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Construction of optically active multimetallic systems of rhodium(I), palladium(II), and ruthenium(II) with a P-chiral tetraphosphine ligand

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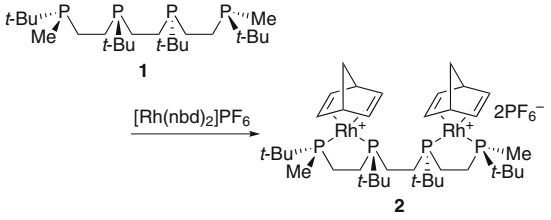
ABSTRACT

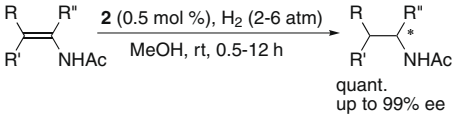
The treatment of optically P-chiral tetraphosphine, (3*S*,6*R*,9*R*,12*S*)-6,9-di-*tert*-butyl-2,2,3,12,13,13-hexamethyl-3,6,9,12-tetraphosphatetradecane (**1**), with rhodium(I), palladium(II), and ruthenium(II) complex precursors led to the selective formation of mono-, di-, or trinuclear homo- or heterometallic complexes, [Rh(**1**)]SbF_6 (**4**), [{Rh(nbd)}$_2$(**1**)]$(SbF_6)_2$ (**3**), [{Pd(η^3-allyl)}$_2$(**1**)]$(SbF_6)_2$ (**5**), [{RuCl(η^5-$C_5(CH_3)_5$)}$_2$(**1**)] (**6**), and [{$RuCl_2$(η^6-benzene)}$_2$($PdCl_2$)(**1**)] (**8**). These complexes were characterized by NMR and X-ray crystallographic analysis.

1. Introduction

Transition metal-catalyzed asymmetric transformation processes are recognized as one of the most important strategies for the production of optically active fine chemicals [1]. Recently, increasing attention has been given to the application of multimetallic catalysis in these asymmetric syntheses, and there have been several important reports of Lewis acid catalysis [2,3]. On the other hand, only a limited number of reports are available regarding transition metal catalysis [4,5]. If the catalytic functions of various transition metals could be integrated in a single catalyst, it would be possible to realize the new catalytic processes. In our previous research, we prepared P-chiral tetraphosphine **1** and applied to transition metal catalysis [6]. Tetraphosphine **1** coordinated to two rhodium atoms to form homobimetallic complex **2** (Eq. (1)). It also exhibited high enantioinduction ability in the asymmetric hydrogenation of various enamides (Eq. (2))



(1)



(2)

In this case, each rhodium center in the complex acted independently as a single catalyst and gave almost the same performance as a rhodium(I) complex of (*S*,*S*)-1,2-bis(*tert*-butyl(methyl)phosphino)ethane (abbreviated to *t*-Bu-BisP*) [7]. Although high enantioselectivity and reactivity were maintained in comparison with the *t*-Bu-BisP* complex, we could not find any new reactivity and selectivity based on the cooperation between two metal centers. Given this background, we planned to design and prepare various types of homo- and heterobimetallic complexes of a P-chiral tetraphosphine in order to realize cooperative asymmetric transition metal catalysis. Herein we describe the selective preparation of various transition metal complexes of P-chiral tetraphosphine **1**, and their crystal structures [8]. As shown in Fig. 1, tetraphosphine **1** was selectively converted into mono-, di-, and trimetallic structures by

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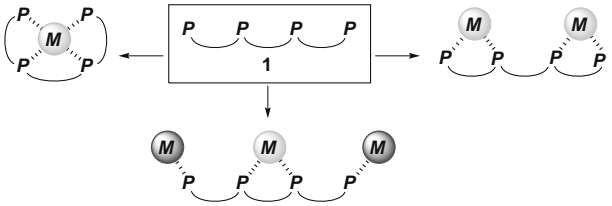


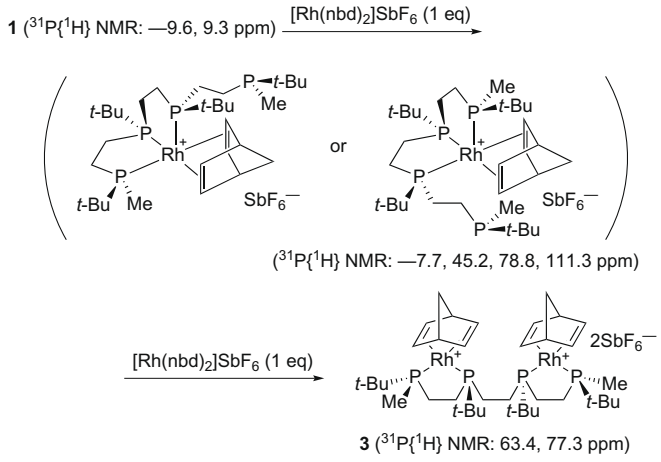
Fig. 1. Three coordination modes of tetraphosphine **1**.

treatment with the metal complex precursors having an appropriate number of free coordination sites.

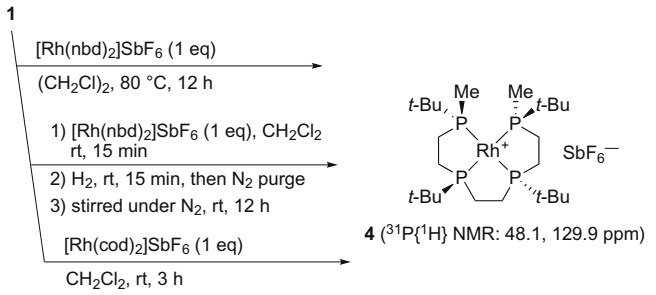
2. Results and discussion

The complexation of P-chiral tetraphosphine **1** with rhodium(I) was carried out with [Rh(diene)$_2$] type precursors. When 2 equiv. of [Rh(nbd)$_2$]SbF$_6$ was employed, the complexation took place smoothly in dichloromethane at room temperature, and dirhodium complex **3** was obtained as the sole product (Scheme 1). The complexation using 1 equiv. of [Rh(nbd)$_2$]SbF$_6$ was also conducted and its reaction was monitored by $^{31}P\{^1H\}$ NMR. The intensities of the signals at −9.6 and 9.3 ppm, which were ascribed to **1,** decreased gradually and new signals at −7.7 ppm (d, $^3J_{P-P}$ = 30 Hz), 45.2 ppm (dt, $^{2+3}J_{P-P}$ = 22 Hz, J_{P-Rh} = 113 Hz), 78.8 ppm (dq, $^{2+3}J_{P-P}$ = 26 Hz, J_{P-Rh} = 130 Hz), and 111.3 ppm (dt, $^{2+3}J_{P-P}$ = 24 Hz, J_{P-Rh} = 126 Hz) appeared within 15 min. No signals assigned to dirhodium(I) complex **3** could be detected during this transformation process. The large coupling constants of the three signals at 45.2, 78.8, and 111.3 ppm (J_{P-Rh} = 113–130 Hz) indicate that the three phosphino groups of the tetraphosphine **1** coordinate to the rhodium center in the facial manner to form an 18-electron pentacoordinated rhodium(I) complex shown in Scheme 1, in which two possible structures can be drawn for the monorhodium(I) intermediate complex. In each case, one norbornadiene ligand would stay on the rhodium(I) center and occupy two equatorial coordination sites adjacent to each other. By P–P homodecoupling experiment, it was found that the phosphorus atoms at −7.7 and 78.8 ppm coupled to each other. The addition of 1 equiv. of [Rh(nbd)$_2$]SbF$_6$ to this solution led to the rapid formation of dirhodium(I) complex **3**.

A different coordination mode was observed when the complexation of **1** with 1 equiv. of [Rh(nbd)$_2$]SbF$_6$ was carried out at 80 °C in dichloroethane (Scheme 2). In this case, ^{31}P NMR signals of **1** disappeared completely and two quartets of doublets newly appeared at 48.1 and 129.9 ppm. The same signals were found



Scheme 1. Formation of dirhodium complex **3**.



Scheme 2. Formation of complex **4**.

when dirhodium complex **3** was treated with free tetraphosphine **1** under hydrogen atmosphere, and the signal at *m/z* = 569, which corresponded to (**1** + Rh), was observed in ESI-MS measurement. This implies that all norbornadiene ligands are dissociated from the rhodium center, and the four phosphino groups of **1** fully coordinate to the same rhodium center to form complex **4** [9]. Use of 1 equiv. of [Rh(cod)$_2$]SbF$_6$ as a rhodium(I) precursor also gave the same complex. Because of weak coordination, cyclooctadiene ligands could be dissociated from the rhodium centers even at ambient temperature. This led to the exclusive formation of **4**, and only trace amounts of the corresponding dinuclear-complex like **3** were detected even when 2 equiv. of [Rh(cod)$_2$]SbF$_6$ was employed. This contrasts the predominant formation of dirhodium complex **3** from [Rh(nbd)$_2$]SbF$_6$. The structure of complex **4** was unequivocally determined by X-ray crystallographic analysis, as shown in Fig. 2. Tetraphosphine **1** coordinates quadridentatively to the Rh center to form distorted square planar complex **4** in which all *tert*-butyl groups are located at quasi axial positions. According to $^{31}P\{^1H\}$ NMR measurement, it was found that the four phosphorus atoms of **4** were magnetically inequivalent and gave the second order multiplet signals corresponds to AA′BB′X spin system (Fig. 3) [8j].

The complexation of **1** with other transition metals exhibiting various coordination patterns was investigated in order to construct various multimetallic systems. Similar to dirhodium complex **2**, dipalladium complex **5** was readily formed when **1** was treated with 2 equiv. of [Pd(η^3-allyl)(cod)]SbF$_6$. Diruthenium complex **6** was also prepared by using [RuCl(η^5-C$_5$(CH$_3$)$_5$)(cod)] (Scheme 3). These three types of complexation have unambiguously occurred because of the simple coordination mode of the precursors; after the removal of diene ligand, [Rh(nbd)]PF$_6$, [Pd(η^3-allyl)]SbF$_6$, and [RuCl(η^5-C$_5$(CH$_3$)$_5$)] would have two coordination sites at *cis* position. The crystal structures of the homobimetallic complexes **2**, **5**, and **6** are shown in Fig. 4. In all three cases, the two metals in five-membered chelate rings are oriented in almost the same direction (“*cis*”-conformation). This fact points to the possibility of developing cooperative dual catalysts for various

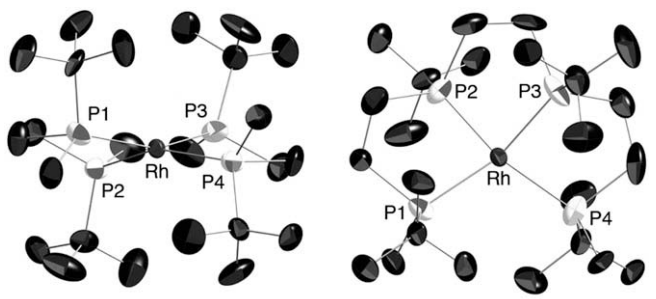


Fig. 2. ORTEP drawings of **4** (front and top views). Ellipsoids are at 50% probability. Hydrogen atoms and SbF$_6^-$ are omitted for clarity.

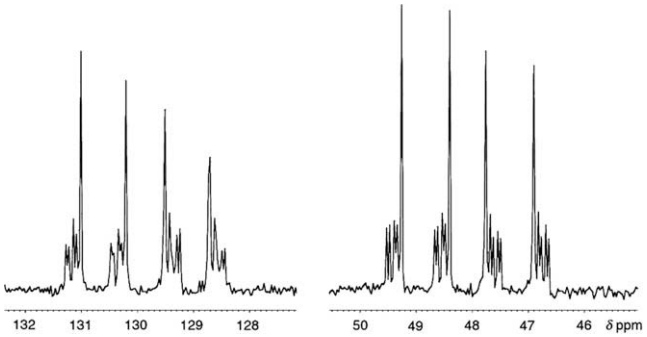
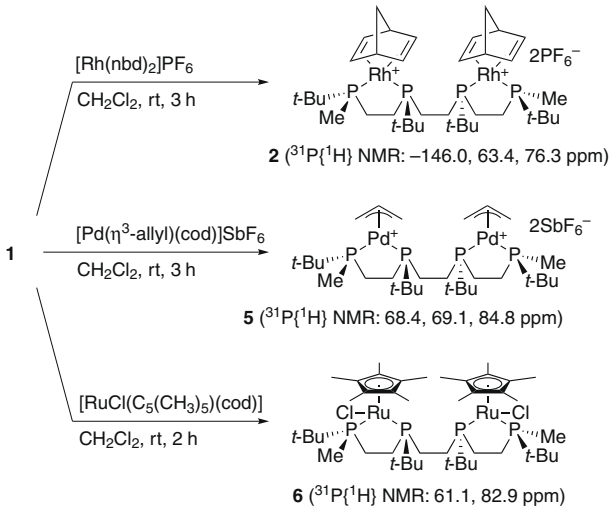


Fig. 3. $^{31}P\{^{1}H\}$NMR spectrum of **4**.



Scheme 3. Preparation of homobimetallic complexes **2**, **5**, and **6**.

asymmetric processes in which two catalytic functions are integrated.

The solution structure of these homobimetallic complexes were examined also by theoretical study (Fig. 5). The DFT calculation of $[\{Rh(nbd)\}_2(\mathbf{1})]^{2+}$ implies that the "*cis*"-conformation (b) is most stable among the three optimized conformations in dichloromethane ($\Delta G_{cis-trans} = -6.3$ kJ/mol), and the "*trans*"-conformation (c) was estimated to be relatively unstable probably due to the steric hindrance between two terminal *tert*-butyl groups of **1**. The dirhodium complex **2** has taken "*twisted*" to "*cis*"-conformation in its single crystal (d), which is in good agreement with the DFT calculation [6]. These results indicates that there would be a good similarity between the crystal structure and solution phase one.

When $[PdCl_2(cod)]$ was employed as a precursor, however, no dipalladium complex was formed and only the mononuclear palladium(II) complex of **1** could be detected by ^{31}P NMR. The spectrum of mononuclear complex **7** indicated that all phosphorus atoms would coordinate to the palladium center according to two kinds of coordination manner, as shown in Fig. 6 [8j,10]. We envisioned that the two terminal phosphino groups would exhibit hemilabile behavior and be able to accept a new metal center for coordination. According to this idea, complex **7** was treated with 1 equiv. of $[RuCl_2(\eta^6\text{-benzene})]_2$ to investigate the formation of heteromultimetallic complexes. Although the reaction was accomplished at 80 °C, no change in the ^{31}P NMR spectrum could be found. This may be because the coordination of the terminal phosphino groups to the palladium center is too strong to exhibit hemilability. On the other hand, when tetraphosphine **1** was treated simultaneously with 1 equiv. of $[PdCl_2(cod)]$ and $[RuCl_2(\eta^6\text{-benzene})]_2$, heterotrinuclear complex **8** was obtained as the main product (Scheme 4). The structure of complex **8** was confirmed by X-ray diffraction analysis, as shown in Fig. 7. The trinuclear Ru(II)–Pd(II)–Ru(II) structure with a C_2 symmetric axis at the palladium center was found and in this case as well, all three metals showed orientation in the same direction.

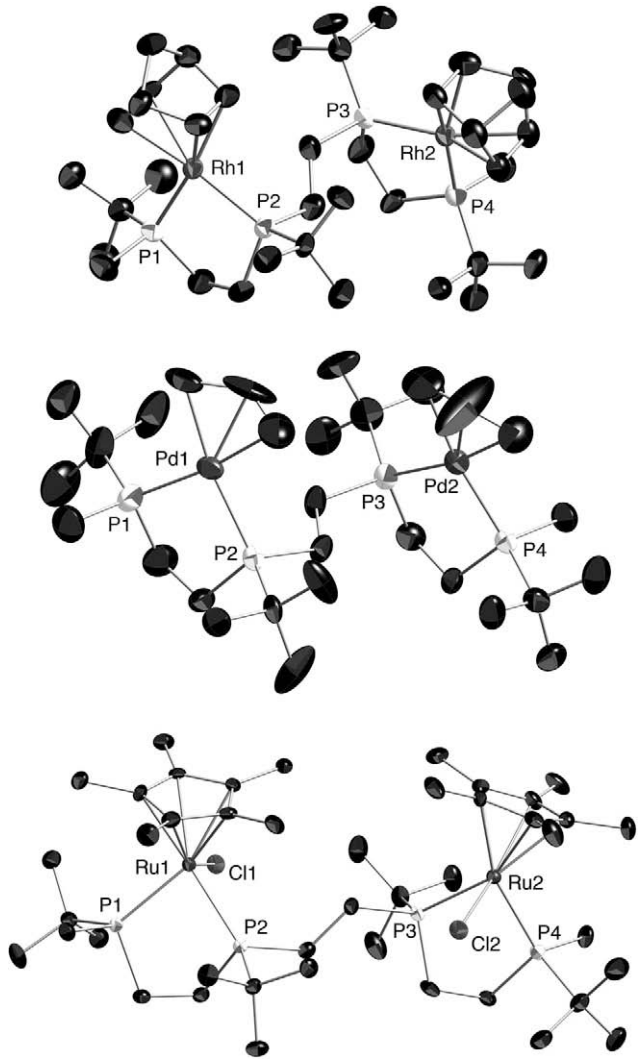


Fig. 4. ORTEP drawings of **2** (top) **5** (middle) and **6** (bottom) ellipsoids are at 50% probability. Hydrogen atoms and SbF_6^- are omitted for clarity.

In summary, the selective preparation of multinuclear complexes of P-chiral tetraphosphine **1** was realized by choosing the appropriate transition metal precursors. In the case of the rhodium(I) complex of **1**, use of $[Rh(nbd)_2]SbF_6$ as precursor produced dinuclear-complex **3** at room temperature, whereas mononuclear rhodium(I) complex **4** coordinating to four phosphine moieties was obtained when $[Rh(cod)_2]SbF_6$ was used. The complexation of **1** with other transition metal precursors was also examined. In addition to homodinuclear complexes **5** (Pd(II)–Pd(II)) and **6** (Ru(II)–Ru(II)), trinuclear heterometallic complex **8** was also prepared from $[PdCl_2(cod)]$ and $[RuCl_2(\eta^6\text{-benzene})]_2$ in which palladium(II) occupied two internal coordination sites to form a five-membered chelate structure, and ruthenium(II) coordinated to the terminal phosphino group in a monodentate manner. In each complex, all metals were found to orient toward the same direction in their single crystal. This conformation ("*cis*"-conformation) was estimated to be favorable even in solution phase by DFT

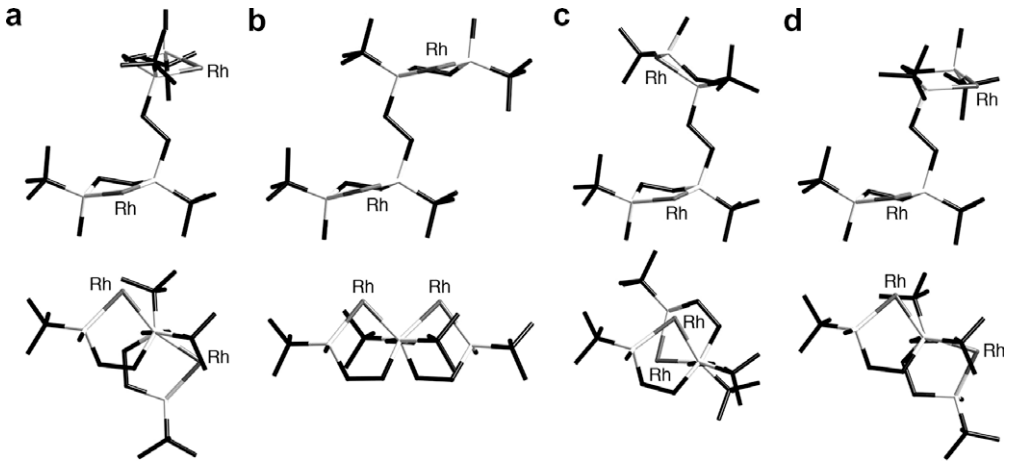
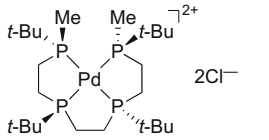
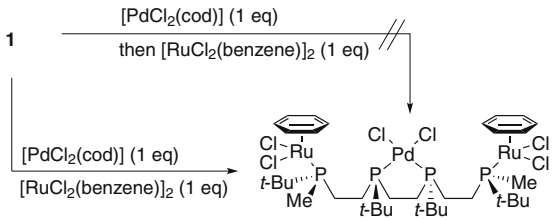


Fig. 5. Comparison of the crystal structure of $[\{Rh(nbd)\}_2(1)]^{2+}$ with its optimized conformations calculated by B3LYP/LANL2DZ (front and top views). (a) Optimized conformation (twisted); (b) optimized conformation (cis); optimized conformation (trans); and (d) crystal structure of **2**. All hydrogen atoms, norbomadiene groups, and counterions are omitted for clarity.



7 ($^{31}P\{^1H\}$ NMR: 85.7, 95.8 ppm)

Fig. 6. Plausible structure of **7**.



8 ($^{31}P\{^1H\}$ NMR: 34.1, 102.8 ppm)

Scheme 4. Preparation of trinuclear Ru–Pd–Ru complex **8**.

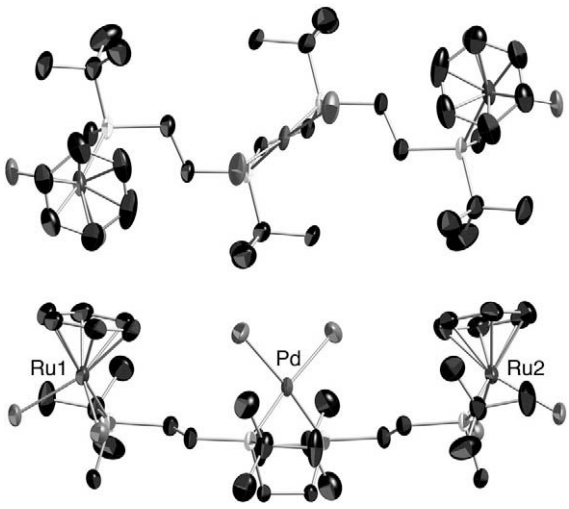


Fig. 7. ORTEP drawings of **8** (front and top views). Ellipsoids are at 50% probability. Hydrogen atoms are omitted for clarity.

calculation. It is expected that these results lead to the development of new cooperative asymmetric catalyses.

3. Experimental

3.1. General

All manipulations were carried out under nitrogen atmosphere. NMR spectra were recorded on a JEOL JNM-ECX (400 MHz for ^1H and 162 MHz for ^{31}P). Chemical shifts were reported in δ ppm referenced to an internal tetramethylsilane standard for ^1H NMR, and to an external 85% H_3PO_4 standard for ^{31}P NMR. ^1H, ^{13}C and $^{31}P\{^1H\}$ NMR spectra were recorded in $CDCl_3$ at 25 °C unless otherwise noted. IR spectra were recorded on a JASCO FT/IR-6300. Optical rotations were measured with a JASCO P-1030 polarimeter with a sodium lamp. MS (ESI) spectra were recorded on a JEOL JMS-T100LC spectrometer. X-ray crystal structure data were collected using a Bruker SMART 1000 CCD, or APEX II diffractometers with Mo Kα radiation. Melting points were measured with a Yanaco MP-500D. Optically active tetraphosphine **1** [6] and all transition metal complexes employed here as starting materials [11–16] were prepared according to the reported procedure.

3.1.1. Preparation of $[\{Rh(nbd)\}_2(\mathbf{1})](SbF_6)_2$ (**3**)

A solution of tetraphosphine **1** (41.7 mg, 0.089 mmol) in freshly distilled dichloromethane (1 mL) was added to a stirred solution of $[Rh(nbd)_2]SbF_6$ [11] (93.1 mg, 0.178 mmol) in dichloromethane (2 mL) under N_2 atmosphere. The solution was stirred at room temperature for 3 h. Then the reaction mixture was filtered, and the solvent was removed under reduced pressure. The residual solid was washed with diethyl ether and dried under reduced pressure to give **3** as an orange powder (78 mg, 69% yield). ^1H NMR (400 MHz, 293 K, $CDCl_3$) δ 1.05 (d, J_{P-H} = 14 Hz, 18H), 1.11 (d, J_{PH} = 14 Hz, 18H), 1.38 (d, J_{P-H} = 8 Hz, 6H), 1.61 (m, 6H), 1.86 (m, 4H), 2.0–2.7 (m, 6H), 4.10 (br s, 2H), 4.16 (br s, 2H), 5.62 (m, 2H), 5.84 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.14 (d, J_{C-P} = 23 Hz), 21.79 (m), 24.00 (m), 26.82 (d, J_{C-P} = 26 Hz), 26.95 (d, J_{C-P} = 26 Hz), 27.58 (m), 33.57 (m), 71.65, 73.36, 82.81 (t, J_{C-P} = 7 Hz), 86.14 (m), 91.82 (m), 92.83 (t, J_{C-P} = 9 Hz); $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$) δ 63.4 (dd, J_{P-Rh} = 149 Hz, $^{2+3}J_{PP}$ = 17 Hz), 77.3 (dm, J_{P-Rh} = 162 Hz); $[\alpha]_D^{24}$ −6.7 (*c* 1.0, $CHCl_3$); m.p. 182–185 °C (decomp); ESI-HRMS Calcd. for $C_{38}H_{70}F_6P_4Rh_2Sb$ $[M-SbF_6]^+$:

1091.1480. Found 1091.1431; IR (ATR): 653, 800, 880, 1089, 1299 cm^{-1}.

3.1.2. Preparation of [Rh(**1**)]SbF_6 (**4**)

A solution of tetraphosphine **1** (97 mg, 0.208 mmol) in freshly distilled dichloromethane (2 mL) was added to a stirred solution of [Rh(cod)$_2$]SbF_6 [12] (115 mg, 0.208 mmol) in dichloromethane (2 mL) under N_2 atmosphere. The solution was stirred at room temperature for 3 h. Then the reaction mixture was filtered, and the solvent was removed under reduced pressure. The residual solid was washed with diethyl ether and dried under reduced pressure to give a yellow-orange powder. Recrystallization from tetrahydrofuran afforded 62 mg (37% yield) of **4** as red crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (d, J_{P-H} = 13 Hz, 18H), 1.18 (d, J_{P-H} = 14 Hz, 18H), 1.38 (d, J_{P-H} = 5 Hz, 6H), 1.3–1.5 (m, 2H), 1.6–1.9 (m, 4H), 2.5–2.8 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.01 (d, J_{C-P} = 8 Hz), 27.17 (m), 28.10, 28.80, 29.04 (m), 33.57 30.13 (m), 33.33 (d, J_{C-P} = 23 Hz), 34.91 (d, J_{C-P} = 27 Hz); ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$) δ 48.1 (m), 129.9 (m); $[\alpha]_D^{24}$ −3.7 (*c* 1.0, $CHCl_3$); m.p. 241–244 °C (decomp); ESI-HRMS Calcd. for $C_{24}H_{54}P_4Rh$ [M−SbF_6]$^+$: 569.2231. Found 569.2187; IR (ATR): 653, 877, 1016, 1294, 1472 cm^{-1}. Anal. Calc. for $C_{24.5}H_{55}ClF_6P_4PhSb_1$(**4**+1/2$CH_2Cl_2$): C, 34.71; H, 6.54. Found: C, 34.97; H, 6.38%.

3.1.3. Preparation of [{Pd(η^3-allyl)}$_2$(**1**)](SbF$_6$)$_2$ (**5**)

A solution of tetraphosphine **1** (80 mg, 0.172 mmol) in freshly distilled dichloromethane (1.5 mL) was added to a stirred solution of [Pd(η^3-allyl)(cod)]SbF_6 [13] (164.7 mg, 0.335 mmol) in dichloromethane (2 mL) under N_2 atmosphere. The solution was stirred at room temperature for 3 h. Then the reaction mixture was filtered and the solvent was removed under reduced pressure. The residual solid was washed with diethyl ether and dried under reduced pressure to give a white powder. Recrystallization from dichloromethane/diethyl ether afforded 103.5 mg (49% yield) of **5** as colorless plates. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 1.04–1.27 (m, 36H), 1.38 (m, 3H), 1.45 (m, 3H), 1.6–2.5 (m, 12H), 2.89 (br m, 0.8H), 3.03 (br m, 2.4H), 3.15 (br m, 0.8H), 4.54 (br m, 1.2H), 4.67 (br m, 0.8H), 4.87 (br m, 0.8H), 4.98 (br m, 1.2H), 5.38 (m, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 7.60 (d, J_{C-P} = 22 Hz), 22.62 (m), 26.24, 26.78, 31.12 (d, J_{C-P} = 26 Hz), 32.39 (m), 34.91 (d, J_{C-P} = 27 Hz), 121.12, 121.72; ^{31}P{^{1}H} NMR (161 MHz, CD_2Cl_2) δ 68.4 (d, $^{2+3}J_{P-P}$ = 26 Hz), 69.1 (d, $^{2+3}J_{P-P}$ = 22 Hz), 84.8 (m); m.p. 133–139 °C; ESI-MS *m/z* 997 ([M−SbF_6]$^+$, 100%), 380 (1/2[M−2SbF_6]$^+$, 22%); IR (ATR): 560, 744, 825, 1193, 1381, 1476 cm^{-1}. Anal. Calc. for $C_{30}H_{64}F_{12}P_4Pd_2Sb_2$: C, 29.22; H, 5.23. Found: C, 29.59; H, 4.87%.

3.1.4. Preparation of [{RuCl(η^5-$C_5(CH_3)_5$)}$_2$(**1**)] (**6**)

A solution of tetraphosphine **1** (40 mg, 0.086 mmol) in freshly distilled dichloromethane (1.5 mL) was added to a stirred solution of [RuCl(η^5-$C_5(CH_3)_5$)(cod)] [14] (65.5 mg, 0.17 mmol) in dichloromethane (1 mL) under N_2 atmosphere. The solution was stirred at room temperature for 12 h. Then the reaction mixture was filtered and the solvent was removed under reduced pressure. The residual solid was washed with diethyl ether and dried under reduced pressure to give a yellow powder. Recrystallization from chloroform/diethyl ether afforded 31 mg (35% yield) of **6** as red prisms. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12 (d, J_{P-H} = 13 Hz, 18H), 1.19 (d, J_{P-H} = 13 Hz, 18H), 1.29 (d, J_{P-H} = 8 Hz, 6H), 1.75 (s, 30H), 1.8–2.1 (m, 6H), 2.2–2.5 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.21 (d, J_{C-P} = 27 Hz), 11.57, 15.37 (d, J_{C-P} = 24 Hz), 24.38 (m), 24.94 (m), 28.41, 29.78, 33.37 (m), 87.79; ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$) δ 61.1 (br s), 82.9 (br s); m.p. 110–114 °C (decomp), ESI-MS: *m/z* 719 ([M−2Cl−Ru−$C_5(CH_3)_5$+O]$^+$, 100%), 1007 ([M−Cl+MeOH]$^+$, 49%); IR (ATR): 698, 810, 878, 1022, 1182, 1362, 1464, 1647, 3405 cm^{-1}. Anal. Calc. for $C_{44}H_{84}Cl_2P_4Ru_2$: C, 52.32; H, 8.38. Found: C, 52.19; H, 8.20%.

3.1.5. Preparation of palladium(II) complex **7**

A solution of tetraphosphine **1** (38 mg, 0.081 mmol) in freshly distilled dichloromethane (1 mL) was added to a stirred solution of [$PdCl_2$(cod)] [15] (23.1 mg, 0.081 mmol) in dichloromethane (1 mL) under N_2 atmosphere. The solution was stirred at room temperature for 2 h. Then the reaction mixture was filtered and the solvent was removed under reduced pressure. The residual solid was washed with diethyl ether and dried under reduced pressure to give **7** as a pale yellow powder. ^{31}P{^{1}H} NMR (161 MHz, CH_2Cl_2) δ 85.7 (s), 95.8 (s); ESI-MS: *m/z* 623 ([M−Cl+O]$^+$, 90%), 658 ([M+O]$^+$, 100%).

3.1.6. Preparation of [{$RuCl_2$(η^6-benzene)}$_2$($PdCl_2$)(**1**)] (**8**)

A solution of tetraphosphine **1** (34.4 mg, 0.073 mmol) in freshly distilled dichloromethane (1.5 mL) was added to a stirred solution of [$RuCl_2$(η^6-benzene)]$_2$ [16] (36.5 mg, 0.073 mmol) and [$PdCl_2$(cod)] (10.8 mg, 0.073 mmol) in dichloromethane (1 mL) under N_2 atmosphere. The solution was stirred at room temperature for 8 h. Then the reaction mixture was filtered and the solvent was removed under reduced pressure. The residual solid was washed with diethyl ether and dried under reduced pressure to give a red powder. Recrystallization from *N*,*N*-dimethylformamide/1,2-dimethoxyethane afforded 32.5 mg (39% yield) of **8** as red cubes. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (d, J_{P-H} = 13 Hz, 18H), 1.35 (d, J_{P-H} = 15 Hz, 18H), 1.40 (d, J_{P-H} = 10 Hz, 6H), 1.9–2.4 (m, 8H), 2.5–2.8 (m, 4H), 5.86 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.75 (d, J_{C-P} = 29 Hz), 20.21 (d, J_{C-P} = 25 Hz), 23.76 (d, J_{C-P} = 21 Hz), 24.69 (m), 28.19, 28.65, 35.27 (d, J_{C-P} = 24 Hz); ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$) δ 34.1 (d, $^3J_{P-P}$ = 43 Hz), 102.8 (dt, $^3J_{P-P}$ = 43 Hz, $^{2+3}J_{P-P}$ = 9 Hz); $[\alpha]_D^{24}$ −7.7 (*c* 1.0, $CHCl_3$), m.p. 159–162 °C (decomp); ESI-MS: *m/z* 857 ([M−3Cl−Ru−benzene]$^+$, 100%), 1107 ([M−Cl]$^+$, 46%); IR (ATR): 700, 812, 888, 1016, 1182, 1288, 1435, 1634, 3504 cm^{-1}. Anal. Calc. for $C_{36}H_{66}C_{l6}P_4PdRu_2$: C, 37.79; H, 5.81. Found: C, 37.87; H, 5.67%.

3.2. Computational details

All calculations were performed using analytical energy gradients of self-consistent-field [17] and density functional theory (DFT) [18]. The latter utilized Becke's three-parameter exchange–correlation functional [19] including the nonlocal gradient corrections described by Lee–Yang–Parr (LYP) [20], as implemented in the GAUSSIAN 03 program package [21]. All calculations were performed using the 6-31G* basis set [22] for hydrogen, carbon and phosphine, and the LANL2DZ basis set [23] for rhodium. The PCM solvation model (dichloromethane, ε = 8.93) was employed for geometry optimizations and single point calculations [24,25]. Frequency calculations were performed on all optimized structures to characterize the stationary points as minima states (no imaginary frequency or negligibly small one), as well as for the calculation of zero-point energies (ZPE), enthalpies (*H*), entropies (*S*), and Gibbs free energies (*G*) at 298.15 K and 1 atm.

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Appendix A. Supplementary material

CCDC 653266, 653268, 653269, and 700893 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary

data (Cartesian coordinates of the optimized structure of **3** associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.10.014.

References

[1] (a) For representative reviews, see: H.B. Kagan, in: J.D. Morrison (Ed.), Asymmetric Synthesis, vol. 5, Academic, Orland, 1985 (Chapter 1);
(b) R. Noyori, Asymmetric Catalysis in Organic Synthesis, Wiley& Sons, New York, 1994;
(c) E.N. Jacobsen, A. Pfaltz, H. Yamamoto, Comprehensive Asymmetric Catalysis, Springer, Berlin, 1999;
(d) I. Ojima, Catalytic Asymmetric Synthesis, 2nd ed., VCH, Weinheim, 2000.

[2] (a) For reviews and recent examples of multifunctional catalyses, see: M. Shibasaki, H. Sasai, T. Arai, Angew. Chem., Int. Ed. 36 (1997) 1236–1256;
(b) H. Sasai, T. Arai, S. Watanabe, M. Shibasaki, Catal. Today 62 (2000) 12–22;
(c) M. Shibasaki, N. Yoshikawa, Chem. Rev. 102 (2002) 2187–2209;
(d) M. Kanai, N. Kato, E. Ichikawa, M. Shibasaki, Synlett (2005) 1491–1508;
(e) S. Handa, V. Gnanadesikan, S. Matsunaga, M. Shibasaki, J. Am. Chem. Soc. 129 (2007) 4900–4901;
(f) Y. Sohtome, Y. Kato, S. Handa, N. Aoyama, K. Nagawa, S. Matsunaga, M. Shibasaki, Org. Lett. 10 (2008) 2231–2234;
(g) S. Handa, K. Nagawa, Y. Sohtome, S. Matsunaga, M. Shibasaki, Angew. Chem., Int. Ed. 47 (2008) 3230–3233.

[3] (a) G.M. Sammis, H. Danjo, E.N. Jacobsen, J. Am. Chem. Soc. 126 (2004) 9928–9929;
(b) C. Mazet, E.N. Jacobsen, Angew. Chem., Int. Ed. 47 (2008) 1762–1765.

[4] G.G. Stanley, Chem. Ind. (Dekker) 62 (1995) 363–372.

[5] (a) M. Kurosu, M. Lin, Y. Kishi, J. Am. Chem. Soc. 126 (2004) 12248–12249;
(b) J.H. Park, S.Y. Kim, S.M. Kim, Y.K. Chung, Org. Lett. 9 (2007) 2465–2468;
(c) S. Podder, J. Choudhury, S. Roy, J. Org. Chem. 72 (2007) 3129–3132;
(d) S. Yamaguchi, T. Katoh, H. Shinokubo, A. Osuka, J. Am. Chem. Soc. 129 (2007) 6392–6393;
(e) J.H. Park, E. Kim, H.-M. Kim, S.Y. Choi, Y.K. Chung, Chem. Commun. (2008) 2388–2390;
(f) S.A. Reed, M.C. White, J. Am. Chem. Soc. 130 (2008) 3316–3318.

[6] T. Imamoto, K. Yashio, V.L. Crépy, K. Katagiri, H. Takahashi, M. Kouchi, I.D. Gridnev, Organometallics 25 (2006) 908–914.

[7] T. Imamoto, J. Watanabe, Y. Wada, H. Masuda, H. Yamada, H. Tsuruta, S. Matsukawa, K. Yamaguchi, J. Am. Chem. Soc. 120 (1998) 1635–1636.

[8] (a) For recent examples of multimetallic complexes of polyphosphines, see: A.L. Airey, G.F. Swiegers, A.C. Willis, S.B. Wild, Inorg. Chem. 36 (1997) 1588–1597;
(b) T. Stampfl, R. Haid, C. Langes, W. Oberhauser, C. Bachmann, H. Kopacka, K.-H. Ongania, P. Bruggeller, Inorg. Chem. Commun. 3 (2000) 387–392;
(c) G. Annibale, P. Bergamini, V. Bertolasi, E. Besco, M. Cattabriga, R. Rossi, Inorg. Chim. Acta 333 (2002) 116–123;
(d) P.K. Bowyer, V.C. Cook, N. Gharib-Naseri, P.A. Gugger, A.D. Rae, G.F. Swieger, A.C. Willis, J. Zank, S.B. Wild, Proc. Natl. Acad. Sci. 99 (2002) 4877–4882;
(e) P. Nair, G.K. Anderson, N.P. Rath, Organometallics 22 (2003) 1494–1502;
(f) P. Nair, G.K. Anderson, N.P. Rath, Inorg. Chem. Commun. 6 (2003) 1307–1310;
(g) S.-I. Aizawa, T. Kawamoto, K. Saito, Chem. Lett. 33 (2004) 1286–1287;
(h) P. Nair, C.P. White, G.K. Anderson, N.P. Rath, J. Organomet. Chem. 691 (2006) 529–537;
(i) S.-I. Aizawa, K. Saito, T. Kawamoto, E. Matsumoto, Inorg. Chem. 45 (2006) 4859–4866;
(j) H.J. Kitto, A.D. Rae, R.D. Webster, A.C. Willis, S.B. Wild, Inorg. Chem. 46 (2007) 8059–8070.

[9] (a) R.B. King, R.N. Kapoor, M.S. Saran, P.N. Kapoor, Inorg. Chem. 10 (1971) 1851–1860;
(b) J.M. Brown, L.R. Canning, J. Organomet. Chem. 267 (1984) 179–190;
(c) M.T. Bautista, K.A. Earl, P.A. Maltby, R.H. Morris, J. Am. Chem. Soc. 110 (1988) 4056–4057.

[10] (a) R. Bartsch, S. Hietkamp, S. Morton, O. Stelzer, Angew. Chem. 94 (1982) 367–368;
(b) L.R. Gray, D.J. Gulliver, W. Levason, M. Webster, J. Chem. Soc., Dalton Trans. (1983) 133–141;
(c) R. Bartsch, S. Hietkamp, S. Morton, H. Peters, O. Stelzer, Inorg. Chem. 22 (1983) 3624–3632;
(d) D.J. Brauer, F. Gol, S. Hietkamp, H. Peters, H. Sommer, O. Stelzer, W.S. Sheldrick, Chem. Ber. 119 (1986) 349–365;
(e) W. Oberhauser, C. Bachmann, P. Brueggeller, Polyhedron 14 (1995) 787–792;
(f) N.R. Champness, W. Levason, S.R. Preece, M. Webster, C.S. Frampton, Inorg. Chim. Acta 244 (1996) 65–72.

[11] U. Köelle, R. Göerissen, T. Wanger, Chem. Ber. 128 (1995) 911–917.

[12] T.V. RajanBabu, T.A. Ayers, G.A. Halliday, K.K. You, J.C. Calabrese, J. Org. Chem. 62 (1997) 6012–6028.

[13] D.A. White, J.R. Doyle, H. Lewis, Inorg. Synth. 13 (1972) 55–65.

[14] N. Oshima, H. Suzuki, Y. Moro-oka, Chem. Lett. (1984) 1161–1164.

[15] D. Drew, J.R. Doyle, A.G. Shaver, Inorg. Synth. 13 (1972) 47–55.

[16] M.A. Bennet, A.K. Smith, J. Chem. Soc., Dalton Trans. (1974) 233–241.

[17] P. Pulay, in: H.F. Schaefer (Ed.), Modern Theoretical Chemistry, vol. 4, Plenum, New York, 1977, p. 153.

[18] R.G. Parr, W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press, New York, 1989.

[19] A.D. Becke, J. Chem. Phys. 98 (1993) 5648–5652.

[20] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785–789.

[21] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong,. C. Gonzalez, J.A. Pople, GAUSSIAN 03, Revision D.02, GAUSSIAN, Inc., Wallingford, CT, 2004.

[22] M.M. Francl, W.J. Pietro, W.J. Hehre, J.S. Binkley, M.S. Gordon, D.J. DeFrees, J.A. Pople, J. Chem. Phys. 77 (1982) 3654–3665.

[23] A. Höllwart, M. Böhme, S. Dapprich, A.W. Ehlers, A. Gobbi, V. Jonas, K.F. Köhler, R. Stegmann, A. Veldkamp, G. Frenking, Chem. Phys. Lett. 208 (1993) 237–240.

[24] J. Tomasi, M. Persico, Chem. Rev. 94 (1994) 2027–2094.

[25] C. Amovilli, V. Barone, R. Cammi, E. Cancés, M. Cossi, B. Mennucci, C.S. Pomelli, J.J. Tomasi, Adv. Quantum Chem. 32 (1999) 227–261.