Homo- and Heteronuclear Complexes of (Pentamethylcyclopentadienyl)rhodium(III) Bearing Bis(diphenylphosphanylmethyl)phenylphosphane

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Keywords: Rhodium / Gold / Copper / Silver / Cluster compounds / P ligands

Reaction of $[Cp^*RhCl_2]_2$ (**1**) with bis(diphenylphosphanylmethyl)phenylphosphane (dpmp) in the presence of KPF_6 generated the mono- or bi-nuclear complexes $[(Cp^*RhCl)(dpmp\text{-}P,P,P)(RhCl_2Cp^*)](PF_6)$ (**2**) or $[Cp^*RhCl(dpmp\text{-}P,P)](PF_6)$ (**3**), depending on the reaction conditions. These complexes have two chiral centers at Rh and the central P atoms, and the diastereomers were separated by successive recrystallization. The structures of **2(B)** with an $R_{Rh}S_P/S_{Rh}R_P$ pair and **3(A)** with an $R_{Rh}S_P/S_{Rh}R_P$ pair were elucidated by X-ray analyses. Reaction of **1** with an excess of dpmp in the presence of Ag(OTf) generated a hetero-tetranuclear complex $[\{Cp^*RhCl_2(dpmp\text{-}P,P,P)Ag\}_2](OTf)_2$ (**4**). An X-ray analysis revealed that each Cp^*RhCl_2 moiety is connected by a terminal P^1 atom of the dpmp ligand and each Ag atom is two-coordinate and is surrounded by another terminal P^3 atom, and a central P^{*2} atom of the other dpmp ligand. A mixture of **1** and dpmp was treated with $Au(SC_4H_8)$ or CuCl in the presence of KPF_6, generating the hetero-tetranuclear complexes $[\{Cp^*RhCl_2(dpmp\text{-}P,P,P)M\}_2](PF_6)_2$ (**7**: M = Au; **8**: M = Cu), in which the structures, except for the Cl-bridged structure of **8**, are fundamentally similar to that of **4**. These complexes were also prepared by the reactions of **3** with $Au(SC_4H_8)$ or CuCl. Complex **3** reacted with AgOTf to afford $[Cp^*Rh(dpmp\text{-}P,P,P)](OTf)_2$ (**5**). Treatment of **3(A)** (a diastereomer with an $R_{Rh}S_{P2}/S_{Rh}R_{P2}$ pair) with **1**, $[(p\text{-cymene})RuCl_2]_2$ or $PdCl_2(cod)$ gave $[Cp^*RhCl(dpmp\text{-}P,P,P)RhCl_2Cp^*](PF_6)$ (**2**) or $[Cp^*RhCl(dpmp\text{-}P,P,P)RuCl_2(p\text{-cymene})](PF_6)$ (**6**), respectively. These addition reactions proceeded stereoselectively.
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Introduction

Triphosphanes, especially bis(diphenylphosphanylmethyl)phenylphosphane (dpmp), play an important role as the backbone in the construction of polynuclear clusters. The chemistry of rhodium, iridium, and gold has been sited by Balch.[1] We have developed systematic syntheses of homo- and hetero-bimetallic and -trimetallic platinum and palladium clusters with tridentate phosphane and isocyanide ligands.[2] These complexes are constructed fundamentally of a square planar framework and contain dpmp, carbon monoxide, halogens and isocyanides as ligands. Octahedral complexes can lead to compounds with diverse dimensionality, in comparison with square-planar complexes.

Recently, we reported the preparation of supramolecular complexes based on quasi-octahedral geometries of rhodium(III) and iridium(III) bearing a pentamethylcyclopentadienyl or arene ruthenium(II) moiety. Thus, the reactions of $[Cp^*MCl_2(\mu\text{-}1,4\text{-}(CN)_2\text{-}2,3,5,6\text{-}Me_4C_6)MCl_2Cp^*]$ (M = Rh, Ir; $Cp^* = C_5Me_5$) with bidentate ligands such as pyrazine, bipyridine and di-isocyanide in the presence of AgOTf ($OTf = CF_3SO_3$) generated tetranuclear complexes with a square core.[3–5] Recently, self-assembled supramolecules with the pentamethylcyclopentadienyl or cyclopentadienyl groups in which the CN group has been generally used as a binary ligand have been reported by several researchers.[6–9]

We are interested in the chemistry of the interaction between quasi-octahedral complexes and dpmp containing three potential coordination sites because of expectation of various coordination modes and polynuclear complexes. We adopted binuclear complexes of rhodium(III), iridium(III) or ruthenium(II) containing pentamethylcyclopentadienyl or arene groups as quasi-octahedral complexes, for which the chemistry has not yet been developed. Here we report the preparation and stereochemistry of mononuclear, binuclear and polynuclear complexes of rhodium(III) bearing dpmp and pentamethylcyclopentadienyl ligands. Part of this work has already been briefly reported.[10]

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Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

DOI: 10.1002/ejic.200300402

Results and Discussion

Reactions of $[Cp^*RhCl_2]_2$ (1) with dpmp in the Presence of KPF_6 or AgOTf

When $[Cp^*RhCl_2]_2$ (**1**) ($Cp^* = C_5Me_5$) was treated with an equivalent of dpmp in the presence of KPF_6 at room temperature, two kinds of complexes [**2(A)** and **2(B)**] with the empirical formula of $[Cp^*{}_2Rh_2Cl_3(\text{dpmp-}P,P,P)](PF_6)$ were isolated by successive recrystallization (Scheme 1). The IR spectrum of **2** showed a peak at ca. 845 cm^{-1} consistent with the presence of a PF_6 anion. The ^1H NMR spectrum of the reaction mixture indicated a ratio of 1.1:1.0 for **2(A):2(B)**. The Cp* protons appeared at $\delta = 1.28$ (d) and 1.55 (t) for **2(A)** and at $\delta = 1.27$ (d) and 1.73 (t) for **2(B)**, respectively. The chemical shift of the Cp* protons in the chelate ring moiety appeared at a lower magnetic field than those of the other Cp* protons since the Rh atom in a chelate ring is sufficiently electron-deficient for the transfer electron density from the Cp* ligand to the rhodium center. The X-ray analysis of **2(B)** revealed that a Rh atom is connected by the terminal and the central P atoms, and another Rh atom is coordinated to another terminal P atom.[10]

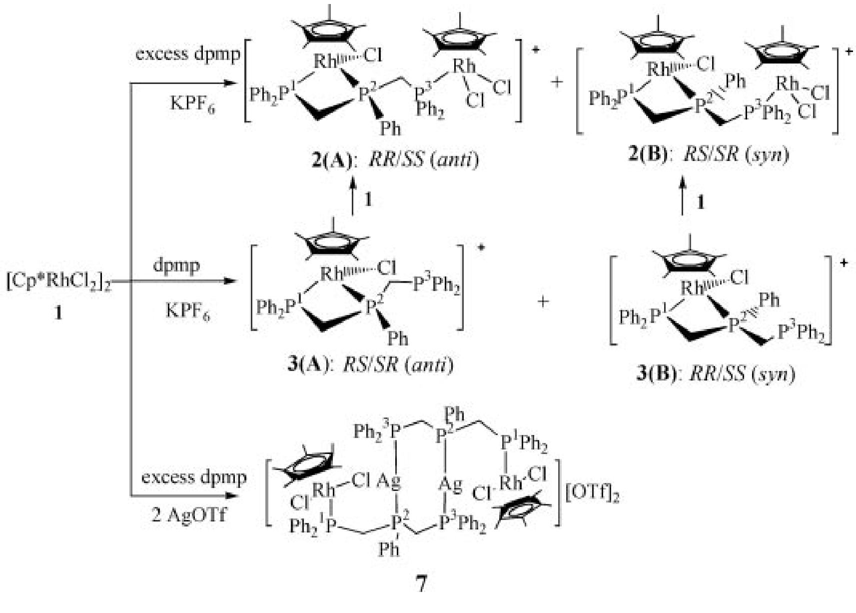
The molecule has two chiral centers namely the Rh and the central P^2 atom. Based on the priority order of the ligands around the two chiral centers,[10] compound **2(B)** was identified as the diastereomer with an $R_{Rh}S_P/S_{Rh}R_P$ pair. Thus **2(A)** is the diastereomer with an $R_{Rh}R_P/S_{Rh}S_P$ pair. The stereochemical difference is that the Cl atom and the P-substituted Ph group occupy the opposite side in **2(A)** and the same side in **2(B)**, where the structure of a **2(A)** type is designated as an *anti*-form and that of a **2(B)** type as a *syn*-form.

The reaction of **1** with an excess of dpmp in the presence of KPF_6 afforded yellow crystals of $[Cp^*RhCl(dpmp)](PF_6)$ (**3**). The ^1H NMR spectrum of the reaction mixture consists of two sets of isomers, **3(A)** and **3(B)**, with an intensity ratio of 2:1, which were separated by successive recrystallization. The X-ray study of **3(A)** revealed its stereochemistry to be that of the diastereomer with an $R_{Rh}S_P/S_{Rh}R_P$ pair (*anti*-form), based on the priority order of the ligands.[10] Thus **3(B)** is assumed to be the $R_{Rh}R_P/S_{Rh}S_P$ pair (*syn*-form). The geometries around the Rh and P^2 centers were found to be similar for **2(A)** and **3(A)**, and for **2(B)** and **3(B)**. In the ^1H NMR spectra, the Cp* protons appeared at $\delta = 1.74$(t) for **3(A)** and at $\delta = 1.78$ for **3(B)**. In the $^{31}P\{^1H\}$ NMR spectrum of **3**, the chemical shifts ($\delta = -24 \approx -30$) of the free P nuclei appeared at the higher magnetic fields by ca. $10 \approx 20$ ppm than those found for the coordinated P nuclei.[11]

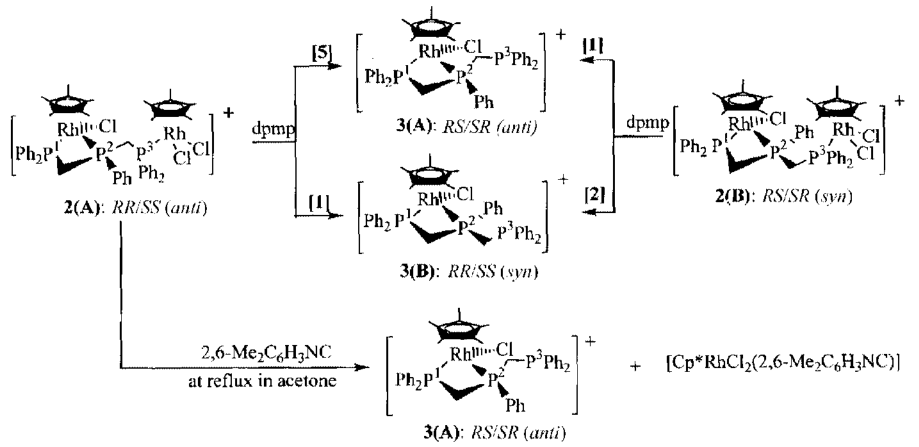
Complex **3(A)** or **3(B)** was treated with **1** at room temperature, exclusively generating **2(A)** or **2(B)**, respectively. The reactions proceeded stereospecifically. Complex **2(A)** was treated with dpmp at room temperature, affording a mixture of **3(A)** and **3(B)** consisting of an approximately 5:1 molar ratio. A similar reaction of **2(B)** gave a mixture of **3(A)** and **3(B)** consisting of an approximately 1:2 molar ratio (Scheme 2). The ratios are reasonable on the basis of the formation ratio in the original reaction of **1** with dpmp. In these reactions the conversion from **2(B)** to **3** and its reverse reaction are slower than inter-conversion between **2(A)** and **3**.

Isomerization from **2(A)** [or, **3(A)**] to **2(B)** [or, **3(B)**] and its reverse reaction did not occur on standing for a long period of time (>100 h) at room temperature. When compound **2(A)** was treated with xylyl isocyanide in acetone at reflux, cleavage of the Rh−P^3 bond occurred, generating **3(A)** and $Cp^*RhCl_2(XylNC)$ (Scheme 2). This reaction suggests a greater bond strength in the chelate ring.

A similar reaction of **1** with dpmp was carried out in the presence of two equivalents of Ag(OTf) which afforded an orange-yellow complex **4**, formulated as $[\{Cp^*RhCl_2(\text{dpmp-}P,P,P)Ag\}_2]\ (OTf)_2$ (Scheme 1). The structure was



Scheme 1. Reactions of $[Cp^*RhCl_2]_2$ **1** with dpmp in the presence of KPF_6 or Ag(OTf)



Scheme 2. Reactions of **2** with dpmp or xylyl isocyanide, where the PF_6 anion has been omitted for clarity. The formation ratio of **3(A)** and **3(B)** is designated in the bracket [].

subsequently confirmed by X-ray analysis (Figure 1). Each Cp^*RhCl_2 moiety is connected by a terminal P^1 atom of the dpmp ligand. Each Ag atom is two-coordinate and is surrounded by another terminal P^3 atom and a central P^{*2} atom of the other dpmp ligand. It is interesting to note that **4** was isolated as an addition product without the abstraction of Cl anions by Ag(OTf).

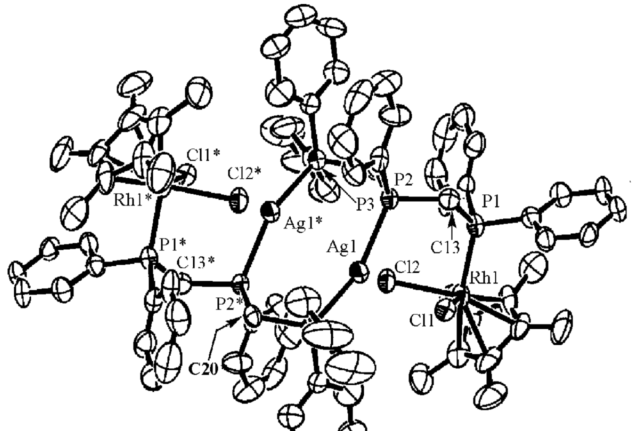


Figure 1. Molecular structure of $4 \cdot H_2O$; the OTf anion and H_2O have been omitted for clarity and thermal ellipsoids have been drawn at the 50% probability level.

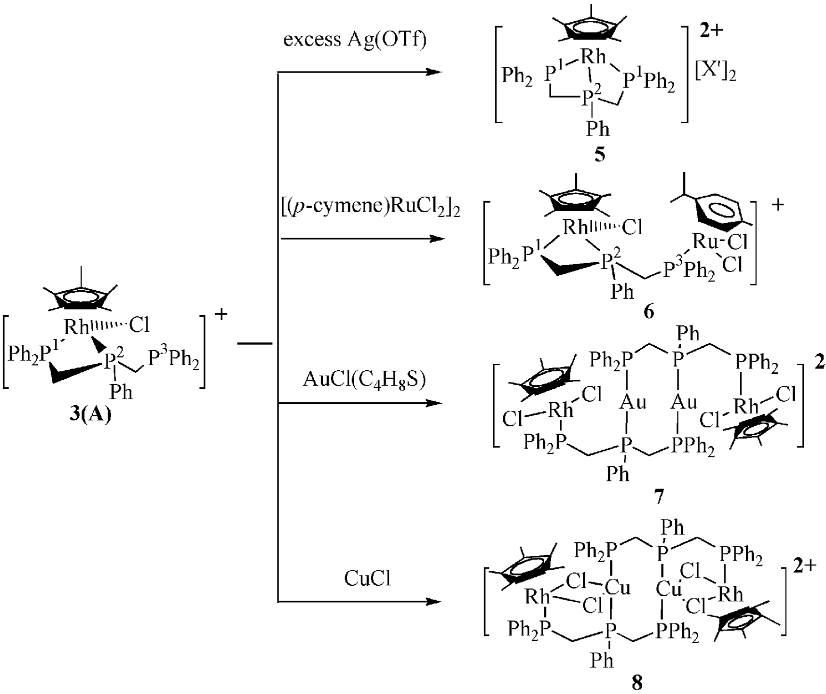
In the ^1H NMR spectrum, the Cp* protons appeared at $\delta = 1.25$ as a doublet, suggesting a symmetric structure. The $^{31}P\{^1H\}$ NMR spectrum showed a double doublet at $\delta = 28.6$ ($J_{PRh} = 146$, $J_{P,P} = 12.9$ Hz) due to the P^1 nucleus coordinated to the rhodium atom and the unresolved signals around $\delta = 2.6$ are due to the other P nuclei.

Reactions of [Cp*RhCl(dpmp-*P,P*)](PF_6) and [$Cp^*_2Rh_2Cl_3$-(dpmp-*P,P,P*)](PF_6)

The mononuclear complex **3** was anticipated as being a potential precursor to hetero- or homo-multiple nuclear complexes. The reactions of **3** are depicted in Scheme 3.

In order to try to extract a Cl anion, **3** was treated with an excess of KPF_6, but only the starting material could be recovered. A similar reaction with AgOTf, however, gave the yellow η^3-complex [Cp*Rh(dpmp-*P,P,P*)]$(OTf)_2$ (**5**) bearing a tridentate ligand as evidenced by the presence of a quadruplet for the Cp* protons in the ^1H NMR spectrum. The X-ray analysis was in agreement with the proposed structure (Figure 2).

When **3(A)** was treated with [(*p*-cymene)$RuCl_2]_2$ at room temperature, a reaction readily occurred, generating a brown complex **6(A)** established from elemental analysis and FAB mass spectrometry as [Cp*RhCl(dpmp-*P,P,P*)$RuCl_2$(*p*-cymene)](PF_6). In the ^1H NMR spectrum, the Cp* protons appeared at δ 1.52 as a triplet and the methyl protons of the isopropyl group showed two doublets at $\delta = 0.52$ and 1.00, due to nonequivalence arising from the chiral centers. The $^{31}P\{^1H\}$ NMR spectrum showed three resonances at $\delta = -12.0$ (dt, $^1J_{RhP2} = {}^2J_{P2P1} = 97.0$, $^2J_{P2P3} = 55.5$ Hz, P^2), -1.41 (t, $^1J_{P1Rh} = {}^2J_{P1P2} = 97.0$ Hz, P^1) and 23.7 (d, $^2J_{P3P2} = 55.5$ Hz, P^3) for the dpmp ligand. The stereochemistry with the *anti*-form ($R_{Rh}R_{P2}/S_{Rh}S_{P2}$) of the starting complex is assumed to be retained. Complex **6** was also prepared from the reaction of **1** with [(*p*-cymene)$RuCl_2]_2$ in a 1:1 molar ratio in the presence of KPF_6. Crystallization of the reaction mixture gave two diastereomers in a 52% yield, consisting of a 1:2 molar ratio of **6(A)** and **6(B)**, suggesting that a chelating formation including a Rh atom is preferable to one with a Ru atom. In the ^1H NMR spectrum of **6(B)**, the Cp* protons appeared at $\delta = 1.73$ and two doublets for the isopropyl protons resulted in magnetic non-equivalence. The $^{31}P\{^1H\}$ NMR



Scheme 3. Reactions of **3(A)**, where the PF_6 anions have been omitted for clarity.

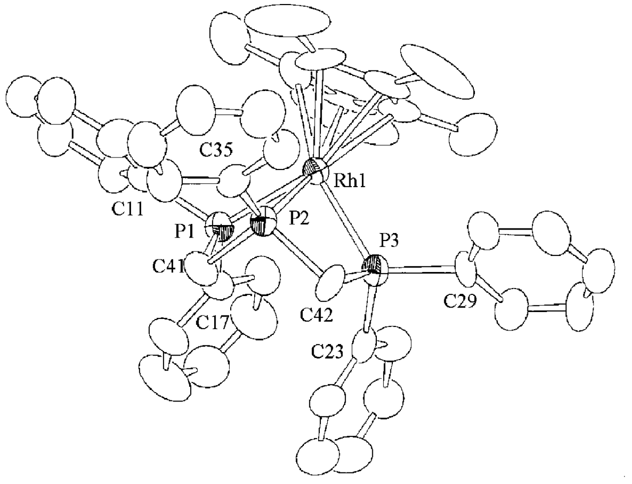


Figure 2. Molecular structure of the cation of **5**; the OTf anions have been omitted for clarity and thermal ellipsoids have been drawn at the 50% probability level.

spectrum showed three resonances at $\delta = -13.8$ (dt, $^1J_{RhP2} = {}^2J_{P2P1} = 105$, $^2J_{P2P3} = 55.0$ Hz, P^2), -10.2 (t, $^1J_{P1Rh} = {}^2J_{P1P2} = 109.0$ Hz, P^1) and 26.6 (d, $^2J_{P3P2} = 55.0$ Hz, P^3) for the dpmp ligand.

Complex **3(A)** reacted readily with $AuCl(SC_4H_8)$ at room temperature, giving the reddish brown complex **7** $[\{Cp^*RhCl_2(dpmp\text{-}P,P,P)Au\}_2](OTf)_2$. X-ray analysis confirmed that the molecular structure is fundamentally similar to that of **4**.[10] Complex **7** was directly generated from **1**, $AuCl(SC_4H_8)$ and dpmp in the presence of KPF_6.

Copper(I) chloride reacted with **3(A)** at room temperature, generating the orange complex $[\{Cp^*RhCl_2(dpmp\text{-}P,P,P)Cu\}_2](PF_6)_2$ (**8**). The ^1H NMR spectrum showed two doublets at $\delta = 1.08$ and 1.20 ppm with an intensity ratio of 1:2 due to the Cp* protons, suggesting the presence of diastereomers arising from two chiral centers (the central P atom of dpmp). Crystals of **8(A)** were suitable for X-ray analysis. The structure, except for the presence of two Cl bridges, is essentially similar to those of **4** and **7**. The stereochemistry was confirmed as an $R_{P2}S_{P2^*}/S_{P2}R_{P2^*}$ pair (Figure 3). Thus complex **8(B)**, with the chemical shift of $\delta = 1.08$, is assumed to be a diastereomer with an $R_{P2}R_{P2^*}/S_{P2}S_{P2^*}$ pair.

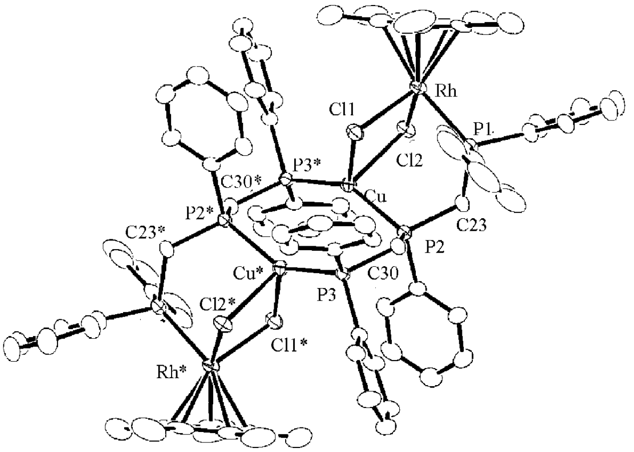
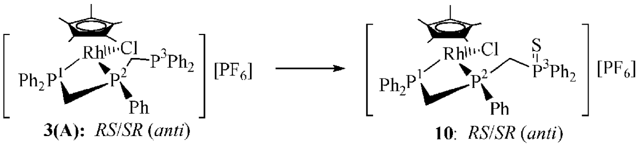


Figure 3. Molecular structure of $8{\cdot}2CH_2Cl_2$; the OTf anions and CH_2Cl_2 molecules have been omitted for clarity and thermal ellipsoids have been drawn at the 50% probability level.

A one-pot synthesis from **1**, an excess of dpmp and CuCl in the presence of KPF_6 can also be used to prepare a mixture of the diastereomers of **8**. The BF_4 anion complex was obtained from the reaction of **1** with dpmp in the presence of $[Cu(MeCN)_4](BF_4)$.

Complex **3(A)** was treated with S_8 at room temperature, affording an orange compound formulated from elemental analysis and FAB mass spectrometry as [Cp*RhCl(dpmp-*P,P,P*)S](PF_6) **9** (Scheme 4). The molecular structure is assumed to be consistent with addition of a S atom to the free terminal P^3 atom. This reaction is similar to the usual reaction of tertiary phosphanes with sulfur.



Scheme 4. Reactions of **3(A)** with sulfur

The substitution reaction of **2(A)** with xylyl isocyanide (XylNC) in the presence of KPF_6 was unsuccessful, leading only to recovery of the starting materials. The reaction in the presence of Ag(OTf), however, gave [(Cp*RhCl)$_2$-(dpmp-*P,P,P*)(XylNC)](OTf)$_2$ (**10**) (Scheme 5). The presence of a terminal isocyanide ligand was confirmed by appearance of a ν(N≡C) band at 2168 cm^{-1} and disappearance of a PF_6 band at ca. 850 cm^{-1}. The ^{1}H NMR spectrum exhibited two resonances at $\delta = 1.48$(t) and 2.00(d) for the Cp* protons. The ^{31}P{^{1}H} NMR spectrum showed three resonances at $\delta = -15.5$(ddd), -2.76(dd) and 28.6(dd) due to the P^2, P^1 and P^3 nuclei, respectively. These spectroscopic data suggest the structure depicted in Scheme 5. Since this complex has three chiral centers namely the two Rh centers and a P^2 atom, formation of two diastereomers was expected. However, no isomers were detected in the ^{1}H NMR spectrum. The stereochemistry for the chelating group in **10** was maintained, but the geometry around the other Rh center remains unknown.

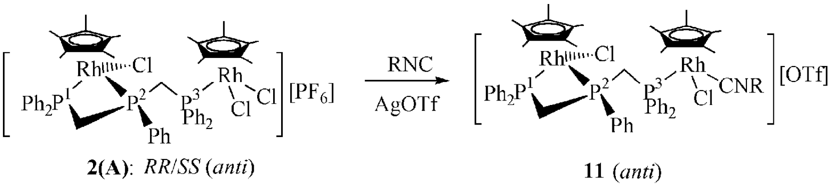
Possible Pathway

A possible route to a hetero-nuclear complex from **1** consists of the initial formation of [Cp*RhCl(dpmp-*P,P*)]Cl **A**, followed by substitution of a Cl anion with the PF_6 or OTf anions to form **B** and AgCl (or KPF_6) (Scheme 6). This proposal was confirmed by the fact that in separate experiments, complex **A** was prepared by the reaction of **1** with an excess of dpmp, and subsequently treated with KPF_6, generating **3**. The next process is the coordination of the resultant AgCl to the free P atom of **3**, generating an intermediate **C**.

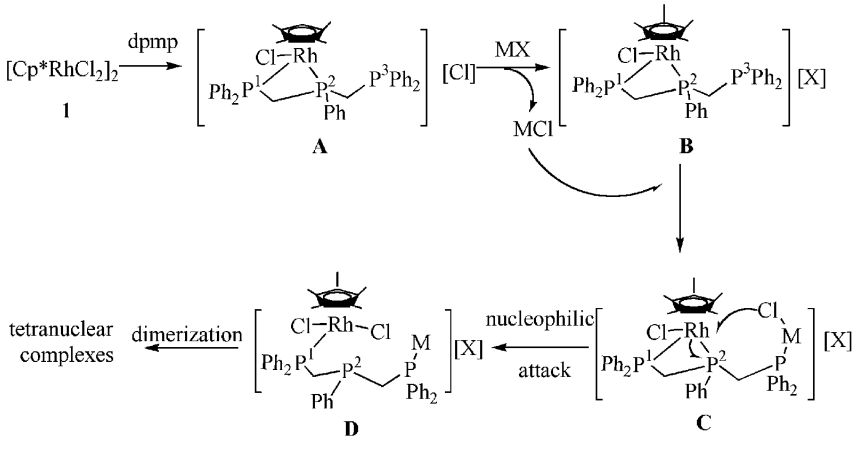
This type of species has been isolated as [Cp*IrCl(dpmp-*P,P,P*)AuCl](PF_6)[12] or [(C_6Me_6)Ru(dpmp-*P,P,P*)AuCl]-(PF_6)[10] by the reactions of [Cp*IrCl(dpmp-*P,P*)](PF_6) or [(C_6Me_6)Ru(dpmp-*P,P*,](PF_6) with AuCl(SC_4H_8). Finally, dimerization of **D** resulting in a nucleophilic attack of the Cl anion to the Rh atom led to formation of tetranuclear complexes.

Molecular Structures

Crystal Structure of 5: A perspective drawing of **5** with the atomic numbering scheme is given in Figure 2, and selected bond lengths and angles are listed in Table 1. The dpmp ligand acts as a tridentate ligand. The average



Scheme 5. Reactions of **2(A)** with xylyl isocyanide in the presence of AgOTf



Scheme 6. Possible pathway for the formation of the hetero-tetranuclear complexes, where MX = AgOTf, [Cu(MeCN)$_4$](PF_6) or AuCl(SC_4H_8) and MCl = AgCl, CuCl or AuCl.

P−Rh−P bite angle has a typical value of 70.9°, except for the P(1)−Rh−P(3) bite angle of 95.2°. The latter wide angle is a result of an unrestrained angle by a methylene chain. The Rh(1)−P(3) length of 2.369(4) Å is longer by ca. 0.05 Å than the average value of other Rh−P bonds.

Structures of 4·H_2O and 8·2CH_2Cl_2: Perspective drawings of **4** and **8** with the atomic numbering scheme are given in Figure 1 and Figure 3, and selected bond lengths and angles are listed in Table 2 and Table 3. Complexes **4** and **8** contain one H_2O and two CH_2Cl_2 solvate molecules, respectively.

Complexes **4** and **8** both have a crystallographically imposed inversion center in the middle of the Ag···Ag* and Cu···Cu vectors like that in the Au···Au vector in **7**.[10] The eight $M_2P_4C_2$ rings (M = Ag, Au, Cu) adopt a chair form to relieve the steric repulsion of the phenyl groups. Each Cp*$RhCl_2$ moiety is connected by a terminal P^1 atom of the dpmp ligand. These compounds have two chiral centers (P^2 and P^{2*}). The priority order of the ligands is M > Ph > C^2 > C^1 for the central P^2 and P^{2*}atoms, where C^1 represents the methylene carbons between the P^1 and P^2 atoms and C^2 is another methylene carbon atom. Complexes **4** and **8** have been identified as the $R_{P2}S_{P2*}/S_{P2}R_{P2*}$ pairs, similarly to **7**.[10]

An Au···Au separation of 3.203(2) Å in **7** suggests the presence of a weak interaction between the two Au centers.[10] However, the measured Ag···Ag separation of 3.385 Å in **4** suggests the absence of a metal−metal bond, since the Ag^I−Ag^I separations of 3.162−3.223 Å in [Ag_3{HC(PPh_2)$_3$}] have also suggested the absence of metal-metal bonds.[14] In comparison, [Ag_2(dpmp)$_2$](NO_3)$_2$, which is considered to have an Ag−Ag bond has an Ag−Ag separation of 3.085(1) Å.[15] A Cu···Cu separation of 3.566 Å in **8** is indicative of the absence of a metal-metal bond.

Since the M···Cl separations of 2.709 and 2.911 Å in **4** [M = Ag], and of 3.05 and 3.15 Å in **7** [M = Au] are longer than those found in each of the M−Cl-bridged bonds,[16] the Ag atoms are two-coordinate and are surrounded by two P atoms (a terminal P^{3*} atom from a dpmp ligand and a central P^2 atom from another dpmp). The P(2)−M−P(3)* angles are 150.3(1)° for **4** and 164.6(1)° for **7**, bent from the linear array to the reverse side against another Ag atom. The Cu···Cl(1) separation of 2.443 Å can be compared with the bridged Cu−Cl bond lengths of 2.448(3) Å in [Ir_2(H)$_4$Cu(CO)$_2$(μ-Cl)Cl(μ-dpma)$_2$]$^+$ [17] and another Cu···Cl(2) separation of 2.568 Å can be assumed to be a weak interaction, although it is somewhat longer. These Cu···Cl interaction cause the P(2)−Cu−P(3)* angle [145.77(7)°] to be more acute than those found in other complexes.

Table 1. Selected bond lengths and angles for [Cp*Rh(dpmp-*P,P,P*)](OTf)$_2$ (**5**)

Rh(1)−P(1)	2.324(3)	Rh(1)−P(2)	2.310(3)	Rh(1)−P(3)	2.369(4)
P(1)−C(41)	1.83(1)	P(2)−C(41)	1.81(1)	P(2)−C(42)	1.82(1)
P(3)−C(42)	1.83(1)				
P(1)−Rh(1)−P(2)	71.0(1)	P(1)−Rh(1)−P(3)	95.2(1)	P(2)−Rh(1)−P(3)	70.7(1)
Rh(1)−P(1)−C(41)	95.8(4)	P(1)−C(41)−P(2)	95.2(5)	Rh(1)−P(2)−C(42)	96.7(4)
P(2)−C(42)−P(3)	95.9(5)	C(41)−P(2)−C(42)	104.7(5)		

Table 2. Selected bond lengths and angles for [{Cp*RhCl(dpmp-*P,P,P*)Ag}$_2$](PF$_6$)$_2$·H_2O (**4**·H_2O)

Ag(1)−Cl(2)	2.706(3)	Ag(1)−P(2)	2.433(3)	Ag(1)−P(3)*	2.392(3)
Rh(1)−Cl(1)	2.425(3)	Rh(1)−Cl(2)	2.441(3)	Rh(1)−P(1)	2.327(3)
P(1)−C(13)	1.85(1)	P(2)−C(13)	1.85(1)	P(2)−C(20)	1.84(1)
P(3)−C(20)	1.84(1)				
Cl(2)−Ag(1)−P(2)	88.32(9)	Cl(2)−Ag(1)−P(3)*	120.2(1)	P(2)−Ag(1)−P(3)*	150.3(1)
Cl(1)−Rh(1)−Cl(2)	89.5(1)	Cl(1)−Rh(1)−P(1)	87.7(1)	Cl(2)−Rh(1)−P(1)	92.7(1)
Ag(1)−Cl(2)−Rh(1)	98.8(1)	Rh(1)−P(1)−C(13)	119.9(4)	P(1)−C(13)−P(2)	120.5(6)
Ag(1)−P(2)−C(13)	112.1(4)	Ag(1)−P(2)−C(20)	112.5(4)	P(2)−C(20)−P(3)	112.3(5)
Ag(1)−P(3)−C(20)	116.6(4)				
Ag(1)···Ag(1)	3.385(2)				

Table 3. Selected bond lengths and angles for [{Cp*RhCl$_2$(dpmp-*P,P,P*)Cu}$_2$](PF$_6$)$_2$·2CH$_2$Cl$_2$ (**8**·2CH$_2$Cl$_2$)

Cu−Cl(1)	3.443(2)	Cu−Cl(2)	2.568(2)	Cu−P(2)	2.249(2)
Cu−P(3)*	2.235(2)	Rh−Cl(1)	2.421(2)	Rh−Cl(2)	2.440(2)
Rh−P(1)	2.329(2)	P(1)−C(23)	1.836(7)	P(2)−C(23)	1.851(7)
P(2)−C(30)	1.839(7)	P(3)−C(30)	1.840(7)		
Cl(1)−Cu−Cl(2)	85.61(6)	Cl(1)−Cu−P(2)	92.02(6)	Cl(1)−Cu−P(3)*	118.80(7)
Cl(2)−Cu−P(2)	95.28(6)	Cl(2)−Cu−P(3)*	101.20(6)	P(2)−Cu−P(3)*	145.77(7)
Cl(1)−Rh−Cl(2)	88.99(6)	Cl(1)−Rh−P(1)	89.63(6)	Rh−Cl(1)−Cu	93.77(7)
Rh−Cl(2)−Cu	90.29(6)	Rh−P(1)−C(23)	101.0(3)	P(1)−C(23)−P(2)	120.0(4)
Cl(2)−Rh(1)−P(1)	88.1(2)				

The M−P lengths increase with M in the order Cu, Au and Ag in accordance with the atomic radii of the metals. The Cl(1)−Rh−Cl(2) and Cl−Rh−P(1) angles which are in the range 87.3−92.7°are nearly perpendicular as a result of the octahedral core. The Rh−Cl bond lengths in the range 2.417−2.440 Å are typical.

Conclusion

The chemistry of dpmp has been limited to square-planar complexes of palladium, platinum and rhodium as well as two coordinate complexes of silver and gold. In this paper the chemistry of dpmp has been extended to the octahedral geometry. Pentamethylcyclopentadienyl rhodium(III) complexes bearing a dpmp ligand may be useful in the strategic synthesis of hetero-polynuclear compounds, where the cluster core could be tuned by the choice of the additional metal complex.

Experimental Section

All procedures were carried out under a nitrogen atmosphere. Dichloromethane was distilled from CaH_2 and diethyl ether was distilled from $LiAlH_4$. Isocyanides,[18] $(Ph_2PCH_2)_2PPh$,[19] $[Cp^*RhCl_2]_2$,[20] and $[Cu(MeCN)_4](BF_4)$[21] were prepared according to the literature. Infrared and electronic absorption spectra were recorded on FT/IR-5300 and U-best30 instruments, respectively. NMR spectra were recorded on a JEOL JNM-ECL-400 spectrometer. ^{1}H NMR spectra were measured at 400 MHz and $^{31}P\{^{1}H\}$ NMR spectra were measured at 161 MHz using 85% H_3PO_4 as an external reference.

Supporting Information: See also the footnote on the first page of this article. (a) Preparation of [(Cp*RhCl)(dpmp-*P,P,P*)(RhCl$_2$-Cp*)](PF$_6$) (**2**). (b) Preparation of [Cp*RhCl(dpmp-*P,P*)](PF$_6$) (**3**). (c) Preparation of [{Cp*RhCl$_2$(dpmp-*P,P,P*)Au}$_2$](PF$_6$)$_2$ (**7**). (c) Crystal structures of **2(B)**·CH$_2$Cl$_2$ and **3(A)**. (d) Table S1. Crystal data for [{Cp*$_2$Rh$_2$Cl$_3$(dpmp-*P,P,P*)}(OTf)$_2$·CH$_2$Cl$_2$ **2(B)**·CH$_2$Cl$_2$, [Cp*Rh(dpmp-*P,P*)](PF$_6$) **3(A)**, and [{Cp*RhCl$_2$(dpmp-*P,P,P*)Au}$_2$](PF$_6$)$_2$ (**7**). (e) Table S2. Selected bond lengths and angles for [Cp*$_2$Rh$_2$Cl$_3$(dpmp-*P,P,P*)](PF$_6$)·CH$_2$Cl$_2$ **2(B)**. (f) Table S3. Selected bond lengths and angles for [Cp*RhCl(dpmp-*P,P*)](PF$_6$) **3(A)**. (g) Table S4. Selected bond lengths and angles for [{Cp*RhCl$_2$(dpmp-*P,P,P*)Au}$_2$](PF$_6$)$_2$ (**7**). (h) Figure S1. ORTEP for **2(B)**. (i) Figure S2. ORTEP for 3(A). (j) Figure S3. ORTEP for **7**.

Preparation of [{Cp*RhCl$_2$(dpmp-*P,P,P*)Ag}$_2$](OTf) (4): A mixture of **1** (52.8 mg, 0.085 mmol), dpmp (107.5 mg, 0.212 mmol) and Ag(OTf) (61.4 mg, 0.239 mmol) was stirred in CH_2Cl_2 (15 mL) and acetone (10 mL) at room temperature. After 4 h the solvent was removed and the solids were washed with diethyl ether and the residue was extracted with CH_2Cl_2. The CH_2Cl_2 solution was concentrated, and diethyl ether was added to give reddish orange crystals (124.0 mg, 67.5%). UV/Vis (CH_2Cl_2): λ_{max} = 392 nm. ^{1}H NMR ($CDCl_3$): δ = 1.25 (d, $J_{H,P}$ = 3.5 Hz, Cp*), 1.90, 2.82, 3.13, 3.48 (m, CH_2), 5.32 (s, CH_2Cl_2), 6.8−8.2 (m, Ph). The $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ = 28.6 (J_{PRh} = 146, $J_{P,P}$ = 12.9 Hz, P1), 2.6 (m, the other P nuclei), −143.6 (sept, J_{PF} = 707.5 Hz, PF_6).

Preparation of [Cp*Rh(dpmp-*P,P,P*)](OTf)$_2$ (5): A mixture of **3** (50 mg, 0.054 mmol) and AgOTf (75.4 mg, 0.293 mmol) in CH_2Cl_2 (15 mL) and acetone (5 mL) was stirred at room temperature. After 3 h, the solvent was removed and the residue was extracted with CH_2Cl_2. The solution was concentrated and diethyl ether was added to form orange crystals (41.8 mg, 72.4%). IR (nujol): $\tilde{\nu}$ = 1255, 1153, 1028 cm^{-1} (OTf). UV/Vis (CH_2Cl_2): λ_{max} = 335, 270 nm. ^{1}H NMR [$(CD_3)_2CO$]: δ = 1.66 (q, J_{PH} = 4.5 Hz, Cp*, 15 H), 5.49 (c, CH_2, 4 H), 7.3−8.4 (c, Ph, 25 H). $^{31}P\{^{1}H\}$ NMR [$(CD_3)_2CO$]: δ = −18.2 (dt, J_{P1P2} = J_{P1Rh} = 97.2 Hz, P^1), −47.4 (q, J_{P2P1} = J_{P2Rh} = 97.2 Hz, P^2), −143.6 (sept, J_{PF} = 707.5 Hz, PF_6). $C_{44}H_{44}F_6O_6P_3RhS_2$ (1042.8): calcd. C 50.68, H 4.25; found C 50.99, H 4.38.

Preparation of [Cp*RhCl(dpmp-*P,P,P*)RuCl$_2$(*p*-cymene)](PF$_6$) (6)

(1) From 3(A) and [(*p*-Cymene)RuCl$_2$]$_2$: A mixture of **3(A)** (50.4 mg, 0.054 mmol) and [(*p*-cymene)RuCl$_2$]$_2$ (19.3 mg, 0.032 mmol) was stirred in CH_2Cl_2 (10 mL) at room temperature for 5 h. The solution was concentrated to ca. 3 mL and diethyl ether was added, affording the yellow complex **6(A)** (43.6 mg, 65.6%). UV/Vis (CH_2Cl_2): λ_{max} = 361 nm. IR (nujol): $\tilde{\nu}$ = 837 cm^{-1}. FAB MS: *m*/*z* = 1085 ([M]$^+$). ^{1}H NMR ($CDCl_3$): δ = 0.53 (d, $J_{H,H}$ = 7.0 Hz, *i*Pr, 3 H), 1.00 (d, $J_{H,H}$ = 7.0 Hz, *i*Pr, 3 H), 1.52 (t, $J_{H,H}$ = 3.5 Hz, Cp*, 15 H), 1.75 (s, *p*-Me, 3 H), 2.41 (sept, $J_{H,H}$ = 7.0 Hz, *i*Pr, 1 H), 4.06 (c, CH_2, 2 H), 3.72 (c, CH_2, 1 H), 4.92 (c, CH_2, 1 H), 5.33, 5.44 (AB system, $J_{H,H}$ = 6.0 Hz, *p*-cymene), 6.8−8.4 (m, ph, 25 H). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ = −12.0 (dt, $^{1}J_{RhP2}$ = $^{2}J_{P2P1}$ = 97.0, $^{2}J_{P2P3}$ = 55.5 Hz, P^2), −1.41 (t, $^{1}J_{P1Rh}$ = $^{2}J_{P1P2}$ = 97.0 Hz, P^1) and 23.7 (d, $^{2}J_{P3P2}$ = 55.5 Hz, P^3), −143.5 (sept, J_{PF} = 707.5 Hz, PF_6).

(2) Direct Reaction: A mixture of $[Cp^*RhCl_2]_2$ (50.0 mg, 0.081 mmol), [(*p*-cymene)RuCl$_2$]$_2$ (50.9 mg, 0.083 mmol), dpmp (94.4 mg, 0.186 mmol) and KPF_6 (43.1 mg, 0.234 mmol) was stirred in CH_2Cl_2 (10 mL) and acetone (10 mL) at room temperature. After 20 h, the solution was evaporated to dryness and the residue extracted with CH_2Cl_2. The CH_2Cl_2 solution was concentrated to ca. 2 mL and diethyl ether was added, affording orange crystals (45.8 mg, 52.1%). The crystals were mainly isolated as the diastereomer **6(B)** based on the NMR spectrum. The ratio of **6(A)** to **6(B)** was 1:2.

6(B): ^{1}H NMR ($CDCl_3$): δ = 0.52 (d, $J_{H,H}$ = 7.0 Hz, *i*Pr, 3 H), 1.05 (d, $J_{H,H}$ = 7.0 Hz, *i*Pr, 3 H), 1.73 (t, $J_{H,H}$ = 4.0 Hz, Cp*, 15 H), 1.80 (s, *p*-Me, 3 H), 2.33(sept, $J_{H,H}$ = 7.0 Hz, *i*Pr, 1 H), 2.69 (dt, $J_{H,H}$ = 16.0, J_{PH} = J_{PH} = 12.0 Hz, CH_2, 1 H), 3.67 (dt, $J_{H,H}$ = 16.0, J_{PH} = J_{PH} = 12.0 Hz, CH_2, 1 H), 4.01 (ddd, $J_{H,H}$ = 16.0, J_{PH} = 7.0, $J_{P'H}$ = 4.0 Hz, CH_2, 1 H), 4.30 (ddd, $J_{H,H}$ = 16.0, J_{PH} = 7.0, J_{PH} = 4.0 Hz, CH_2, 1 H), 4.68, 5.20 (AB system, $J_{H,H}$ = 5.5 Hz, *p*-cymene), 7.0−8.5 (m, ph, 25 H). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ = −13.8 (dt, $^{1}J_{RhP2}$ = $^{2}J_{P2P1}$ = 105, $^{2}J_{P2P3}$ = 55.0 Hz, P^2), −10.2 (t, $^{1}J_{P1Rh}$ = $^{2}J_{P1P2}$ = 109.0 Hz, P^1) and 26.6 (d, $^{2}J_{P3P2}$ = 55.0 Hz, P^3), −143.5 (sept, J_{PF} = 707.5 Hz, PF_6).

Preparation of [{Cp*Rh(μ-Cl)$_2$(dpmp-*P,P,P*)Cu}$_2$](PF$_6$)$_2$ (8)

(1) One-Pot Synthesis: A mixture of **1** (32.9 mg, 0.053 mmol), dpmp (60.8 mg, 0.12 mmol) and CuCl (56.1 mg, 0.175 mmol) was stirred in CH_2Cl_2 (5 mL) and acetone (5 mL) for 24 h. The solvent was then removed and the residue extracted with CH_2Cl_2. The solution was concentrated to ca. 3 mL and diethyl ether was added, affording red crystals (47.6 mg, 43.7%).

(2) From 3: Complex **8** (16.9%) was prepared from **3(A)** and CuCl. UV/Vis (CH_2Cl_2): λ_{max} = 387, 235 nm. IR (nujol): $\tilde{\nu}$ = 835 cm^{-1}.

^{1}H NMR (CD_2Cl_2): δ = 1.10 (d, $J_{H,P}$ = 3.5 Hz), 1.26 (d, J_{PH} = 3.5 Hz, Cp*), 2.1−3.3 (m, CH_2), 6.9−8.05 (c, Ph). $C_{84}H_{88}Cl_4Cu_2F_{12}P_8Rh_2\cdot 1/2CH_2Cl_2$ (2090.6): calcd. C 48.55, H 4.29; found C 48.52, H 4.25.

Preparation of [{Cp*Rh(μ-Cl)$_2$(dpmp-*P,P,P*)Cu}$_2$](BF$_4$)$_2$: The BF_4 anion complex (11.1%) was prepared from **1** (0.051 mmol), dpmp (0.011 mmol) and $[Cu(MeCN)_4](BF_4)$ (0.13 mmol). The complex was established as a BF_4 anion analog of **8** by comparison with the ^{1}H NMR spectrum of **8**.

Preparation of [Cp*RhCl(dpmp=S)](PF$_6$) (9): A mixture of **3(A)** (50.9 mg, 0.055 mmol) and S_8 (7.8 mg, 0.030 mmol) was stirred in CH_2Cl_2 (5 mL) at room temperature. After 51 h, the solvent was removed under reduced pressure. After the residue was extracted with CH_2Cl_2, the solution was concentrated to ca. 2 mL, and diethyl ether was added, affording a yellow powder (16.7 mg, 31.7%). UV/Vis (CH_2Cl_2): λ_{max} = 359, 260 (sh) nm. IR (nujol): $\tilde{\nu}$ = 837 cm^{-1} (PF_6). FAB MS: *m*/*z* = 811 ([M]$^+$). ^{1}H NMR ($CDCl_3$): δ = 1.64 (t, $J_{H,P1}$ = J_{HP2} = 4.0 Hz, Cp*, 15 H), 4.3−4.9 (m, CH_2, 2 H), 6.8−8.1 (c, Ph, 25 H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 35.6 (d, J_{P3P2} = 31.5 Hz, P^3), 0.92 (dd, J_{P1Rh} = 114.0, J_{P1P2} = 94.0 Hz, P1), −15.5 (ddd, J_{RhP2} = 114.0, J_{P2P3} = 31.5, J_{P2P1} = 94.0 Hz, P2), −143.6 (sept, J_{PF} = 707.5 Hz, PF_6). $C_{42}H_{44}ClF_6P_4RhS$ (957.1): calcd. C 49.56, H 4.45; found C 49.71, H 4.53.

Preparation of [{Cp*RhCl}(dpmp-*P,P,P*){RhCl(XylNC)Cp*}](OTf)$_2$ (10): To a mixture of **3(A)** (50.6 mg, 0.045 mmol) and Ag(OTf) (27.4 mg, 0.167 mmol) in CH_2Cl_2 (10 mL) and acetone (5 mL) was added XylNC (13.9 mg, 0.107 mmol) at room temperature. After the reaction mixture was stirred for 24 h usual workup of the mixture gave orange crystals of **10** (35.2 mg, 52.3%). IR (nujol): $\tilde{\nu}$ = 2168 cm^{-1} (N≡C). UV/Vis (CH_2Cl_2): λ_{max} = 342 nm. ^{1}H NMR ($CDCl_3$): δ = 1.48 (t, J_{PH} = 4.0 Hz, Cp*, 15 H), 1.56 (d, $^2J_{PH}$ = 3.8 Hz, Cp*, 15 H), 2.00 (s, *o*-Me, 6 H), 4.10 (m, CH_2, 1 H), 4.51 (m, CH_2, 1 H), 4.90 (m, CH_2, 2 H), 6.8−8.0 (c, 25 H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 28.6 (dd, $^1J_{RhP3}$ = 122.2, $^2J_{P3P2}$ = 50.1 Hz, Rh(CNR)−P, P^3), −2.76 (dd, $^1J_{RhP1}$ = 113.1, $^2J_{P2P1}$ = 98.0 Hz, RhCl−P, P^1), −15.3 (ddd, $^1J_{RhP2}$ = 111.1, $^2J_{P2P1}$ = 98.0, $^2J_{P2P3}$ = 50.1 Hz, RhCl−P, P^2). $C_{63}H_{68}Cl_2F_6NO_6P_3Rh_2S_2$ (1483.0): calcd. C 50.02, H 4.62, N 0.94; found C 50.11, H 4.71, N 1.13.

Preparation of [(Cp*RhCl)(dpmp-*P,P*)]Cl (A): A mixture of [Cp*RhCl$_2$]$_2$ (30.5 mg, 0.049 mmol) and dpmp (55.2 mg, 0.109 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 24 h. After the removal of the solvent, the residue was washed with diethyl ether and crystallized from CH_2Cl_2 and diethyl ether to give orange crystals (28.8 mg, 36.0%). FAB MS: *m*/*z* = 780 [M$^+$]. UV/Vis (CH_2Cl_2): λ_{max} = 356, ca. 270 (sh) nm. ^{1}H NMR ($CDCl_3$): δ = 1.81 (t, *J* = 3.8 Hz, Cp*, 15 H), 3.47 (m, CH_2, 2 H), 4.24 (m, CH_2, 1 H), 5.30 (s, CH_2Cl_2), 5.49 (m, CH_2, 1 H), 7.0−7.7 (c, 25 H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −5.10 ppm (dd, J_{P3Rh} = 115.6, J_{P2P3} = 99.0 Hz, RhCl−P, P^3), −11.0 (ddd, J_{P2Rh} = 114.1, J_{P2P3} = 99.0, J_{P2P1} = 46.5 Hz, RhCl−P, P^2), −29.4 (d, J_{P1P2} = 46.5 Hz, CH_2P, P^1). $C_{42}H_{44}Cl_2P_3Rh\cdot 3/4CH_2Cl_2$ (879.2): calcd. C 58.40, H 5.22; found C 58.03, H 5.47. The structure is assumed to be similar to that of **3(B)**, based on the ^{1}H NMR spectrum.

Reaction of 2(A) with Xylyl Isocyanide: A mixture of **2(A)** (50 mg, 0.041 mmol) and xylyl isocyanide (26.9 mg, 0.205 mmol) was heated to reflux in acetone (15 mL). After 5 h, the solvent was removed and the residue was extracted with CH_2Cl_2. The solution was concentrated and diethyl ether was added, affording a dark brown solid of [Cp*RhCl$_2$(XylNC)] (30 mg, 78%). Workup of the mother liquor gave **3(A)** (10.3 mg, 57.2%).

X-ray Data Collection: All complexes were recrystallized from CH_2Cl_2/diethyl ether. The cell constants for **5** were determined from 20 reflections on a Rigaku four-circle automated diffractometer AFC5S. Data collection was carried out using a Rigaku AFC5S diffractometer. Intensities were measured by the 2θ−ω scan method using Mo-K_α radiation (λ = 0.71069).

Table 4. [{Cp*RhCl$_2$(dpmp-*P,P,P*)Ag}$_2$](OTf)$_2\cdot$H$_2$O (**4**·H$_2$O), [Cp*Rh(dpmp-*P,P,P*)](OTf)$_2$ (**5**), and [{Cp*RhCl$_2$(dpmp-*P,P,P*)-Cu}$_2$](OTf)$_2\cdot$2CH$_2$Cl$_2$ (**8**)

Complex	**4**·H$_2$O$^{[a]}$	**5**$^{[b]}$	**8**·2CH$_2$Cl$_2$$^{[a]}$
Empirical formula	$C_{86}H_{88}Ag_2Cl_4F_6O_7P_6Rh_2S_2$	$C_{44}H_{44}F_6O_6P_3RhS_2$	$C_{86}H_{92}Cl_8Cu_2F_{12}P_8Rh_2$
Formula mass	2160.95	1042.77	2217.97
Crystal system	orthorhombic	triclinic	monoclinic
Space group	*Pccn* (no. 46)	*P*1 (no. 2)	*P*2$_1$/*c* (no. 14)
a /Å	31.7839(7)	12.725(10)	13.573(1)
b /Å	14.632(3)	18.23(2)	13.1107(5)
c /Å	19.9580(7)	10.90(1)	25.2635(6)
α /°	90	99.54(10)	90
β /°	90	101.70(9)	103.74(2)
γ /°	90	107.63(6)	90
V	5648(1)	2289(3)	4227(2)
Z	4	2	2
$D_{calcd.}$ /gcm^{-3}	1.546	1.513	1.643
μ(Mo-K_α) /cm^{-1}	10.89	6.39	12.79
$2\theta_{max}$	55.0	50.0	55.0
No. measured (unique)	10851	8036	10231
No. observed	5923 [$I > 3.0\sigma(I)$]	2864 [$I > 2.0\sigma(I)$]	6807 [$I > 3.0\sigma(I)$]
No. variable	523	559	532
R; *Rw*	0.090; 0.114$^{[c]}$	0.062; 0.075$^{[c]}$	0.155; 0.207$^{[d]}$
*R*1	0.090(5923 ref)	0.062	0.074(4155 ref)
GOF	3.22	1.09	2.13

[a] Measured on a Quantum CCD Rigaku AFC7 instrument. [b] Measured on a Rigaku AFC5S instrument. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = (\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega F_o^2)^{1/2}$ and $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $I > 3.0\sigma(I)$. [d] $R = \Sigma(F_o^2 - F_c^2)/\Sigma F_o^2$, $R_w = (\Sigma\omega F_o^2 - F_c^2)^2/\Sigma\omega(F_o^2)]^{1/2}$ and $R1 = \Sigma||F_o| - |F_c|| /\Sigma|F_o|$ for $I > 2.0\sigma(I)$.

Throughout the data collection the intensities of the three standard reflections were measured after every 200 reflections as a check of the stability of the crystals and no decay was observed. Absorption corrections were made using the ψ scan methods.

The measurements for $\mathbf{4}\cdot H_2O$ and $\mathbf{8}\cdot 2CH_2Cl_2$ were made on an MSC/ADSC Quantum CCD/Rigaku AFC7 diffractometer, using Mo-K_α radiation at 0 °C under a cold nitrogen stream. Four preliminary data frames were measured at 0.5° increments of ω in order to assess the crystal quality and preliminary unit cell parameters were calculated. The cell parameters were refined using all reflections measured in the range $2.8° < 2\theta < 40°$. The intensity images were measured at 0.5° intervals of ω for a duration of 20 s. The frame data were integrated using the d*TREK program package, and the data sets were corrected for absorption using the REQAB program.

The crystal parameters along with the details of the data collections are summarized in Table 4. Intensities were corrected for Lorentz and polarization effects. Atomic scattering factors were taken from the usual tabulation of Cromer and Waber.[22] Anomalous dispersion effects were included in $F_{calcd.}$;[23] the values of $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[24] All calculations were performed using the teXsan crystallographic software package.[25]

Determination of the Structures: All complexes were solved by direct methods (SIR92) except **7** which was solved by Patterson methods (DIRDIF94 PATTY) . The non-hydrogen atoms of all complexes were refined anisotropically using full-matrix least-squares based on F^2 or F values. All hydrogen atoms were calculated in ideal positions with a C−H distance of 0.95 Å. The crystal data are listed in Table 4.

CCDC-190355 for $\mathbf{4}\cdot H_2O$, -213525 for **5** and -190357 for $\mathbf{8}\cdot 2CH_2Cl_2$ contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

The authors would like to thank Professor Shigetoshi Takahashi and Dr Fumie Takei of The Institute of Scientific and Industrial Research, Osaka University for performing the FAB mass spectrometry measurements. This work was partially supported by a Grant-in Aid for Scientific Research from the Ministry of Education, Science, Culture and Sports, Japan.

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Received June 26, 2003
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