas two methyl-carbon atoms of the isopropyl group sit on the benzene ring plane. The Ru(1)P(1)C(23)C(24) and P(1)C(23)C(24)C(29) torsion angles are −162 and −90°, respectively. The naphthalene ring is perpendicular to the rhombus Ru(1)Cl(1)Ru(1)*Cl(1)* lying on the position near the two middle points of the Ru(1) and Cl(1) atoms and of the Ru(1)* and Cl(1)* atoms (Fig. 10). The Ru–Cl_{br} and Ru–Cl^*_{br} bond lengths are 2.439(3) Å and 2.459(3) Å, respectively, compared with the Ru–Cl_{term} bond lengths for **8b** and **11a**. TheRu(1)–P(1) bond length of 2.396 Å is longer than those found in **8b** and **11a**, suggesting the steric strain of a four-ring structure.

3.3.6. Structures of *18b*

A perspective drawing with an atomic numbering scheme is given in Fig. 9, and selected bond lengths and angles are listed in Table 8. Each rhodium atom is surrounded by Cl and P atoms, and terminal carbon atom of isocyanide ligand. Each rhodium moiety located mutually on the both sides of the naphthalene ring with the Rh···Rh separation of 7.44 Å, being shorter by

Table 6
Selected bond lengths (Å) and angles (°) of [(Cp*RhCl (1,8-dpmn-*P*,*P*′)](OTf) (**12**)

Bond lengths					
Rh(1)–Cl(1)	2.387(2)	Rh(1)–P(1)	2.352(2)	Rh(1)–P(2)	2.344(2)
P(1)–C(35)	1.867(6)	P(2)–C(46)	1.859(9)	C(35)–C(36)	1.513(9)
C(44)–C(46)	1.511(9)				
Bond angles					
Cl(1)–Rh(1)–P(1)	88.29(5)	Cl(1)–Ru(1)–P(2)	87.17(6)	P(1)–Ru(1)–P(2)	96.04(5)
Ru(1)–P(1)–C(35)	120.9(2)	P(1)–C(35)–C(36)	117.2(4)	C(35)–C(36)–C(45)	126.7(6)
C(36)–C(45)–C(44)	127.3(5)	C(45)–C(44)–C(46)	125.6(5)	Ru(1)–P(2)–C(46)	122.6(2)
P(2)–C(46)–C(44)	120.7(4)				

Table 7
Selected bond lengths (Å) and angles (°) of [{(*p*-cymene)Ru(μ-Cl)}$_2$(μ-1,8-dpmn-*P*,*P*′)](OTf)$_2$ (**15a**)

Bond lengths					
Ru(1)–Cl(1)	2.439(3)	Ru(1)–Cl(1)*	2.459(3)	Ru(1)–P(1)	2.396(3)
P(1)–C(23)	1.86(1)	C(23)–C(24)	1.48(1)	P(1)–C(11)	1.833(10)
P(1)–C(17)	1.83(1)				
Bond angles					
Cl(1)–Ru(1)–Cl(1)*	79.78(9)	Cl(1)–Ru(1)–P(1)	91.01(9)	Cl(1)*–Ru(1)–P(1)	91.57(9)
Rh(1)–Cl(1)–Ru(1)*	98.56(9)	Ru(1)–P(1)–C(23)	113.2(3)	P(1)–C(23)–C(24)	121.5(7)
Ru(1)···Ru(1)*	3.71	P(1)···P(1)*	4.60	Cl(1)···Cl(1)*	3.14

Table 8
Selected bond lengths (Å) and angles (°) of [{Cp*RhCl(MesNC)}$_2$(μ-1,8-dpmn-*P*,*P*′)](OTf) (**18b**)

Bond lengths					
Rh(1)–Cl(1)	2.395(1)	Rh(1)–P(1)	2.326(1)	Rh(1)–C(11)	1.962(4)
P(1)–C(33)	1.854(1)	C(33)–C(34)	1.490(6)	C(11)–N(1)	1.144(5)
Rh(2)–Cl(2)	2.400(1)	Rh(2)–P(2)	2.340(1)	Rh(2)–C(67)	1.964(5)
P(2)–C(44)	1.868(4)	C(42)–C(44)	1.509(6)	C(67)–N(2)	1.156(6)
Rh(1)···Rh(2)	7.44	P(1)···P(2)	5.54	Cl(1)···Cl(2)	5.78
Bond angles					
Cl(1)–Rh(1)–P(1)	90.03(4)	Cl(1)–Rh(1)–C(11)	88.8(1)	P(1)–Ru(1)–C(11)	91.0(1)
Rh(1)–P(1)–C(33)	110.5(1)	P(1)–C(33)–C(34)	114.8(3)	Rh(1)–C(11)–N(1)	169.9(4)
C(11)–N(1)–C(12)	167.9(5)				
Cl(2)–Ru(2)–P(2)	89.85(4)	Cl(2)–Ru(2)–C(67)	84.2(1)	P(2)–Ru(2)–C(67)	93.7(1)
Ru(2)–P(2)–C(44)	111.4(1)	P(2)–C(44)–C(42)	116.8(3)	Ru(2)–C(67)–N(2)	168.3(4)
C(11)–N(1)–C(12)	167.9(5)				

approximately 1.5 Å than that in the parent complex **5**, whereas the P···P separation of 5.44 Å is not different. The Rh–C–N and C–N–C angles are nearly linear with approximately 170°. The Rh–P, Rh–Cl and Rh–C bond lengths are in usual values.

The torsion angles of the naphthalene ring in μ-coordinated complexes **5**, **8b**, **10** and **18b** are approximately ±15°, whereas those in chelating complexes **11a** and **12** are approximately ±2°. For example, the torsion angle of the C(34)C(43)C(42)C(41) bond in **18b** is −164.4(4)° and that of the C(36)C(45)C(44)C (43) bond in **11a** is −1.7°. These data indicated the presence of the great strain of the naphthalene ring arising from an anti-form of the metal moieties in the μ-l,8-dpmn complexes.

4. Supplementary material

A listing of atomic coordinates, thermal parameters, bond lengths and angles and torsion angles are available from the Cambridge Structural Database.

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