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Synthesis, Reactivities, and Coordination Chemistry of Tris(2-isopropoxyphenyl)phosphine

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ABSTRACT: *A phosphine bearing three 2-isopropoxyphenyl groups, $P\{C_6H_4[2\text{-}O(i\text{-}Pr)]\}_3$ (**1**), was synthesized. Phosphine **1** readily reacted with CH_2Cl_2 and $ClCH_2CH_2Cl$ at 25°C to give the corresponding phosphonium salts $[RCH_2P\{C_6H_4[2\text{-}O(i\text{-}Pr)]\}_3]X$ (**2**: R=X=Cl, **3**: R=CH_2Cl, X=BF_4). Platinum, palladium, and rhodium complexes with ligand **1**, $[PtCl_2(\mathbf{1})_2]$ (**4**), $[PdCl_2(\mathbf{1})_2]$ (**5**), $[\{PdCl(\mathbf{1})\}_2(\mu\text{-}Cl)_2]$ (**6**), and $[RhCl(cod)(\mathbf{1})]$ (**7**) were synthesized and their structures were determined by X-ray crystallography, which revealed that ligand **1** works as a monodentate ligand in these complexes.* © 2014 Wiley Periodicals, Inc. Heteroatom Chem. 25:628–635, 2014; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21174

INTRODUCTION

In recent years, much attention has been focused on the chemistry of transition metal complexes bearing tripodal tetradentate ligands from the viewpoints of the activation of small molecules, the stabilization of reactive species with unusual electric and geometric structures, catalytic activities, and so on [1–6]. Although there are many reports on tripodal tetradentate ligands bearing nitrogen or phosphorus atoms, the chemistry of those bearing one phosphine and three chalcogenoether moieties is less explored. Such ligands are expected to show unique structures and reactivities derived from the lability of the coordination of chalcogenoether moieties to transition metals and the property of phosphine as an anchor ligand. As for PO_3-type ligands, there are many reports on transition metal complexes bearing tris(2,4,6-trimethoxyphenyl)phosphine or tris(2,6-dimethoxyphenyl)phosphine, which work as mono-, bi-, tri-, or tetradentate ligands [7–12]. Some complexes with tris(2-methoxyphenyl)phosphine have been synthesized [13–18], and this phosphine ligand, in most of its complexes, coordinates to transition metals only by the phosphine part without the coordination of the oxygen atoms. However, the studies on other PO_3-type tripodal tetradentate ligands are relatively rare.

On the other hand, we have recently reported the synthesis and structure of group 10 metal complexes bearing a PS_3-type ligand (tris(2-isopropylthiophenyl)phosphine) [19]. In this paper, we present synthesis and properties of a PO_3-type ligand, tris(2-isopropoxyphenyl)phosphine (**1**), and its transition metal complexes.

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Dedicated to 77th birthday of Professor Renji Okazaki.

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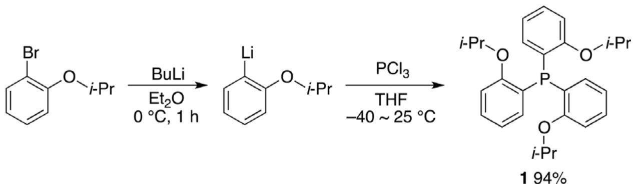


SCHEME 1 Synthesis of phosphine ligand **1**.

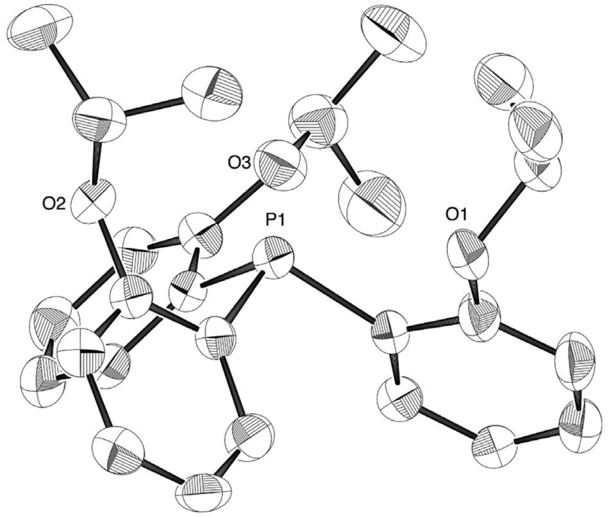
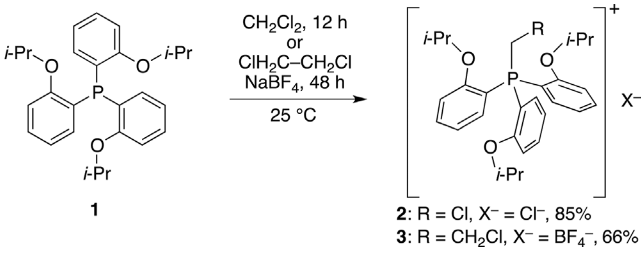


FIGURE 1 ORTEP drawing of **1** with thermal ellipsoids (30% probability). Hydrogen atoms were omitted for clarity.

RESULTS AND DISCUSSION

Synthesis of Tris(2-isopropoxyphenyl)phosphine **1**

After 1-bromo-2-isopropoxybenzene [20] was lithiated by the treatment with butyllithium in ether at 0°C according to the reported method [21], the solvents were replaced by tetrahydrofuran (THF). The reaction of resulting 2-isopropoxyphenyllithium with PCl_3 in THF at –40°C to 25°C gave tris(2-isopropoxyphenyl)phosphine (**1**) in good yield (Scheme 1). The structure of **1** was determined by ^{1}H, ^{13}C, and ^{31}P NMR spectra and X-ray crystallography.



SCHEME 2 Reactions of ligand **1** with dichloromethane and 1,2-dichloroethane.

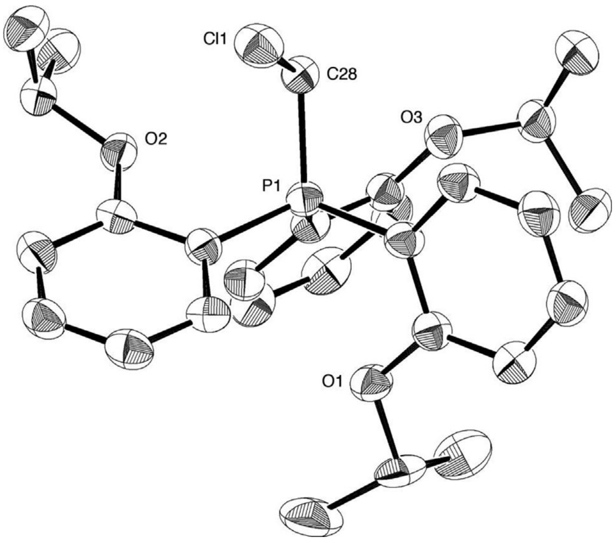


FIGURE 2 ORTEP drawing of **2** with thermal ellipsoids (50% probability). Hydrogen atoms, a counter anion, and a solvent molecule were omitted for clarity. Selected bond lengths (Å): P1–C28, 1.823(5).

The ORTEP drawing of phosphine **1** showed that the three oxygen atoms were situated in the same side of the lone pair of the phosphorus (Fig. 1). This preorganized structure suggests that ligand **1** can work as a tetradentate ligand.

Reactions of Phosphine **1** *with Haloalkanes*

When a solution of phosphine **1** in CH_2Cl_2 was stirred at 25°C for 12 h, the reaction of **1** with CH_2Cl_2 proceeded to give the corresponding phosphonium chloride **2** as colorless crystals in 85% yield (Scheme 2). The structure of **2** was determined by the ^{1}H NMR spectrum and X-ray crystallography (Fig. 2). It has been reported that tris(2,4,6-trimethoxyphenyl)phosphine also undergoes a similar reaction with CH_2Cl_2 to afford the corresponding phosphonium chloride [22]. Higher reactivities of these phosphines compared with triphenylphosphine and tris(2-isopropylthiophenyl)phosphine, which are stable in haloalkanes at 25°C, can be explained by the mesomeric effect of methoxy groups. This effect results in the increase in electron density in the phosphorus center of these phosphines, and the phosphorus center having high nucleophilicity attacks the carbon atom of CH_2Cl_2.

Phosphine **1** also reacts with 1,2-dichloroethane in the presence of $NaBF_4$ at 25°C to afford the corresponding phosphonium tetrafluoroborate **3** in 66% yield (Scheme 2). The structure of **3** was determined by the ^{1}H NMR spectrum and X-ray crystallography (Fig. 3).

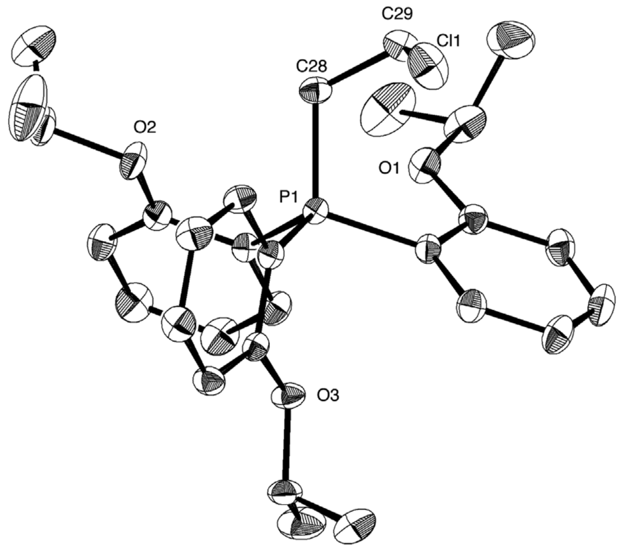
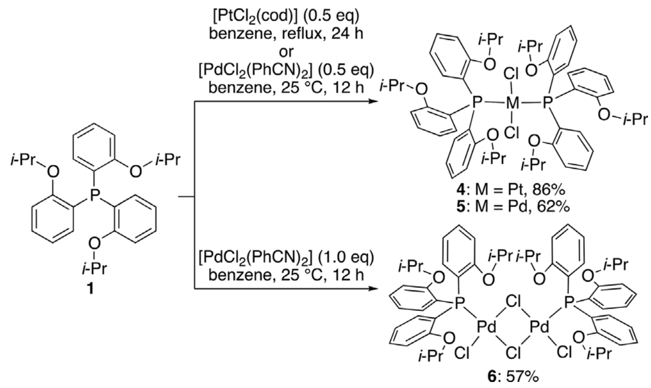


FIGURE 3 ORTEP drawing of **3** with thermal ellipsoids (50% probability). Hydrogen atoms and a counter anion were omitted for clarity. Selected bond lengths (Å): P1–C28, 1.8214(16).



SCHEME 3 Synthesis of group 10 metal complexes with **1**.

Synthesis of Transition Metal Complexes with PO_3 Ligand **1**

When ligand **1** was treated with 0.5 molar amounts of [$PtCl_2$(cod)] in refluxing benzene for 24 h, dichloridoplatinum complex **4** bearing two PO_3 ligands was obtained as pale yellow crystals in 86% yield (Scheme 3). The reaction of **1** with 0.5 molar amounts of [$PdCl_2(PhCN)_2$] in benzene at 25°C for 12 h also gave the corresponding complex **5** bearing two PO_3 ligands in 62% yield. On the other hand, the reaction of **1** with equimolar amount of [$PdCl_2(PhCN)_2$] in benzene at 25°C for 12 h resulted in the formation of dipalladium complexes **6**, a dimer of dichloridopalladium complex bearing one PO_3 ligand, in 57% yield.

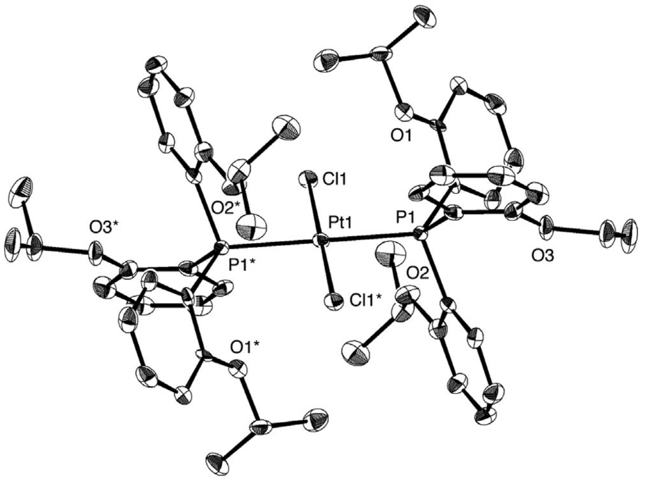


FIGURE 4 ORTEP drawing of **4** with thermal ellipsoids (50% probability). Hydrogen atoms and solvent molecules were omitted for clarity. Two independent molecules exist in the unit cell. Since the structures of these two molecules are similar to each other, only one molecule is shown. Selected bond lengths (Å) and angles (deg): Pt1–P1, 2.326(2); Pt1–Cl1, 2.313(2); Cl1–Pt1–P1, 93.29(7); Cl1*–Pt1–P1, 86.71(7).

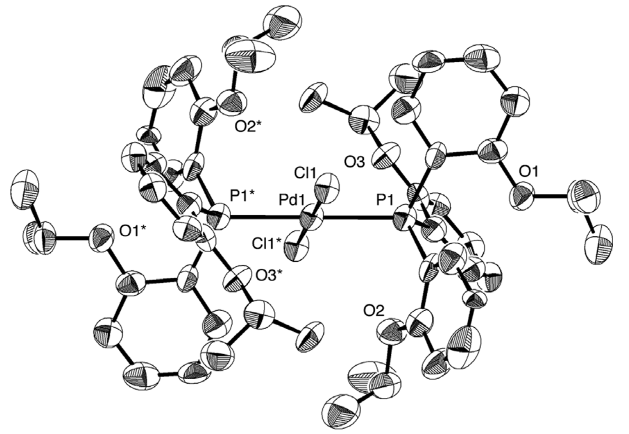


FIGURE 5 ORTEP drawing of **5** with thermal ellipsoids (50% probability). Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1–P1, 2.342(2); Pd1–Cl1, 2.318(2); Cl1–Pd1–P1, 86.29(7); Cl1*–Pd1–P1, 93.71(7).

The structures of these complexes **4–6** were determined by the ^{1}H NMR spectrum and X-ray crystallography. The X-ray analyses of **4** and **5** (Figs. 4 and 5) indicated the trans configuration of the phosphine ligands and the square planar structures around the palladium and platinum centers. It is suggested that no interaction exists between the oxygen atoms and the metal centers, since the shortest metal–oxygen distances (Pt1···O1: 3.4993(2) Å in **4**, Pd1···O1: 3.534(7) Å in **5**) are longer than the sum of van der Waals' radii of metals and oxygen (Pt···O: 3.24 Å and Pd···O: 3.15 Å) [23, 24], respectively.

Figure 6 shows the molecular structure of dipalladium complex **6**, which has *syn* configuration to the Pd(μ-Cl)$_2$Pd part and the square planar structures around the two palladium atoms. There have

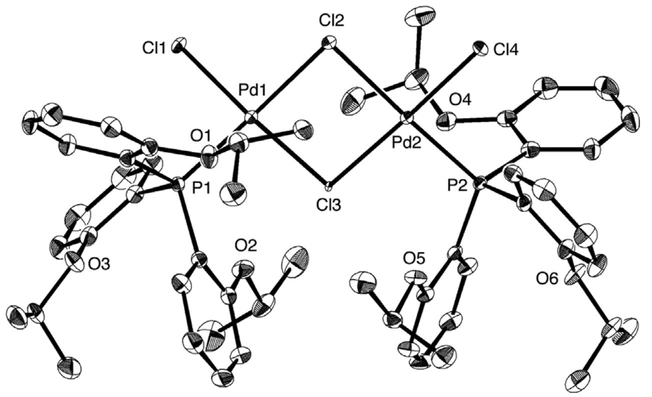
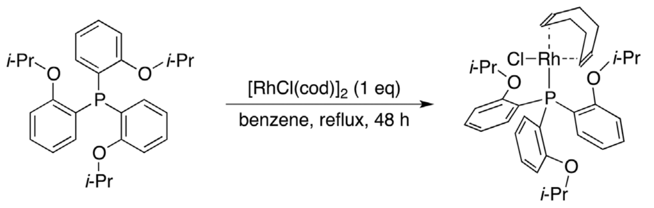


FIGURE 6 ORTEP drawing of **6** with thermal ellipsoids (50% probability). Hydrogen atoms and solvent molecules were omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1–P1, 2.2413(7); Pd1–Cl1, 2.2992(7); Pd1–Cl2, 2.4293(7); Pd1–Cl3, 2.3359(6); Pd2–P2, 2.2435(7); Pd2–Cl4, 2.2928(7); Pd2–Cl2, 2.4340(7); Pd2–Cl3, 2.3411(7); P1–Pd1–Cl1, 88.10(3); Cl1–Pd1–Cl2, 91.05(2); Cl2–Pd1–Cl3, 86.21(2); Cl3–Pd1–P1, 95.32(2); P2–Pd2–Cl4, 87.33(3); Cl4–Pd2–Cl2, 91.84(2); Cl2–Pd2–Cl3, 85.99(2); Cl3–Pd2–P2, 95.57(2).

been reported some *syn*-LClPd(μ-Cl)$_2$PdClL complexes which are stabilized by chelating ligands (L-L) [25–27], however, the *syn*-complexes bearing monodentate ligands are very rare. The *syn*-structure of **6** in the crystalline state is very interesting, although its reason is not clear. Since the Pd1–O1 distance [3.040(2) Å] is slightly shorter than the sum of van der Waals' radii of palladium and oxygen (3.15 Å) [23, 24] and the Pd2–O4 distance [3.170(2) Å] is near to this value, the existence of very weak interaction between these atoms is suggested.

The ^{1}H NMR spectra of **4–6** at 25°C showed broad peaks. The measurement at 60°C resulted in the observation of sharp peaks in the ^{1}H NMR spectra of **4** and **5**, although the ^{1}H NMR spectrum of **6** at 60°C did not show sufficiently sharp peaks. These results suggest the restricted rotation of the P–C bonds in these complexes (**4–6**).

The reaction of ligand **1** with [RhCl(cod)]$_2$ in refluxing benzene for 48 h afforded the corresponding choloridorhodium complex **7** bearing ligand **1** and a cod ligand in 74% yield (Scheme 4). The structure of **7** was determined by the ^{1}H NMR spectroscopy and X-ray crystallography (Fig. 7).



1 **7**: 74%

SCHEME 4 Synthesis of rhodium complex with **1**.

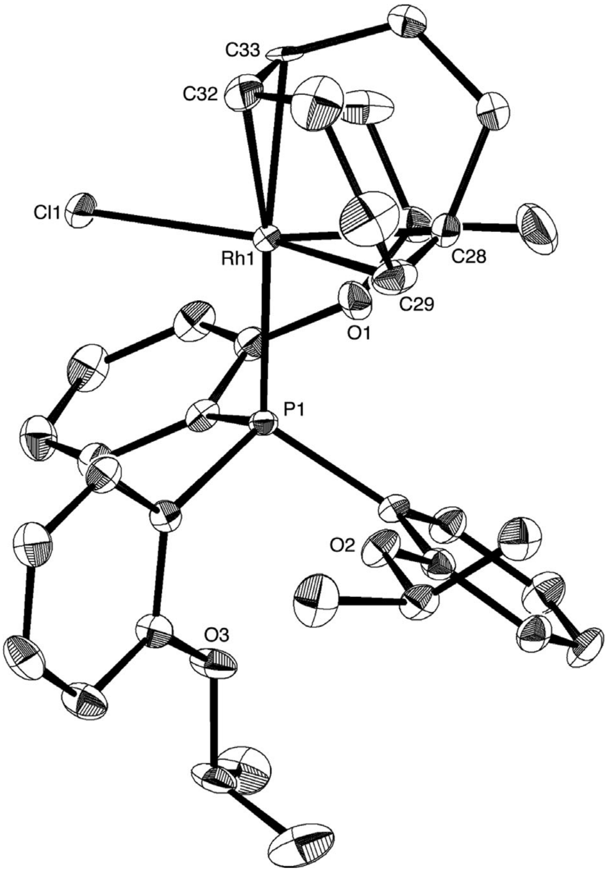


FIGURE 7 ORTEP drawing of **7** with thermal ellipsoids (50% probability). Hydrogen atoms and a solvent molecule were omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh1–P1, 2.3526(7); Rh1–Cl1, 2.3725(8); Rh1–C28, 2.115(3); Rh1–C29, 2.108(3); Rh1–C32, 2.209(3); Rh1–C33, 2.201(3); C28–C29, 1.407(4); C32–C33, 1.381(5); P1–Rh1–Cl1, 88.89(3); P1–Rh1–C28, 96.17(8); P1–Rh1–C29, 93.04(9); Cl1–Rh1–C32, 89.97(9); Cl1–Rh1–C33, 88.39(9); C28–Rh1–C29, 38.92(12); C28–Rh1–C32, 90.47(12); C28–Rh1–C33, 81.47(12); C29–Rh1–C32, 81.37(12); C29–Rh1–C33, 96.21(12); C32–Rh1–C33, 36.50(12).

The X-ray analysis showed that ligand **1** works as a monodentate ligand and complex **7** has a square planar structure if the alkene parts are considered to coordinate to the rhodium(I) center with the π-electron. The Rh–P, Rh–Cl, and Rh–C bond lengths are normal [28], and the C28–C29 and C32–C33 bond lengths are intermediate values between single and double bonds, suggesting the coordination of π-electrons of the C–C double bonds to the rhodium center. Since the Rh1–O1 distance [3.421(2) Å] is slightly shorter than the sum of van der Waals' radii of rhodium and oxygen (3.52 Å) [23, 24], it is suggested that very weak interaction exists between these atoms.

CONCLUSIONS

Tris(2-isopropoxyphenyl)phosphine (**1**) was synthesized by the reaction of 2-isopropoxyphenyllithium with PCl_3. Phosphine **1** has high nucleophilicity and readily reacts with haloalkanes such as dichloromethane and 1,2-dichloroethane at 25°C to give the corresponding phosphonium salts $[RCH_2P\{C_6H_4[2\text{-}O(i\text{-}Pr)]\}_3]X$ (**2**: R=X=Cl, **3**: $R{=}CH_2Cl$, $X{=}BF_4$). The reaction of **1** with $[PtCl_2(cod)]$, $[PdCl_2(PhCN)_2]$, and $[RhCl(cod)]_2$ resulted in the formation of the corresponding transition metal complexes $[PtCl_2(\mathbf{1})_2]$ (**4**), $[PdCl_2(\mathbf{1})_2]$ (**5**), $[\{PdCl(\mathbf{1})\}_2(\mu\text{-}Cl)_2]$ (**6**), and $[RhCl(cod)(\mathbf{1})]$ (**7**), in which ligand **1** works as a monodentate ligand.

EXPERIMENTAL

General Procedures

All reactions were carried out under an argon atmosphere unless otherwise noted. THF and ether were purified by distillation from sodium diphenylketyl before use. All solvents used in the reactions were purified by the reported methods. Wet column chromatography (WCC) was performed with Merck Silica Gel 60 (70-230 mesh ASTM). The ^{1}H NMR (500 or 300 MHz) spectra were measured in $CDCl_3$ or C_6D_6 with a JEOL JNM-λ500 or JEOL JNM-AL300 spectrometer using $SiMe_4$ (0 ppm) as internal standards. The ^{13}C NMR (126 MHz) and ^{31}P NMR (202 MHz) spectra were measured in $CDCl_3$ or C_6D_6 with a JEOL JNM-λ500 spectrometer using $CDCl_3$ (77.0 ppm) as an internal standard for ^{13}C NMR spectroscopy and H_3PO_4 (85%) in D_2O (0 ppm) as an external standard for ^{31}P NMR spectroscopy.

*Synthesis of Tris(2-isopropoxyphenyl)phosphine (**1**)*

To an ether solution (20 mL) of 1-bromo-2-isopropoxybenzene (2.00 g, 9.30 mmol) was added a hexane solution of *n*-butyllithium (1.54 M, 6.3 mL, 9.77 mmol) at 0°C. After stirring at 0°C for 1 h, ether was removed under reduced pressure and THF (20 mL) and trichlorophosphine (0.24 mL, 2.7 mmol) were successively added at –40°C. The reaction mixture was stirred for 12 h during which time the mixture was gradually warmed to 25°C. After addition of a saturated aqueous solution of NH_4Cl, the mixture was extracted with ether/chloroform. The organic layer was washed with brine and dried with anhydrous Na_2SO_4. After the filtration, the solvents were removed under reduced pressure. The residue was separated by WCC (SiO_2, hexane:chloroform = 1:2) to afford **1** (1.11 g, 0.112 mol, 94%) as colorless crystals. **1**: Colorless crystals; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.11 (d, $^3J_{HH} = 6.0$ Hz, 18H), 4.49 (sep, $^3J_{HH} = 6.0$ Hz, 3H), 6.78 (dd, $^3J_{HH} = 8.0, 8.0$ Hz, 3H), 6.84 (dd, $^3J_{HH} = 8.0$ Hz, $J_{HP} = 4.0$ Hz, 3H), 6.88 (dd, $^3J_{HH} = 8.0, 8.0$ Hz, 3H), 7.25 (dd, $^3J_{HH} = 8.0$ Hz, $J_{HP} = 8.0$ Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 21.7 (CH_3), 70.1 (CH), 112.1 (CH), 120.1 (CH), 126.1 (d, $J_{CP} = 13.4$ Hz, C), 129.2 (CH), 134.8 (d, $^2J_{CP} = 6.3$ Hz, CH), 159.7 (d, $J_{CP} = 14.5$ Hz, C). ^{31}P{^{1}H}NMR (202 MHz, $CDCl_3$) δ –32.9.

*Reaction of Tris(2-isopropoxyphenyl)phosphine (**1**) with Dichloromethane*

A dichloromethane solution (5 mL) of phosphine **1** (122 mg, 0.279 mmol) was stirred at 25°C for 12h. After the filtration of the reaction mixture, the solvent was removed under reduced pressure. The residue was recrystallized from hexane/chloroform to give (chloromethyl)tris(2-isopropoxyphenyl)phosphonium chloride (**2**) (123.0 mg, 0.236 mmol, 85%). **2**: Colorless crystals; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.05 (d, $^3J_{HH} = 6.0$ Hz, 18H), 4.77 (sep, $^3J_{HH} = 6.0$ Hz, 3H), 4.92 (d, $^2J_{HP} = 6.6$ Hz, 2H), 7.18–7.22 (m, 6H), 7.44 (dd, $^3J_{HH} = 7.2$ Hz, $^3J_{HP} = 15$ Hz, 3H), 7.84 (dd, $J = 7.5, 7.5$ Hz, 3H).

*Reaction of Tris(2-isopropoxyphenyl)phosphine (**1**) with 1,2-Dichloroethane*

A 1,2-dichloroethane solution (5 mL) of phosphine **1** (122 mg, 0.279 mmol) and sodium tetrafluoroborate (296 mg, 2.70 mmol) was stirred at 25°C for 48 h. After the filtration of the reaction mixture, the solvent was removed under reduced pressure. The residue was recrystallized from hexane/chloroform to give (2-chloroethyl)tris(2-isopropoxyphenyl)phosphonium tetrafluoroborate (**3**) (108.0 mg, 0.184 mmol, 66%). **3**: Colorless crystals; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (d, $^3J_{HH} = 6.0$ Hz, 18H), 3.50–3.57 (m, 2H), 3.66–3.74 (m, 2H), 4.77 (sep, $^3J_{HH} = 6.0$ Hz, 3H), 7.11–7.24 (m, 9H), 7.80 (dd, $J = 7.5, 7.5$ Hz, 3H).

TABLE 1 Crystal Data and Refinement Details for **1**, **2**·H_2O, and **3**

Characteristic	**1**	**2**·*H_2O*	**3**
Empirical formula	$C_{27}H_{33}O_3P$	$C_{28}H_{37}Cl_2O_4P$	$C_{29}H_{37}BClF_4O_3P$
Formula weight	436.50	539.45	586.82
Temperature	208(2) K	123(2) K	173(2) K
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (#14)	$P2_1/c$ (#14)	$P2_1/c$ (#14)
a (Å)	11.362(5)	11.227(2)	10.4614(8)
b (Å)	15.369(6)	20.605(3)	15.5486(13)
c (Å)	14.761(6)	13.694(3)	18.7462(15)
α (deg)	90	90	90
β (deg)	100.615(5)	112.927(2)	102.0077(10)
γ (deg)	90	90	90
V (Å^3)	2533.5(19)	2917.7(10)	2982.5(4)
Z	4	4	4
D_{calc} (Mg m^{-3})	1.144	1.228	1.307
Absorption coefficient (mm^{-1})	0.132	0.307	0.235
Crystal size (mm^3)	0.30 × 0.20 × 0.05	0.40 × 0.30 × 0.20	0.40 × 0.30 × 0.30
θ range	3.33–25.50°	2.55–25.50°	3.53–25.50°
Number of reflections measured	16,471	19,395	19,409
Number of independent reflections	4,704	5,425	5,469
R_{int}	0.0884	0.0393	0.0197
Completeness	99.5%	99.7%	98.5%
Data/restraints/parameters	4,704/0/286	5,425/0/317	5,469/0/352
Goodness-of-fit on F^2	1.006	1.247	1.091
Final R indices [$I > 2\sigma(I)$]^a	$R_1 = 0.1181$ $wR_2 = 0.2911$	$R_1 = 0.1044$ $wR_2 = 0.2469$	$R_1 = 0.0409$ $wR_2 = 0.0975$
R indices (all data)^a	$R_1 = 0.2125$ $wR_2 = 0.3656$	$R_1 = 0.1064$ $wR_2 = 0.2484$	$R_1 = 0.0414$ $wR_2 = 0.0978$
Largest difference peak and hole (e Å^{-3})	0.631 and –0.520	1.426 and–0.841	0.690 and –0.398

$^a R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [(\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.

*Synthesis of Dichloridobis[tris(2-isopropoxyphenyl)phosphine]platinum (**4**)*

A mixture of phosphine **1** (122 mg, 0.279 mmol) and dichlorido (η-cycloocta-1,5-diene)platinum (52 mg, 0.139 mmol) in benzene (5 mL) was stirred at reflux for 24 h. After the filtration of the reaction mixture, the filtrate was evaporated to dryness and the residue was recrystallized from hexane/chloroform to give dichlorido bis[tris(2-isopropoxyphenyl)phosphine]platinum (**4**) (126 mg, 0.120 mmol, 86%). **4**: Pale yellow crystals, ^{1}H NMR (300 MHz, $CDCl_3$, 60°C) δ 0.90 (brs, 36H), 4.34 (sep, $^3J_{HH} = 6.0$ Hz, 6H), 6.64 (d, $^3J_{HH} = 7.5$ Hz, 6H), 6.76 (dd, $J = 7.5$, 7.5 Hz, 6H), 7.21 (m, 12H).

*Synthesis of Dichloridobis[tris(2-isopropoxyphenyl)phosphine]palladium (**5**)*

A mixture of phosphine **1** (122 mg, 0.279 mmol) and dichloridobis(benzonitrile)palladium (52 mg, 0.136 mmol) in benzene (5 mL) was stirred at 25°C for 12 h. After the filtration of the reaction mixture, the filtrate was evaporated to dryness and the residue was recrystallized from hexane/chloroform to give dichloridobis[tris(2-isopropoxyphenyl)phosphine]palladium (**5**) (98 mg, 0.0860 mmol, 62%). **5**: Orange crystals, ^{1}H NMR (300 MHz, $CDCl_3$, 60°C) δ 0.90 (brs, 36H), 4.35 (sep, $^3J_{HH} = 6.0$ Hz, 6H), 6.63–6.79 (m, 18H), 7.22 (d, $^3J_{HH} = 7.5$ Hz, 6H). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) δ 14.7.

*Synthesis of Dichloridodi(μ-dichlorido)-bis[tris(2-isopropoxyphenyl)phosphine]-dipalladium (**6**)*

A mixture of phosphine **1** (61 mg, 0.140 mmol) and dichloridobis(benzonitrile)palladium (52 mg, 0.136 mmol) in benzene (5 mL) was stirred at 25°C for 12 h. After the filtration of the reaction mixture, the filtrate was evaporated to dryness and the residue was recrystallized

TABLE 2 Crystal Data and Refinement Details for **4**·2(CHCl$_3$), **5**, and **6**·2(CHCl$_3$)

Characteristic	**4**·*2(CHCl$_3$)*	**5**	**6**·*2(CHCl$_3$)*
Empirical formula	$C_{56}H_{68}Cl_8O_6P_2Pt$	$C_{54}H_{66}Cl_2O_6P_2Pd$	$C_{56}H_{68}Cl_{10}O_6P_2Pd_2$
Formula weight	1377.73	1050.31	1466.34
Temperature	153(2) K	123(2) K	153(2) K
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P*-1(#2)	*P*-1(#2)	*P*-1(#2)
a (Å)	10.1641(8)	10.270(3)	14.0926(2)
b (Å)	15.9127(13)	12.197(3)	14.7747(2)
c (Å)	18.8640(14)	12.737(3)	18.7058(4)
α (deg)	88.282(7)	111.849(3)	70.615(3)
β (deg)	85.163(6)	108.135(3)	82.914(4)
γ (deg)	85.249(6)	102.208(3)	60.342(3)
V (Å^3)	3028.9(4)	1306.8(6)	3188.75(8)
Z	2	1	2
D_{calc} (Mg m^{-3})	1.511	1.335	1.527
Absorption coefficient (mm^{-1})	2.768	0.566	1.079
Crystal size (mm^3)	0.30 × 0.20 × 0.10	0.20 × 0.10 × 0.05	0.30 × 0.20 × 0.10
θ range	2.63–25.50°	2.92–25.50°	3.29–28.28°
Number of reflections measured	19,529	8,941	27,915
Number of independent reflections	10,472	4,568	14,435
R_{int}	0.0336	0.0636	0.0259
Completeness	93.0%	93.7%	91.2%
Data/restraints/parameters	10,472/0/661	4,568/0/296	14,435/0/685
Goodness-of-fit on F^2	1.480	1.063	1.181
Final R indices [$I > 2\sigma(I)$]^a	$R_1 = 0.0709$ $wR_2 = 0.1429$	$R_1 = 0.0874$ $wR_2 = 0.2066$	$R_1 = 0.0420$ $wR_2 = 0.0851$
R indices (all data)^a	$R_1 = 0.0743$ $wR_2 = 0.1441$	$R_1 = 0.1297$ $wR_2 = 0.2410$	$R_1 = 0.0435$ $wR_2 = 0.0856$
Largest difference peak and hole (e Å^{-3})	0.928 and –1.000	0.743 and –1.086	1.256 and –0.795

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [(\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

from hexane/chloroform to give dichloridobis[tris(2-isopropoxyphenyl)phosphine]palladium (**6**) (49 mg, 0.040 mmol, 57%) as red crystals. **6**: Red crystals, ^{1}H NMR (300 MHz, CDCl$_3$, 60°C) δ 0.4–2.0 (br m, 36H), 4.64 (brs, 6H), 6.5–8.0 (br m, 24H).

*Synthesis of Chlorido(η-cycloocta-1,5-diene)[tris(2-isopropoxyphenyl)-phosphine]rhodium (**7**)*

A mixture of phosphine **1** (61 mg, 0.140 mmol) and bis[chlorido(η-cycloocta-1,5-diene)rhodium] (69 mg, 0.140 mmol) in benzene (5 mL) was stirred at reflux for 48 h. After the filtration of the reaction mixture, the filtrate was evaporated to dryness and the residue was recrystallized from hexane/chloroform to give chlorido(η-cycloocta-1,5-diene)[tris-(2-isopropoxyphenyl)phosphine]rhodium (**7**) (74 mg, 0.104 mmol, 74%). **7**: Orange crystals, ^{1}H NMR (300 MHz, CDCl$_3$, 60°C) δ 1.01 (brs, 18H), 1.87 (m, 4H), 2.36 (m, 4H), 4.10 (brs, 2H), 4.45 (brs, 3H), 5.26 (brs, 2H), 6.72 (dd, $^3J_{\text{HH}} = 7.5$ Hz, $^3J_{\text{HP}} = 3.8$ Hz, 3H), 6.84 (dd, $^3J_{\text{HH}} = 7.5, 7.5$ Hz, 3H), 7.21 (dd, $^3J_{\text{HH}} = 7.5, 7.5$ Hz, 3H), 7.77 (brs, 3H). ^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$): δ 17.5 (d, $^1J_{\text{PRh}} = 149$ Hz).

X-Ray Crystallography of **1**, **2**·*H$_2$O*, **3**, **4**·*2(CHCl$_3$)*, **5**, **6**·*2(CHCl$_3$), and* **7**·*CHCl$_3$*

Single crystals of **1**, **2**·H$_2$O, **3**, **4**·2(CHCl$_3$), **5**, **6**·2(CHCl$_3$), and **7**·CHCl$_3$ suitable for X-ray structural analysis were obtained by slow recrystallization from hexane/chloroform. The crystals were mounted on a glass fiber. The intensity data were collected on a Rigaku R-AXIS IV^{++} diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71070 Å). The structures were solved by direct methods (SHELXS-97 [29]), and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97 [29]). All the nonhydrogen atoms were refined anisotropically, and all hydrogens were placed using AFIX instructions. The structural data are shown in Tables 1–3. CCDC numbers 989009 for **1**, 989010 for **2**·H$_2$O, 989011 for

TABLE 3 Crystal Data and Refinement Details for $\mathbf{7}\cdot\mathrm{CHCl_3}$

Characteristic	$\mathbf{7}\cdot CHCl_3$
Empirical formula	$C_{36}H_{46}Cl_4O_3PRh$
Formula weight	802.41
Temperature	153(2) K
Crystal system	Triclinic
Space group	*P*-1(#2)
a (Å)	10.5754(5)
b (Å)	12.8454(9)
c (Å)	14.1061(7)
α (deg)	86.224(5)
β (deg)	71.757(4)
γ (deg)	89.165(5)
V (Å^3)	1815.94(18)
Z	2
D_{calc} (Mg m^{-3})	1.467
Absorption coefficient (mm^{-1})	0.843
Crystal size (mm^3)	0.20 × 0.15 × 0.15
θ range	3.44–25.50°
Number of reflections measured	12,420
Number of independent reflections	6,295
R_{int}	0.0244
Completeness	93.2%
Data/restraints/parameters	6,295/0/406
Goodness-of-fit on F^2	1.106
Final R indices [$I > 2\sigma(I)$]^a	$R_1 = 0.0378$ $wR_2 = 0.0856$
R indices (all data)^a	$R_1 = 0.0392$ $wR_2 = 0.0865$
Largest difference peak and hole (e Å^{-3})	0.719 and –1.067

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [(\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.

3, 989012 for **4**·2(CHCl$_3$), 989013 for **5**, 989014 for **6**·2(CHCl$_3$), and 989015 for **7**·CHCl$_3$ contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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