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Note

Preparation and properties of sandwiched trinuclear palladium(II) complexes with tridentate phosphine and phosphine sulfide ligands

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ABSTRACT

The central phosphino group of tripodal tetradentate tris[2-(diphenylphosphino)ethyl]phosphine (pp_3) was selectively oxidized by the reaction with diethyl disulfide to give tridentate phosphine ligand pOp_3. The terminal phosphino groups were reacted with sulfur to give pOp_3 trisulfide (pOp_3S_3). Three palladium(II) ions were sandwiched in the two pOp_3 and pOp_3S_3 ligands to form the trinuclear complexes with three trans(*P*) and trans(*S*) PdX_2 (X = Cl, Br, I) moieties, respectively. The tripodal triphosphine, 1,1,1-tris(diphenylphosphinomethyl)ethane (*i*-p_3), and its mono- and tri-sulfide, which have shorter carbon chains compared with pOp_3, form the mononuclear dichloro palladium(II) complexes with cis(*P*) and cis(*S*) geometries. Difference in the catalytic activity for the C–C coupling reaction was discussed in connection with the coordinated groups and geometries of the complexes.

1. Introduction

Structure, properties, and reaction mechanisms of five-coordinate trigonal-bipyramidal d^8 metal complexes have been investigated so far by using the tripodal tetradentate ligands with soft donors such as tris[2-(diphenylphosphino)ethyl]phosphine (pp_3) [1–12], tris[2-(diphenylphosphino)ethyl]amine (np_3) [3–5,13–15], tris[2-(diphenylarsino)ethyl]amine (nas_3) [4,6,13]. On the other hand, employing tripodal tridentate ligands is of interest because equivalent coordination of the three donor atoms of the tripodal ligands does not make usual square-planar or trigonal-bipyramidal structures of the d^8 metal complexes. In this work, we have attempted selective oxidation of the central phosphino group of pp_3 to give the Pd(II) complex with the tripodal tridentate ligand considering that the phosphine phosphorus is a good donor for Pd(II) while the phosphine oxide is scarcely coordinated to Pd(II). The coordination behavior of the pp_3 monooxide ligand (pOp_3) was compared with that of 1,1,1-tris(diphenylphosphinomethyl)ethane (*i*-p_3), which is a smaller tripodal tridentate ligand with shorter carbon chains.

Recently, some phosphine sulfides have been employed as the bound ligands for the palladium catalyst [16–18] instead of phosphine. The phosphine sulfide group can act as a good π acceptor and a quite weak σ donor compared with the phosphino group. The π^* orbital of the sulfur–phosphorus double bond is moderately low and can accept electrons from Pd(0) to stabilize the catalytically active species. On the other hand, the formation of the substrate adduct and subsequent catalytic reaction on Pd(II) seem not to be blocked because the phosphine sulfide group is not a strong σ donor for Pd(II). Therefore, comparison between phosphine complexes and the corresponding phosphine sulfide ones in the catalytic reaction is of importance from the viewpoint of coordination chemistry. Under the circumstances, the syntheses of the Pd(II) complexes with the phosphine sulfide of the tripodal tridentate phosphines also have been undertook, and the catalytic activities for the C–C coupling reaction were compared with those of the corresponding phosphine complexes.

2. Experimental

2.1. Reagents

Tris[2-(diphenylphosphino)ethyl]phosphine (pp_3, Aldrich), 1,1,1-tris (diphenylphosphinomethyl)ethane (*i*-p_3, Aldrich), diethyl disulfide (Aldrich), sulfur (Wako), potassium tetrachloropalladate (II) ($K_2[PdCl_4]$, Aldrich), tetrakis(acetonitrile)palladium(II) tetrafluoroborate ($[Pd(CH_3CN)_4](BF_4)_2$, Aldrich), tetra(*n*-butyl)ammonium bromide (Bu_4NBr, Wako), tetra(*n*-butyl)ammonium iodide (Bu_4NI, Wako), iodobenzene (Kanto Chemical), and styrene (Wako) were used for preparation or catalytic reaction without further purification.

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2.2. Preparation of complexes

2.2.1. Tris[2-(diphenylphosphino)ethyl]phosphine monoxide (pOp_3)

To a solution containing pp_3 (0.22 g, 0.33 mmol) in deoxygenated chloroform (ca. 10 cm^3) was added diethyl disulfide (0.043 g, 0.35 mol). The solution was stirred at room temperature for 48 h, and to this was added diethyl ether. The resultant colorless crystals were recrystallized from deoxygenated chloroform a few times until the ^{31}P NMR signal for the terminal phosphine oxide groups was not observed. Yield: 0.12 g (53%). Anal. Found: C, 73.03; H, 6.08%. Calcd for $C_{42}H_{42}OP_4$: C, 73.46; H, 6.16%. $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ −12.6 (*d*, terminal), 50.0 (*q*, central), $^3J_{P-P} = 42$ Hz.

2.2.2. $[Pd_3Cl_6(pOp_3)_2]$ (**1**)

To a solution containing $K_2[PdCl_4]$ (0.28 g 0.86 mmol) in deoxygenated water (ca. 20 cm^3) was added a solution containing pOp_3 (0.39 g, 0.57 mmol) in deoxygenated chloroform (ca. 10 cm^3), and the mixture was stirred at room temperature for 2 h. The chloroform layer was concentrated, and to this was added diethyl ether. The resultant yellow crystals were collected by filtration and air-dried. Yield: 0.29 g (51%). Anal. Found: C, 52.13; H, 4.59%. Calcd for $C_{84}H_{84}Cl_6O_2P_8Pd_3\cdot 0.5CHCl_3\cdot 0.5C_4H_{10}O$: C, 51.89; H, 4.51%. $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ 18.8 (terminal), 51.5 (central), $^2J_{P-P} = 300$ Hz, $^3J_{P-P} = 23$ Hz.

2.2.3. $[Pd_3Br_6(pOp_3)_2]$ (**2**)

To a solution containing pOp_3 (0.23 g 0.33 mmol) and Bu_4NBr (0.33 g, 1.02 mmol) in deoxygenated chloroform (ca. 10 cm^3) was added a solution containing $[Pd(CH_3CN)_4](BF_4)_2$ (0.22 g, 0.50 mmol) in deoxygenated acetonitrile (ca. 20 cm^3), and the solution was stirred at room temperature for 2 h, and then concentrated. To this was added diethyl ether to give yellow crystals which were recrystallized from chloroform Yield: 0.16 g (42%). Anal. Found: C, 44.22; H, 3.60%. Calcd for $C_{84}H_{84}Br_6O_2P_8Pd_3\cdot CHCl_3$: C, 44.55; H, 3.74%. $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ 17.3 (terminal), 51.6 (central), $^2J_{P-P} = 280$ Hz, $^3J_{P-P} = 22$ Hz.

2.2.4. $[Pd_3I_6(pOp_3)_2]$ (**3**)

The orange iodo complex **3** was prepared by a procedure similar to that for the bromo complex **2** using Bu_4NI instead of Bu_4NBr. Yield: 0.20 g (47%). Anal. Found: C, 39.49; H, 3.30%. Calcd for $C_{84}H_{84}I_6O_2P_8Pd_3\cdot CHCl_3$: C, 39.67; H, 3.33%. $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ 10.9 (terminal), 51.7 (central), $^2J_{P-P} = 170$ Hz, $^3J_{P-P} = 14$ Hz. The single crystals suitable for an X-ray analysis were obtained by recrystallization from chloroform.

2.2.5. pOp_3 trisulfide (pOp_3S_3)

A solution containing pOp_3 (0.33 g, 0.48 mmol) and sulfur (0.059 g, 1.8 mmol) in deoxygenated chloroform (ca. 25 cm^3) was stirred at room temperature for 1 h. To this was added diethyl ether to give colorless crystals. Yield: 0.32 g (85%). Anal. Found: C, 64.19; H, 5.56%. Calcd for $C_{42}H_{42}OP_4S_3$: C, 64.63; H, 5.41%. $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ 44.6 (*d*, terminal), 51.1 (*q*, central), $^3J_{P-P} = 54$ Hz.

2.2.6. $[Pd_3Cl_6(pOp_3S_3)_2]$ (**4**)

To a solution containing $K_2[PdCl_4]$ (0.24 g 0.74 mmol) in water (ca. 20 cm^3) was added a solution containing pOp_3S_3 (0.38 g, 0.49 mmol) in deoxygenated chloroform (ca. 10 cm^3), and the mixture was stirred at room temperature for 2 h. The chloroform layer was concentrated, and to this was added diethyl ether. The resultant reddish brown crystals were collected by filtration and air-dried. Yield: 0.32 g (60%). Anal. Found: C, 47.40; H, 4.23%. Calcd for $C_{84}H_{84}Cl_6O_2P_8Pd_3S_6\cdot 0.5CHCl_3\cdot 0.5C_4H_{10}O$: C, 47.34; H, 4.11%. $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ 45.5 (*q*, central), 53.1 (*d*, terminal), $^3J_{P-P} = 60$ Hz; 51.1 (*d*, terminal), 56.8 (*q*, central), $^3J_{P-P} = 64$ Hz. The single crystals suitable for an X-ray analysis were obtained by recrystallization from chloroform.

2.2.7. $[Pd_3Br_6(pOp_3S_3)_2]$ (**5**)

To a solution containing pOp_3S_3 (0.28 g 0.36 mmol) and Bu_4NBr (0.36 g, 1.12 mmol) in deoxygenated chloroform (ca. 20 cm^3) was added a solution containing $[Pd(CH_3CN)_4](BF_4)_2$ (0.23 g, 0.52 mmol) in deoxygenated acetonitrile (ca. 20 cm^3), and the solution was stirred at room temperature for 2 h, and then concentrated To this was added diethyl ether to give red crystals which were recrystallized from chloroform. Yield: 0.20 g (46%). Anal. Found: C, 40.98; H, 3.33%. Calcd for $C_{84}H_{84}Br_6O_2P_8Pd_3S_3\cdot CHCl_3$: C, 41.10; H, 3.45%. $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ 45.4 (*q*, central), 52.5 (*d*, terminal), $^3J_{P-P} = 60$ Hz; 49.6 (*d*, terminal), 56.1 (*q*, central), $^3J_{P-P} = 64$ Hz.

2.2.8. $[PdCl_2(i\text{-}p_3)]$ (**6**)

To a solution containing $K_2[PdCl_4]$ (0.20 g 0.61 mmol) in deoxygenated water (ca. 20 cm^3) was added a solution containing *i*-p_3 (0.38 g, 0.61 mmol) in deoxygenated chloroform (ca. 10 cm^3), and the mixture was stirred at room temperature for 2 h. The chloroform layer was concentrated, and the resultant white solid was collected by filtration and air-dried. Yield: 0.41 g (76%). Anal. Found: C, 56.50; H, 4.60%. Calcd for $C_{41}H_{39}Cl_2P_3Pd\cdot H_2O\cdot 0.5CHCl_3$: C, 56.66; H, 4.75%. $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ −29.6 (*s*), 16.6 (*s*).

2.2.9. $[PdCl_2(i\text{-}p_3S)]$ (**7**)

A solution containing **6** (0.14 g 0.16 mmol) and sulfur (0.0069 g, 0.22 mmol) in deoxygenated chloroform (ca. 10 cm^3) was stirred at room temperature for 1 h. The reaction solution was concentrated, and the resultant white solid was collected by filtration and air-dried. Yield: 0.10 g (73%). Anal. Found: C, 57.39; H, 4.60%. Calcd for $C_{41}H_{39}Cl_2P_3PdS\cdot H_2O$: C, 57.79; H, 4.85%. $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ 15.3(*s*), 33.3(*s*).

2.2.10. *i*-p_3 trisulfide (*i*-p_3S_3)

A solution containing *i*-p_3 (0.56 g, 0.90 mmol) and sulfur (0.086 g, 2.7 mmol) in deoxygenated chloroform (ca. 10 cm^3) was stirred at room temperature for 1 h. The reaction solution was concentrated, and to this was added diethyl ether. The resultant white crystals were collected by filtration. Yield: 0.51 g (71%). Anal. Found: C, 64.09; H, 5.26%. Calcd for $C_{41}H_{39}P_3S_3$: C, 64.31; H, 5.45%. $^{31}P\{^1H\}$ NMR ($CHCl_3$): δ 33.4 (*s*).

2.2.11. $[PdCl_2(i\text{-}p_3S_3)]$ (**8**)

To a solution containing $K_2[PdCl_4]$ (0.14 g 0.43 mmol) in water (ca. 10 cm^3) was added a solution containing *i*-p_3S_3 (0.30 g, 0.42 mmol) in chloroform (ca. 50 cm^3), and the mixture was stirred at room temperature for 2 h. The chloroform layer was concentrated, and the resultant orange solid was collected by filtration and air-dried. Yield: 0.19 g (44%). Anal. Found: C, 49.82; H, 4.11%. Calcd for $C_{41}H_{39}Cl_2P_3PdS_3\cdot CHCl_3$: C, 49.59; H, 3.96%. $^{31}P\{^1H\}$ NMR (CH_3CN): δ 33.0(*s*), 34.8 (*s*).

2.3. Crystal structure determination

The measurements of **3**·4$CHCl_3$ and **4**·4$CHCl_3$ were made on a Rigaku Mercury CCD X-ray diffractometer using graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation at 200 K. Cell Parameters were refined using the program CrystalClear (Rigaku and MSC, version 1.3, 2001) and the collected data were reduced using the program CrystalStructure (Rigaku and MSC, version 3.8, 2006). Empirical absorption corrections were applied. The structures were solved by direct methods using SIR 92 [19] and refined by full-matrix least-squares techniques using SHELXL-97 [20]. All non-hydrogen atoms for **3** and **4** were refined anisotropically and

hydrogen atoms were included in calculated positions. The iodine atom (I4) in **3**·4$CHCl_3$ was found to be disordered over two sites in a ratio of 0.5:0.5. The structure of **4**·4$CHCl_3$ contains voids comprised of a disordered solvent molecule.

Crystal data for **3**·4$CHCl_3$: $C_{88}H_{88}Cl_{12}I_6O_2P_8Pd_3$, $M = 2931.34$, triclinic, space group P-1, $a = 15.151(9)$ Å, $b = 17.622(13)$ Å, $c = 21.49(4)$ Å, $\alpha = 85.14(9)^\circ$, $\beta = 81.51(9)^\circ$, $\gamma = 70.09(8)^\circ$, $V = 5331(11)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.826$ g cm^{-3}, $\mu = 2.701$ mm^{-1}, $F(000) = 2824$, $T = 200(2)$ K, $R1 = 0.1264$, wR2 = 0.3195 for 19347 ($I > 2\sigma(I)$).

Crystal data for **4**·4$CHCl_3$: $C_{88}H_{88}Cl_{18}O_2P_8Pd_3S_6$, $M = 2575.00$, trigonal, space group R-3, $a = 26.86(4)$ Å, $c = 25.68(3)$ Å, $V = 16046(36)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.599$ g cm^{-3}, $\mu = 1.230$ mm^{-1}, $F(000) = 7752$, $T = 200(2)$ K, $R1 = 0.0820$, wR2 = 0.2209 for 6532 ($I > 2\sigma(I)$).

2.4. Measurements

^{31}P and ^{1}H NMR spectra were recorded on a JEOL JNM-A400 FT-NMR spectrometer operating at 160.70 and 399.65 MHz. In order to determine the chemical shifts of ^{31}P NMR signals, a 3 mm o.d. NMR tube containing the sample solution was coaxially mounted in a 5 mm o.d. NMR tube containing deuterated water as a lock solvent and phosphoric acid as a reference.

2.5. General procedure for the C–C coupling reaction

Reactions of iodobenzene (5.7 g, 28 mmol) with styrene (3.2 g, 30 mmol) in DMF (10 cm^3) were carried out under nitrogen at 120 °C in the presence of tributylamine (14 g, 76 mmol) as a base and trinuclear complexes **1** or **4** (3.8×10^{-3} mmol) or mononuclear complexes **6**, **7**, **8**, or [PdCl(pp_3)]Cl (1.1×10^{-2} mmol) as a catalysts. The yields were calculated by the ^{1}H NMR intensity of the *ortho* protons of stilbene formed on the basis of the intensity of the ethylene protons of bis(2-butoxyethyl) ether contained as an internal reference and followed as a function of time.

3. Results and discussion

The molecular structures of **3** and **4** obtained by X-ray analyses were shown in Figs. 1 and 2, respectively. Both complexes take the trinuclear structure in which the three Pd(II) ions are sandwiched between two pOp_3 or pOp_3S_3 ligands by coordination of phosphine phosphorus or phosphine sulfide sulfur atoms, respectively. All the Pd(II) ions have the square-planar trans geometry, and the Pd(II)–P and Pd(II)–S bond distances are in the range of those reported for trans(*P*) [21,22] and trans(*S*) [17] geometries with multidentate phosphine and phosphine sulfide ligands, respectively. The clear difference in molecular structures of **3** and **4** is that both central phosphine oxide oxygen atoms are directed outside in the trinuclear structure of **3** while one oxygen atom is inversed to be directed inside for **4** as shown in the ^{31}P NMR spectra below.

The ^{31}P NMR spectra of the single crystals of **3** in chloroform showed two signals for the terminal phosphino groups at 10.9 ppm and the central phosphine sulfide groups at 51.7 ppm. Since the AA′XX′ spin systems are made up of the three sets of two chemically equivalent coordinated terminal phosphorus atoms trans to each other (A and A′) and the two central phosphorus atoms (*X* and *X*′), virtual $^{2}J_{P-P}$ coupling through the Pd(II) ions should be observed for the sandwiched trinuclear structure of **3**. The ^{31}P NMR spectral simulation [23] actually gave a large $^{2}J_{P-P}$ value (170 Hz) characteristic of the trans(*P*) geometry (Fig. 3) [21,24], and this fact indicates that the complex **3** maintains the sandwiched trinuclear structure in solution. The ^{31}P NMR simulation also revealed that the complex **1** and **2** have a similar sandwiched trinuclear structure with trans(*P*) geometry showing the large virtual $^{2}J_{P-P}$ coupling (300 Hz for **1** and 280 Hz for **2**).

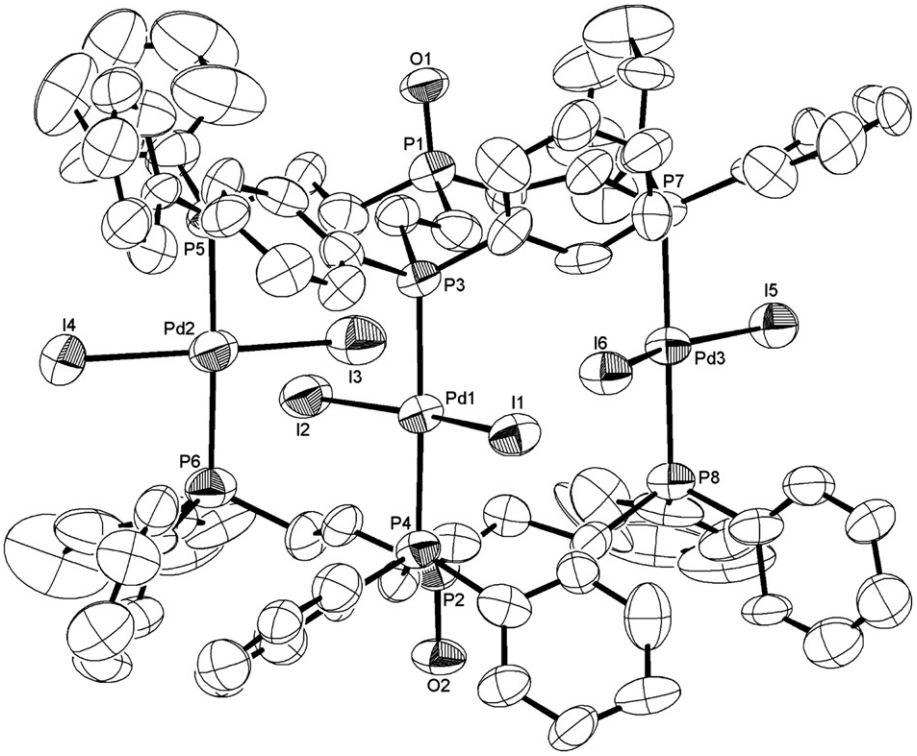

Fig. 1. ORTEP diagram of **3**.

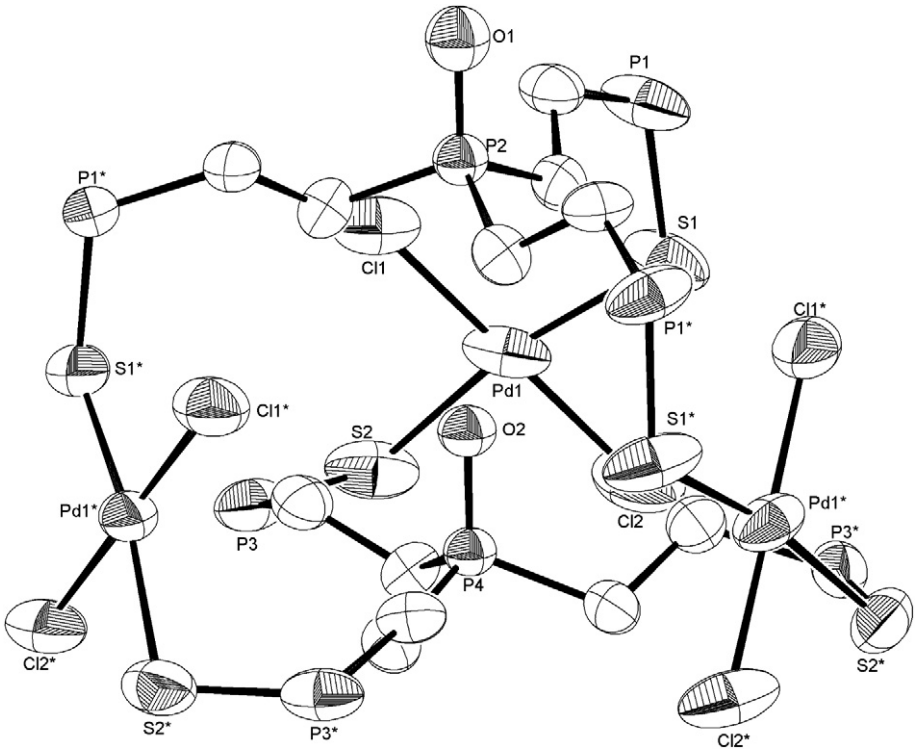

Fig. 2. ORTEP diagram of **4**. The peripheral phenyl rings are omitted for clarity.

The ^{31}P NMR spectrum for crystals of **4** dissolved in chloroform exhibits two sets of signals for the pOp_3S_3 ligand with different $^3J_{P-P}$ values between the terminal and central phosphorus atoms, 64 Hz and 60 Hz (Fig. 4). The former pOp_3S_3 ligand shows the signal for the central phosphine oxide group at lower field than that for the terminal phosphine sulfide groups as observed for the free pOp_3S_3 ligand (see Experimental Section), while the latter pOp_3S_3 ligand shows the reverse order of chemical shifts (Fig. 4). Considering that the natural conformation of the free pOp_3S_3 ligand may correspond to that for the ligand with phosphine oxide group (P2═O1) directed outside in **4** of which the conformation is also observed for the free tris[2-(diphenylphosphino)ethyl]phosphine tetrasulfide (pp_3S_4) ligand in the solid state (Fig. S1), the former pOp_3S_3 ligand can be assigned to the ligand with phosphine oxide groups directed outside, and consequently, the latter to that with phosphine oxide group directed inside. The bromo complex **5** dissolved in chloroform showed the ^{31}P NMR spectra with two set of signals for pOp_3S_3 quite similar to that for **4** indicating that **5** takes the sandwiched trinuclear structure with two kinds of pOp_3S_3 conformation.

While the *i*-p_3 ligand is a tripodal tridentate ligand with equivalent three diphenylphosphino groups, the ^{31}P NMR spectrum of **6** in chloroform showed signals for coordinated phosphino groups at 16.6 ppm and relatively small free phosphino group at −29.6 ppm (Fig. 5(a)) indicating that **6** takes the square-planar geometry with two coordinated phosphino groups at the cis position and one pendent free phosphino group in which *i*-p_3 acts as

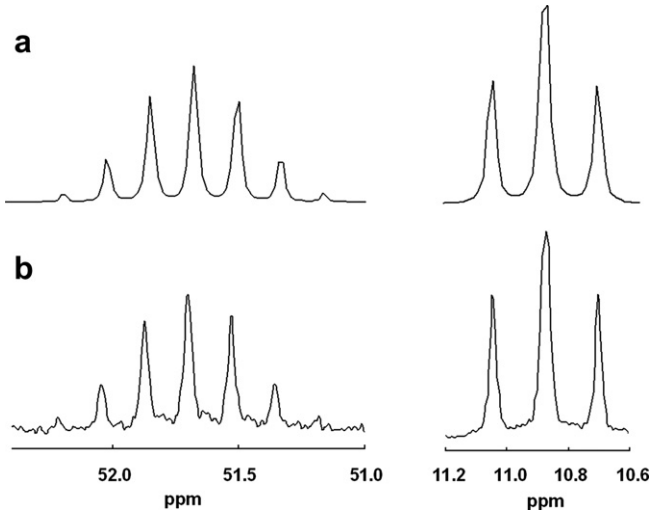

Fig. 3. Simulated (a) and observed (b) ^{31}P NMR spectral of **3**. The simulated spectrum is depicted by using $^2J_{P-P}$ = 170 Hz and $^3J_{P-P}$ = 14 Hz.

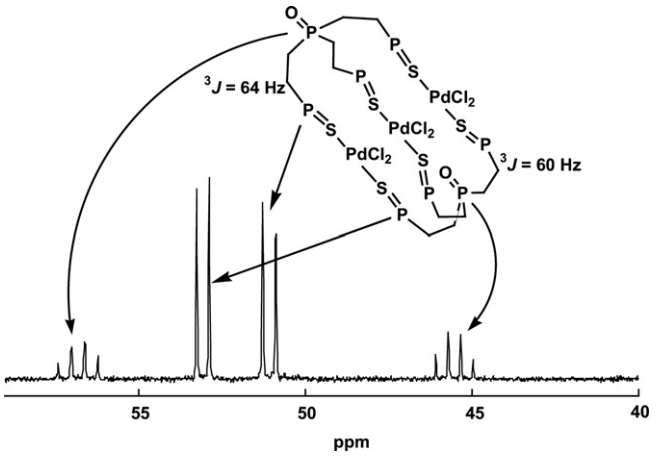

Fig. 4. ^{31}P NMR spectrum of **4**.

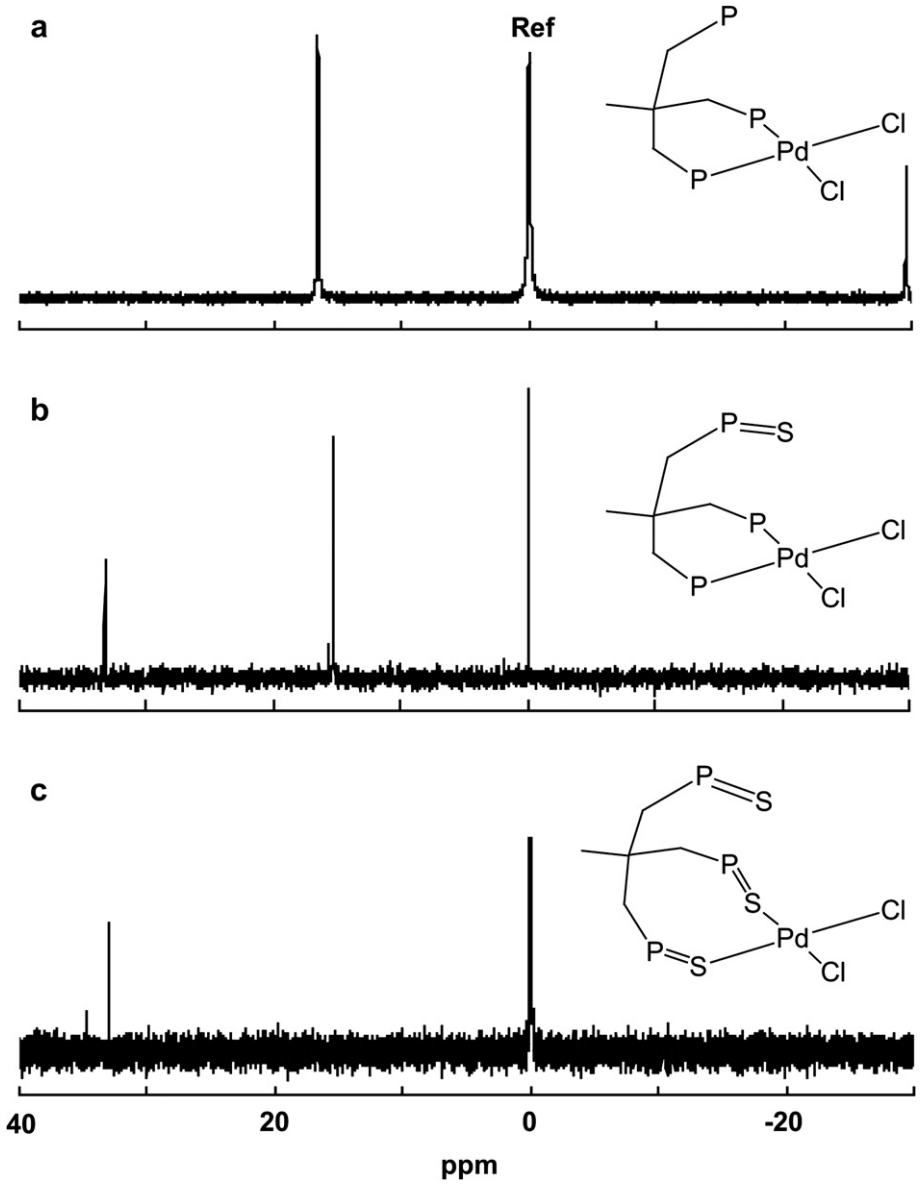

Fig. 5. ^{31}P NMR spectra of **6** (a), **7** (b), and **8** (c). Ref denotes the signal for D_3PO_4 in the outer D_2O.

the bidentate ligand with six-membered chelate ring. The pendent free phosphino group of **6** changed to phosphine sulfide (33.3 ppm) by the reaction of **6** with sulfur to give **7** keeping the cis(*P*) geometry (Fig. 5(b)). The ^{31}P NMR for **8** showed two kinds of signals for phosphine sulfide groups (Fig. 5(c)). The large and small signals were assigned to the two coordinated and one free phosphine sulfide groups indicating the cis(*S*) geometry of **8**.

The ^{31}P NMR spectrum of the reaction solution of pp_3 with diethyl disulfide showed that the central phosphino group was selectively oxidized and the most of the terminal phosphino groups remained unoxidized. A small amount of the phosphine dioxide with the oxidized terminal phosphino group was completely removed by repeated recrystallizations from deoxygenated chloroform. The pure phosphine trisulfide, pOp_3S_3, was prepared from the pure phosphine monoxide, pOp_3, with excess of sulfur.

The ^{31}P NMR spectra of the reaction solutions of $K_2[PdCl_4]$ with pOp_3 and with pOp_3S_3 in which the metal:ligand molar ratio was 3:2, showed that the trinuclear complexes, **1** and **4**, were formed almost quantitatively, respectively. Furthermore, the reaction solutions with metal:ligand ratio of 1:1 only gave the respective trinuclear complexes and free ligands. These facts indicate that the pOp_3 and pOp_3S_3 trinuclear complexes are thermodynamically much more stable than the corresponding 1:1 mononuclear complexes having a eight-membered chelate ring and one terminal pendent phosphino group for the pOp_3 ligand and a ten-membered chelate ring and one pendent phosphine sulfide group for the pOp_3S_3 ligand, respectively, to maintain the square-planar geometry. Contrarily, the carbon chains of the *i*-p_3 and *i*-p_3S_3 ligands are too short to form the trinuclear structure and consequently, gave the mononuclear complexes.

The reaction solutions of **1** or **2** with 6 equiv. of Bu_4NI in chloroform gave the ^{31}P NMR spectrum of **3**. On the other hand, the sulfide complex was not formed by the reactions of **1** or **2** with excess sulfur in chloroform at 50 °C for 5 h. These facts indicate that the sandwiched trinuclear structure was maintained during the substitution reaction of halide ions and the pOp_3 ligand was not dynamically dissociated in solution. Considering that ^{31}P NMR signals for the free pOp_3S_3 ligand was observed by the reaction of **4**

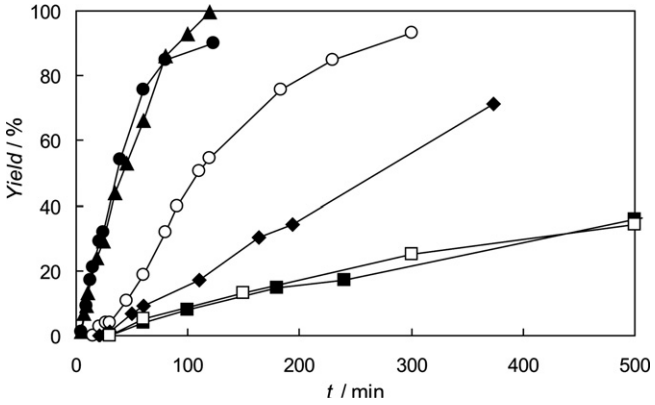

Fig. 6. Changes in the yield of stilbene with time in Mizoroki–Heck reaction catalyzed by 1 (○), 4 (●), 6 (■), 7 (□),8 (▲), and [PdCl(pp_3)]Cl (◆).

or **5** with Bu_4NI, the pOp_3S_3 trinuclear Pd(II) complexes are more labile than the pOp_3 ones due to the weak σ donating ability of phosphine sulfide.

Catalytic activities of **1**, **4**, **6**, **7**, and **8** were evaluated by carrying out the Mizioroki–Heck reaction using iodobenzene and styrene as the substrates and was compared with that of the pp_3 complex [PdCl(pp_3)]Cl. Changes in the yield of formed stilbene with time were followed by ^{1}H NMR under the same conditions in which the concentration of the catalysts were normalized on the basis of the Pd(II) concentration (see Section 2). The appreciable induction period was observed for the phosphine-coordinated complexes, **1**, **6**, **7**, and [PdCl(pp_3)]Cl, while the phosphine sulfide complexes **4** and **8** started the reaction almost instantly (Fig. 6). This fact indicates that the prereduction of phosphine sulfide Pd(II) complexes to the catalytically active Pd(0) species readily proceeds compared with the phosphine complexes. Acceleration of the reaction for **4** and **8** is attributed to stabilization of the zerovalent oxidation state of palladium in the phosphine sulfide complexes by the π-accepting ability of the phosphine sulfide groups, which can keep higher concentration of the catalytically active Pd(0) species compared with the phosphino groups. Furthermore, the weaker σ donation of the phosphine sulfide to Pd(II) is of great advantage to the migratory insertion of Pd(II) to give the acceleration of the catalytic cycle. The catalytic activity of **1** appears to be higher than the other phosphine complexes **6** and **7** with square-planar cis(*P*) geometry and [PdCl(pp_3)]Cl with five-coordinate trigonal-bipyramidal structure. It is probable that the trans(*P*) geometry of **1** is relatively thermodynamically unstable to facilitate the formation of the catalytically active species.

Appendix A. Supplementary data

CCDC 800188 and 800189 contain the supplementary crystallographic data for **3** and **4**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.03.018.

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