Synthesis and Structures of a Chiral Phosphine-Phosphoric Acid Ligand and its Rhodium(I) Complexes

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Abstract: The synthesis and characterization of a novel chiral phosphine-phosphoric acid ligand, (*R*)-3-diphenylphosphino-1,1'-binaphthyl-2,2'-diyl hydrogenphosphate (**2**) and its rhodium(I) complexes are described. The single-crystal X-ray diffraction analysis of **2** showed the intermolecular hydrogen-bonding network of the phosphoric acid moiety. The reactions of **2** with [RhCl(cod)]₂ in the presence of KO^{*t*}Bu or with [Rh(acac)(CO)]₂ (acac = acetylacetonate) gave P,O-chelating rhodium(I) complexes [Rh(**2**-H⁺)(cod)] **3** or [Rh(**2**-H⁺)(CO)]₂ **4**, respectively. Their molecular structures were determined by single-crystal X-ray diffraction.

1. Introduction

Since the seminal reports by Akiyama and Terada,¹ chiral phosphoric acids and derivatives have attracted much attention in the construction of efficient chiral

environments not only in organocatalysis, but also in transition metal catalysis due to their multifunctionality such as Brønsted acidity/basicity, hydrogen-bonding units and counteranions toward metals.²⁻⁶ Recently, cooperative dual catalysis, in particular combining transition metal catalysis and organocatalysis by chiral phosphoric acids, has emerged as a useful strategy for asymmetric synthesis.⁷ Thus, the design and synthesis of new chiral ligands containing a phosphoric acid (or phosphate) moiety in the same molecule are important for the development of efficient asymmetric catalysis. Such catalysts are predicted to increase catalytic performance compared to the mixing of two separate catalysts.

Despite these considerations, there are only a few examples of transition metal catalysts containing a phosphoric acid moiety in the same molecule. We have previously synthesized a chiral *N*-heterocyclic carbene (NHC) ligand bearing an *m*-terphenyl-based diorganophosphate moiety as an anionic *N*-substituent.⁸ The NHC-phosphate-copper catalysts, which were prepared *in situ* from the corresponding imidazolium zwitterion and copper salts in the presence of a base, were utilized in an enantioselective boron conjugate addition to an α,β -unsaturated ester (Scheme 1). However, the effect of the phosphate moiety on the enantioselectivity in this transformation was unclear. Recently, Nishibayashi et al. disclosed an elegant cooperative dual catalysis using diruthenium complexes bearing a chiral phosphoramidate group for enantioselective propargylic alkylations of propargylic alcohols with enecarbamates (Scheme 2).⁹ This study suggested the importance of ligand-substrate interactions through hydrogen bonding for high enantioselectivity.¹⁰

Scheme 1. Our previous study on the copper-catalyzed enantioselective boron conjugate addition to an α,β -unsaturated ester with an NHC-phosphate ligand.⁸

Scheme 2. Nishibayashi et al.'s study on the ruthenium-catalyzed enantioselective propargylic alkylation of propargylic alcohol with enecarbamate.⁹

Herein, we report the synthesis and characterization of a chiral phosphine-phosphoric acid ligand, which possesses both a tertiary phosphine as a metal-coordination site and a BINOL-derived phosphoric acid as a Brønsted acid or an anionic coordination site in the same molecule (Scheme 3). The *P,O*-chelation properties of the phosphine-phosphoric acid ligands toward rhodium(I) complexes were demonstrated by

NMR and single-crystal X-ray diffraction analysis.

Scheme 3. Expected features of phosphine-phosphoric acid ligands.

2. Results and Discussion

The synthesis of a chiral phosphine-phosphoric acid **2**, composed of a (*R*)-BINOL-derived phosphoric acid moiety and a diphenylphosphino group at the 3-position, is shown in Scheme 4.^{11–14} The reaction of a diphenylphosphino-substituted (*R*)-BINOL at the 3-position **1**, which was easily prepared from commercially available (*R*)-BINOL according to Endo and Shibata's report,^{14a} with POCl_3 in pyridine followed by hydrolysis was carried out to introduce the phosphate group. The phosphoric acid diester **2** was isolated in 54% yield after acidic work-up with aqueous HCl followed by recrystallization from EtOH/ CH_3CN .¹⁵ The ^{31}P NMR spectrum of **2** in CDCl_3 showed two singlet signals at $\delta = -14.5$ and 4.5 ppm, which were assigned to the P atoms of the triarylphosphine and the diorganophosphoric acid moieties, respectively. There was no acid-base interaction between the tertiary phosphine and the phosphoric acid moiety on the basis of the ^{31}P chemical shift values.^{16,17} In the ^1H NMR spectrum, the OH group on **2** exhibited a broad signal with a variable chemical shift ($\delta = \text{ca. } 5\sim 11$ ppm).

Scheme 4. Synthesis of phosphine-phosphoric acid **2**.

The single-crystal X-ray diffraction of **2** elucidated the three-dimensional structure in the solid state,¹⁸ as shown in Figure 1. The asymmetric cell contained two independent molecules of **2** with acetonitrile as a solvent molecule, and each diorganophosphoric acid moiety was connected through an intermolecular hydrogen-bonding network (P2–O1···O6–P4, 2.461 Å; P2–O2···O5–P4, 2.515 Å, in Figure 1b). Importantly, there were no intra- or intermolecular interactions between the diphenylphosphino group and the phosphoric acid moiety in **2** (P1···O1, 4.732 Å; P1···O2, 3.529 Å; P1···O5, 3.538 Å; P1···O6, 5.209 Å) in the solid state or in solution as supported by the ³¹P NMR analysis (*vide supra*).

Figure 1

Figure 1. ORTEP drawing of **2** with thermal ellipsoids drawn at the 20% probability level. Hydrogen atoms on the carbon atoms and CH₃CN molecules are omitted for the sake of clarity. (a) Molecular structure and (b) hydrogen-bonding network (dashed blue lines) of **2**. Selected bond lengths (Å): P2–O1 [1.516 (4)], P2–O2 [1.471 (3)], P2–O3 [1.587 (3)], P2–O4 [1.584 (3)].

A diorganophosphate has a metal coordination ability similar to those of carboxylate and sulfonate ligands. A number of metal phosphate complexes have been utilized in catalysis and materials science.¹⁹ Thus, we investigated the coordination behavior of the phosphine-phosphoric acid ligand toward Rh(I) complexes. Specifically, the reaction of **2** with [RhCl(cod)]₂ in the presence of KO^tBu in benzene at room temperature gave an air- and moisture-stable Rh(I) complex [Rh(**2**-H⁺)(cod)] **3** in 59% yield (Scheme 5). The ³¹P NMR spectrum in CDCl₃ exhibited two doublet signals at 20.0 (¹J_{Rh-P} = 154 Hz) and 5.5 (²J_{Rh-P} = 2 Hz) ppm, which were assigned to the P atoms of the tertiary phosphine and the diorganophosphate attached to the Rh center, respectively (Figure 2). The small value of the second-order Rh-P coupling constant (²J_{Rh-P} = 2 Hz) indicates that the phosphate anion binds to the Rh center.^{8,20} In fact, the molecular structure of **3** with the η¹-O-coordination of the phosphate group was unambiguously confirmed by single-crystal X-ray diffraction analysis (recrystallization from CH₂Cl₂/EtOH) (Figure 3).

Scheme 5. Synthesis of [Rh(**2**-H⁺)(cod)] (**3**).

Figure 2

Figure 2. ³¹P NMR spectrum (161.8 MHz, CDCl₃) of [Rh(**2**-H⁺)(cod)] **3**.

Figure 3

Figure 3. ORTEP drawing of $[\text{Rh}(\mathbf{2}-\text{H}^+)(\text{cod})]$ **3** with thermal ellipsoids drawn at the 20% probability level. Hydrogen atoms are omitted for the sake of clarity. Selected bond lengths ($\text{\AA}$): Rh1–P1 [2.3120 (17)], Rh1–O1 [2.088 (4)], Rh1–C33 [2.116 (9)], Rh1–C34 [2.132 (8)], Rh1–C37 [2.248 (7)], Rh1–C38 [2.215 (6)].

Furthermore, the *P,O*-chelation property of the phosphine-phosphoric acid ligand **2** was demonstrated by the use of $[\text{Rh}(\text{acac})(\text{CO})_2]$ (acac = acetylacetonate) as a Rh(I) source. As shown in Scheme 6, the reaction between **2** and $[\text{Rh}(\text{acac})(\text{CO})_2]$ in CH_2Cl_2 proceeded smoothly to provide an air- and moisture-stable dinuclear Rh(I) complex $[\text{Rh}(\mathbf{2}-\text{H}^+)(\text{CO})]_2$ **4** in 67% yield. In this case, the phosphoric acid moiety of **2** underwent deprotonation by the acac ligand on $[\text{Rh}(\text{acac})(\text{CO})_2]$. The ^{31}P NMR spectrum of **4** in CDCl_3 showed two doublet of doublet signals at 45.4 ($^1J_{\text{Rh-P}} = 189 \text{ Hz}$; $^3J_{\text{P-P}} = 8 \text{ Hz}$) and 10.2 ($^2J_{\text{Rh-P}} = 3 \text{ Hz}$; $^3J_{\text{P-P}} = 8 \text{ Hz}$) ppm, which were assigned to the P atoms of the tertiary phosphine and the diorganophosphate attached to the Rh center, respectively (Figure 4). The infrared spectrum of **4** gave a carbonyl stretching band at $\nu = 1981.6 \text{ cm}^{-1}$, indicating that the electron density at the Rh(I) center was comparable to that of $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$ ($\nu = 1977.6 \text{ cm}^{-1}$).²¹

Scheme 6. Synthesis of $[Rh(2-H^+)(CO)]_2$ **4**.

Figure 4

Figure 4. ^{31}P NMR spectrum (161.8 MHz, $CDCl_3$) of $[Rh(2-H^+)(CO)]_2$ **4**.

Single crystals of **4** suitable for X-ray diffraction analysis were obtained by recrystallization from CH_2Cl_2 /hexane, and its molecular structure with the *P,O*-chelating motif was unambiguously confirmed (Figure 5). Selected bond lengths and angles for **4** are summarized in Table 1. Each Rh center of the eight-membered dirhodacycle is bridged by two phosphate moieties and adopts a square-planar coordination geometry. The nearly equivalent length of the P–O bonds in the dirhodacycle

indicated the delocalization of a negative charge over the phosphate moiety [P(2)–O(1) 1.500 (5) Å; P(2)–O(2) 1.475 (5) Å; P(4)–O(6) 1.485 (6) Å; P(4)–O(7) 1.483 (6) Å].

Figure 5

Figure 5. ORTEP drawing of $[Rh(2-H^+)(CO)]_2$ **4** with thermal ellipsoids drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (deg) for [Rh(**2**-H⁺)(CO)]₂ **4**.

Bond lengths	(Å)	Angles	(deg)
Rh1–P1	2.211 (2)	P1–Rh1–O1	95.54 (15)
Rh1–O1	2.093 (5)	P1–Rh1–C33	87.1 (3)
Rh1–O7	2.111 (5)	O7–Rh1–O1	83.4 (2)
Rh1–C33	1.775 (10)	O7–Rh1–C33	94.7 (3)
P2–O1	1.500 (5)	P1–Rh1–O7	168.91 (15)
P2–O2	1.475 (5)	O1–Rh1–C33	175.4 (3)
Rh2–P3	2.218 (2)	P3–Rh2–O6	95.55 (16)
Rh2–O2	2.142 (6)	P3–Rh2–C66	86.0 (3)
Rh2–O6	2.107 (5)	O2–Rh2–O6	86.2 (2)
Rh2–C66	1.784 (9)	O2–Rh2–C66	92.4 (3)
P4–O6	1.485 (6)	P3–Rh2–O2	173.69 (14)
P4–O7	1.483 (6)	O6–Rh2–C66	177.8 (3)

3. Conclusion

A new chiral phosphine-phosphoric acid **2**, which possesses both a tertiary phosphine and a BINOL-derived phosphoric acid in the same molecule, was synthesized and characterized. The phosphine and phosphoric acid moieties in **2** exhibited no acid-base interaction, leaving the P center free from hydrogen-bonding. X-ray crystallographic analysis of **2** showed a three-dimensional molecular structure with an intermolecular hydrogen-bonding network of the phosphoric acid moiety. The P,O-chelation properties

of **2** toward rhodium(I) complexes such as $[\text{Rh}(\mathbf{2}-\text{H}^+)(\text{cod})]$ **3** and $[\text{Rh}(\mathbf{2}-\text{H}^+)(\text{CO})]_2$ **4** were demonstrated by ^{31}P NMR and single-crystal X-ray diffraction analysis. Investigations into the applications of the phosphine-phosphoric acid ligands for enantioselective catalysis are currently in progress.²²

4. Experimental

4.1 General

NMR spectra were recorded on a JEOL JNM-ECXII 400 spectrometer, operating at 400 MHz for ^1H NMR, 100.5 MHz for ^{13}C NMR and 161.8 MHz for ^{31}P NMR. Chemical shift values for ^1H , ^{13}C , and ^{31}P NMR spectra were referenced to Me_4Si (0 ppm), the residual solvent (77.0 ppm), and H_3PO_4 (0 ppm), respectively. High-resolution ESI mass spectra were recorded on a Thermo Fisher Scientific Exactive mass spectrometer at the Instrumental Analysis Division, Equipment Management Center, Creative Research Institution, Hokkaido University. High-resolution FD mass spectrum was recorded on JEOL JMS-T100GCv mass spectrometer at the GC-MS & NMR Laboratory, Research Faculty of Agriculture, Hokkaido University. Melting points were determined on a micro melting point apparatus (Yanaco: MP-500D). TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F₂₅₄. Silica gel (Kanto Chemical Co., Silica gel 60 N, spherical, neutral) was used for column chromatography. All reactions were carried out under a nitrogen or argon atmosphere. Materials were obtained from commercial suppliers or prepared according to standard

procedures unless otherwise noted. Diol **1** was synthesized according to the reported procedure with slight modifications.^{14a}

4.2 Preparation of phosphine-phosphoric acid **2**

Diol **1** (470.5 mg, 1.0 mmol) was placed in a 20-mL two-necked flask containing a magnetic stirring bar, and was dissolved in pyridine (6 mL). Next, POCl₃ (112 μ L, 1.2 mmol, 1.2 equiv.) was added to the flask at 0 °C, and the mixture was stirred at room temperature for 12 h. Subsequently, water (1 mL) was added to the solution, and the resulting mixture was vigorously stirred at room temperature for 1.5 h. Next, 6M HCl aq. was added to the flask, and the resulting mixture was extracted with CH₂Cl₂. The combined organic layer was further washed with 2M HCl aq., dried over Na₂SO₄, filtered, and concentrated. The crude product was purified by recrystallization from EtOH/CH₃CN (1:10) to give **2** as a pale yellow solid (293.6 mg). Compound **2** contained 1/3 equivalents of CH₃CN on the basis of the ¹H NMR analysis. Thus, the isolated yield of **2** was calculated to be 54% (286.2 mg). Mp: 213–214 °C. ¹H NMR (CDCl₃): δ 7.13 (br s, 1H), 7.24–7.52 (m, 18H), 7.70 (d, J = 8.0 Hz, 1H), 7.88–7.93 (m, 2H). ¹³C NMR (CDCl₃): Due to the complexity of the spectrum, complete signal assignment based on P–C coupling was difficult and is not shown here. δ 120.90, 121.21, 121.81, 125.38, 125.77, 126.45, 126.87, 127.10, 127.20, 128.44–129.56 (m), 131.15, 131.31, 131.57, 132.22, 133.17, 133.62–133.88 (m), 134.56, 134.75, 136.19, 147.14, 147.23, 148.72, 148.81, 148.90, 148.99. ³¹P NMR (CDCl₃): δ –14.5, 4.5. HRMS-ESI (m/z): [M–H][–] calcd for C₃₂H₂₁O₄P₂, 531.09206; found: 531.09242. $[\alpha]_D^{25}$ =

–351.3 (*c* 1.00, CHCl₃).

4.3. Preparation of [Rh(2–H⁺)(cod)] **3**

In an N₂-filled glove box, phosphine-phosphoric acid **2** (21.3 mg, 40 μmol), [RhCl(cod)]₂ (9.9 mg, 20 μmol, 0.5 equiv.) and KO^{*t*}Bu (4.5 mg, 40 μmol) were placed in a 5-mL vial containing a magnetic stirring bar. Next, benzene (2 mL) was added to the vessel, and the mixture was stirred at room temperature for 11 h. The crude mixture was filtered through Celite with benzene, and the filtrate was evaporated under vacuum. The crude product was purified by recrystallization from CH₂Cl₂/EtOH to give [Rh(2–H⁺)(cod)] **3** as a yellow solid (18.1 mg). Compound **3** contained 1/2 equivalent of EtOH on the basis of the ¹H NMR analysis. Thus, the isolated yield of **3** was calculated to be 59% (17.6 mg). Mp: >205 °C (decomp.). ¹H NMR (CDCl₃): δ 1.62–1.73 (m, 1H), 1.87–2.00 (m, 1H), 2.06–2.21 (m, 3H), 2.44–2.69 (m, 3H), 2.70–2.85 (m, 1H), 3.22 (br-s, 1H), 5.31 (br-m, 1H), 5.89 (br-m, 1H), 7.16–7.21 (m, 1H), 7.25–7.43 (m, 5H), 7.45–7.52 (m, 3H), 7.53–7.59 (m, 6H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 10.0 Hz, 2H), 7.92 (d, *J* = 8.8 Hz, 1H), 8.24–8.31 (m, 2H). ¹³C NMR (CDCl₃): Due to the complexity of the spectrum, complete signal assignment based on P–C and Rh–C coupling was difficult and is not shown here. δ 27.55, 28.80, 31.14, 34.39, 68.13 (d, *J* = 14 Hz), 72.46 (d, *J* = 15 Hz), 106.75–106.94 (m), 107.47–107.65 (m), 121.30, 121.92, 123.62, 124.03, 124.72, 125.61, 125.82, 126.91–127.37 (m), 128.29, 128.56, 128.67, 129.03, 129.14, 129.31, 129.77, 130.51–130.81 (m), 131.28, 131.41, 132.29, 133.38, 133.77–133.94 (m), 135.78, 135.91, 149.40–149.66 (m). ³¹P

NMR (CDCl₃): δ 5.5 (d, $^2J_{\text{Rh-P}} = 2$ Hz), 20.0 (d, $^1J_{\text{Rh-P}} = 154$ Hz). HRMS-FD (m/z): Calcd for C₄₀H₃₃O₄P₂Rh, 742.09091; found: 742.09274. $[\alpha]_{\text{D}}^{24} = +10.3$ (c 1.00, CHCl₃).

4.4. Preparation of [Rh(2-H⁺)(CO)]₂ **4**

In an N₂-filled glove box, phosphine-phosphoric acid **2** (21.3 mg, 40 μ mol) and [Rh(acac)(CO)₂] (10.3 mg, 40 μ mol, 1 equiv.) were placed in a 5-mL vial containing a magnetic stirring bar. Next, CH₂Cl₂ (2 mL) was added to the vessel, and the mixture was stirred at room temperature for 0.5 h. The volatiles were removed under vacuum. The crude product was purified by recrystallization from CH₂Cl₂/hexane to give [Rh(2-H⁺)(CO)]₂ **4** as a yellow solid (18.0 mg). Compound **4** contained 1/5 equivalents of CH₂Cl₂ on the basis of the ¹H NMR analysis. Thus, the isolated yield of **4** was calculated to be 67% (17.8 mg). Mp: >180 °C (decomp.). ¹H NMR (CDCl₃): δ 7.25–7.36 (m, 8H), 7.40–7.57 (m, 24H), 7.69 (d, $J = 7.6$ Hz, 2H), 7.90–7.97 (m, 4H), 8.05–8.12 (m, 4H). ¹³C NMR (CDCl₃): Due to the complexity of the spectrum, complete signal assignment based on P–C and Rh–C coupling was difficult and is not shown here. δ 120.68, 121.52, 123.68 (br), 124.03, 124.54, 125.09, 125.96, 126.27, 127.08, 127.92, 128.42–128.74 (m), 129.18, 130.34, 130.92–131.31 (m), 131.92, 132.30, 132.51, 133.75, 133.87, 135.65, 148.70–148.85 (m), 149.31, 149.41, 184.92 (dd, $^2J_{\text{P-C}} = 24$ Hz, $^1J_{\text{Rh-C}} = 78$ Hz). ³¹P NMR (CDCl₃): δ 10.2 (dd, $^2J_{\text{P-Rh}} = 3$ Hz, $^3J_{\text{P-P}} = 8$ Hz), 45.4 (dd, $^1J_{\text{P-Rh}} = 189$ Hz, $^3J_{\text{P-P}} = 8$ Hz). HRMS-FD (m/z): Calcd for C₆₆H₄₂O₁₀P₄Rh₂, 1323.98385; found: 1323.98494. $[\alpha]_{\text{D}}^{23} = +11.0$ (c 1.00, CHCl₃). IR (ATR): 1981.6 cm⁻¹ (Rh–CO).

4.5. X-Ray crystallographic analysis

Data were collected on a Rigaku Mercury CCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71075 \text{ \AA}$), and processed using the CrystalClear software.²³ Structures were solved by a direct method using SIR2004,²⁴ and refined by full-matrix least-square method using SHELXL-97²⁵ for **2**·0.5(CH₃CN) and SHELXL-2013²⁵ for **3** and **4**. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on the calculated positions and refined using a riding model. Absolute configurations were deduced based on the Flack parameters.²⁶ All calculations were performed using the CrystalStructure software package.²⁷ The supplementary crystallographic data for this paper can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystal data for **2**·0.5(CH₃CN) (CCDC 1413278; recrystallization from EtOH/CH₃CN; the single crystal contains **2** and CH₃CN in a 2:1 ratio.) 2[C₃₂H₂₂O₄P₂]·CH₃CN, $M = 1105.99$, monoclinic, space group = $P2_1$ (#4), $a = 12.475(3) \text{ \AA}$, $b = 8.340(2) \text{ \AA}$, $c = 27.633(7) \text{ \AA}$, $\beta = 100.146(4)^\circ$, $V = 2830.0(12) \text{ \AA}^3$, $T = 150 \text{ K}$, $Z = 2$, density (calc.) = 1.298 g/cm^3 , total reflections = 23321, unique reflections = 11228 ($R_{\text{int}} = 0.044$), GOF = 1.067, Flack parameter = 0.03 (10). $R_1 = 0.0608$ [$I > 2\sigma(I)$], $wR_2 = 0.1617$ (all data). Crystal data for **3** (CCDC 1413279; recrystallization from CH₂Cl₂/EtOH; the structure **3** contains two symmetrically independent molecules of similar conformation.) Large accessible voids remained in the structure probably due to the highly disordered solvent molecules. Thus, the SQUEEZE program in PLATON was employed for analysis.²⁸

Although the high $U(\text{eq})$ value compared to neighbors for the C80 atom of the cyclooctadiene moiety was observed in the checkCIF/PLATON test,²⁹ the carbon atom was assigned correctly. $\text{C}_{40}\text{H}_{33}\text{O}_4\text{P}_2\text{Rh}$, $M = 742.55$, orthorhombic, space group = $P2_12_12$ (#18), $a = 26.314(3) \text{ \AA}$, $b = 29.654(4) \text{ \AA}$, $c = 11.0055(13) \text{ \AA}$, $V = 8587.8(18) \text{ \AA}^3$, $T = 150 \text{ K}$, $Z = 8$, density (calc.) = 1.149 g/cm^3 , total reflections = 72481, unique reflections = 19392 ($R_{\text{int}} = 0.081$), GOF = 1.021, Flack parameter = $-0.006(15)$. $R_1 = 0.0576 [I > 2\sigma(I)]$, $wR_2 = 0.1128$ (all data).

Crystal data for **4** (CCDC 1413280; recrystallization from $\text{CH}_2\text{Cl}_2/\text{hexane}$). Large accessible voids remained in the structure probably due to the highly disordered solvent molecules. Thus, the SQUEEZE program in PLATON was employed for analysis.²⁸

$\text{C}_{66}\text{H}_{42}\text{O}_{10}\text{P}_4\text{Rh}_2$, $M = 1324.76$, tetragonal, space group = $P4_3$ (#78), $a = 26.165(4) \text{ \AA}$, $c = 10.4806(16) \text{ \AA}$, $V = 7175.1(19) \text{ \AA}^3$, $T = 230 \text{ K}$, $Z = 4$, density (calc.) = 1.226 g/cm^3 , total reflections = 54552, unique reflections = 13939 ($R_{\text{int}} = 0.065$), GOF = 1.106, Flack parameter = $-0.019(13)$. $R_1 = 0.0520 [I > 2\sigma(I)]$, $wR_2 = 0.1070$ (all data).

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Figure(s)

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$C_{32}H_{22}O_4P_2$

(*R*)-3-Diphenylphosphino-1,1'-binaphthyl-2,2'-diyl hydrogenphosphate **2**

$[\alpha]_D^{25} = -351.3$ (*c* 1.00, $CHCl_3$)

Source of chirality: (*R*)-(+)-1,1'-Bi-2-naphthol

Absolute configuration: (*R*)

$C_{40}H_{33}O_4P_2Rh$

Compound $[Rh(2-H^+)(cod)]$ **3**

$[\alpha]_D^{24} = +10.3$ (*c* 1.00, $CHCl_3$)

Source of chirality: (*R*)-(+)-1,1'-Bi-2-naphthol

Absolute configuration: (*R*)

$C_{66}H_{42}O_{10}P_4Rh_2$

Compound $[Rh(2-H^+)(CO)]_2$ **4**

$[\alpha]_D^{23} = +11.0$ (*c* 1.00, $CHCl_3$)

Source of chirality: (*R*)-(+)-1,1'-Bi-2-naphthol

Absolute configuration: (*R,R*)