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Preparation and reactions of the (pentamethylcyclopentadienyl)rhodium(III) complexes bearing 1,1′-bis(diphenylphosphinomethyl)ferrocene (dpmf) or 1,1′-bis(diphenylphosphino)ferrocene (dppf)☆

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Abstract

Reactions of [Cp*RhCl$_2$]$_2$ with 1,1′-bis(diphenylphosphinomethyl)ferrocene (dpmf) or 1,1′-bis(diphenylphosphino)ferrocene (dppf) gave the bridged complex [Cp*RnCl$_2$]$_2$(μ-diphos) (**1**: diphos = dpmf; **2**: diphos = dppf). Reaction with dppf in the presence of NaPF$_6$ gave the cationic chelated [Cp*RhCl(dppf-*P,P′*)](PF$_6$) complex **3**. Complex **1** reacted with xylyl isocyanide (XylNC) in the presence of NaPF$_6$ to yield [Cp$_2^*$Rh$_2$Cl$_2$(μ-dpmf)(XylNC)$_2$](PF$_6$)$_2$, **4**, in low yield. [Cp*Rh(dppf-*P,P′*)(MeCN)](PF$_6$)$_2$, **5a**, was prepared from **3**, NaPF$_6$ and AgNO$_3$ in MeCN. The acetonitrile ligand in this complex was replaced readily with Lewis bases (L), such as CO and isocyanides, to form [Cp*Rh(dppf-*P,P′*)(L)](PF$_6$)$_2$, **5**. Structures of **2**, **3** and **5d** (L = *p*-TosCH$_2$NC) were confirmed by X-ray analyses, in which their molecules have the piano stool structure. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: dpmf; dppf; Rhodium

1. Introduction

The use of ferrocenyl phosphines as ligands in co-ordination chemistry and catalytic reactions is well-known [1]. Many of the metal complexes of 1,1′-bis(diphenylphosphino)ferrocene (dppf) are catalytically active in some organic reactions, such as C–C couplings [2], hydroformylation [3], etc. It has been reported that the bite size and angle of dppf contribute to catalytic activities [1] and the conformation of ferrocenyl moiety thus plays an important role. The ferrocenyl moiety in dppf takes a wide variety of conformations, such as *syn*periplanar, *syn*clinal, *anti*clinal, *anti*periplanar, etc., when dppf co-ordinates to the metals ([1]a).

1,1′-Bis[(diphenylphosphino)methyl]ferrocene (dpmf) formed by introduction of a methylene group between the cyclopentadienyl ring and P atom is less rigid than dppf. This paper is interested in differences of structures and reactivities between dppf and dpmf. As part of ongoing studies, the preparation of dpmf, and palladium and nickel complexes of dpmf, were reported and they have macrocyclic dinuclear or tetranuclear structures bridged by two dpmf ligands [4]. The authors recently reported the reactions of bis[dichloro(η^6-arene)ruthenium(II)] with dpmf or dppf [5]. They now report the synthesis, structures and reactions of the bridged or chelating complexes derived from the treatment of dpmf or dppf with bis[dichloro(η^5-pentamethylcyclopentadienyl)rhodium(III)], [Cp*RhCl$_2$]$_2$, bearing an isoelectronic structure with bis[dichloro(η^6-

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☆ Dedicated to the memory of the late Professor Rokuro Okawara.

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Table 1
Crystal data of $[(\eta^5\text{-}C_5Me_5)_2Rh_2Cl_2(\mu\text{-dppf})]$ **2**, $[(\eta^5\text{-}C_5Me_5)RhCl(\text{dppf-}P,P')](PF_6)$ **3**, and $[(\eta^5\text{-}C_5Me_5)Rh(\text{dppf-}P,P')(p\text{-}MeC_6H_5SO_2CH_2NC)](PF_6)$ **5d**

Compound	**2**	**3**	**5d**
Formula	$C_{54}H_{55}P_2Cl_4FeRh_2$	$C_{44}H_{43}P_3F_6CLFeRh$	$C_{53}H_{52}NO_2P_4Fe_{12}SFeRh$
Molecular weight	1172.47	972.94	1277.69
Color	Red–violet	Orange	Pink
Crystal size (mm^3)	0.40 × 0.30 × 0.20	0.40 × 0.20 × 0.10	0.40 × 0.30 × 0.20
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
a (Å)	15.19(1)	14.987(2)	16.203(5)
b (Å)	16.836(9)	16.734(4)	18.081(5)
c (Å)	12.36(1)	16.025(2)	20.350(4)
α (°)	104.75(5)	90.0	90.0
β (°)	111.61(5)	92.94(1)	105.35(2)
γ (°)	95.39(5)	90.0	90.0
V (Å^3)	2780(4)	4013(1)	5749(2)
Z	2	4	4
$D_{calc.}$ (g cm^{-3})	1.400	1.610	1.476
μ, (cm^{-1})	5.38	10.18	7.64
F(000)	1192	1976	2592
No. of reflections	9811	7336	10 509
No. of data ($I > 3.0\sigma(I)$)	4332	2854	2846
No. of variables	558	505	511
R; R_w[a]	0.079; 0.097	0.054; 0.062	0.068; 0.075
GOF[b]	2.73	1.51	1.98

[a] $R = \Sigma \|F_o| - |F_c\|/\Sigma |F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)2/\Sigma w|F_o|^2]^{1/2}$ $(w = 1/\sigma^2(F_o))$.

[b] $\text{GOF} = [\Sigma w(|F_o| - |F_c|)^2/\Sigma (\text{No} - \text{Nv})]^{1/2}$, where No = number of data, Nv = number of variables.

arene)ruthenium(II)]. A preliminary part of this study has been described [6].

2. Experimental

All reactions were carried out under nitrogen atmosphere. Bis[dichloro(η^5-pentamethylcyclopentadienyl)rhodium(III)] [7], dpmf [4], dppf [8] and isocyanides ($2,6\text{-}Me_2C_6H_3NC$ (= XylNC), $2,4,6\text{-}Me_3C_6H_2NC$ (= MesNC)) [9] were prepared according to the literature. $p\text{-}MeC_6H_4SO_2CH_2NC$ (= $TosCH_2NC$) was commercially available. (l)-3-(PhMeHCNHCO)C_6H_4NC was given by Miss F. Takei of Osaka University. Dichloromethane and diethyl ether were distilled over CaH_2. The IR spectra were measured on an FT/IR-5300. NMR spectroscopy was carried out on a Bruker AC250. ^{1}H-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.

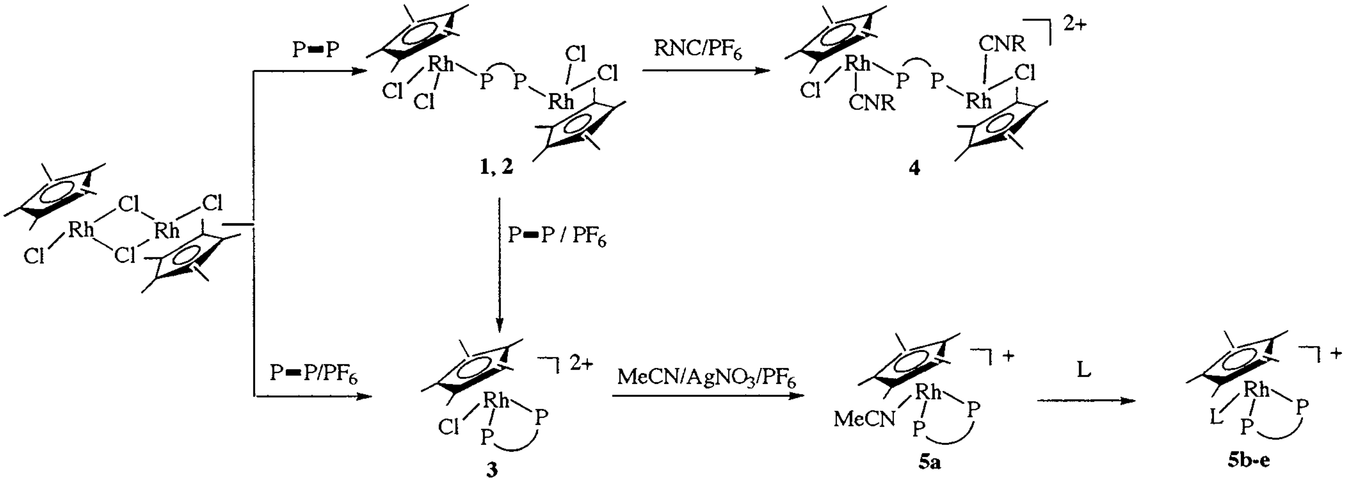
2.1. Preparation of $[Cp^*RhCl_2]_2(\mu\text{-dpmf})$, 1

To a solution of $[Cp^*RhCl_2]_2$ (31 mg, 0.05 mmol) in CH_2Cl_2 (10 ml), dpmf (29 mg, 0.05 mmol) was added at room temperature (r.t.). After stirring for 2 h, the solvent was reduced to ca. 3 ml under reduced pressure and diethyl ether was added to give red–orange crystals of **1** (42 mg, 70%). ^{1}H-NMR($CDCl_3$): δ (ppm) 1.29 (d, $J_{PH} = 3.4$ Hz, C_5Me_5), 3.19, 3.62 (s, C_5H_4), 3.67 (d, $J_{PH} = 3.4$ Hz, PCH_2), 7.3–7.7 (m, Ph). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ (ppm) 33.86 (d, $J_{RhP} = 141$ Hz). Anal. Calc. for $C_{56}H_{62}C_4P_2FeRh_2$: C, 56.03; H, 5.21. Found: C, 56.26; H, 5.00.

Complex $[Cp^*RhCl_2]_2(\mu\text{-dppf})$ **2** (78%) was prepared from the reaction of $[Cp^*RhCl_2]_2$ with dppf according to a method similar to that for **1**. ^{1}H-NMR ($CDCl_3$, at r.t.): δ (ppm) 1.21 (d, $J_{PH} = 3.4$ Hz, C_5Me_5), ca. 4.0 (b, C_5H_4), 7.2–7.9 (m, Ph); (at 50°C): δ (ppm) 1.23 (d, $J_{PH} = 3.4$ Hz, C_5Me_5), 4.07, 4.16 (b, C_5H_4), 7.2–7.8 (m, Ph). $^{31}P\{^1H\}$-NMR ($CDCl_3$ at r.t.): δ (ppm) ca. 22 (b); (at 50°): δ (ppm) 22.98 (d, $J_{RhP} = 146$ Hz). Anal. Calc. for $C_{54}H_{58}C_4P_2FeRh_2$: C, 55.32; H, 4.99. Found: C,54.72;H, 4.79.

2.2. Preparation of $[Cp^*RhCl(\text{dppf-}P,P')](PF_6)$, 3

To a solution of $[Cp^*RhCl_2]_2$ (31 mg, 0.05 mmol) and dppf (56 mg, 0.1 mmol) in a mixture of CH_2C1_2 (5 ml) and acetone (5 ml), $NaPF_6$ (84 mg, 0.5 mmol) was added at r.t. After the mixture was stirred for 3 h, the solvent was removed under reduced pressure. The residue was extracted with CH_2CI_2 (2 × 10 ml). The solution was concentrated to ca. 3 ml and diethyl ether was added to give red–orange crystals of **3** (82 mg, 84%). IR (nujol): 841 cm^{-1} (PF_6). ^{1}H-NMR (CD_3COCD_3): δ (ppm) 1.20 (t, $J_{PH} = 3.7$ Hz, C_5Me_5),



Scheme 1. Reactions of $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ and its related complexes. (P—P = dmpf-P,P′ for **1** and **4**; dppf-P,P′ for **2**, **3** and **5**: L = CO, RN).

4.27, 4.48, 4.53, 5.19 (s, C_5H_4), 7.5–7.9 (m, *Ph*). $^{31}P\{^1H\}$-NMR (CD_3COCD_3): δ (ppm) 37.94 (d, J_{RhP} = 145 Hz, dppf), − 143.1 (sep. J_{PF} = 707 Hz, PF_6). Anal. Calc. for $C_{44}H_{43}Cl_2P_3F_6FeRh_2$: C, 57.07; H, 5.43. Found: C, 56.65; H, 5.12.

2.3. Preparation of $[Cp^*_2Rh_2Cl_2(\mu\text{-}dpmf)(XylNC)_2](PF_6)_2$, 4

To a solution of **1** (60 mg, 0.05 mmol) and xylyl isocyanide (13 mg, 0.1 mmol) in a mixture of CH_2Cl_2 (5 ml) and acetone (5 ml), $NaPF_6$ (84 mg, 0.5 mmol) was added at r.t. After the mixture was stirred for 3 h, the solvent was removed under reduced pressure. The residue was extracted with CH_2Cl_2 (2 × 10 ml). The solvent was removed to dryness and recrystallization of the residual oil from MeOH/diethyl ether gave orange crystals of **4** (8 mg, 11%). IR (nujol): 2170 (N≡C), 841 cm^{-1} (PF_6). ^1H-NMR (CD_2Cl_2): δ (ppm) 1.44 (d, J_{PH} = 3.6 Hz, C_5Me_5), 2.16 (s, *o-Me*), 2.60, 2.96, 3.15, 3.99 (s, C_5H_4), 333 (t, $J_{HH} = J_{PH}$ = 15 Hz, PCH), 3.79 (q, J_{HH} = 15 Hz, J_{PH} = 7.5 Hz, PCH), 7.0–7.8 (m, *Ph*). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): δ (ppm) 39.69 (d, J_{RhP} = 123 Hz, dpmf), − 142.5 (sep., J_{PF} = 711 Hz, PF_6). Anal. Calc. for $C_{74}H_{80}Cl_2N_2P_4F_{12}FeRh_2$: C, 52.85; H, 4.79; N, 1.67. Found: C, 52.69; H, 4.50; N, 1.67.

2.4. Preparation of $[Cp^*Rh(dppf\text{-}P,P')(MeCN)](PF_6)_2$, 5a

To a solution of **3** (97 mg, 0.10 mmol) and $NaPF_6$ (84 mg, 0.5 mmol) in MeCN (20 ml), $AgNO_3$ (17 mg, 0.1 mmol) was added at r.t. After stirring for 3 h, the solvent was removed under reduced pressure. The residue was extracted with CH_2Cl_2 (2 × 10 ml). The solution was concentrated to ca. 5 ml and diethyl ether was added to give brown crystals of **5a** (86 mg, 77%). IR (nujol): 2313, 2278 (C≡N), 841 cm^{-1} (PF_6). ^1H-NMR (CD_3COCD_3): δ (ppm) 1.32 (t, J_{PH} = 3.9 Hz, C_5Me_5), 3.43 (s, *Me*CN), 4.47, 4.64, 4.75, 4.92 (s, C_5H_4), 7.7–8.0 (m, *Ph*). $^{31}P\{^1H\}$-NMR (CD_3COCD_3): δ (ppm) 41.74 (d, J_{Rhp} = 133 Hz, dppf), − 143.1 (sep., J_{PF} = 707 Hz, PF_6). Anal. Calc. for

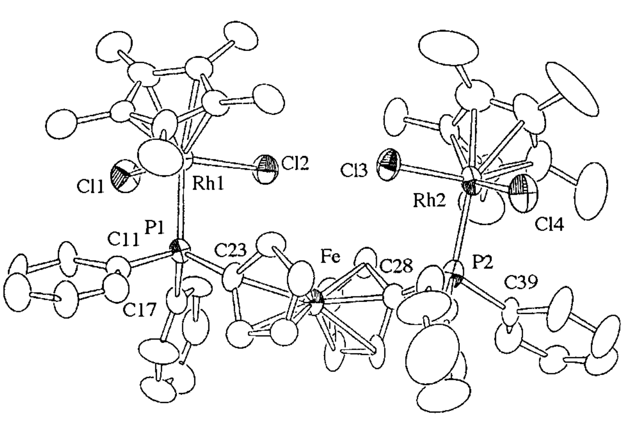


Fig. 1. Structure of **2**. Hydrogen atoms were omitted for clarity.

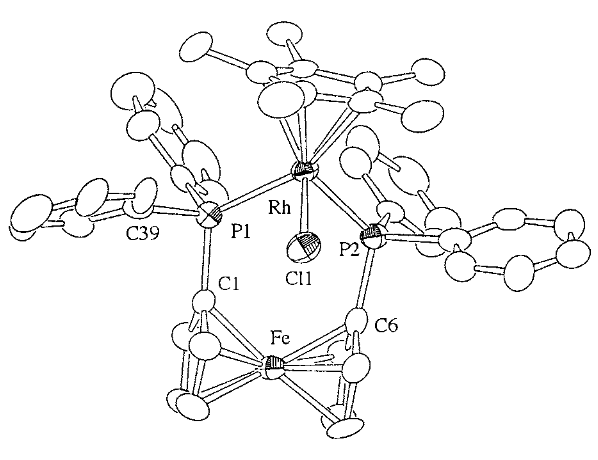


Fig. 2. Structure of **3**. The PF_6 and hydrogen atoms were omitted for clarity.

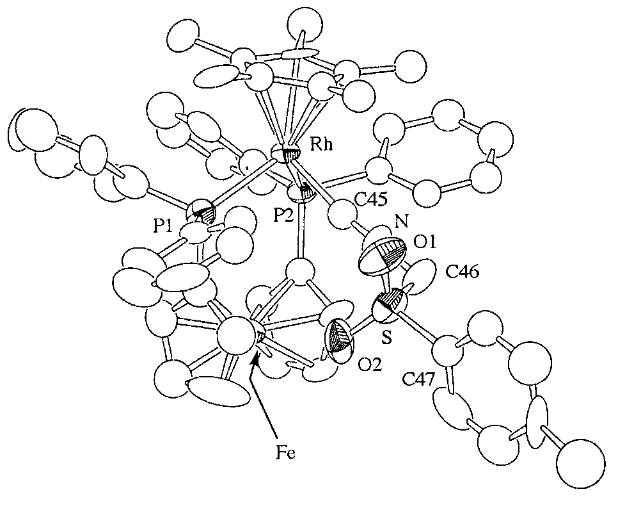


Fig. 3. Structure of **5d**. The PF_6 and hydrogen atoms were omitted for clarity.

$C_{46}H_{46}N_2P_4F_{12}FeRh$: C, 49.18; H, 4.13; N, 1.25. Found: C, 48.82; H, 3.84; N, 1.21.

*2.5. Preparation of [Cp*Rh(dppf-P,P′)(XylNC)](PF_6)$_2$, **5b***

To a solution of **5a** (25 mg, 0.022 mmol) in CH_2Cl_2 (10 ml), xylyl isocyanide (4 mg, 0.03 mmol) was added at r.t. After stirring for 2 h, the solution was concentrated to ca. 3 ml and diethyl ether was added to give pink crystals of **5b** (22 mg, 80%). IR (nujol): 2147 (N≡C), 841 cm^{-1} (PF_6). ^1H-NMR (CD_2Cl_2): δ (ppm) 1.32 (t, $J_{PH} = 3.9$ Hz, C_5Me_5), 2.30 (s, *o-Me*), 4.46, 4.54, 4.57 (s, C_5H_4), 7.3–8.0 (m, *Ph*). $^{31}P\{^1H\}$-NMR (CD_2Cl_2): δ (ppm) 43.22 (d, $J_{RhP} = 127$ Hz, dppf), -142.6 (sep., $J_{PF} = 713$ Hz, PF_6). Anal. Calc. for $C_{53}H_{52}Np_4F_{12}Rh$: C, 52.45; H, 4.32; N, 1.15. Found: C, 51.96; H, 4.08; N, 1.15.

Table 2
Selected bond lengths and angles of [(η^5-C_5Me_5)2Rh_2Cl_2(μ-dppf)] **2**[a]

Bond length (Å)			
Rh–Cl(1)	2.394(5)	Rh–Cl(2)	2.388(5)
Rh–P(1)	2.349(5)		
Rh–C_{av}(Cp*)	2.19	Fe–C_{av}(Cp)	2.05
Bond angles (°)			
Cl(1)–Rh–Cl(2)	92.5(2)	Cl(1)–Rh–P(1)	88.1(2)
Cl(2)–Rh–P(1)	89.9(2)	Rh–P(l)–C(11)	110.2(6)
Rh–P(1)–C(17)	119.3(6)	Rh–P(l)–C(23)	116.3(6)
C(11)–P(1)–C(17)	100.7(8)	C(ll)–P(1)–C(23)	104.5(7)
C(17)–P(1)–C(23)	103.8(8)	C(23)–Fe–C(28)	158.6(7)
Torsion angle (°)			
Rh–P(1)–C(23)–Fe	−84(1)	Rh–P(2)–C(28)–Fe	−84(1)
P(1)–C(23) –Fe–C(28)	72(2)	P(2)–C(28) –Fe–C(23)	74(2)

[a] Cp* = C_5Me_5, Cp = C_5H_4.

Analogously, other isocyanide complexes [Cp*Rh(dppf-*P,P′*)(RNC)](PF_6)$_2$ (**5c**: R = Mes; **5d**: R = *p*-TosCH_2; **5e**: 3-(*l*)-PhCHMeNHCO)C_6H_4)] were prepared from the substitution reaction of **5a** with the appropriate isocyanide. **5c** (pink, yield 95%): IR (nujol): 2153 (N≡C), 837 cm^{-1} (PF_6). ^1H-NMR (CD_3COCD_3): δ (ppm) 1.49 (t, $J_{PH} = 3.9$ Hz, C_5Me_5), 2.41 (s, *o-Me*), 2.44 (s, *p-Me*), 4.60, 4.75, 4.79, 4.85 (s, C_5H_4), 7.26 (s, *m-H* of MesNC), 7.8–8.0 (m, *Ph*). $^{31}P\{^1H\}$-NMR (CD_3COCD_3): δ (ppm) 42.82 (d, $J_{RhP} = 127$ Hz, dppf), -143.1 (sep., $J_{PF} = 707$ Hz, PF_6). Anal. Calc. for $C_{54}H_{54}NP_4F_{12}FeRh$: C, 52.83; H, 4.43; N, 1.14. Found: C, 52.17; H, 4.48; N, 0.99.

5d (brown, yield 91%): IR (nujol): 2186 (N≡C), 1595 (SO_2), 843 cm^{-1} (PF_6). ^1H-NMR (CD_3COCD_3): δ (ppm) 1.49 (t, $J_{PH} = 3.9$ Hz, C_5Me_5), 2.57 (s, *p-Me*), 4.51, 4.65, 4.83, 5.12 (s, C_5H_4), 6.70 (s, CH_2), 7.6–8.2 (m, *Ph*). $^{31}P\{^1H\}$-NMR (CD_3COCD_3): δ (ppm) 47.09 (d, $J_{RhP} = 127$ Hz, dppf), -143.1 (sep., $J_{PF} = 707$ Hz, PF_6). Anal. Calc. for $C_{53}H_{52}NO_2SP_4F_{12}FeRh$: C, 49.82; H, 4.10; N, 1.10. Found: C, 49.85; H, 3.92; N, 1.23.

5e (brown, yield 81%): IR (nujol): 3401 (NH), 2164 (N≡C), 1657 (C=O), 839 cm^{-1} (PF_6). ^1H-NMR (CD_3COCD_3): δ (ppm) 1.53 (t, $J_{PH} = 3.9$ Hz, C_5Me_5), 1.63 (d, $J_{HH} = 7.0$ Hz, CH_3), 4.54, 4.65, 4.89, 4.92 (s, C_5H_4), 5.38 (q, $J_{HH} = 7.0$ Hz, *CH*), 7.3–8.6 (m, *Ph*). $^{31}P\{^1H\}$-NMR (CD_3COCD_3): δ (ppm) 47.14 (d, $J_{RhP} = 127$ Hz, dppf), -143.1 (sep., $J_{PF} = 707$ Hz, PF_6). Anal. Calc. for $C_{60}H_{57}N_2OP_4F_{12}FeRh$: C, 54.07; H, 4.31; N, 2.10. Found: C, 53.62; H, 4.20; N, 2.22.

*2.6. Preparation of [Cp*Rh(dppf-P,P′)(CO)](PF_6)$_2$, **5f***

Through a solution of **5a** (25 mg, 0.022 mmol) in CH_2Cl_2 (10 ml), CO was bubbled for 10 min at r.t. After stirring for 1 h, the solution was concentrated to ca. 3 ml and diethyl ether was added to give brown crystals of **5f** (12 mg, 53%). IR (nujol): 2074 (C≡O), 839 cm^{-1} (PF_6). ^1H-NMR (CD_3COCD_3): δ (ppm) 1.62 (t, $J_{PH} = 4.1$ Hz, C_5Me_5), 4.62, 4.80, 5.00, 5.26 (s, C_5H_4), 7.8–8.1 (m, *Ph*). $^{31}P\{^1H\}$-NMR (CD_3COCD_3): δ (ppm) 49.98 (d, $J_{RhP} = 122$ Hz, dppf), -143 2 (sep., $J_{PF} = 707$ Hz, PF_6). Anal. Calc. for $C_{45}H_{43}OF_{12}P_4FeRh$: C, 48.67; H, 3.90. Found: C, 48.65; H, 4.12.

2.7. Crystallography

Complexes **2**, **3** and **5d** were recrystallized from CH_2Cl_2/diethyl ether. Cell constants were determined from 15–20 reflections on a Rigaku four-circle automated AFC5S diffractometer. The crystal along with data collection parameters are summarized in Table 1. Data collection was carried out on a Rigaku AFC5S diffractometer. Intensities were measured by the $2\theta-\omega$ scan method using graphite-monochromated Mo–K_α radiation ($\lambda = 0.71069$ Å). Throughout the data collec-

Table 3
Selected bond lengths and angles of [(η^5-C_5Me_5)RhCl(dppf-*P*,*P′*)](PF_6) **3**[a]

Bond length (Å)			
Rh–Cl(1)	2.411(3)	Rh–P(1)	2.364(3)
Rh–P(2)	2.365(3)	Rh–C_{av}(Cp)	2.25
Fe–Cav(Cp)	2.02		
Bond angle (°)			
Cl(1)–Rh–P(1)	88.9(1)	Cl(1)–Rh–P(2)	90.0(1)
P(1)–Rh–P(2)	95.6(1)	Rh–P(1)–C(1)	119.6(4)
Rh–P(2)–C(6)	120.4(4)	C(1)–Fe–C(6)	107.4(4)
P(1)–C(1)–Fe	131.5(6)	P(2)–C(6)–Fe	129.7(6)
Torsion angle (°)			
Rh–P(1)–C(1)–Fe	−04(1)	Rh–P(2)–C(6)–Fe	26.3(10)
P(1)–C(1) –Fe–C(6)	−0.8(10)	P(2)–C(6) –Fe–C(1)	0.1(9)

[a] Cp* = C_5Me_5, Cp = C_5H_4.

tion, 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 empirical ψ rotation. Atomic scattering factors were taken from the usual tabulation of Cromer and Waber [10]. Anomalous dispersion effects were included in F_{calc} [11]; the values of $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [12]. All calculations were performed using the teXsan crystallographic software package of the Molecular Structure Corporation.

The structures of **2**, **3** and **5d** were solved by Patterson methods (DIRDIF92) and refined by a full-matrix least-squares methods based on *F* values. All non-hydrogen atoms for **2** and **3** were refined anisotropically, and hydrogen atoms were calculated at the ideal positions with the C–H distance of 0.95 Å. For **5d**, 33 carbon atoms were refined isotropically and other non-hydrogen atoms, anisotropically. Final difference Fourier syntheses of **2** and **3** had no peak greater than 2.08 eÅ^{-3}.

3. Results and discussion

3.1. Reactions of [Cp*$RhCl_2$]$_2$ with dpmf or dppf

When [Cp*$RhCl_2$]$_2$ was treated with dpmf or dppf in a 1:1 ratio at r.t., red–orange crystals, formulated as [Cp*$RhCl_2$]$_2$(dpmf) **1** or [Cp*$RhCl_2$]$_2$(dppf) **2**, were obtained in ca. 70% yields (Scheme 1). In the ^{1}H-NMR spectra ($CDCl_3$) the pentamethylcyclopentadienyl groups appeared at δ 1.29 ppm for **1** and δ 1.21 ppm for **2** as a doublet consisting of the coupling constant value of $J_{PH} = 3.4$ Hz. A similar P–H coupling behavior has been observed in Cp*$RhCl_2$[PPh_2(2-O-6-$MeOC_6H_3$)] [13]. Arbitrary α- or β-protons of the ferrocenyl rings of dpmf complex **1** showed two singlets at δ 3.19 and 3.62 ppm, whereas those of dppf **2** appeared at ca. δ 4 ppm as a broad peak, in which α- and β-protons could not be distinguished within the NMR time scale at ambient temperature. When it was measured at 50°C, the spectrum separated as two broad peaks at δ 4.07 and 4.16 ppm. In the ^{31}P{^{1}H}-NMR spectra, complex **1** showed a doublet at δ 33.86 ppm ($J_{RhP} = 141.0$ Hz), but **2** showed a broad peak at δ 21.80 ppm without showing a clear J_{PH} coupling constant value, as well as in the ^{1}H-NMR spectrum. The spectrum at 50°C showed a doublet consisting of $J_{RhP} = 146.2$ Hz. The elemental analysis and spectroscopic results showed that the molecule has a dimeric structure bridged by the dpmf or dppf ligand. The X-ray analysis of **2** supported the proposed structure (Fig. 1).

When [Cp*$RhCl_2$]$_2$ was treated with two equivalents of dppf in the presence of excess $NaPF_6$ at r.t., red–orange crystals, **3**, formulated as [Cp*RhCl(dppf)](PF_6) were obtained in high yield. Complex **3** was also prepared by the reaction of **2** with dppf in the presence of $NaPF_6$. The IR spectrum showed a strong peak at 841 cm^{-1} due to a PF_6 group. The ^{1}H-NMR spectrum in CD_3COCD_3 showed a triplet at δ 1.20 ppm for the Cp* protons and four singlets in the range from δ 4.2 to 5.2 ppm for the ferrocenyl ring protons, as has been observed in [(η_6-arene)RuCl(dppf *P*,*P′*)](PF_6) having the chelated structure [5]. The X-ray analysis showed the dppf chelated structure (Fig. 2). A similar reaction with dpmf was carried out in the presence of excess $NaPF_6$, and a trace of yellow powder was obtained, but it could

Table 4
Selected bond lengths and angles of [(η_5-C_5Me_5)Rh(dppf-*P*,*P′*)(*p*-$MeC_6H_4SO_2CH_2NC$)] (PF_6)$_2$ **5d**[a]

Bond length (Å)			
Rh–P(1)	2.387(4)	Rh–P(2)	2.397(5)
Rh–C(45)	2.02(2)	C(45)–N(1)	1.10(2)
N(1)–C(46)	1.37(2)	C(46)–S(1)	1.81(2)
S(1)–O(1)	1.41(1)	S(1)–O(2)	1.40(1)
Rh–C_{av}(Cp*)	2.27	Fe–C_{av}(Cp)	2.01
Bond angle (°)			
P(1)–Rh–P(2)	97.0(2)	P(1)–Rh–C(45)	90.8(5)
P(2)–Rh–C(45)	89.4(5)	Rh–P(1)–C(6)	118.2(6)
Rh–P(2)–C(1)	119.3(5)	C(1)–Fe–C(6)	110.3(7)
P(1)–C(6)–Fe	131.9(10)	P(2)–C(1)–Fe	126.8(9)
Rh–C(45)–N(1)	170(1)	C(45)–(N1)–C(46)	178(1)
N(1)–C(46)–S(1)	109(1)	C(46)–S(1)–0(1)	106.5(9)
C(46)–S(1)–O(2)	106.8	C(47)–S(1)–0(1)	109.9(9)
C(47)–S(1)–O(2)	110.0(8)		
Torsion angle (°)			
Rh–P(1)–C(6)–Fe	−14(1)	Rh–P(2)–C(1)–Fe	33(1)
P(1)–C(6)–Fe–C(1)	−7(1)	P(2)–C(1)–Fe–C(6)	3(1)

[a] Cp* = C_5Me_5; Cp = C_5H_4.

Table 5
Structural parameters of the ferrocenyl skeleton

Complex	τ, (°)[a]	θ (°)[b]	δ_P (°)[c]	C_A–Fe–C_B (°)	P···P (Å)	Conformation
2	142.9	3.33	−0.28, −0.25	158.6(7)	6.84	*Anti*clinal (eclipsed)
3	3.0	2.95	−0.17, −0.13	107.4(4)	3.50	*Syn*periplanar
5d	−2.5	0.97	−0.06, −0.23	110.3(7)	3.58	*Syn*periplanar

[a] The torsion angle is defined as C_A–X_A–X_B–C_B, where C_A is carbon atom in Cp ring A that is bonded to a P atom (likewise for C_B), and X_A and X_B are the centroids of the two Cp rings.

[b] θ is the dihedral angle between the two Cp rings.

[c] δ_P is the deviation of the linked P atom from the same plane. A positive sign means that the P atom is on the same side of the Cp* ring as the Fe atom.

not be characterized. No chelated complexes were obtained.

3.2. Reactions of the dpmf and dppf complexes (**1**, **2** and **3**)

When complex **1** was treated with xylyl isocyanide in the presence of $NaPF_6$, replacement of a Cl anion with the isocyanide occurred to give red–orange crystals, **4**, formulated as $[Cp^*_2Rh_2Cl_2(XylNC)_2(dpmf)](PF_6)_2$ from the elemental analysis, as depicted in Scheme 1. However, a similar reaction with dppf complex **2** did not give any isolatible complexes. The IR spectrum of **4** showed two characteristic bands at 2170 and 841 cm^{-1}, suggesting the presence of the terminal isocyanide and PF_6 groups.

An attempt to replace a Cl anion of **3** with an isocyanide in the presence of $NaPF_6$ was carried out in a mixture of CH_2Cl_2 and MeOH, and the starting material **3** was recovered. However, when $AgNO_3$ was added to a mixture of **3** and $NaPF_6$ in MeCN, brown crystals of **5a**, formulated as [Cp*Rh(dppf)(MeCN)]$(PF_6)_2$, were obtained in 77% yield. The IR spectrum showed the presence of the C≡N bond and PF_6 group. The ^{1}H-NMR spectrum in CD_3COCD_3 indicated a triplet at δ 1.32 ppm and a singlet at δ 3.43 ppm, assignable to the Cp* and acetonitrile protons, respectively. Each of the ferrocenyl protons also appeared as four singlets derived from the chelated structure. A similar acetonitrile complex of ruthenium(I), [Cp*Ru(dppf)(MeCN)](BF_4)] has been prepared from the reaction of [Cp*RuCl(dppf)] with $AgBF_4$ in MeCN [14]. The acetonitrile ligand of **5a** was readily replaced with Lewis bases such as isocyanide and CO to give the corresponding complex [Cp*Rh(dppf-*P*,*P′*)(L)]$(PF_6)_2$ (**5b**: L = XylNC; **5c**: L = MesNC; **5d**: TosCH$_2$NC; **5e**: L = (*l*)-3-(PhMeHCNHCO)C_6H_3NC; **5f**: L = CO) (Scheme 1). The detailed structure was confirmed by X-ray analysis of **5d** (Fig. 3).

In the $^{31}P\{^1H\}$-NMR spectra of **5** in CD_3COCD_3, the chemical shift of the chelated ligand increased in the order as MeCN < MesNC < TosCH$_2$NC, (*l*)-3-(PhCH-MeNHCO)C_6H_3NC < CO, and a similar fashion was also observed for the chemical shift of the methyl protons on the Cp* ring. Increase of π-acceptor ability of ligands was accompanied by the result of the downfield shift of the chemical shift of the Cp* protons and the P nuclei. This suggested that the electron density on the P and Cp* ring decreased with increase of π-acceptor ability. A similar trend has been observed in the chelated diphosphine complexes, [(η^6-arene)Rh(diphos)]-(BF_4) [15].

3.3. Structures of **2**, **3** and **5d**

The selected bond lengths and angles, and structural parameters of the ferrocenyl skeleton are summarized in Tables 2–5. The conformations of ferrocenyl skeleton are classified by six categories from the torsion angles of τ [1], in which the conformation between two ferocenyl rings are *anti*clinal (eclipsed) with the P···P separation of 6.84 Å for **2** and *syn*periplanar with the P···P separation of ca. 3.5 Å for **3** and **5d**. The dihedral angles between two ferrocenyl rings are 1–3°, not being different from those found in arene–ruthenium complexes containing dpmf or dppf ligand [5].

4. Supplementary materials

Complete atomic co-ordinates, thermal parameters, bond lengths and angles, and a listing of observed and calculated structure factors are available from Y. Yamamoto on request.

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References

[1] (a) K.S. Gan, T.S.A. Hor, in: A. Togni, T. Hayashi (eds.), Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Material Science, VCH, Whinheim, 1995, p. 1. (b) P.J. Stang, H. Plenyuk, J. Fan, A.M. Arif, Organometallics 15 (1996) 904.

[2] (a) T. Ohe, N. Miyaura, A. Suzuki, J. Org. Chem. 58 (1993) 2201. (b) M. Sato, A. Miyaura, A. Suzuki, Chem. Lett. (1989) 1405. (c) W.J. Thompson, J. Gaudino, J. Org. Chem. 49 (1984) 5237.

[3] O.R. Hughe, J.D. Unruh, J. Mol. Catal. 12 (1981) 71.

[4] Y. Yamamoto, T. Tanase, I. Mori, Y. Nakamura, J. Chem. Soc. Dalton Trans. (1994) 3191.

[5] F.-J. Ma, Y. Yamamoto, J. Organomet. Chem., in press.

[6] F.-J. Ma, Y. Yamamoto, J. Organomet. Chem. 545–546 (1997) 577.

[7] J.W. Kang, K. Moseley, M. Maitlis, J. Am. Chem. Soc. 91 (1969) 5971.

[8] J.J. Bishop, A. Davison, M.L. Katcher, D.W. Lichtenberg, R.E. Merrill, J.C. Smart, J. Organomet. Chem. 27 (1971) 241.

[9] H.M. Walborsky, G.E. Niznik, J. Org. Chem. 37 (1972) 187.

[10] D.T. Cromer, J.T. Waber, International Tables for X-ray Crystallography, vol. IV, Table 2.2A, The Kynoch Press, Birmingham, UK, 1974.

[11] J.A. Ibers, W.C. Hamilton, Acta Crystallogr. 17 (1964) 781.

[12] D.C. Creagh, W.J. McAuley, in: A.J.C. Wilson (ed.), International Tables for X-ray Crystallography, Vol. C, Table 4.2.6.8, Kluwer, Boston, 1992, pp. 219–222.

[13] X.-H. Han, Y. Yamamoto, J. Organomet. Chem. in press.

[14] M. Sato, M. Asai, J. Organomet. Chem. 508 (1996) 121.

[15] E.T. Singewald, C.S. Slone, C.L. Stern, C.A. Mirkin, G.P.A. Yap, L.M. Liable-Sands, A.L. Rheingold, J. Am. Chem. Soc. 119 (1997) 3048.