# Syntheses and structures of bowl-shaped triarylphosphines and their palladium(II) complexes

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## Abstract

Novel bowl-shaped triarylphosphines, tris(2,2″,6,6″-tetraalkyl[1,1′:3′,1″-terphenyl]-5′-yl)phosphines (TRMP: alkyl = methyl; TRIP: alkyl = isopropyl), were prepared by lithiation of the corresponding *m*-terphenyl bromides followed by reaction with $PCl_3$. X-ray crystallographic analysis revealed that the phosphorus center of TRMP is embedded in the shallow bowl-shaped cavity of 16 Å diameter and 2.1 Å depth formed by three radially extended *m*-terphenyl units. Its cone angle was estimated to be as large as 174°. In the crystal structure of TRIP, the depth of the cavity and cone angle increased to 3.3 Å and 206°, respectively, because of the different arrangement of the *m*-terphenyl units. In contrast with TRMP, which can form the mononuclear complex, $PdCl_2(TRMP)_2$ (**6**), in the reaction with $PdCl_2$, treatment of TRIP (1 or 3 eq.) with $PdCl_2$ produced the trinuclear palladium(II) chloride complex, $[(PdCl_2)_3(TRIP)_2]$ (**8**), as a single product. X-ray crystallography established the structure of **8**, where the trimer of $PdCl_2$ is terminated by two TRIP ligands. The formation of the different types of $PdCl_2$ complexes was explained in terms of the difference in the cavity shape of TRMP and TRIP.
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*Keywords:* Phosphine ligands; Bowl-shaped molecules; Palladium; Crystallographic analysis

## 1. Introduction

The molecular design of sterically demanding tertiary phosphines has been attracting increasing attention [1]. By modulating their steric bulkiness, the number of the ligands introduced to the metal center can be controlled, which leads to the facilitation of the formation of catalytically active low-coordinate species. Usually, increasing the steric bulk of monodentate phosphines means the increase of the steric congestion around the phosphorus center. Although severe steric shielding of a metal center by bulky phosphine ligands enables the control of the coordination number, it concomitantly reduces the reactivity of the complex toward substrate molecules. We

have been investigating the stabilization of highly reactive species by utilizing bowl-shaped molecules [2], and previously designed the triarylmethane [3a], triarylsilane [3b], and triarylgermane [3c] derivatives **1–3** (Scheme 1). In these molecules, the radially extended *m*-terphenyl units form a large cavity around the central functionality. The reactive species embedded in the bowl-shaped cavity of these molecules can be prevented from dimerization or self-condensation effectively, whereas their reactivity towards appropriate molecules is not so much degenerated because there is a relatively large space around the central functionality. For example, an *S*-nitrosothiol bearing the Trm group (TrmSNO) was successfully obtained as stable crystals [3a]. A bowl-shaped silanol, TRMS-OH, undergoes no self-condensation reaction even under the conditions where $Ph_3SiOH$ affords the corresponding disiloxane, $Ph_3SiOSiPh_3$, while it can readily react with trimethylsilanol generated in situ
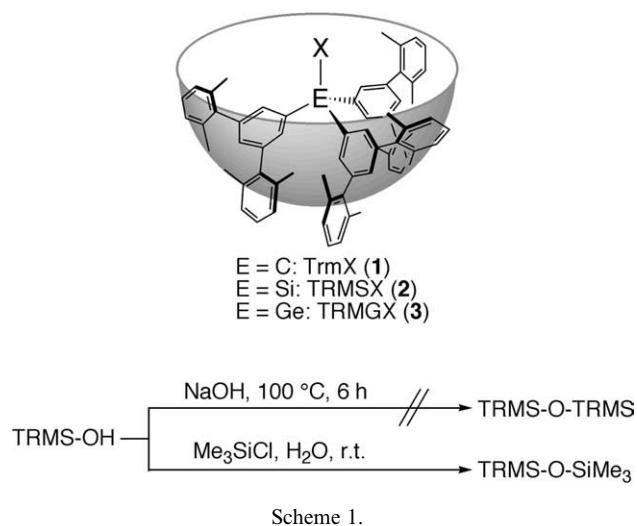
Scheme 1.

to produce the corresponding condensation product (Scheme 1) [3b]. A germanol bearing the similar framework, TRMG-OH, was also found to be extremely resistant to self-condensation [3c].

If the central atom of these molecules is replaced by a phosphorus atom, very bulky phosphine ligands without severe steric congestion in the vicinity of the phosphorus center are expected to be obtained. Recently, Tatsumi and co-workers [4] and our group [5] independently reported the synthesis of a bowl-shaped triarylphosphine, tris(2,2″,6,6″-tetramethyl[1,1′:3′,1″-terphenyl]-5′-yl)phosphine (denoted as TRMP, Fig. 1). We have also communicated the application of TRIP, in which the methyl groups of TRMP are replaced by isopropyl groups [6]. Herein, we report the syntheses and full characterization of these bowl-shaped phosphines and their palladium(II) complexes including the first example of the [(PdX$_2$)$_3$(PR$_3$)$_2$]-type trinuclear complex.

## 2. Results and discussion

### 2.1. Syntheses of triarylphosphines TRMP and TRIP

TRMP was prepared by lithiation of *m*-terphenyl bromides **4** [7] with *n*-butyllithium followed by reaction
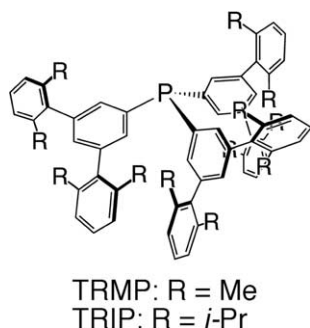
with PCl$_3$ in 92% yield (Scheme 2). For preparation of TRIP, the use of *t*-butyllithium instead of *n*-butyllithium for lithiation of bromide **5** [8] gave better results, although the yield was moderate. Usually, the compounds composed of oligophenylene units show poor solubility, which is one of the largest problems of such kind of aromatic compounds. By contrast, both TRMP and TRIP were soluble in various solvents such as chloroform, benzene, and hexane. This is probably due to the dendritic structure of these phosphines. The $^{31}$P NMR (CDCl$_3$) spectra of TRMP and TRIP showed the signals at $\delta_P$ −7.16 and −6.60, respectively, which are almost the same as that of PPh$_3$ ($\delta_P$ −6.0) [9]. In the $^1$H NMR (CDCl$_3$) spectrum of TRMP at room temperature, a single methyl signal was observed. Similarly, TRIP showed the signals for only one kind of isopropyl group: two nonequivalent methyl signals and one methine signal, which was similar to *m*-terphenyl bromide **5**. These results indicate the rapid rotation of the P–C bonds of TRMP and TRIP on the NMR time scale, in spite of their seemingly congested structures.

### 2.2. Crystal structures of TRMP and TRIP

The structures of TRMP and TRIP were established by X-ray crystallographic analysis. ORTEP drawings are shown in Fig. 2 with the selected bond lengths and angles. The structure of TRMP belongs to the $P\bar{3}$ trigonal space group, where the number of molecules in the asymmetric unit is 1/3. The *m*-terphenyl groups are arranged in a propeller shape, and the dihedral angle between the aromatic ring attached to the phosphorus atom and the plain containing the $C_3$ axis and the P–C bond is 52.7° (Fig. 3). The phosphorus atom of TRMP is embedded in a shallow bowl-type cavity with a diameter of ca. 16 Å as shown in Fig. 4. There is a relatively large space without any alkyl substituent around the phosphorus center. The cone angle of TRMP is estimated to be 174°, which is comparable with that of tri-*t*-butylphosphine (182°) and much larger than that of PPh$_3$ (145°) [9]. On the other hand, the C–P–C bond angle of TRMP is 102.61(6)°, which is almost the same as that of triphenylphosphine (103°) in contrast to other bulky phosphines such as P(Mes)$_3$ (110°) [10] and P(Tip)$_3$ (Tip = 2,4,6-triisopropylphenyl) (112°) [11].



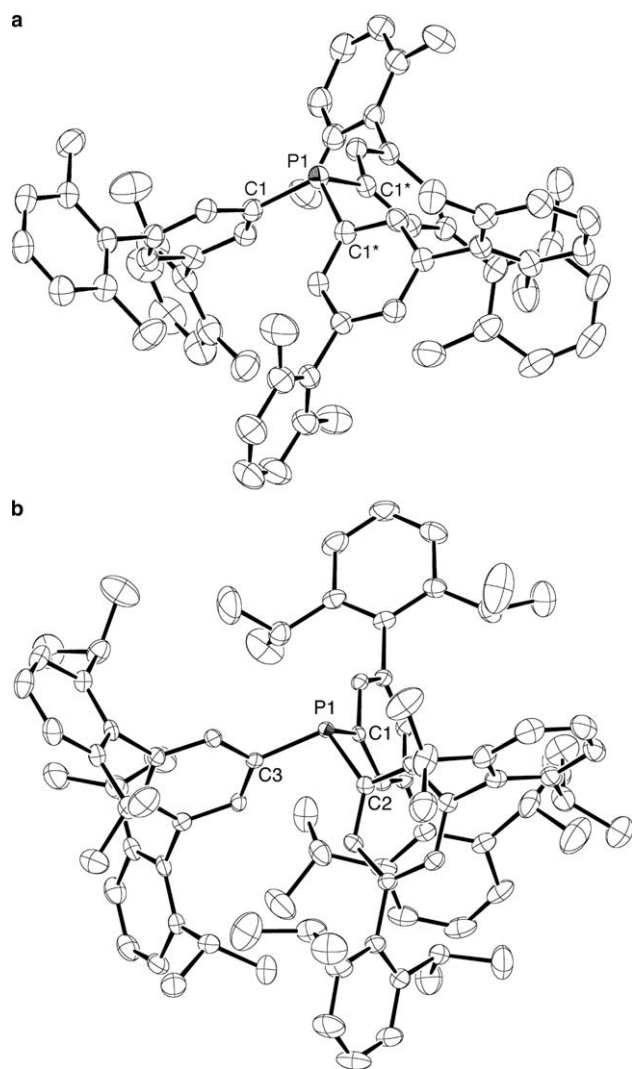Fig. 1. Bowl-shaped phosphines bearing *m*-terphenyl units.



Scheme 2.

a



b
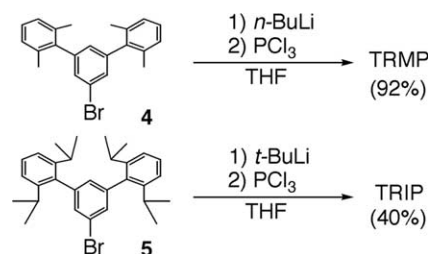


Fig. 2. ORTEP drawings of (a) TRMP and (b) TRIP (50% probability). Selected bond lengths (Å) and angles (°) for (a): P(1)–C(1),1.8329(16); C(1)–P(1)–C(1)*, 101.61(6). For (b): P(1)–C(1), 1.829(3); P(1)–C(2), 1.830(3); P(1)–C(3), 1.836(3); C(1)–P(1)–C(2), 101.52(13); C(2)–P(1)–C(3), 103.48(13); C(1)–P(1)–C(3), 104.52(13).
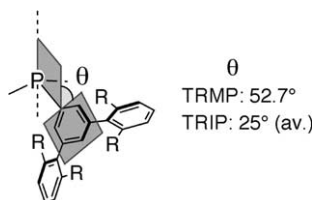


θ
TRMP: 52.7°
TRIP: 25° (av.)

Fig. 3. Dihedral angles between the aromatic ring attached to the phosphorus atom and the plain containing the (pseudo) $C_3$ axis and the P–C bond.

These results indicate that, in TRMP bearing a dendritic framework, the molecular size is enlarged in comparison with PPh$_3$ without increasing steric repulsion among the three $m$-terphenyl groups. Similar results for the C–E–C (E = element) bond angles were found for compounds **2**
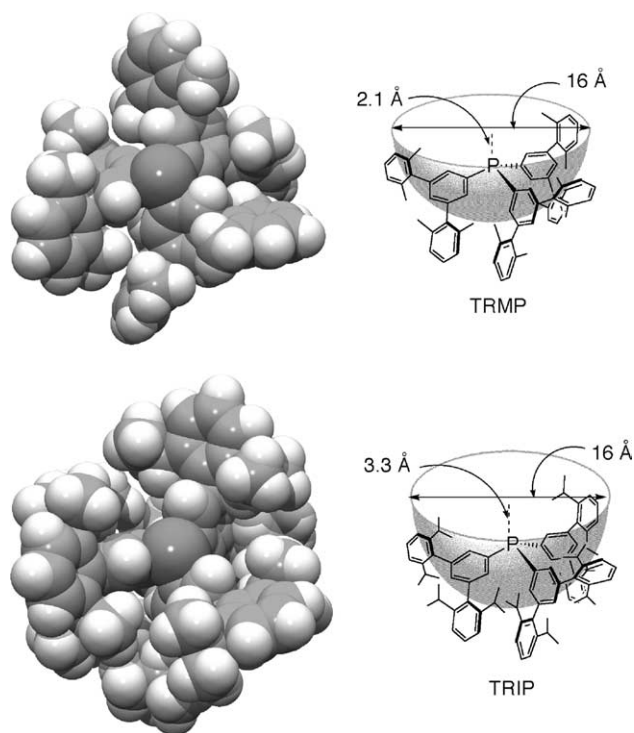


Fig. 4. Space-filling models of the crystal structures of TRMP and TRIP.

and **3**, the silicon and germanium analogues of TRMP; the averaged C–Si–C and C–Ge–C angles of the silanol (**2**, X = OH) [3b] and the germanol (**3**, X = OH) [3c] are 109° and 111°, respectively, which are almost the same as those of Ph$_3$SiOH (110°) [12] and Ph$_3$GeOH (112°) [13].

TRIP crystallizes in the $P\bar{1}$ triclinic space group, where the asymmetric unit contains one molecule of TRIP and two molecules of chloroform. Although the diameter of TRIP is almost the same as that of TRMP, the depth of the cavity increases from 2.1 Å in TRMP to 3.3 Å in TRIP (Fig. 4). This increase in the depth in TRIP is mainly caused by the arrangement of the $m$-terphenyl units. The dihedral angles between the aromatic ring attached to the phosphorus atom and the plain containing the pseudo $C_3$ axis and the P–C bond are 22.0°, 24.0°, and 29.7° (av. 25°) (Fig. 3), which are much smaller than that of TRMP. Such a vertical arrangement of the $m$-terphenyl units in TRIP is likely to minimize the steric repulsion among the bulky isopropyl groups in the bottom side of the molecule. Because of such structural changes, the cone angle of TRIP is much enlarged in comparison with TRMP. It is estimated to be 206°, which is even larger than that of P($t$-Bu)$_3$. In spite of such enlargement of the cone angle, however, the averaged C–P–C bond angle of TRIP (103°) is almost the same as those of PPh$_3$ and TRMP. These results indicate the characteristics of the dendrimer-type framework again.

## 2.3. Synthesis of a palladium(II) chloride trimer complex

The reactions of tertiary phosphines with palladium(II) halides usually produce the 2:1 complexes $[PdX_2(PR_3)_2]$ (X = halide) or the 2:2 complexes $[(PdX_2)_2(PR_3)_2]$, and bulky phosphine ligands tend to favor the formation of 2:2 complexes [14]. However, there has been no example of the 2:3 trinuclear complex $[(PdX_2)_3(PR_3)_2]$ to date probably because of the lack of an appropriate bulky phosphine ligand. Usually, increasing the steric bulk of a phosphine means the increase of steric congestion around the phosphorus center. The substituents in the close vicinity of the phosphorus, however, often cause the intramolecular cyclometallation. For example, the reactions of trimesitylphosphine with palladium(II) chloride afford only the cyclometallated dinuclear complex under a wide range of reaction conditions [15]. Such internally metallated complexes are of interest in view of their catalytic utility [16], but their formation is undesirable for the synthesis of the complex with the phosphine ligands in the intact form. The bowl-shaped phosphines, TRMP and TRIP, have no substituent in the ortho positions of phosphorus that induces the cyclometallation, whereas their molecular sizes are large as a whole. It is expected that these phosphines are useful for the control of the number of the coordinated ligands on the metal center without intramolecular side reactions. However, Tatsumi et al. [4a] reported that, even in the case of TRMP, the reactions with $PdCl_2$ in the ratio of 1:2 and 1:1 (Pd/ligand) yielded the corresponding mononuclear complex, $[PdCl_2(TRMP)_2]$ (6), and the dinuclear complex, $[(PdCl_2)_2(TRMP)_2]$ (7), respectively. These results prompted us to examine the reaction of TRIP with $PdCl_2$. Although based only on indirect evidence, there have been several reports about the formation of a $PdCl_2$ trimer terminated by organic ligands at each end [17]. On the other hand, there has been no example of the characterization of a $PdCl_2$ trimer complex bearing phosphine ligands, $[(PdCl_2)_3(PR_3)_2]$.

When $PdCl_2$ was treated with an equimolar amount of TRIP in refluxing ethanol/THF, the trinuclear palladium(II) chloride complex, $[(PdCl_2)_3(TRIP)_2]$ (8), was obtained as a single product (Scheme 3). The $^1H$ NMR spectrum (CDCl$_3$) of the crude product revealed that the reaction proceeded almost quantitatively. In the $^{31}P$ NMR spectrum (CDCl$_3$), the signal of 8

appeared at $\delta_P = 34.77$ ppm. The structure of 8 was determined by X-ray crystallographic analysis (vide infra). Complex 8 is soluble in chloroform, dichloromethane, toluene, and acetone, but hardly soluble in ether and ethanol. In the open atmosphere, 8 is stable both in the solid state and in solution. It should be noted that, even when an excess amount (3 eq.) of TRIP was used in this reaction, only trinuclear complex 8 and unreacted TRIP were observed in the $^{31}P$ NMR spectrum of the reaction mixture, and no other complexes were detected (Scheme 3). The similar results were obtained when $PdCl_2(PhCN)_2$ was used as an alternative palladium chloride source, which is known to be in equilibrium with $[PdCl_2]_n$ [18]. Treatment of $PdCl_2(PhCN)_2$ with TRIP (2 eq.) in refluxing benzene resulted in the formation of only complex 8 (Scheme 3). In the reactions of tertiary phosphines thus far reported, including TRMP, the $[PdCl_2(PR_3)_2]$-type complexes were formed when an excess of phosphine ligand was added. The present results suggest that, unlike other phosphines, only one molecule of TRIP can be introduced to one palladium atom because the phosphorus center of TRIP is embedded in the deep bowl-shaped cavity.

## 2.4. Structures of palladium(II) complexes

The yellow single crystals of $[(PdCl_2)_3(TRIP)_2]$ (8) suitable for X-ray crystallographic analysis were obtained by recrystallization from CHCl$_3$, and its structure was established by X-ray crystallographic analysis. The ORTEP drawings and space-filling model of 8 are shown in Fig. 5 with the selected bond lengths and angles, and the comparison of the bond lengths with those of related complexes is shown in Table 1. This is the first structural analysis of a $PdCl_2$ trimer complex although the crystal structures of several π-allyl complexes with a $Pd_3Cl_4$ bridge such as 10–12 have been reported [19–21].

The structure of $8 \cdot 10CHCl_3$ belongs to the the $P\bar{1}$ triclinic space group, which contains three Pd atoms linked by bridging chloride ligands with the Pd(2) atom residing at a crystallographic inversion center. The solvent molecules (omitted for clarity in Fig. 5) are located outside the cavity of the TRIP ligand. It is known that in the crystal structure of $PdCl_2$ the bridging chlorines form an infinite polymeric ribbon [18]. The structure of 8 can be regarded as a $PdCl_2$ trimer cut out from the polymeric chain of $[PdCl_2]_n$ by two phosphine ligands. The space-filling model (Fig. 5(b)) shows that the trimer of $PdCl_2$ is encapsulated by two TRIP ligands bearing a deep cavity. This figure also suggests that the formation of the isomer of 8 with two TRIP ligands in the cis positions would be sterically difficult. The bond length of Pd(1)–Cl(3) is substantially longer than that of Pd(1)–Cl(1), indicating that the trans influence of the phosphine ligand is stronger than that of the
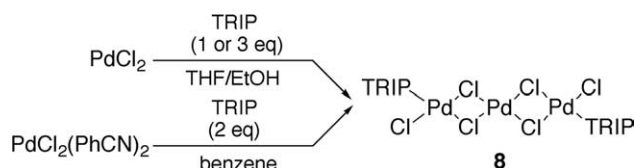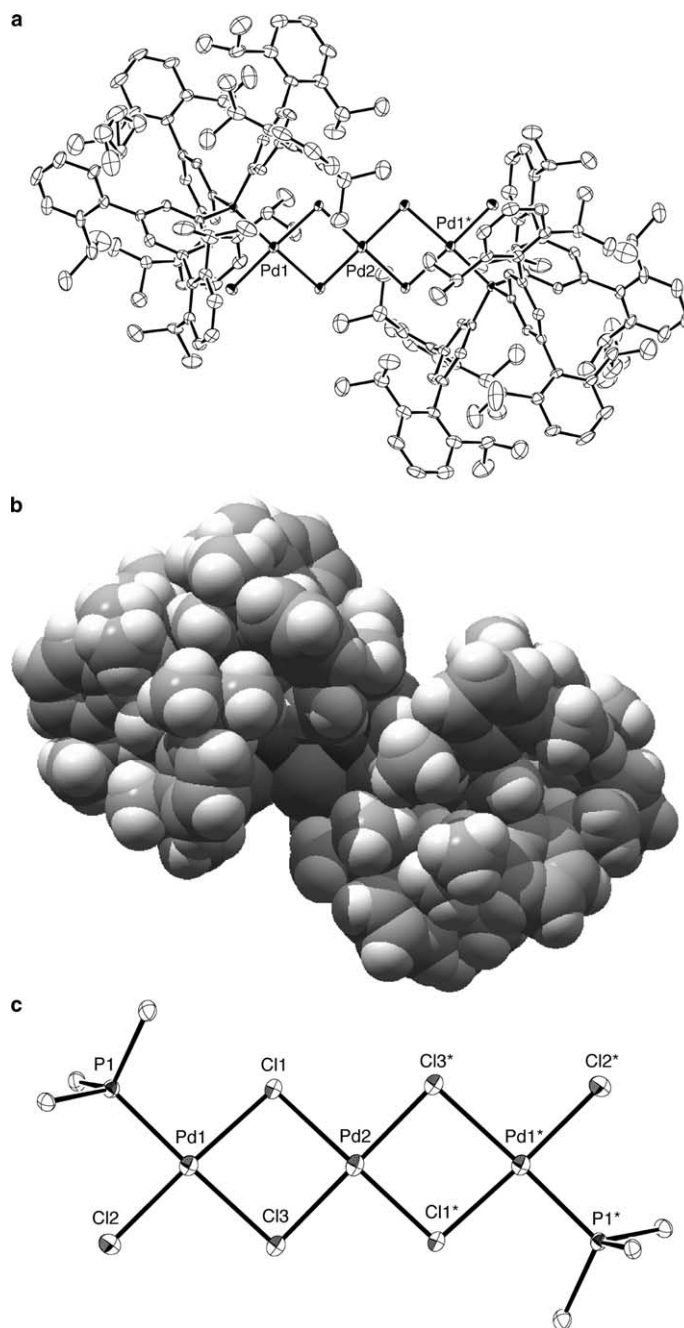


Scheme 3.

Fig. 5. Crystal structure of **8**. (a) ORTEP drawing (50% probability), (b) space filling model, and (c) ORTEP drawing of partial structure (50% probability). Selected bond lengths (Å) and angles (°): Pd(1)–Cl(1), 2.3389(14); Pd(1)–Cl(2), 2.2782(14); Pd(1)–Cl(3), 2.4214(15); Pd(1)–P(1), 2.2249(14); Pd(2)–Cl(1), 2.2901(14); Pd(2)–Cl(3), 2.3054(14); P(1)–Pd(1)–Cl(3), 176.26(5); Cl(1)–Pd(1)–Cl(2), 176.48(5).
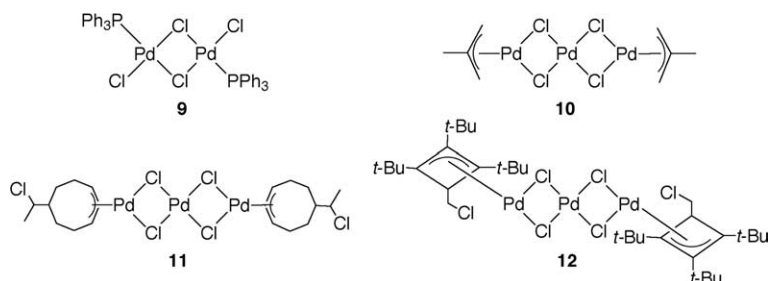
chloride. Similar asymmetry in the Pd–Cl bond lengths due to the *trans* influence has also been reported for many dinuclear palladium chloride phosphine complexes, such as [(PdCl$_2$)$_2$(PPh$_3$)$_2$] (**9**) [22] (Table 1). Concerning the internal four-membered rings, there is no significant difference between the Pd(2)–Cl(1) and Pd(2)–Cl(3) distances, both of which are close to the Pd–(μ-Cl) bond lengths in the central PdCl$_4$ unit of the chloride-bridged trinuclear palladium(II) complexes

**10–12** (2.29–2.31 Å) [19–21] as well as the Pd–Cl bond length of [PdCl$_2$]$_n$ (2.31 Å) [23] (Table 1).

The $^1$H NMR spectrum of **8** in CDCl$_3$ at room temperature showed the signals for only one kind of isopropyl group, which is the same signal pattern as those of TRIP and *m*-terphenyl bromide **5** (Fig. 6). These results indicate that in this complex the P–C bonds of the TRIP ligands as well as the P–Pd bonds are rotating rapidly on the NMR time scale in spite of the seemingly congested

Table 1
Selected bond lengths (Å) for the $PdCl_2$ complexes and related complexes

| Complex | Pd–Cl | | | | Pd–P | Reference |
|---|---|---|---|---|---|---|
| | Central $PdCl_4$ | *trans* to Cl | *trans* to P | Terminal PdCl | | |
| **8** | 2.2901(14) | 2.3389(14) | 2.4214(15) | 2.2782(14) | 2.2249(14) | This work |
| | 2.3054(14) | | | | | |
| **9** | | 2.339 | 2.426 | 2.266 | 2.241 | [22] |
| $[PdCl_2]_n$ | 2.31 | – | – | – | – | [23] |
| **10** | 2.313(9) | – | – | – | – | [19] |
| | 2.297(9) | | | | | |
| **11** | 2.297(1) | – | – | – | – | [20] |
| | 2.286(2) | | | | | |
| **12** | 2.300(2) | – | – | – | – | [21] |
| | 2.308(2) | | | | | |

structure, and that the space around the phosphorus center of **8** is large enough to ensure the rapid rotation of these bonds.

For comparison, the palladium(II) mononuclear complex bearing TRMP ligands, $[PdCl_2(TRMP)_2]$ (**6**), was prepared. The synthesis of **6** was first reported by Tatsumi et al. [4a] although the details of the experimental procedures were not described. The crystal structure of **6** is shown in Fig. 7, and the selected bond lengths and angles are summarized in Table 2. The palladium atom resides at a crystallographic inversion center. The Pd–P bond lengths are close to that of $[PdCl_2(PPh_3)_2]$ (**13**) (Table 2). Although the TRMP ligand has a bowl-shaped
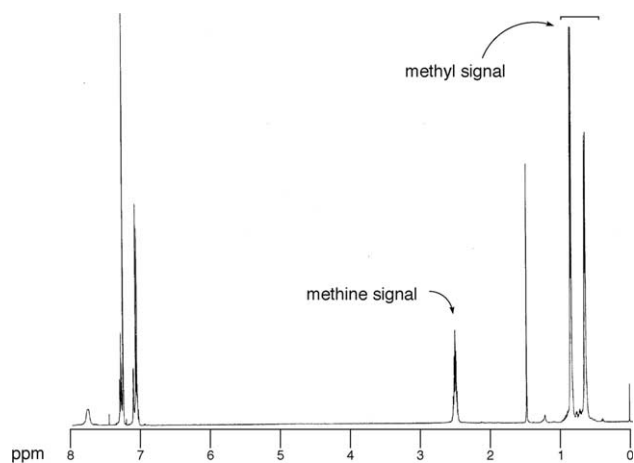

Fig. 7. ORTEP drawing of $PdCl_2(TRMP)_2$ (**6**) (50% probability).


Fig. 6. $^1H$ NMR spectrum (500 MHz, $CDCl_3$) of $[(PdCl_2)_3(TRIP)_2]$ (**8**).

Table 2
Selected bond lengths (Å) and angles (°) of $[PdCl_2(phosphine)_2]$ complexes

| Complex | Pd–Cl | Pd–P | P–Pd–Cl | Reference |
|---|---|---|---|---|
| $[PdCl_2(TRMP)_2]$ (**6**) | 2.2859(9) | 2.3247(8) | 93.23(3), 86.77(3) | This work |
| $[PdCl_2(PPh_3)_2]$ (**13**) | 2.290(1) | 2.337(1) | 92.0(1) | [24] |

framework, its brim is "chipped" as shown in Fig. 4. Because of these chips, two TRMP ligands can be in gear with each other and coordinate to one palladium atom in complex **6**. The comparison of the structures of the trinuclear complex **8** and the mononuclear complex **6** indicate that the deeper bowl-shaped cavity with a full brim of the TRIP ligand suppressed its coordination to the same palladium atom and enabled the formation of the $[(PdX_2)_3(PR_3)_2]$-type complex.

## 3. Conclusion

Novel bowl-shaped triarylphosphines, TRMP and TRIP, where the radially extended *m*-terphenyl units form a large cavity, were synthesized and fully characterized. Whereas the cone angles of TRMP and TRIP were estimated to be as large as 174° and 206°, respectively, there is a large and inert space around their phosphorus center because of the absence of any substituent in the ortho positions of phosphorus. The reaction of TRIP, which has a deeper bowl-shaped cavity, with $PdCl_2$ produced the trinuclear palladium(II) chloride complex, $[(PdCl_2)_3(TRIP)_2]$ (**8**), as a single product, presenting the first example of a structurally characterized $PdCl_2$ trimer complex. These bowl-shaped phosphines are expected to work as potent ligands in catalytic reactions. Recently, Tsuji et al. [25] utilized TRMP for the efficient rhodium-catalyzed hydrosilylation of ketones. Investigations on the reactivity of the metal complexes bearing TRMP and TRIP are currently in progress.

## 4. Experimental

All reactions were carried out under argon atmosphere with standard Schlenk or vacuum line techniques. Melting points were determined on a Yanaco micro melting point apparatus. All melting points were uncorrected. THF was purified by distillation from sodium diphenylketyl under argon atmosphere before use. Chloroform-*d* was distilled from calcium hydride before use. Phosphorus trichloride was distilled from calcium hydride before use. The $^1H$ NMR (500 MHz) and $^{13}C$ NMR (126 MHz) spectra were measured with a Bruker Avance500 spectrometer and a Bruker DRX-500 spectrometer using a residual peak of deuterated solvents as an internal standard. The $^{31}P$ NMR (109 MHz) spectra were measured with a JEOL Excalibur270 spectrometer using 85% $H_3PO_4$ as an external standard. Atmospheric pressure chemical ionization (APCI) mass spectra were recorded with a Shimadzu LC-MS-QP 8000α spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, The University of Tokyo.

### 4.1. Synthesis of tris(2,2″,6,6″-tetramethyl[1,1′:3′,1″-terphenyl]-5′-yl)phosphine (TRMP)

*n*-Butyllithium (1.53 M hexane solution, 5.36 mmol) was added to a solution of *m*-terphenyl bromide **4** (1.83 g, 5.01 mmol) in THF (30 mL) at −70 °C. The mixture was stirred at −70 °C for 25 min. $PCl_3$ (150 µL, 1.72 mmol) was added to this solution and the mixture was stirred at −70 °C for 2 h and at room temperature for 2 h. After removal of the solvent, the residue was treated with degassed $H_2O$, and extracted with degassed $CHCl_3$ under argon. The extracts were dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was washed thoroughly with degassed ethanol to give TRMP as colorless crystals (1.41 g, 92%). M.p. 284–287 °C. $^1H$ NMR (500 MHz, $CDCl_3$) δ 1.86 (s, 36H), 6.87 (s, 3H), 7.01–7.13 (m, 24H). $^{31}P$ NMR (109 MHz, $CDCl_3$) δ −7.16. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 20.67 (s), 127.05 (s), 127.17 (s), 130.21 (s), 132.52 (d, $J_{PC} = 18.9$ Hz), 135.65 (s), 137.78 (d, $J_{PC} = 13.1$ Hz), 141.20 (s), 141.64 (d, $J_{PC} = 6.9$ Hz). APCI-MS *m/z* 888 [M + H]⁺.

### 4.2. Synthesis of tris(2,2″,6,6″-tetraisopropyl[1,1′:3′,1″-terphenyl]-5′-yl)phosphine (TRIP)

*tert*-Butyllithium (2.36 M hexane solution, 6.14 mmol) was added to a solution of *m*-terphenyl bromide **5** (1.42 g, 2.97 mmol) in THF (25 mL) at −70 °C. The mixture was stirred at −70 °C for 25 min. $PCl_3$ (84 µL, 0.963 mmol) was added to this solution and the mixture was stirred at −70 °C for 2.5 h and at room temperature for 2 h. After removal of the solvent, the residue was treated with degassed $H_2O$, and extracted with degassed $CHCl_3$ under argon. The extracts were dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was washed thoroughly with degassed ethanol to give TRIP as colorless crystals (0.475 g, 40%). M.p. 345 °C. $^1H$ NMR (500 MHz, $CDCl_3$) δ 0.77 (d, $J_{HH} = 6.8$ Hz, 36H), 0.95 (d, $J_{HH} = 6.8$ Hz, 36H), 2.52 (sept, $J_{HH} = 6.8$ Hz, 12H), 6.97 (s, 3H), 7.10 (d, $J_{HH} = 7.8$ Hz, 12H), 7.26 (t, $J_{HH} = 7.8$ Hz, 6H), 7.50 (dd, $J_{PH} = 8.7$ Hz, $J_{HH} = 1.6$ Hz, 6H). $^{31}P$ NMR (109 MHz, $CDCl_3$) δ −6.60. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 23.60 (s), 23.99 (s), 30.38 (s), 122.41 (s), 127.91 (s), 131.58 (s), 133.45 (d, $J_{PC} = 23.2$ Hz), 135.60 (d, $J_{PC} = 13.7$ Hz), 138.77 (s), 140.61 (d, $J_{PC} = 8.6$ Hz), 146.61 (s). Anal. Calc. for $C_{90}H_{113}OP$: C, 87.05; H, 9.17. Found: C, 86.89; H, 9.27%. APCI-MS *m/z* 1224 [M + H]⁺.

### 4.3. Synthesis of [PdCl₂ (TRMP)₂] (6)

A solution of TRMP (282.6 mg, 0.319 mmol) in THF (15 mL) was added to a solution of $PdCl_2$ (15 mg, 0.0846 mmol) in ethanol (10 mL) at room temperature.

The mixture was refluxed for 3 h. After removal of the solvent, the residue was treated with $CHCl_3$ and filtered. After evaporation of the solvent, the residue was recrystallized from $CHCl_3$/hexane to give [$PdCl_2(TRMP)_2$] (**6**) as yellow crystals (148.8 mg, 90%). M.p. 335 °C (dec). $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 1.75 (s, 72H), 6.89 (s, 6H), 6.97 (d, $J_{HH} = 7.6$ Hz, 24H), 7.07 (t, $J_{HH} = 7.6$ Hz, 12H), 7.46 (m: virtual coupling, 12H). $^{31}P$ NMR (109 MHz, $CDCl_3$) $\delta$ 22.47. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) $\delta$ 20.69 (s), 127.06 (s), 127.16 (s), 130.34 (m: virtual coupling), 131.92 (s), 133.69 (m: virtual coupling), 135.84 (s), 140.67 (s), 140.91 (m: virtual coupling).

### 4.4. Synthesis of [$(PdCl_2)_3$ $(TRIP)_2$] (**8**)

A solution of TRIP (134.9 mg, 0.110 mmol) in THF (30 mL) was added to a solution of $PdCl_2$ (29.8 mg, 0.168 mmol) in ethanol (10 mL) at room temperature. The mixture was refluxed for 3 h. After removal of the solvent, the residue was treated with $CHCl_3$ and filtered. After evaporation of the solvent, the residue was washed with hexane and recrystallized from $CHCl_3$/hexane to give [$(PdCl_2)_3(TRIP)_2$] (**8**) as yellow crystals (80.3 mg, 49%). M.p. 380 °C (dec). $^1H$ NMR (500 MHz, $CDCl_3\delta$) 0.69 (d, $J_{HH} = 6.8$ Hz, 72H), 0.89 (d, $J_{HH} = 6.8$ Hz, 72H), 2.53 (sept, $J_{HH} = 6.8$ Hz, 24H), 7.07 (d, $J_{HH} = 7.8$ Hz, 24H), 7.10 (s, 6H), 7.29 (t, $J_{HH} = 7.8$ Hz, 12H), 7.76 (d, $J_{PH} = 9.3$ Hz, 12H). $^{31}P$ NMR (109 MHz, $CDCl_3$) $\delta$ 34.77. $^{13}C\{^1H\}$ NMR

(126 MHz, $CDCl_3$) $\delta$ 23.64 (s), 24.02 (s), 30.31(s), 122.65 (s), 126.72 (d, $J_{PC} = 57$ Hz), 128.10 (s), 133.72 (brs), 134.15 (s), 137.78 (s), 140.77 (m: virtual coupling), 146.80 (s). Anal. Calc. for $C_{180}H_{222}Cl_6P_2Pd_3$: C, 72.56; H, 7.51. Found: C, 72.27; H. 7.79%. In the reaction of TRIP (133.0 mg, 0.109 mmol) with $PdCl_2(PhCN)_2$ (21 mg, 0.055 mmol) in benzene (15 mL) at reflux temperature for 2 h, the $^{31}P$ NMR spectrum of the reaction mixture showed only the signals of complex **8** and TRIP.

### 4.5. X-ray crystallographic analysis of TRMP, TRIP, **6**, and **8**

Single crystals of TRMP · 1.5THF were grown from its THF/hexane solution at room temperature under argon atmosphere. Single crystals of TRIP · 2$CHCl_3$ were grown from its $CHCl_3$ solution at −20 °C under argon atmosphere. Single crystals of **6** · 4$CHCl_3$ and **8** · 10$CHCl_3$ were grown from their $CHCl_3$ solution at room temperature in the open atmosphere. The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.71069$ Å). The structures were solved by the direct method and refined by full-matrix least-squares on $F^2$ using SHELXL-97 [26]. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were idealized by using the riding models. Crystallographic data for TRMP · 1.5THF, TRIP · 2$CHCl_3$, **6** · 4$CHCl_3$, and **8** · 10$CHCl_3$ are listed in Table 3.

Table 3
Crystallographic data for TRMP · 1.5THF, TRIP · 2$CHCl_3$, **6** · 4$CHCl_3$, and **8** · 10$CHCl_3$

| | TRMP · 1.5THF | TRIP · 2$CHCl_3$ | **6** · 4$CHCl_3$ | **8** · 10$CHCl_3$ |
|---|---|---|---|---|
| Formula | $C_{72}H_{75}O_{1.5}P$ | $C_{92}H_{113}Cl_6P$ | $C_{136}H_{130}Cl_{14}P_2$ | $C_{190}H_{232}Cl_{36}P_2P$ |
| Formula weight | 995.29 | 1462.49 | 2429.04 | 4173.10 |
| $T$ (K) | 120 | 120 | 120 | 120 |
| Crystal system | Trigonal | Triclinic | Monoclinic | Triclinic |
| Space group | $P\bar{3}$ | $P\bar{1}$ | $P2_1/n$ | $P\bar{1}$ |
| $a$ (Å) | 15.1903(8) | 14.855(5) | 14.071(5) | 15.920(6) |
| $b$ (Å) | 15.1903(8) | 14.885(4) | 29.425(11) | 17.486(7) |
| $c$ (Å) | 14.2841(11) | 21.813(7) | 16.724(7) | 20.339(8) |
| $\alpha$ (°) | 90 | 76.152(12) | 90 | 82.825(16) |
| $\beta$ (°) | 90 | 84.394(13) | 117.548(4) | 71.934(14) |
| $\gamma$ (°) | 120 | 67.948(10) | 90 | 74.785(14) |
| $V$ (Å$^3$) | 2854.4(3) | 4340(2) | 6139(4) | 5189(4) |
| $Z$ | 2 | 2 | 2 | 1 |
| $D_{calc}$ (g cm$^{-3}$) | 1.158 | 1.119 | 1.314 | 1.336 |
| Reflections collected | 19 592 | 28 146 | 37 069 | 33 449 |
| Unique reflections | 3324 | 14 872 | 10 192 | 17 768 |
| $R_{int}$ | 0.0229 | 0.0340 | 0.0454 | 0.0326 |
| $F(0\,0\,0)$ | 1068 | 1564 | 2520 | 2152 |
| $\mu$(Mo K$\alpha$) (mm$^{-1}$) | 0.093 | 0.258 | 0.532 | 0.783 |
| Limiting indices | $-18 \leqslant h \leqslant 17$, | $-17 \leqslant h \leqslant 13$, | $-16 \leqslant h \leqslant 16$, | $-18 \leqslant h \leqslant 18$, |
| | $-18 \leqslant k \leqslant 18$, $-16 \leqslant l \leqslant 13$ | $-17 \leqslant k \leqslant 17$, $-25 \leqslant l \leqslant 25$ | $-33 \leqslant k \leqslant 34$, $-19 \leqslant l \leqslant 19$ | $-20 \leqslant k \leqslant 17$, $-23 \leqslant l \leqslant 24$ |
| Restraints/parameters | 0/263 | 0/971 | 0/733 | 0/1075 |
| Goodness-of-fit on $F^2$ | 1.058 | 1.096 | 1.096 | 1.057 |
| $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0494$, $wR_2 = 0.1465$ | $R_1 = 0.0816$, $wR_2 = 0.1720$ | $R_1 = 0.0483$, $wR_2 = 0.1117$ | $R_1 = 0.0676$, $wR_2 = 0.1606$ |
| $R$ indices (all data) | $R_1 = 0.0541$, $wR_2 = 0.1520$ | $R_1 = 0.1051$, $wR_2 = 0.1865$ | $R_1 = 0.0524$, $wR_2 = 0.1141$ | $R_1 = 0.0905$, $wR_2 = 0.1779$ |

## 5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 265230, 216987, 265231, and 216988 for TRMP · 1.5THF, TRIP · 2CHCl$_3$, **6** · 4CHCl$_3$, and **8** · 10CHCl$_3$, respectively. Copies of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc. cam.ac.jk or www: http://www.ccdc.cam.ac.uk).

## Acknowledgements

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